

# Measurement Control Workshop Instructional Materials

---

Philip Gibbs/Brookhaven National Laboratory  
Cary Crawford/Pacific Northwest National Laboratory  
Brent McGinnis/Pacific Northwest National  
Laboratory/Insolves, LLC

April 2014

**BNL-106051-2014-IR**

**BROOKHAVEN**  
NATIONAL LABORATORY

*a passion for discovery*



U.S. DEPARTMENT OF  
**ENERGY**

Office of  
Science



**BNL-106051-2014-IR**

***Measurement Control Workshop Instructional Materials***

Philip Gibbs  
Brookhaven National Laboratory

Cary Crawford  
Pacific Northwest National Laboratory

Brent McGinnis  
Pacific Northwest National Laboratory / Insolves LLC

April 2014

**Nonproliferation and National Security Department  
Brookhaven National Laboratory**

**U.S. Department of Energy  
National Nuclear Security Administration  
Office of International Material Protection and Cooperation**

## **DISCLAIMER**

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or any third party's use or the results of such use of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof or its contractors or subcontractors. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Notice: This manuscript has been authored by employees of Brookhaven Science Associates, LLC under Contract No. DE-AC02-98CH10886 with the U.S. Department of Energy. The publisher by accepting the manuscript for publication acknowledges that the United States Government retains a non-exclusive, paid-up, irrevocable, world-wide license to publish or reproduce the published form of this manuscript, or allow others to do so, for United States Government purposes.

## **Executive Summary**

An essential element in an effective nuclear materials control and accountability (MC&A) program is the measurement of the nuclear material as it is received, moved, processed and shipped. Quality measurement systems and methodologies determine the accuracy of the accountability values. Implementation of a measurement control program is essential to ensure that the measurement systems and methodologies perform as expected. A measurement control program also allows for a determination of the level of confidence in the accounting values.

This report is a compilation of workshop materials consisting of lectures on various aspects of measurement control, including calibration, basic statistics and measurement models, analysis of measurement method qualification data, control charts, inventory difference analysis, and measurement control for specific measurement systems.

The objectives of these materials are to identify, study, and discuss best practices in measurement and measurement control for the accountability of nuclear material. Presentation is envisioned to be through classroom instruction and discussion related to physical and error measurement models, uncertainty estimation, measurement control, and other areas of interest related to measurements. Several practical and hands-on exercises are included for demonstration of the various measurement concepts contained in the lecture/discussion sessions.

### **Mode of Instruction**

The suggested mode of instruction for these materials is lecture, demonstrations, and participant-led practical exercises.

### **Participants**

Participants attending this workshop should currently, or in the near future, be responsible for measurements and/or measurement control or material accountability at their facilities. It is suggested that the ideal participant pool consist of several MC&A “teams” that include MC&A specialists, measurement experts, and statisticians.

**Workshop length** - 5 training days

# Exercise 1

## LEU Conversion and Fuel Fabrication Facility Overview

---

### Session Objectives:

After the session the participants will understand the following:

1. Understand the Facility and Process that will be used as the teaching basis for the workshop.
2. Understand the MBA Division and Key Measurement Points .
3. Understand the physical (e.g., powder, gas, sintered pellet, etc.) and chemical (e.g., oxide, fluoride, etc.) forms of LEU in the process.
4. Understand the Measurement Methods applicable to the facility and process.

### Estimated Time:

0.5 hours large group discussion

### Materials needed:

1. Handout – **Appendix A** from the **Nuclear Safety Guide HAD501/01 – “Nuclear Material Accountancy of LEU Conversion and Fuel Fabrication Facilities”**.
2. Presentation

### Instructions:

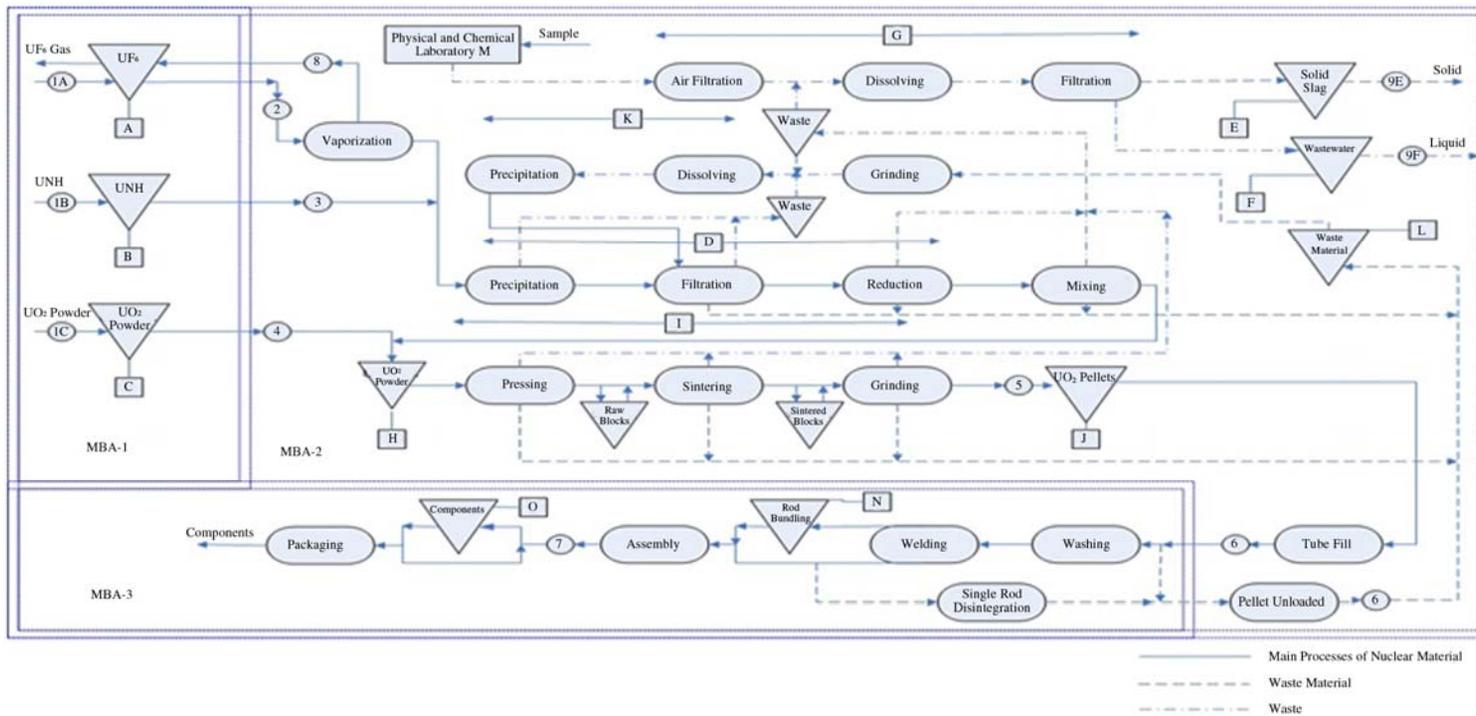
This is a large group instructor led discussion.

- 1) Participants are provided Appendix A from the **Nuclear Safety Guide HAD501/01 – “Nuclear Material Accountancy of LEU Conversion and Fuel Fabrication Facilities”**.
- 2) The instructor, using a presentation developed from the guide, will review appendix A with participants identifying the information pertaining to session objectives 1 through 4.

**Nuclear Safety Guide HAD501/01**  
**Nuclear Material Accountancy of LEU Conversion and Fuel Fabrication Facilities**  
**Appendix A**

1. According to the current level of manufacturing processes and technical management in our country, the target control volume of nuclear material accountancy is temporarily set to  $0.48\% * \text{input volume} + 2\sigma_{\text{MUF}}$ .
2. In order to facilitate understanding and mastering of this guidance, a typical facility is now taken as an example to demonstrate how nuclear material accountancy and evaluation work.

**A1. Facility MBA Division and Key Measurement Points**



**Figure 1. Facility MBA Division and Key Measurement Points**

**Nuclear Safety Guide HAD501/01**  
**Nuclear Material Accountancy of LEU Conversion and Fuel Fabrication Facilities**  
**Appendix A**

Table A1-1 Description of Flow KMPs

KMPs	Description	Material Type	Container	Sampling Method	Measurement Method
1A	UF <sub>6</sub> flow received by MBA-1	UF <sub>6</sub>	Gas tank	Provided by the dispatch side	b - gas tank weighing; e - gravimetric method; i - mass spectrometry
1B	UNH flow received by MBA-1	UNH	Tank	One sample for each tank	b - tank weighing; e - gravimetric method; i - mass spectrometry
1C	UO <sub>2</sub> flow received by MBA-1	UO <sub>2</sub> Powder	Tank	Take 3 tanks from the 40 tanks of each batch, then take one sample for each tank	b - powder weighing; e - gravimetric method; i - mass spectrometry
2	UF <sub>6</sub> flow for transfer, measured in MBA-2	UF <sub>6</sub>	Gas tank	N/A	b - weight difference between full tank and empty tank; i&e - coefficients of KMP-1A weight methods and mass spectroscopy
3	UNH flow for transfer, measured in MBA-2	UNH	Tank	N/A	b - UNH pipeline flowmeter; i&e - coefficients of KMP-1B weight methods and mass spectroscopy
4	Pressurized UO <sub>2</sub> flow, measured in MBA-2	Powder	Tank	Take 3 tanks from the 40 tanks of each batch, then take one sample for each tank	b - powder weighing; e - gravimetric method; i - mass spectrometry or measured value from KMP-1C
5	Sintered pellet flow, stored in MBA-2	Pellets	Pallet	5 random pellets from each batch	b - pellet pallet weighing; e - gravimetric method

**Nuclear Safety Guide HAD501/01**  
**Nuclear Material Accountancy of LEU Conversion and Fuel Fabrication Facilities**  
**Appendix A**

Table A1-1 Description of Flow KMPs (Continued)

KMPs	Description	Material Type	Container	Sampling Method	Measurement Method
6	Rods assembled in MBA-2 and delivered to MBA-3	Clad and welded fuel rods	Cladding	N/A	b - pellet stack weighing; e - gravimetric method from KMP-5
6	Unqualified pellet flow, returned by MBA-3 to MBA-2	Pellets	Rod	N/A	Values from rod assembly
7	Components flow dispatched from MBA-3	Components	Cladding	N/A - values of rods from KMP-5 and KMP-6	Sum of values from KMP-5 and KMP-6
8	Surplus materials measured in MBA-2	UF <sub>6</sub>	Gas tank	N/A	b - mass difference; e - coefficients from KMP-1A
9E	Solid waste measured in MBA-2	Various materials	Drum	N/A	NDA $\gamma$ - counts
9F	Liquid waste measured in MBA-2	Liquid waste	Drum	Mix each drum before sampling	b - drum weighing; e - fluorescence spectrometry

\* b = batch measurement, e = element analysis, i = isotope analysis

**Nuclear Safety Guide HAD501/01**  
**Nuclear Material Accountancy of LEU Conversion and Fuel Fabrication Facilities**  
**Appendix A**

Table A1-2 Description of Inventory KMPs

KMPs	Description	Material Type	Container	Sampling Method	Measurement Method
A	UF <sub>6</sub> stored in MBA-1	Solid in gas tanks	Gas tank	Item seal verification	Values from KMP-1A
B	UNH stored in MBA-1	UNH	Tank	N/A	Coefficients from KMP-1B b - UNH tank weighbridge
C	UO <sub>2</sub> powder stored in MBA-1	UO <sub>2</sub> Powder	Tank	Item seal verification	KMP-K values
D	Hold-up volume of UF <sub>6</sub> - UO <sub>2</sub> transfer in MBA-2	ADU and uranium oxide	Process equipment	N/A	γ-ray measuring instrument
E	Waste stored in MBA-2	Various solid	Drum	N/A	NDA γ-ray counts
F	Waste stored in MBA-2	Liquid	Drum	Mix each drum before sampling	b - drum weighing e - fluorescence spectrometry
G	Hold-up volume of waste treatment in MBA-2	Various materials	Equipment	N/A	γ-ray measuring instrument
H	UO <sub>2</sub> powder stored in MBA-2	UO <sub>2</sub> Powder	Tank	Item seal verification or sampling	Values from KMP-4 or: b - powder weighing; e - gravimetric method ; i - mass spectroscopy
I	Hold-up volume of pellet manufacturing	UO <sub>2</sub> Powder and pellets	Equipment	N/A	γ-ray measuring instrument
J	KMP-7 values	Sintered pellets stored in MBA-2	Pellets	Pallet	Item verification

**Nuclear Safety Guide HAD501/01**  
**Nuclear Material Accountancy of LEU Conversion and Fuel Fabrication Facilities**  
**Appendix A**

Table A1-2 Description of Inventory KMPs (Continued)

KMPs	Description	Material Type	Container	Sampling Method	Measurement Method
K	Sintered pellets stored in MBA-2	ADU and metal uranium	Process equipment	N/A	KMP-7 values
L-1	Hold-up volume of scrap recovery in MBA-2	ADU	Drum	Mix each drum before sampling	$\gamma$ -ray measuring instrument
L-2	Scraps stored in MBA-2	Dirty powder	Drum	Mix each drum before sampling	b - scrap weighing; e - titration
L-3	Scraps stored in MBA-2	Grinding residues	Tank	Mix each drum before sampling	b - scrap weighing; e - titration
L-4	Scraps stored in MBA-2	Raw material scraps	Drum	N/A	b - scrap weighing; e - titration
L-5	Scraps stored in MBA-2	Sinter scraps	Drum	5 random pellets from each drum	b - scrap weighing; e - calculate from weight of UO <sub>2</sub> and lubricants
M	MBA-2 laboratory inventory	Various samples	Glass bottles	N/A	b - scrap weighing; e - gravimetric method
N	MBA-3 rod inventory	Rod	Cladding	Item verification	Different b, e and i
O	MBA-3 component inventory	Components	Cladding	Item verification	KMP-6 values

\* b = batch measurement, e = element analysis, i = isotope analysis

**Nuclear Safety Guide HAD501/01**  
**Nuclear Material Accountancy of LEU Conversion and Fuel Fabrication Facilities**  
**Appendix A**

A2. Measurement Methods

1) Gravimetric method, for determination of uranium factor in UF<sub>6</sub>, UO<sub>2</sub>, pellets and scraps (i.e. the weight percentage). Put the sample (UO<sub>2</sub>) in a burned crucible which has known tare. Burn in a muffle furnace at the temperature of 900±25°C until UO<sub>2</sub> is completely converted into U<sub>3</sub>O<sub>8</sub>. Conduct impurity analysis on the sample at the same time. Calculate weight ratio of U<sub>3</sub>O<sub>8</sub> and U, and calculate the uranium weight percentage of the corresponding samples (UF<sub>6</sub>, UO<sub>2</sub>).

2) K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> Redox titration method: for determination of uranium percentage in slag and waste.

3) Mass spectroscopy, for determination of U-235 enrichment.

4) Fluorescent spectrometry, for determination of uranium concentration in liquid waste.

5) Non-destructive assay (NDA): for determination of uranium concentration in solid waste.

6) Volume measurement.

a) For each batch of filtrate (from the conversion and scrap recovery section), measure the volume with a level gauge, then deliver the filtrate to the natural evaporation pool. Typical delivery volume of a single batch is approximately 1890 L.

b) For centrifuged grinding slurry, measure the supernatant volume with a glass level gauge (approximately 56 L).

7) Mass measurement: Weigh the UF<sub>6</sub> drums with a 4000 kg scale.

A3. Evaluation of 6-Month Material Accountancy of a Model Factory

Brief process of the reference factory: A pellet manufacturing and rod assembly factory with two production lines with a daily production of 1t. The material is UF<sub>6</sub> and the product is fuel rod bundles. All scraps are converted into U<sub>3</sub>O<sub>8</sub> then processed into UO<sub>2</sub>. Enrichment mix only takes place in UNH during scrap recovery. Liquid waste is stored in the natural evaporation pool. Solid waste is stored at location or sent to the disposal facility.

Calculation of  $\sigma_{MUF}$  is listed in Table A2. The comments for (a), (b) and (c) in Table A2 are as follows:

a) Unless otherwise specified as kg, all the others refer to the numbers of items which are affected by random errors and short-term systematic errors;

b) Percent error is a unit for relative standard deviation;

c) When opening and closing inventory are equal, sample and analyze the long-term systematic error.

Calculated results from Table A2 are listed below:

**Nuclear Safety Guide HAD501/01**  
**Nuclear Material Accountancy of LEU Conversion and Fuel Fabrication Facilities**  
**Appendix A**

Measurement Method	Random Error (kg) <sup>2</sup>	Short-term Systematic Error (kg) <sup>2</sup>	Long-term and Short- term Systematic Error (kg) <sup>2</sup>
Weight	27.07	299.52	404.05
Sampling	46.15		2787.84
Volume	0.08		46.10
U - sample	23.83	125.05	2640.4
Sum	97.13	424.57	5878.39

Total  $\sigma^2_{\text{MUF}}=97.13+424.57+5878.39=6400.09 \text{ (kg)}^2$

Total  $\sigma_{\text{MUF}}=80.00 \text{ kg}$

Calculated from Table A3

$\text{MUF}=\text{B}+\text{I}-\text{O}-\text{E}$

$=17890.0+117600-117573.00-17890.0=27.00 \text{ kg}$

$\text{LEMUF}=2 \cdot \sigma_{\text{MUF}}=160 \text{ kg}$

$\therefore \text{MUF} < \text{LEMUF}$

$\therefore$  Zero true MUF can not be denied at a confidence level of 95%. The uranium balance of the model factory is closed. The true MUF range is:

$-133 \text{ kg} < \text{True MUF} < 187 \text{ kg}$

**Nuclear Safety Guide HAD501/01**  
**Nuclear Material Accountancy of LEU Conversion and Fuel Fabrication Facilities**  
**Appendix A**

Table A2 Calculation examples of  $\sigma_{MUF}$  for uranium at a material balance period of 6 months

Measurement	Material	Type	Method ID	Pieces or volumes affected by error types <sup>(a)</sup>			$\sigma$ (b)			$\sigma^2 \text{kg}^2 \text{U}$		
				Random Error	Short-term Systematic Error	Long-term Systematic Error	Random Error	Short-term Systematic Error	Long-term Systematic Error	Random Error	Short-term Systematic Error	Long-term Systematic Error
Weight	UF6	1	W1	84	17	84	0.40	0.60	0.15	13.44	149.76	158.76
Weight	Scraps	2E	W1	84	17	84	0.40	0.60	0.15	13.44	149.76	158.76
Weight	Sintered pellets (rods)	2A	W14	23400	—	23400	0.30	—	0.20	0.002	—	21.9
Weight	Sintered pellets (rods)	2A	W15	23400	—	23400	0.30	—	0.20	0.002	—	21.9
Weight	Unused powder	3A	W2	270	—	135 (2)	8g	—	6g			
Weight	Hard slag	3C	W2	20	—	10 (2)	8g	—	6g			
Weight	ADU	3G	W2	40	—	20 (2)	8g	—	6g			
Weight	Dirty powder	3I	W2	20	—	10 (2)	—	—	6g			
				$\Sigma$ 350		175 (2)	8g			$\Sigma$ 0.023		$\Sigma$ 2.21
Weight	Unused powder (debris recycling)	3A	W3	270	—	135 (2)	8g	—	6g			
Weight	Raw pellets	3B	W4	20	—	10 (2)	8g	—	6g	0.0013	—	0.007
Weight	Raw pellets	3B	W5	20	—	10 (2)	8g	—	6g	0.0013	—	0.007
Weight	Raw pellets (in pallets)	3B	W6	1000	—	500 (2)	8g	—	6g	0.064	—	18.00
Weight	Sintered pellets (in pallets)	3C	W7	1000	—	500 (2)	8g	—	6g	0.064	—	18.00
Weight	Sintered pellets (in boats)	3D	W8	20	—	10 (2)	8g	—	6g	0.001	—	0.007
Weight	Sintered pellets (in boats)	3D	W9	20	—	10 (2)	8g	—	6g	0.001	—	0.007
Weight	Grinding slurry	3H	W11	20	—	10 (2)	8g	—	6g	0.001	—	0.007
Weight	Grinding slurry	3H	W12	20	—	10 (2)	8g	—	6g	0.001	—	0.007
Weight	U <sub>3</sub> O <sub>8</sub>	3C	W13	500	—	250 (2)	8g	—	6g	0.032	—	4.50
Weight										$\Sigma$ 27.0	$\Sigma$ 299.52	$\Sigma$ 404.07
Sampling	ADU	3G	S1	80	—	—	6%	—	(3.0%) <sup>C</sup>	28.80	—	576.00 <sup>C</sup>
Sampling	Grinding slurry	3H	S2	40	—	—	3%	—	(2%) <sup>C</sup>	5.184	—	92.16 <sup>C</sup>
Sampling	Dirty powder	3I	S3	40	—	—	3%	—	(0.5%) <sup>C</sup>	10.404	—	11.56 <sup>C</sup>
Sampling	Liquid waste	2D	S4	176	—	—	5%	—	15%	1.76	—	2787.74
Sampling										$\Sigma$ 46.184		$\Sigma$ 2787.84

**Nuclear Safety Guide HAD501/01**  
**Nuclear Material Accountancy of LEU Conversion and Fuel Fabrication Facilities**  
**Appendix A**

Continued

Measurement	Material	Type	Method ID	Pieces or volumes affected by error types <sup>(a)</sup>			$\sigma$ (b)			$\sigma^2 \text{kg}^2 \text{U}$		
				Random Error	Short-term Systematic Error	Long-term Systematic Error	Random Error	Short-term Systematic Error	Long-term Systematic Error	Random Error	Short-term Systematic Error	Long-term Systematic Error
Volume	Liquid waste (first line)	2D	V1	1659	—	158(Kg)	5%	—	3%	0.0376	—	22.468
Volume	Liquid waste (second line)	2D	V2	1659	—	158(Kg)	5%	—	3%	0.0376	—	22.468
Volume	Liquid waste (debris recycling)	2D	V3	378	—	36(Kg)	5%	—	3%	0.009 $\Sigma$ 0.08	—	1.166 $\Sigma$ 46.10
U-sample	UF <sub>6</sub>	1	U1	17	—	117432(Kg)	0.013%	—	0.005%	13.74	—	34.475
U-sample	UF <sub>6</sub> Scraps	2C	U1	17	—	—	0.013%	—	0.005%	—	—	—
U-sample	Sintered UO <sub>2</sub> (rods)	2A	U2	488	—	117000Kg	0.02%	0.02	0.015%	1.122	—	308.00
U factor	Unsintered UO <sub>2</sub> (rods)	3A, 3B	U3	—	10920Kg (9 batches)	—	—	0.3%	—	—	119.246	—
U factor	Sintered UO <sub>2</sub> (Inventory)	3C, 3D, 3F	U4	—	14400Kg (12 batches)	—	—	0.3%	—	—	1.555	—
U-sample	U <sub>3</sub> O <sub>8</sub>	3E	U5	—	8500Kg (17 batches)	—	—	0.10%	—	—	4.25	—
U-sample	Grinding slurry	3H	U7	40	—	—	0.04%	—	—	0.001	—	—
U-sample	ADU	3G	U6	80	—	—	0.04%	—	—	0.001	—	—
U-sample	Dirty powder	3I	U8	40	—	—	0.04%	—	—	0.0102	—	—
U-sample	Waste drums	2B	U2351	470	—	188Kg	15%	—	20%	1.692	—	1413.76
U-sample	Filter	2C	U2351	240	—	48Kg	15%	—	20%	0.216	—	92.16
U-sample	Liquid waste	2D	Ug	176	—	352Kg	10%	—	8%	7.04	—	792.0

**Nuclear Safety Guide HAD501/01**  
**Nuclear Material Accountancy of LEU Conversion and Fuel Fabrication Facilities**  
**Appendix A**

Table A3 6-Month Balance Data of Uranium Material

Material Balance Composition	U%	Pieces	kgU/Piece	Total Amount of Uranium (kg)
Transfer-in UF <sub>6</sub>	67.60	84	1400	117600
Transfer-out Rod (UO <sub>2</sub> pellets)	88.10	46800	2.5	117000
Waste drums	—	470	0.4	188
Filter	—	240	0.2	48
Liquid waste	50ppm	176	1.2	211
UF <sub>6</sub> hold-up volume	67.6	84	1.5	126
Inventory*				
Unused UO <sub>2</sub> powder	87.6	300	17	5100
Raw pellets	87.6	20	18	360
Sintered pellets (in pallets)	88.10	1000	6	6000
Sintered pellets (in boats)	88.10	20	18	360
U <sub>3</sub> O <sub>8</sub> Powder	84.5	250	17	4250
Hard slag	88.10	40	21	840
ADU	60.0	40	10	400
Grinding slurry	80.0	20	12	240
Dirty powder	86.0	20	17	340

Note: It is assumed that the opening inventory is equal to the closing inventory to simplify the calculation.



## Module 1

### Measurement Control Program Workshop

#### Objectives and Overview

### Learning Objectives

- To apply results of measurement control programs to determine if Inventory Differences (ID) are significant in the accountability of nuclear material
- To understand the elements of a measurement control program

Module 1 - 2

### Elements of a Comprehensive Measurement Control Program (MCP)

1. Data Quality Objectives
2. Measurement Method Selection & Qualification
3. Traceable Reference Materials (Standards)
4. Physical/Environmental Conditions MC
5. Scales and Balances Program
6. Analytical Quality Control
7. Sampling Verification
8. Statistical Programs & Statistical Control Limits
9. Proficiency Testing Programs
10. Accreditation by Recognized Accrediting Body

Module 1 - 3

### Key Concepts

- Measurements have uncertainty
- Different types of measurement errors
- Methods for estimating the uncertainty of measurement
- National & international standards related to measurements and measurement uncertainty
- Metrology vocabulary definitions
  - International Vocabulary of Basic and General Terms in Metrology (VIM)

Module 1 - 4

## IDs Are Not Zero Because

---

- **Measurement uncertainty: measurement system effects**
  - **Location of material**
    - In calorimeter, on scale, etc.
    - For example, heat distribution, weight distribution, etc.
  - **Calibration of scales**
  - **Fluctuations in air pressure, temperature, etc.**

Module 1 - 5

## IDs Are Not Zero Because

---

- **Measurement uncertainty:**
  - Non-measurement system effects**
    - Power fluctuations
    - Electronic functioning of equipment
    - Non-homogeneity of material being measured
    - Statistical nature of radioactive decay
    - Improper or incomplete background measurements

Module 1 - 6

## IDs Are Not Zero Because

---

- **Sampling effects**
  - Improper or incomplete blending in a destructive analysis sample
- **Nondestructive Analysis (NDA) limitations**
  - Material composition of the NDA standards does not match the material composition of the measured items
  - Failure to account for background effects

Module 1 - 7

## IDs Are Not Zero Because

---

- **Accounting system effects**
  - Better measurement to correct estimates
  - Decay, rounding errors, etc.
- **Human error**
  - Clerical mistakes (transcription errors, etc.)
  - Failure to follow procedures

Module 1 - 8

## IDs Are Not Zero Because

- **Unmeasured streams or inventories**
  - Solids entrained in liquid systems settle in tanks
  - Holdup can take the form of material associated with specific equipment
- **Factors or estimates**

Module 1 - 9

## MCP Element #1 Data Quality Objectives

- The IAEA's International Target Values (ITVs) for uncertainty components in measurements of nuclear material should be considered
- **Maximum Permissible Error VIM 4.26 (5.21) limit of error**
  - Extreme value of measurement error, with respect to a known reference quantity value, permitted by specifications or regulations for a given measurement, measuring instrument, or measuring system
    - NOTE 1 Usually, the term "maximum permissible errors" or "limits of error" is used where there are two extreme values
    - NOTE 2 The term "tolerance" should not be used to designate 'maximum permissible error'
- **Target Uncertainty VIM 2.34**
  - Measurement uncertainty specified as an upper limit and decided on the basis of the intended use of measurement results

Module 1 - 10

## MCP Element #2 Measurement Method Selection and Qualification

- Method selections are based on target values
- A documented method is used on an identified periodic basis to ensure that a measurement method shall demonstrate acceptable performance before being used for performing accountability measurements
- **Verification VIM 2.44**
  - Provision of objective evidence that a given item fulfills specified requirements
- **Validation VIM 2.45**
  - Verification, where the specified requirements are adequate for an intended use

Module 1 - 11

## MCP Element #3 Traceable Reference Materials (Standards)

- Calibration and working standards are traceable, as well as representative of the type and composition of the material being measured when the matrix affects the measured values
  - Such standards will have smaller uncertainties associated with their reference values than the uncertainties of the measurement method in which they are used. Should be < 1/3 of the method's uncertainty.
- **Metrological traceability VIM 2.41 (6.10)**
  - Property of a measurement result whereby the result can be related to a reference through a documented unbroken chain of calibrations, each contributing to the measurement uncertainty.

Module 1 - 12

#### MCP Element #4

##### Physical/Environmental Conditions Measurements & Control

- The desired quality of measurements may require adequate control of environmental conditions or correcting measurements to standard conditions.
- The precision and accuracies of volume and density as well as environmental temperatures, pressure, and humidity measurements are determined and assured where applicable.
- Environmental parameters are specified for various measurement method in national standards and guides.

Module 1 - 13

#### MCP Element #5

##### Scales and Balances Program

- This program should include:
  - Selection of weighing equipment “fit for purpose”
  - OIML R 76-1, 3.7.1 "The standard weights or standard masses used for the verification of an instrument shall not have an error greater than 1/3 of the maximum permissible error of the instrument for the applied load"
  - Selecting standards with  $\leq 1/3$  the uncertainty of the balance load being tested
  - Periodic independent calibration & maintenance
  - Accuracy checks prior to and after scales or balances are used for MC&A measurements and
  - Routine statistical evaluation QC data to evaluate performance & calculate current uncertainty estimates and control limits.

Module 1 - 14

#### MCP Element #6

##### Analytical Measurement Control Programs

- Analytical Measurement Control Programs include:
  - Standards preparation for:
    - Calibration,
    - Measurement quality control (QC),
    - Analyst training & testing and
    - Method validation.
  - MC programs for measurement system verification, (QC standard measurements are within control limits) before making measurements for accountability or process control.
  - Data from the assay of known and unknown QC standards samples are used to calculate new uncertainty estimates & control limits.

Module 1 - 15

#### MCP Element #7

##### Sampling Verification

- The uncertainty associated with each sampling method is determined and monitored. Multiple samples are used to validate homogeneity.
- Comparison of density measurements on sequential samples drawn from a tank can assure adequate mixing and representative samples.
- ITVs address sampling uncertainties in the computation of uncertainty of accountability measurements.

Module 1 - 16

## MCP Element #8 Statistical Programs and Control Limits

- **Statistical Program**

A documented program for the statistical evaluation of measurement data for determining control limits, calibration limits, and precision and accuracy levels for each measurement system used for accountability. The objective is to ensure the quality of measurement and measurement control data and to provide estimates of uncertainty on inventory and inventory control

- **Statistical Control Limits**

Control limits are calculated and monitored with documented procedures in place to address out-of-control conditions for processes and measurement systems

- For example, limits are established so that the measurement system is not used for accountability measurements until the system is demonstrated to be within statistical control

Module 1 - 17

## MCP Element #9 Proficiency Testing

- Participation in inter-laboratory sample exchange programs provides external validation of measurement system performance.
- **Training:** Each facility shall have a documented plan for the training of measurement personnel. It shall specify training, qualification, and requalification requirements for each measurement method.
- Qualification program shall ensure measurement personnel demonstrate acceptable levels of proficiency before performing measurements, and are re-qualified according to requirements in the training plan.

Module 1 - 18

## MCP Element #10 Accreditation

- **Performed by a formal accrediting body to recognized international standards (ISO 17025 General requirements for the competence of testing and calibration laboratories)**
- **International Laboratory Accreditation Cooperation (ILAC) promotes acceptance of accredited test & calibration laboratories**
  - Accreditation bodies must meet the requirements and accepted as signatories to the ILAC Mutual Recognition Arrangement. Each accreditation body that is a signatory to the Arrangement agrees to abide by its terms and conditions and by the ILAC evaluation procedures

Module 1 - 19

## Summary

- Introduced how the results of measurement control programs to determine if Inventory Differences (ID) are significant for accountability of nuclear material
- Introduced the basic elements of a measurement control program

Module 1 - 20



## Module 1 Exercise

### Hypothetical Facility Overview

### Objectives

- Understand the Facility and Process that will be used as the teaching basis for the workshop.
- Understand the MBA Division and Key Measurement Points .
- Understand the physical (e.g., powder, gas, sintered pellet, etc.) and chemical (e.g., oxide, fluoride, etc.) forms of LEU in the process.
- Understand the Measurement Methods applicable to the facility and process.

### Reference

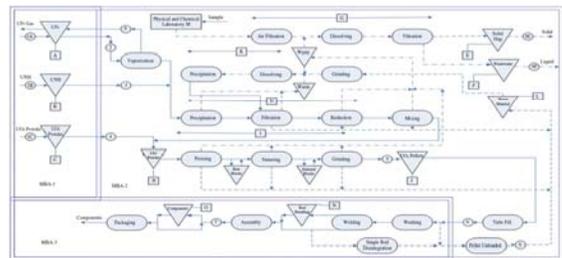
*Note: See handout*

“Nuclear Safety Guide HAD501/01

Nuclear Material Accountancy of  
LEU Conversion and Fuel Fabrication Facilities

Appendix A”

### Process Diagram and Flow MBA Division and Key Measurement Points



### Description of Key Measurement Points

*Note: Refer to Table A1-1 in Handout*

- Column 1 – Identifier of KMP – relates to diagram of process
- Column 2 – Description of the process step
- Column 3 – Material Type – chemical and/or physical form
- Column 4 – Sampling method
- Column 5 – Measurement method

### Description of Inventory at KMPs

*Note: Refer to Table A1-2 in Handout*

- Column 1 – Identifier of KMP – relates to diagram of process
- Column 2 – Description of the process step
- Column 3 – Material Type – chemical and/or physical form
- Column 4 – Sampling Method
- Column 5 – Measurement method

### Description of Measurement Methods

*Note: Refer to Section A.2 in Handout*

- Gravimetric method, for determination of uranium factor in  $UF_6$ ,  $UO_2$ , pellets and scraps
- $K_2Cr_2O_7$  Redox titration method: for determination of uranium percentage in slag and waste
- Mass spectroscopy, for determination of U-235 enrichment
- Fluorescent spectrometry, for determination of uranium concentration in liquid waste
- Non-destructive assay (NDA): for determination of uranium concentration in solid waste
- Volume measurement
- Mass measurement

### Description of Measurement Errors

*Note: Refer to Table A.2 in Handout*

< Discussion >

### Other information

*Note: Refer to Table A.3 and Calculation in Section A.2 in Handout*

**This information will be used in the final module on Friday:**

- Table A.3 – Six Month Balance Data of Uranium Material
- MUF Calculation – End of Section A.2

### Summary

- Reviewed the Facility and Process that will be used as the teaching basis for the workshop.
- Reviewed the MBA Division and Key Measurement Points .
- Reviewed the physical (e.g., powder, gas, sintered pellet, etc.) and chemical (e.g., oxide, fluoride, etc.) forms of LEU in the process.
- Reviewed the Measurement Methods applicable to the facility and process.



## Module 1-2

### U.S. Department of Energy Requirements and other References

### Objectives

- To understand the DOE requirements for measurement and measurement control programs
- To understand the facility measurement and measurement control program and its relationship to DOE requirements
- To introduce US and international standards related to measurement control programs and measurement uncertainty [ANSI (15.51), ISO(17025), BIPM (GUM), STR (IAEA Target Values), etc.]

Module 1-2 - 2

### DOE requirements for measurement & measurement control programs

- DOE Order 474.2, approved 6-27-2011 "Nuclear Material Control and Accountability"
- DOE Standard 1194-2011, approved June 2011 "Nuclear Materials Control and Accountability"

Module 1-2 3

### DOE Order 474.2, approved 6-27-2011 "Nuclear Material Control & Accountability"

Attachment 1."Contractor Requirements Document DOE 474.2 Nuclear Material Control And Accountability"

#### (3) Measurement Objectives.

- (a) The measurements program must provide measured values with uncertainties sufficient to detect theft or diversion of nuclear material.
- (b) The measurement control program must assure the quality of measurements made for MC&A purposes.

Module 1-2 4

### (3) Measurement Objectives. (Continued)

#### 3. MEASUREMENTS METRICS.

*The measurement program element provides quantitative and qualitative data about nuclear materials* for accounting, inventories, and transfers. Measured values are essential for establishing category levels and determining protection requirements for nuclear materials.

- a. The quantity of all nuclear material types present on inventory is determined using identified measurement systems, measurement services, technically justified values or accepted shipper's values when approved by the DOE line management.

Module 1-2 5

### 3. MEASUREMENTS METRICS (Continued)

- b. *Measurements and measurement uncertainties are determined and reported for each measured value using methodologies and statistical terminology accepted by voluntary consensus standards bodies.* Other methodologies are only used with sufficient justification and approved in the MC&A plan.
- c. *Sources of measurement error* that are key contributors to the total measurement limit of error for a material balance period are identified and used to estimate systematic and random errors.
- d. Before use (beginning of the work day), the proper functioning of measurement systems is checked against standards.

Module 1-2 6

**3. MEASUREMENTS METRICS** (Continued)

- e. Key measurement points are established during construction of or changes to process lines, and documented in project documentation. Key measurement points are included in operational (process and transfer) procedures.
- f. The site/facility operator demonstrates that uncertainties remain applicable and are consistent with target values established by the site.
- g. Measurement methods are qualified, formally documented, periodically validated, and approved in the MC&A plan.

Module 1-2 7

**3. MEASUREMENTS METRICS** (Continued)

- h. Potential sources of sampling error for bulk measurements are identified and samples are representative of the materials being sampled. If sampling is required to establish accountability measurements, the program describes how the representativeness/homogeneity is determined and periodically tested or updated.
- i. Capability exists to confirm type and quantity of nuclear material present. For each type of nuclear material at the site, measurement methods are identified which are capable of confirming presence of nuclear materials and verifying nuclear material quantities. Nuclear materials not amenable to verification measurement must be identified and documented in the MC&A Plan.

Module 1-2 8

**3. MEASUREMENTS METRICS** (Continued)

- j. Measurements are traceable to the National Institute of Standards and Technology (NIST) or New Brunswick Laboratory (NBL) standards.
- k. Measurement systems are calibrated on a defined frequency, including the frequency and methodology for recertifying the measurement standards.
- l. The measurement program identifies target values for each MC&A measurement method, referencing national and international sources as applicable and defines the methodology, including frequency, by which uncertainties are compared to the target values and performance is assessed.

Module 1-2 9

**3. MEASUREMENTS METRICS** (Continued)

- m. A methodology exists for ensuring that measurement systems are in control when accountability measurements are made, and evidence exists that accounting values are established only when measurement systems are in control.
- n. A statistical control system exists that includes establishing control limits, determining out-of-control conditions, returning control to out-of-control measurement systems, and analyzing trends and outliers.
- o. The technical basis for the measurement and measurement control program is documented, and the documentation is either included or referenced in the MC&A Plan.

Module 1-2 10

**DOE Standard for NMC&A  
DOE-STD-1194-2011 dated June 2011.**

- The Technical Standard provides an acceptable MC&A approach commonly or typically used throughout the DOE and NRC.
- In the final analysis, DOE line management reviewer make a judgment as to whether the site/facility operator can achieve, with high probability, the objectives stated in DOE O 474.2.”

Module 1-2 11

**DOE-STD-1194-2011** (Continued)

6.1.4.2 Measurements Training

- Training plan that covers personnel who make measurements (e.g., DA, NDA, sampling, process measurements etc.)
- Performance criteria for the personnel making the measurements
- Covers periodic qualification and requalification as part of the measurement control plan for a KMP
- Personnel shall be knowledgeable of the standards and their values for each measurement system. Where sampling of bulk material is necessary, personnel shall be familiar with the sampling and sub-sampling programs

Module 1-2 12

**DOE-STD-1194-2011** (Continued)

**6.3.1 Specifications [Measurements] (Types) Three types of measurements are used for accountability purposes:**

- Accountability measurements shall be used to establish initial values for nuclear materials and to replace existing values with more accurate measured values.
- Verification measurements shall be used to validate the accounting system values when necessary, e.g., at time of physical inventory for non-tamper-indicating items or in response to a security anomaly that could have resulted in a theft or diversion of nuclear material.
- Confirmation measurements shall be used to validate the presence of nuclear material for transfers, and to determine nuclear material presence under anomalous conditions.

Module 1-2 13

**DOE-STD-1194-2011** (Continued)

**6.3.2 Measurement Methods & Procedures**

- When a weight or mass measurement method is used for accountability purposes, a daily check of both accuracy and linearity shall be performed.
- Accountability measurement methods shall be selected to minimize the uncertainty of the inventory difference, maximize the loss detection sensitivity of the MC&A system, and assure the quality of the measurement results consistent with the consequences of the loss of the material.
- Target values for precision and accuracy, established and approved by DOE line management, shall be used as performance goals.
- All measurement systems generating accountability values shall be in the measurement control program.
- A measurement control program shall quantify the random and systematic errors in all quantitative measurements used to assess the statistical significance of inventory differences and shipper/receiver differences.

Module 1-2 14

**DOE-STD-1194-2011** (Continued)

- Target values for precision and accuracy, established and approved by DOE line management, shall be used as performance goals. Performance during qualification shall be documented to validate that the method can be performed with the material types for which the method is qualified
- 6.3.4.1 All measurement systems generating accountability values shall be in the measurement control program.
- 6.3.4.2 A measurement control program shall quantify the random and systematic errors in all quantitative measurements used to assess the statistical significance of inventory differences and shipper/receiver differences.

Module 1-2 15

**The Guide to the Expression of Uncertainty in Measurement (GUM)**

Published in 1993 by ISO in the name of BIPM, IEC, IFCC, ISO, IUPAC, IUPAP and OIML.

1. Promote full information on how uncertainty statements are arrived at and,
2. Provide a basis for the international comparison of measurement results

Current documents:

- JCGM 100:2008 is current GUM Guide
- JCGM 104:2009 is an intro to the GUM Guide
- JCGM 200:2008 is the current VIM

Module 1-2 16

**ANSI/INMM N15.51-2012 for Methods of Nuclear Materials Control --Measurement Control Program – Nuclear Materials –Analytical Chemistry Laboratory**

- Guide for setting up an analytical laboratory measurement control program
- It was based on ANSI/INMM 15.41-1984 “derivation of measurement control programs – general principle”
- Provides basic principles which address both technical and administrative aspects of measurement processes.

Module 1-2 17

**Other Reference Documents**

- ISO/IEC 17025 “General requirements for the competence of testing & calibration laboratories”
- ISO 9001/9002 contains requirements for calibration, inspection and testing.
- American National Standards for Calibration ANSI/NCSL Z540-1-1994 “Calibration Laboratories and Measuring and Test Equipment - General Requirements”
- IAEA STR – 368 “International Target Values for Measurement Uncertainties in Safeguarding Nuclear Materials”, Vienna, November 2010 (ITVs)

Module 1-2 18

## Summary

---

- Reviewed the DOE requirements for measurement and measurement control programs
- Discussed the facility measurement and measurement control program and its relationship to DOE requirements
- Introduced US and international standards related to measurement control programs and measurement uncertainty [ANSI (1551), ISO(17025), BIPM (GUM), STR (IAEA Target Values), etc.]

Module 1 -2 19

# **Answer for Module 2 Slide 17**

## **Exercise – Calculate the mean**

---

**Our metrologist weighed a 100 gram mass standard 20 times. The results are shown in the table below. Based on the formulas presented previously, calculate the mean weight.**

100.64	97.55	100.62	110.00	100.67
99.11	102.22	107.40	112.58	101.14
95.41	106.86	103.77	98.53	99.59
93.91	101.17	104.28	96.99	108.41

**Answer:  $\bar{X} = 102.04$**

# Answer for Slide Module 2 Slide 35

i	$X_i$	$(X_i - \bar{X})^2$
1	100.64	1.97
2	99.11	8.60
3	95.41	43.99
4	93.91	66.14
5	97.55	20.18
6	102.22	0.03
7	106.86	23.21
8	101.17	0.76
9	100.62	2.02
10	107.40	28.70
11	103.77	2.98
12	104.28	5.01
13	110.00	63.32
14	112.58	111.04
15	98.53	12.34
16	96.99	25.53
17	100.67	1.88
18	101.14	0.81
19	99.59	6.01
20	108.41	40.55

Variance 465.08

Std. Dev. 21.57

# Answers for Module 2 Slide 37

---

**Calculate the mean, variance, and standard deviation for the Technician 1 and Technician 2**

	Technician 1	Technician 2
Mean	105.19	99.63
Variance	3.63	21.05
Standard Deviation	1.91	4.59

# Answers for Module 2 Slide 37

---

**Technician 1 is the least accurate but most precise so potentially the better candidate. This is assuming you can quantify and correct their measurement bias.**

## **Notes:**

- **Typically it is easier to correct and/or manage bias in a process than to reduce the variability of Technician 2.**
- **Regardless a review of each technician's technique compared to a qualified technician will typically provide insight into the cause of each technician's errors.**

Observation Weighing Number:	Measurement Value
1	100.64
2	99.11
3	95.41
4	93.91
5	97.55
6	102.22
7	106.86
8	101.17
9	100.62
10	107.40
11	103.77
12	104.28
13	110.00
14	112.58
15	98.53
16	96.99
17	100.67
18	101.14
19	99.59
20	108.41
Average	
Variance	
Standard Deviation	

*Note: Insert average Excel Function in the cell to the left*

*Note: Insert Variance Excel Function in the cell to the left*

*Note: Insert Standard Deviation Excel Function in the cell*

*for data in rows B2 through B21 (reference slide 2-17)*  
*for data in rows B2 through B21 (reference slide 2-31)*  
*to the left for data in rows B2 through B21 (reference slide 2-31)*

Observation	Technician 1	Technician 2
1	105	95
2	102	95
3	102	99
4	105	102
5	106	97
6	107	107
7	108	98
8	108	103
9	104	101
10	105	103
11	107	109
12	104	100
13	103	100
14	105	91
15	107	98
16	105	96
Mean/Average		
Variance		
Standard Deviation		
BIAS (target = 100)		

*Note: Insert average Excel Function in the cell.*

*Note: Insert Variance Excel Function in the cell.*

*Note: Insert Standard Deviation Excel Function in the cell.*

*Note: Value for BIAS = target (100 grams) - "I"*

*Is to the left (e.g., B18 and C18 selecting data in rows 2-17 for columns B and C respectively)*  
*Is to the left (e.g., B19 and C19 selecting data in rows 2-17 for columns B and C respectively)*  
*in the cell to the left (e.g., B20 and C20 selecting data in rows 2-17 for columns B and C respectively)*  
*Mean/Average"*



# **Module 2**

---

# **Statistics Review**

# Objectives

---

- Review basic statistical terms and concepts
- Review Mean/Average and how it is calculated
- Review the concept of a “Probability Distribution” and the Normal Distribution
- Review Variance and Standard Deviation and how they are calculated
- Review the concepts of “Bias” and “Fit for Purpose”
- Review how to add random error from multiple sources
- Review how the magnitude of an error affects the total error

# Populations

---

**A population is the complete set of elements to be studied.**

**Examples:**

- All measurements made with a particular instrument or method
- All analyses performed by a certain technician
- All uranium destructive analyses made by a certain laboratory over a given time period
- All items created by a particular process

# Parameters

---

**A parameter is a numeric result that describes the population.**

**Examples:**

- **Concentration of uranium in the process solution**
- **Ratio of Pu/U in a mixed oxide**
- **Amount of Pu in a container**

**Parameters are typically unknown.**

# Samples

---

- **The only way to know the exact value of a parameter is to examine every element in the population.**
- **Typically it is not feasible to look at every element so samples are taken from the population or an attribute is observed that correlates to the parameter in which we are interested.**

# Data

---

- **The sample is observed or measured in some fashion.**
- **Data results from observations or measurements.**

# Statistics

---

- **Data is summarized to provide statistics.**
- **A statistic is a numeric result that describes a sample.**
- **Statistics are used to estimate unknown parameters.**

# Estimation and Confidence Intervals

---

- **Calculated statistics will rarely equal the exact value of an unknown parameter so uncertainty is reported with any parameter that is estimated.**
- **Confidence intervals are a range of values that contain the unknown parameter within a stated confidence level.**
  - **Example: Based on the measurements taken, we are 95% confident that the uranium content of the item is between 1,500 and 1,900 grams.**

# Statistical Inference

---

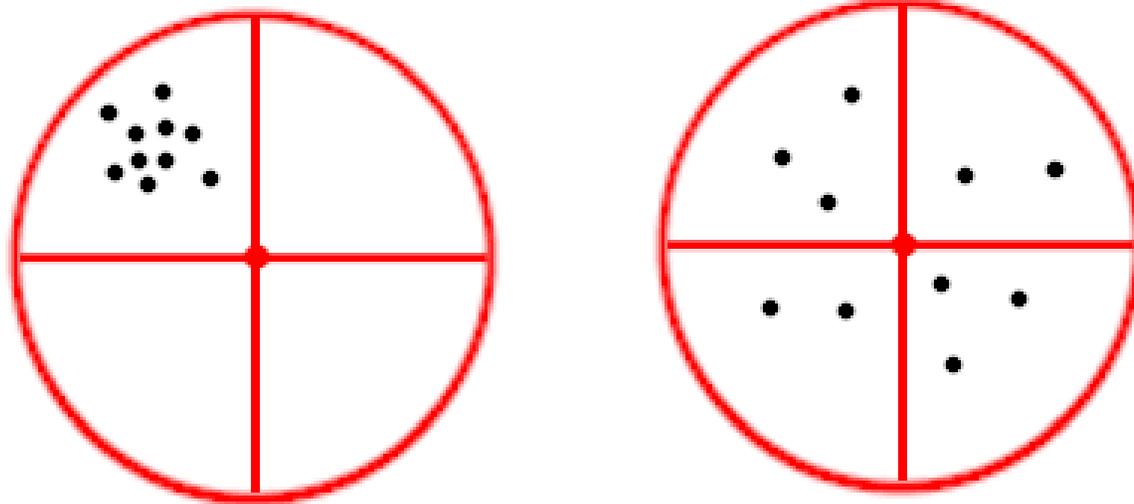
## Statistical inference supports the decision making processes

- Is the average weight of an item from a particular process equal to 1.5kg (e.g., manufacturing tolerance)?
- Is the inventory difference significantly different from zero (e.g., Safeguards and Safety question)?
- Is a measurement method meeting the accuracy and precision requirements established for it?
- Is a new technician able to meet the job requirements for making uranium analyses?

# Accuracy and Precision are two important characteristics of measurements

---

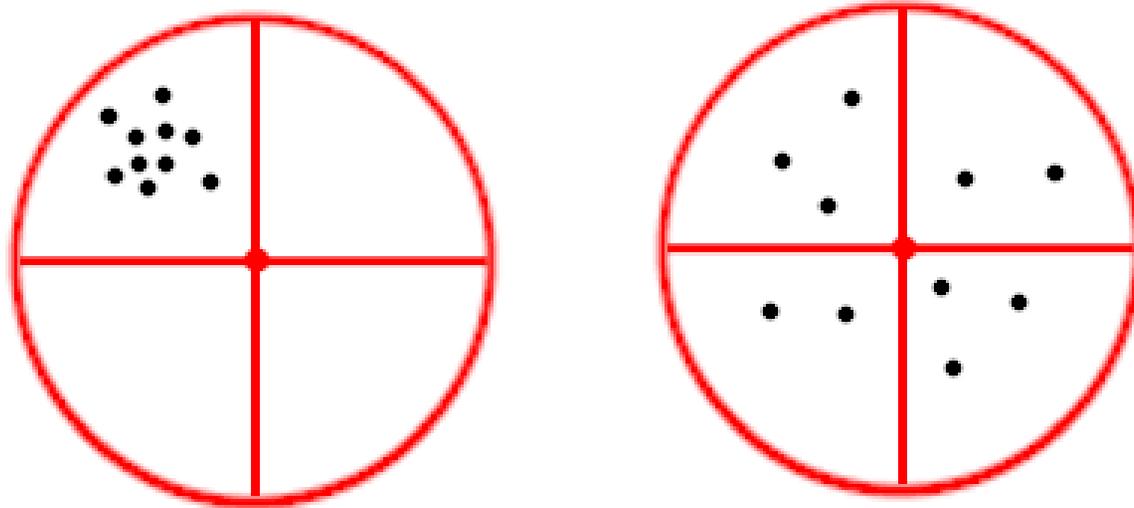
- If the process mean or average is close to the target center, it is said to be accurate.
- If the process has little variation, it is said to be precise. Another term used is dispersion.



# Accuracy and Precision – cont'd.

---

- The shooter on the right is the most accurate. Although the shots are widely scattered, the mean or average is close to the target center.
- The shooter on the left has the least variation between shots and is thus more “precise”. This shooter’s shots are less dispersed.



# Measures of Central Location (i.e., accuracy)

Measure	Description	Formula	Excel Function
Mean/Average	The sum of the sample values divided by the sample size. The sample statistic $\bar{x}$ is an unbiased estimate of the population $\mu$ .	$\bar{x} = \frac{\sum_{i=1}^{i=n} x_i}{n}$	=AVERAGE(data_range)
Median	The middle value after the sample values have been sorted into order by magnitude. If there are an even number of values in the sample, the average of the two middle values.		=MEDIAN(data_range)
Mode	The most common value in the sample.		=MODE(data_range)

# Measures of Dispersion (i.e., precision)

Measure	Description	Formula	Excel Function
Range	The difference between the largest and smallest values in the sample.		=MAX(data_range)-MIN(data_range)
Variance	An estimate of the variation or dispersion of the process from which the sample is drawn. The sample statistic “S <sup>2</sup> ” is an unbiased estimate of the population parameter $\sigma^2$ .	$s^2 = \frac{\sum_{i=1}^{i=n} (x_i - \bar{x})^2}{n - 1}$	=VAR(data_range)
Standard Deviation	The square root of the variance. Often preferred as a measure of the process variation. The sample statistic “s” is an estimator of the population parameter $\sigma$ . This method of calculating the standard deviation is known as the Root Mean Square Error (RMSE) method.	$s = \sqrt{\frac{\sum_{i=1}^{i=n} (x_i - \bar{x})^2}{n - 1}}$	=STDEV(data_range)

# Part 2

---

**Calculating Measures of Central Location  
(e.g., average or mean)**

**Mean or Average** – The sum of all values being considered divided by the total number of values in the set.

---

**Calculate the mean of the 5 numbers below:**

1 8 3 6 2

**Formula:**

$$\text{Xbar (e.g., Mean)} = \frac{X_1 + X_2 + X_3 + \dots + X_n}{n}$$

**OR**

$$\bar{x} = \frac{\sum_{i=1}^n x_i}{n}$$

**Mean or Average** – The sum of all values being considered divided by the total number of values in the set.

---

**Calculate the mean of the 5 numbers below:**

**1 8 3 6 2**

**Answer:**

$$\text{XBar} = \frac{1+8+3+6+2}{5} = 4$$

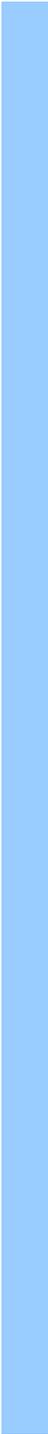
# Exercise – Calculate the mean

---

**Our metrologist weighed a 100 gram mass standard 20 times. The results are shown in the table below. Based on the formulas (or Excel function) presented previously, calculate the mean weight.**

100.64	97.55	100.62	110.00	100.67
99.11	102.22	107.40	112.58	101.14
95.41	106.86	103.77	98.53	99.59
93.91	101.17	104.28	96.99	108.41

**Note: Use the “Spreadsheet 1 Module 2” to calculate the average or mean.**



---

**< See Answer Handout >**

# Part 3

---

**Calculating Measures of Dispersion  
Variance and Standard Deviation  
(Random Error)**

# How were the weight measurements dispersed from the previous exercise?

---

Our metrologist weighed a 100 gram mass standard 20 times. The results are shown in the table below.

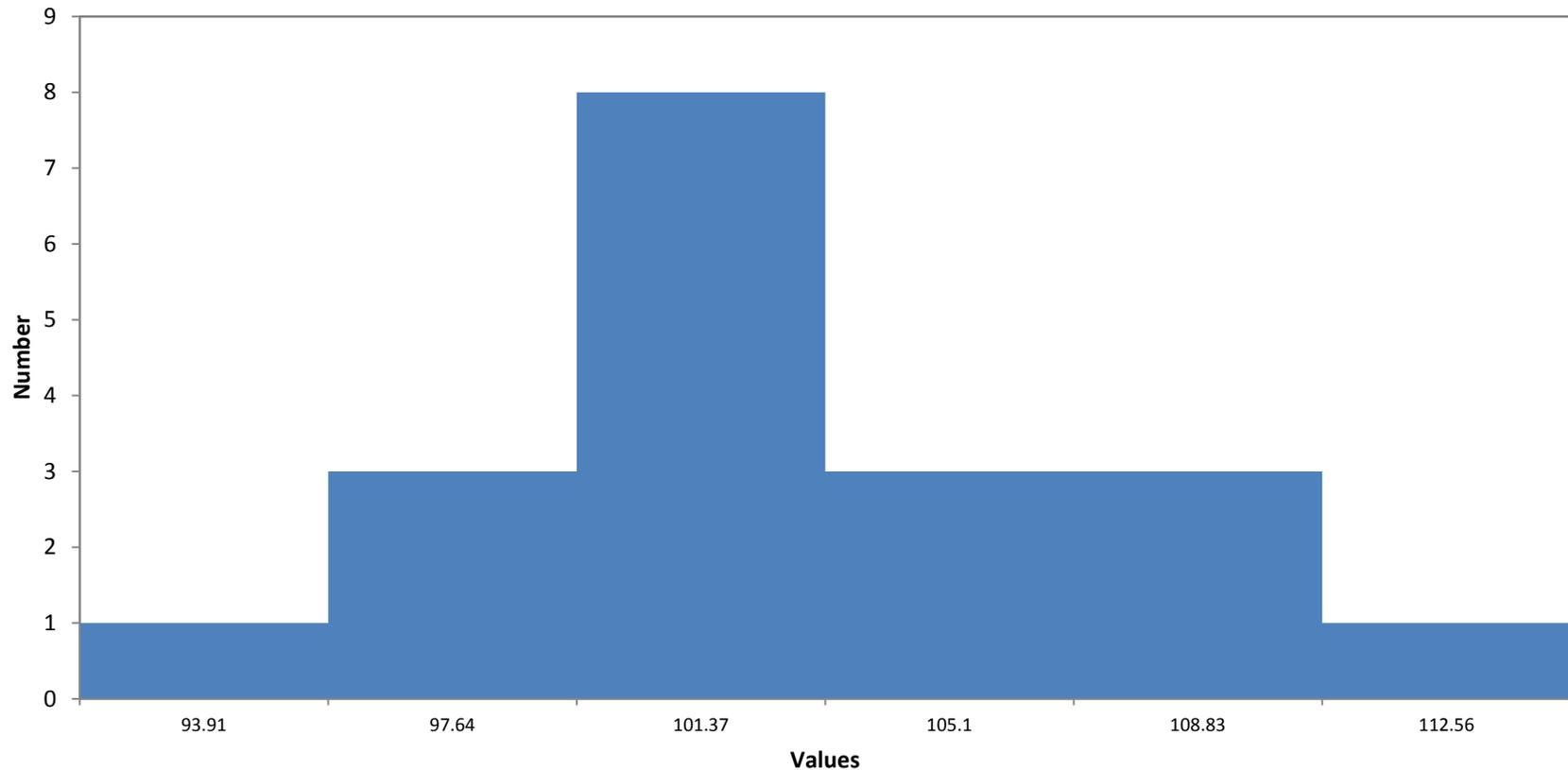
100.64	97.55	100.62	110.00	100.67
99.11	102.22	107.40	112.58	101.14
95.41	106.86	103.77	98.53	99.59
93.91	101.17	104.28	96.99	108.41

**X-Bar = 102.04**

# Histograms are a way to show variation (precision) graphically

---

Histogram of Weight Measurements



# Example histogram/distribution summing the rolling of 2-5 dice

---



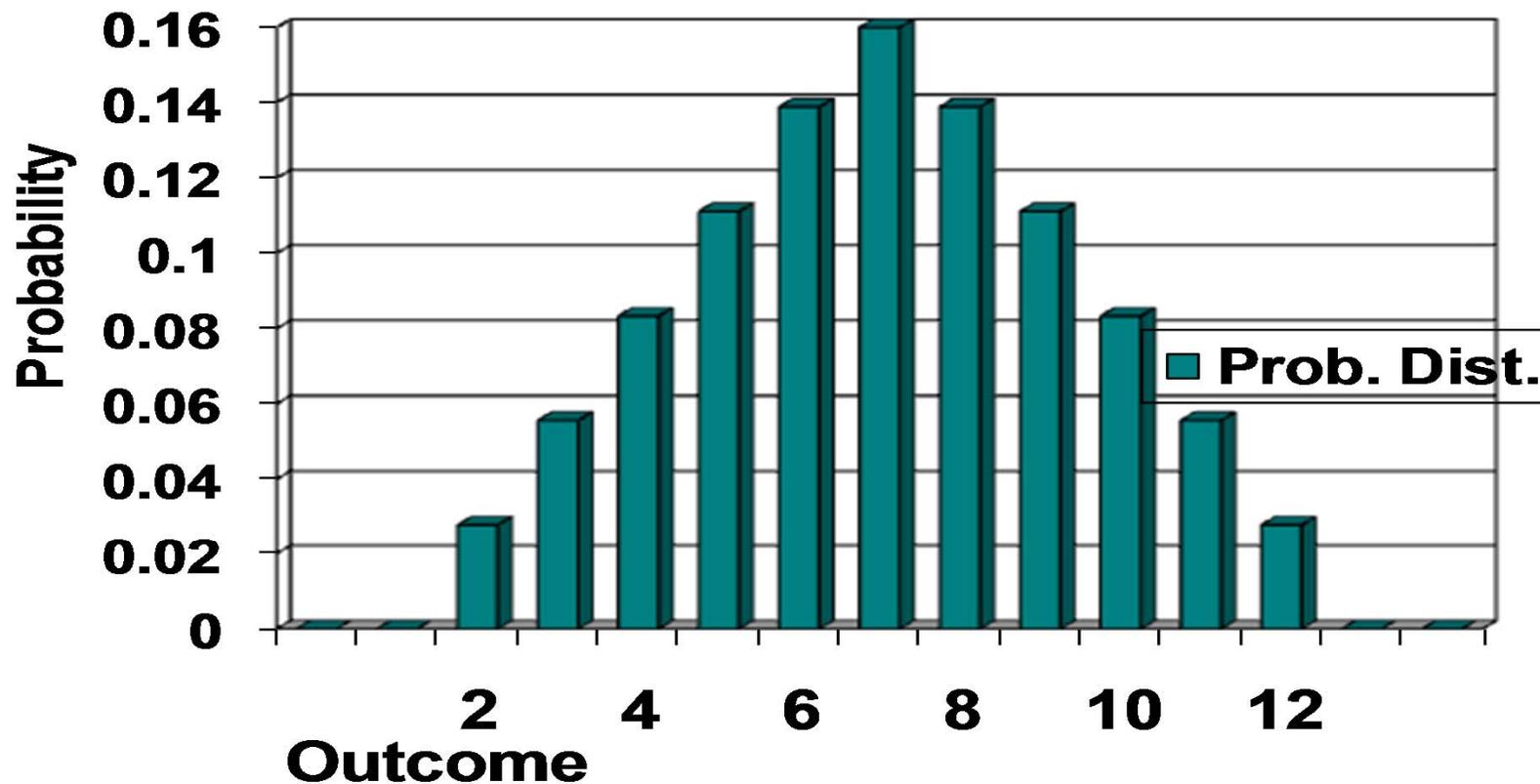
## Probability Distribution for rolling Dice

- Roll dice 30 times.
- Record the outcomes in column one on the table.
- Record the sum of the two dice in column two.
- Tabulate the frequencies.
- Plot the data on the histogram.
  
- REPEAT for 3 dice
- REPEAT for 5 dice

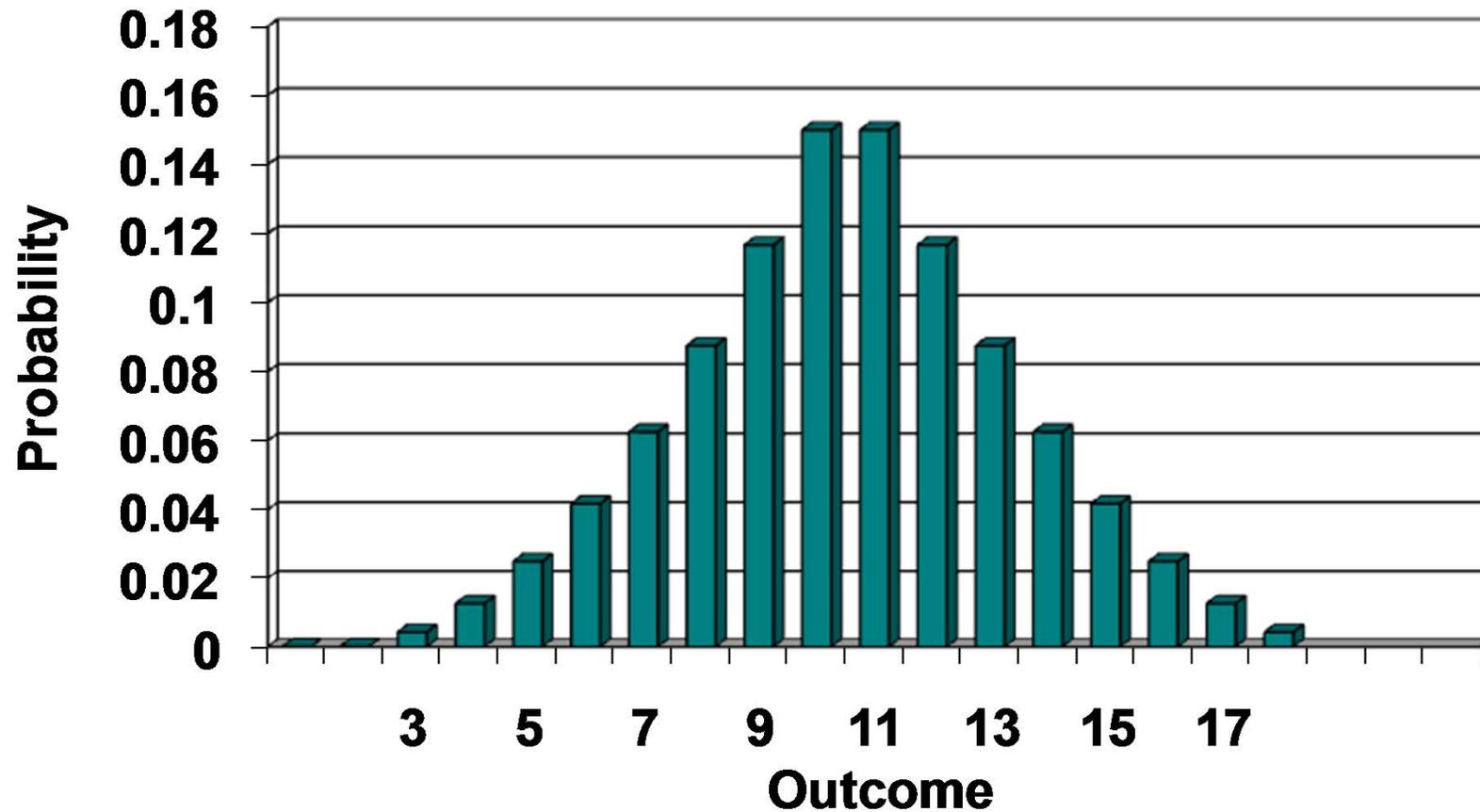
# Two Dice



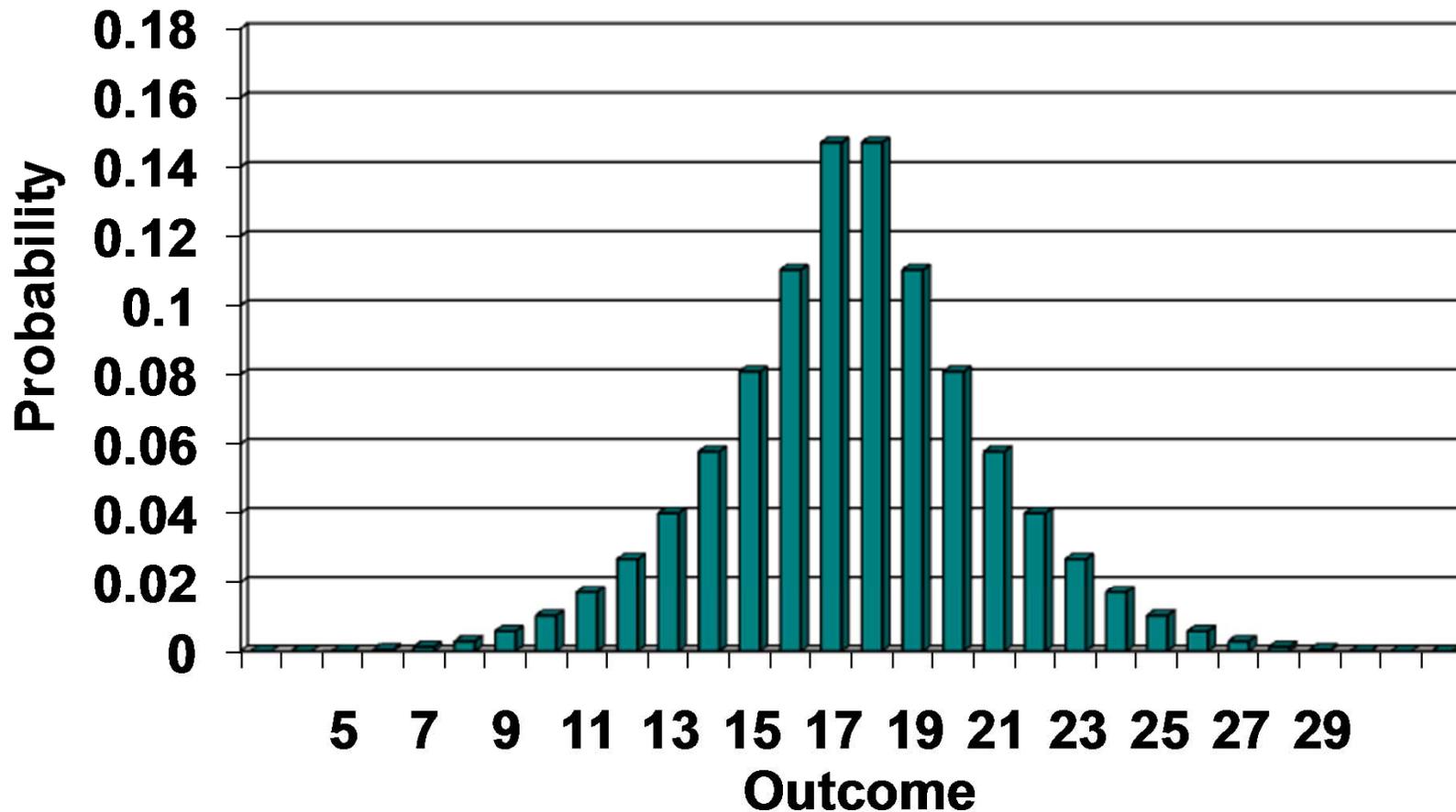
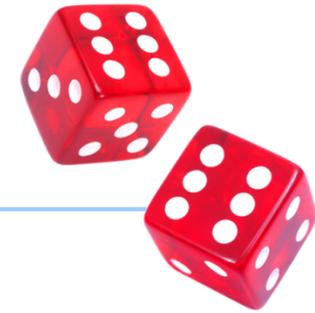
## Probability Distribution for Two Dice



# Probability Distribution for Three Dice



# Probability Distribution for Five Dice



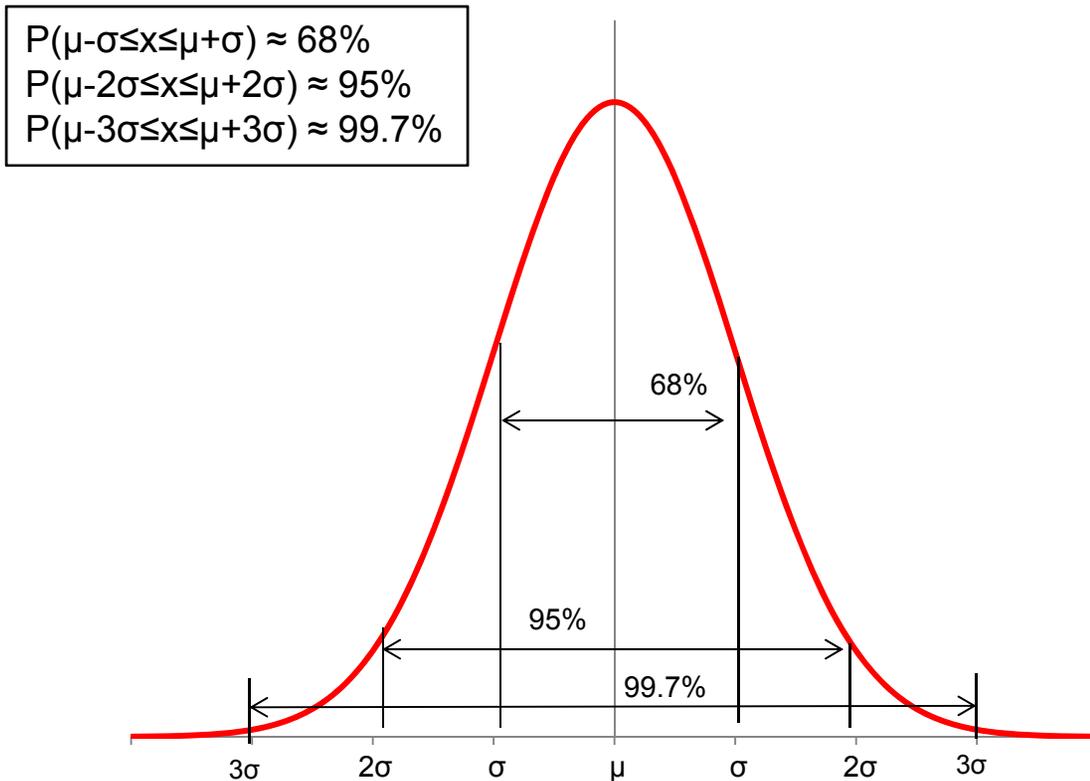
**Measurement control requires a “hard number” for variation (precision) to objectively compare and manage measurement processes.**

---

- **Variance** – An estimate of the variation or dispersion of the process from which the sample is drawn. The sample statistic “ $s^2$ ” is an unbiased estimate of the population parameter  $\sigma^2$ .
- **Standard Deviation** – The square root of the variance. Often preferred as a measure of the process variation. The sample statistic “ $s$ ” is an estimator of the population parameter  $\sigma$ . This method of calculating the standard deviation is known as the Root Mean Square Error (RMSE) method.

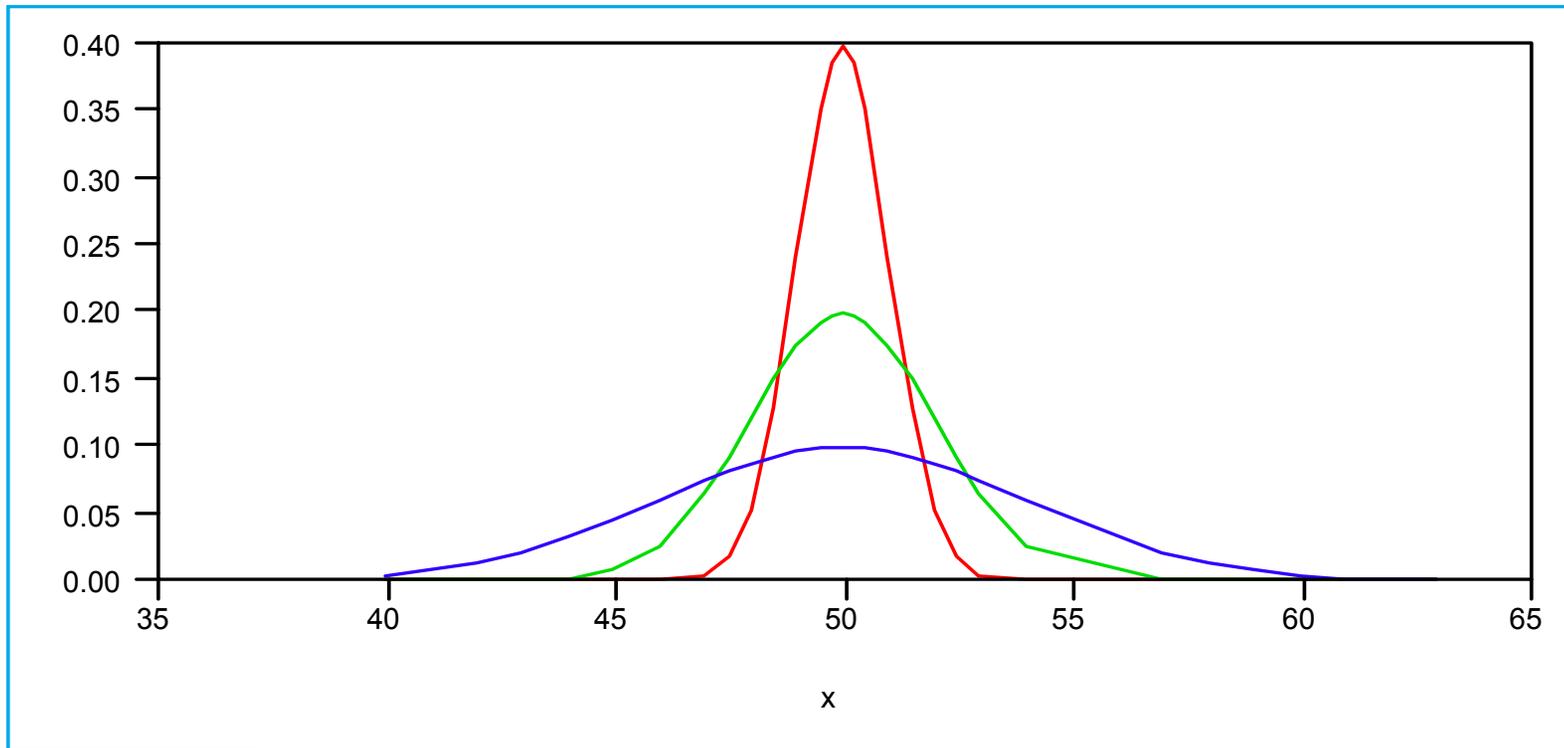
**The Normal Distribution and the math behind it are used to transition the “histogram” into a hard number describing dispersion (precision).**

---

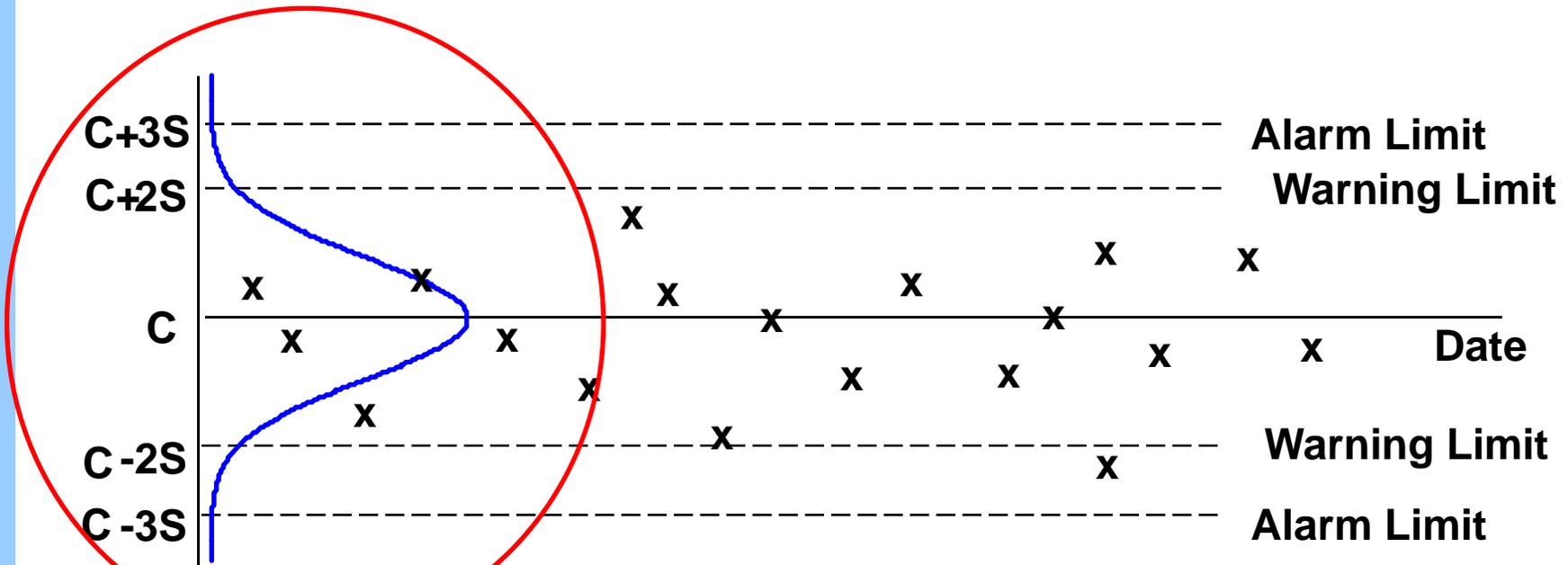


# Normal Distribution with different amounts of dispersion (precision).

Three Normal distributions with the same mean or average, but different levels of precision



# *“Look ahead “* to module on Control Charts



- Generally, 95% of the measurement control data should fall between  $C \pm 2s$
- Generally, 99.7% of the measurement control data should fall between  $C \pm 3s$

# Calculation of the Variance

---

Calculate the variance of the 5 numbers below:

1   8   3   6   2

Formula:

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

# Calculation of the Variance 1 of 2– cont'd

---

1) Index	2) Data	3) Mean	4) Difference between data values and the mean	5) The square of column 4
i	$X_i$	Xbar	$(X_i - \text{Xbar})$	$(X_i - \text{Xbar})^2$
1	1	4	-3	9
2	8	4	4	16
3	3	4	-1	1
4	6	4	2	4
5	2	4	-2	4

$$\sum_{i=1}^{i=n} (x_i - \bar{x})^2 = 34$$

## Calculation of the Variance 2 of 2 – cont'd

---

$$s^2 = \frac{\sum_{i=1}^{i=n} (x_i - \bar{x})^2}{n-1} = \frac{34}{5-1} = 8.5$$

# Standard Deviation – square root of the Variance

---

- The reason the standard deviation is usually preferred because it is in the same units as the original data, not “square units”.
- The statistic is represented by “s”. The corresponding process parameter is called “ $\sigma$ ” (sigma).

$$s = \sqrt{\frac{\sum_{i=1}^{i=n} (x_i - \bar{x})^2}{n-1}}$$

# Calculation of the Standard Deviation – cont'd

---

$$s = \sqrt{\frac{\sum_{i=1}^n (x_i - \bar{x})^2}{n-1}} = \sqrt{\frac{34}{5-1}} = \sqrt{8.5} = 2.915$$

# Calculate the Variance and Standard Deviation of the weight measurements from the previous exercise.

---

**Our metrologist weighed a 100 gram mass standard 20 times. The results are shown in the table below. Based on the formulas (or Excel Functions) presented previously, calculate the variance and standard deviation.**

100.64	97.55	100.62	110.00	100.67
99.11	102.22	107.40	112.58	101.14
95.41	106.86	103.77	98.53	99.59
93.91	101.17	104.28	96.99	108.41

**Note: Use the “Spreadsheet 1 Module 2” to calculate and add the variance and standard deviation. Same spreadsheet as used for the mean exercise.**



---

**< See Answer Handout >**

# Exercise – Using measurements and statistics to select a new technician

---

Two technicians are being considered for a position in the laboratory. Each is given 100 gram weight and they weigh it 16 times. The results are shown below. Who is best for the job?

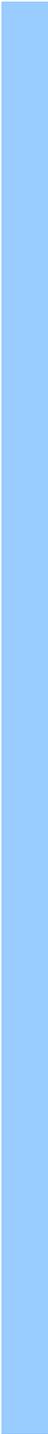
## Technician 1:

105	102	102	105	106	107	108	108
104	105	107	104	103	105	107	105

## Technician 2:

95	95	99	102	97	107	98	103
101	103	109	100	100	91	98	96

Note: Use the “Technician Selection spreadsheet” to calculate the mean, variance, and standard deviation

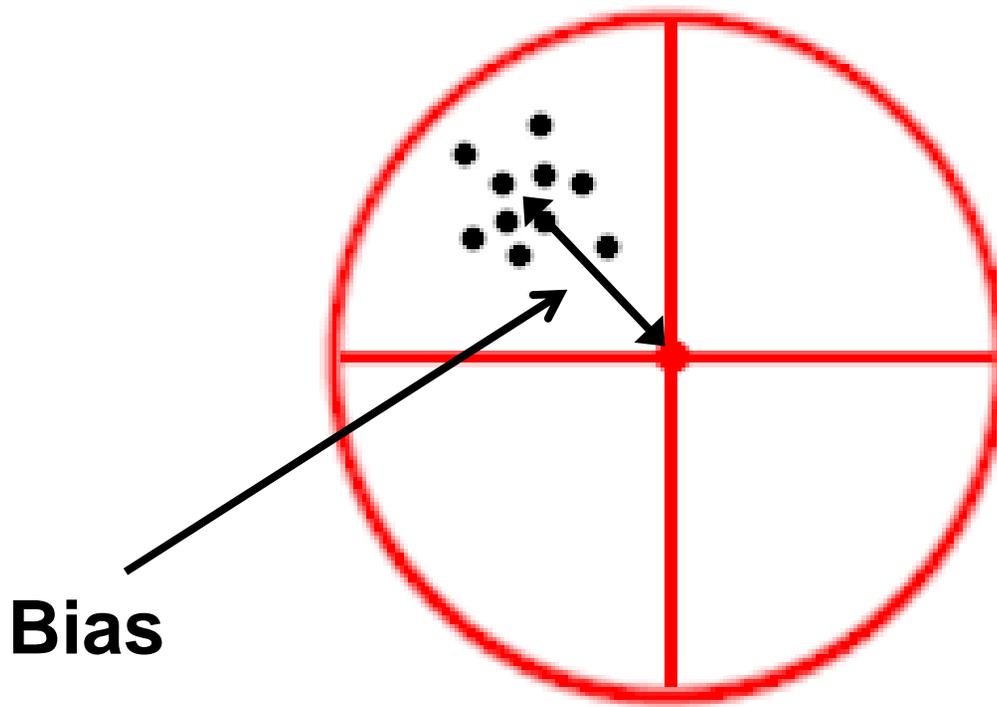


---

**< See Answer Handout >**

**Bias (Systematic Error)– the difference between the sample mean and the target mean (or true value)**

---



# Bias – the difference between the sample mean and the target mean (or true value)

---

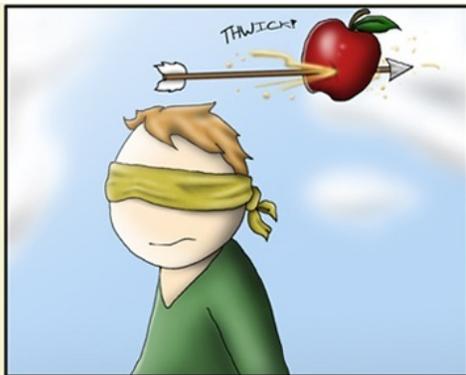
Technician 1 and Technician 2 both measured a 100 gram weight.

	Technician 1	Technician 2
Mean	105.19	99.63
Variance	3.63	21.05
Standard Deviation	1.91	4.59
<b>Bias</b>	105.19-100 = <b>5.19</b>	99.63-100= <b>-0.37</b>

# “Fit for Purpose” is a phrase used during the workshop

Simply stated it means that the measurement has the accuracy and precision to meet the engineering requirements that have been established for that particular measurement (*i.e., defined in process and/or MC&A measurement plans*).

Fit for Purpose



Not Fit for Purpose



# Systematic Error (Bias)

Accurate

Inaccurate

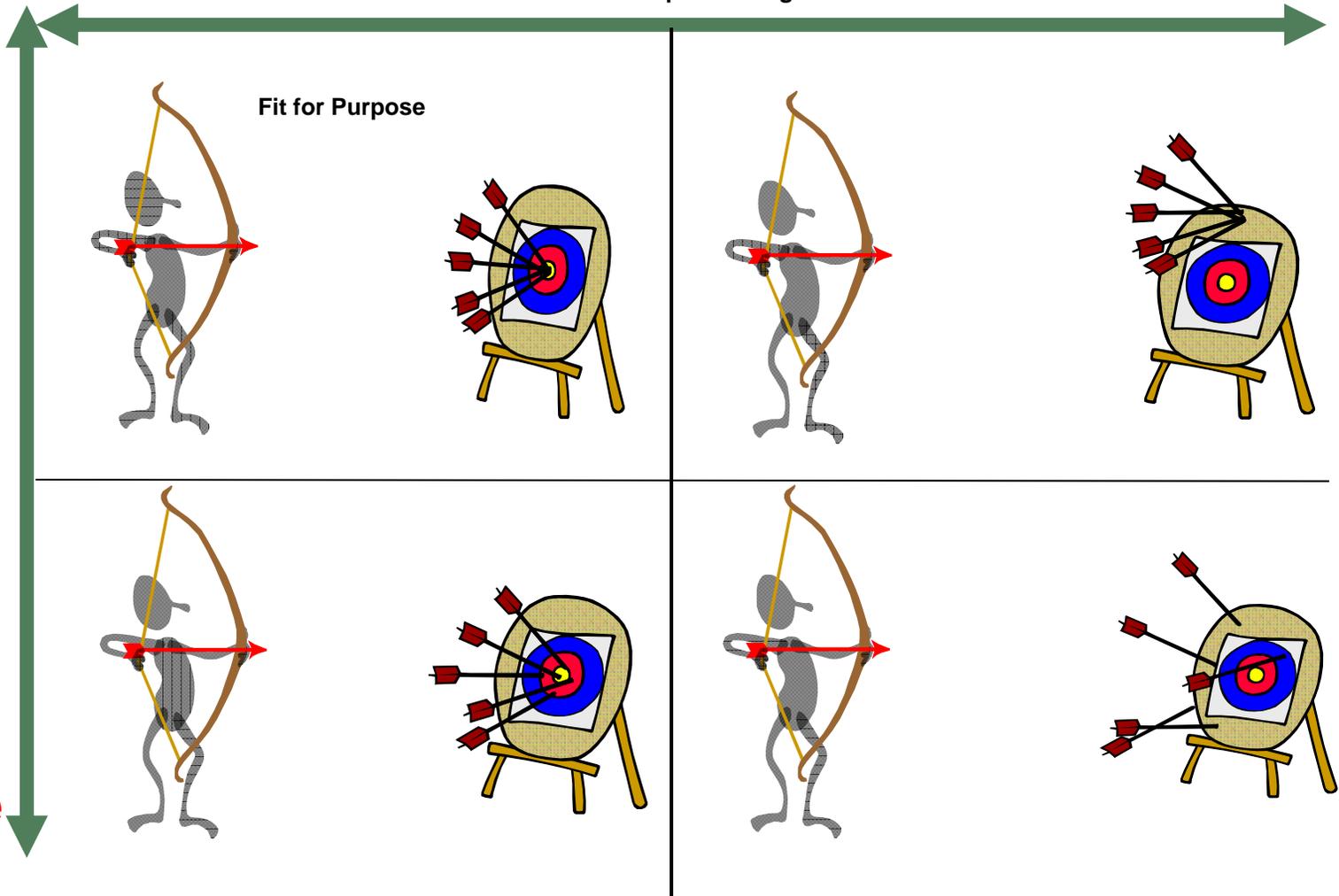
Mean with respect to target

Precise

Random Error

Variance / Standard Deviation

Imprecise



# Combining Errors from multiple sources

---

***Note: This subject will be covered in more detail in sections on variance propagation and calibration. For this example assume the bias is corrected so only random errors are considered. Rule is Variances get added. Standard Deviations do not.***

**Example of combining Process (method) and Standard random uncertainty:**

$$U_{\text{total}} = \sqrt{(S_{\text{process}})^2 + (S_{\text{standard}})^2}$$

**Note: called square root of the sum of squares**

# Ratio of Standard Uncertainty to Method (Process) Uncertainty

$$U_{\text{total}} = \sqrt{(S_{\text{process}})^2 + (S_{\text{standard}})^2}$$

- 10 to 1 ratio:  $100.5 = \sqrt{(100)^2 + (10)^2}$

Increase of 0.5% due to standard

**GUM recommended goal**

- 4 to 1 ratio:  $103.1 = \sqrt{(100)^2 + (25)^2}$

Increase of 3.1% due to standard

- 1 to 1 ratio:  $141.42 = \sqrt{(100)^2 + (100)^2}$

Increase of 41.4% due to standard

## Ratio of Standard Uncertainty to Method (Process) Uncertainty – *Continued*

---

*Example impact for 4 to 1 ratio, process to standard, with the 3.1% increase (from previous slide):*

$$\text{4 to 1 ratio: } 103.1 = \sqrt{(100)^2 + (25)^2}$$

Increase of 3.1% due to standard

**Assume the error of 103.1 is units of decagrams (tenths of a gram) which means the error in grams is 0.1031 grams. That would mean on the weighing of a 1000 gram item the standard uncertainty would have added only 3.1 mg (0.0031g) to the total uncertainty.**

**In this example the standard uncertainty is having negligible impact.**

# Summary

---

- Reviewed basic statistical terms and concepts
- Reviewed Mean/Average and how it is calculated
- Reviewed the concept of a “Probability Distribution” and the Normal Distribution
- Reviewed Variance and Standard Deviation and how they are calculated
- Reviewed the concepts of “Bias” and “Fit for Purpose”
- Reviewed how to add random error from multiple sources
- Reviewed how the magnitude of an error affects the total error

# Exercises

## Introduction to Statistics

---

### Session Objectives:

After the session the participants will be able to do the following:

1. Calculate the mean (average), variance, and standard deviation for a group of data by hand or by using Microsoft Excel

### Estimated Time:

The exercises are instructor led so the time is included as part of the presentation time.

### Materials Needed:

1. One computer with Microsoft Excel for each group of 5 students
2. Microsoft Excel workbooks a through c should be loaded on student computers
  - a. Filename = Module 2 – Statistical Review.xls
  - b. Filename = Module 2 Var and Stddev by hand.xls
  - c. Filename = Module 2 - Technician Selection.xls
3. The students should be familiar with Excel
4. Pencil and paper

### Instructions:

1. There are 3 instructor led exercises within Module 2. Using Microsoft Excel the instructor will lead students through the steps of calculating the mean, variance, and standard deviations for sets of data.
  - a. Exercise 1 is on Slide 17 – Calculate the mean
  - b. Exercise 2 is on Slides 30-34 – Calculate the variance and standard deviation without the Excel functions
  - c. Exercise 3 is on Slide 35 – Calculate the variance and standard deviation with the Excel functions
  - d. Exercise 4 is on Slide 37 – Calculate the mean, variance, and standard deviation and use that data to contrast the performance of 2 technicians.

1) Index	2) Data	3) Mean	4) Difference between data values and the mean	5) The square of column 4
i	$X_i$	Xbar	$(X_i - \text{Xbar})$	$(X_i - \text{Xbar})^2$
1	1	4	-3	9
2	8	4	4	16
3	3	4	-1	1
4	6	4	2	4
5	2	4	-2	4

Sum of  $(X_i - \text{Xbar})^2$

**34**

1) Index	2) Data	3) Mean	4) Difference between data values and the mean	5) The square of column 4
i	$X_i$	Xbar	$(X_i - \text{Xbar})$	$(X_i - \text{Xbar})^2$
1			0	0
2			0	0
3			0	0
4			0	0
5			0	0

0

# Exercises

## Measurement Models

---

### Session Objectives:

After the session the participants will be able to do the following:

1. Understand the calculations of variances for functions involving measurements
2. Understand the application to measurement models

### Estimated Time:

There are six (6) exercises in this module. The completion times are as follows:

1. Exercise #1 – 30 minutes
2. Exercise #2 – 20 minutes
3. Exercise #3 – 15 minutes
4. Exercise #4 – 20 minutes
5. Exercise #5 – 45 minutes
6. Exercise #6 – 30 minutes

These exercises will require 160 minutes or approximately 2.5 hours to complete.

### Materials Needed:

1. One computer with Microsoft Excel for each group of 4 to 5 students
2. The students must be familiar with the use of Excel
3. Pencil and paper
4. Spreadsheet support personnel

### Instructions:

1. There are six (6) exercises in this module
2. Students can work individually or in groups
3. The exercises are included in the presentation
4. Students will be requested to complete a particular exercise
5. Each exercise will then be discussed

### Exercise #1

Let  $x_1, \dots, x_n$  be independent, identically distributed (iid)  $N(\mu, \sigma^2)$ .

Compute the following:

1.  $E(x_1 - x_2) = 0$
2.  $E(x_1 + 2x_2 - x_3 - x_4 + 5) = \mu + 5$
3.  $E(x_1 + \dots + x_n) = n\mu$
4.  $E((x_1 + \dots + x_n)/n)$  or  $E(\bar{x}) = \mu$
5.  $V(x_1 - 2x_2 - 5) = 5\sigma^2$
6.  $V(x_1 + \dots + x_n) = n\sigma^2$
7.  $V((x_1 + \dots + x_n)/n) = V(\bar{x}) = \sigma^2/n$

### Exercise #2

Questions related to measurement models:

1. How are the model terms different between the additive and relative models?
  - **Additive terms are in the same units as the measurement, while relative terms are fractions or percentages**
2. How would a plot of the absolute differences look for an additive model?
  - **The absolute differences should have the same variance or spread over the measurement range**
3. How would a plot of the measurement values look for a relative model?
  - **The measurement values should have an increasing variance over the measurement range**
4. How would a plot of the relative differences look for a relative model?
  - **The absolute differences should have the same variance or spread over the measurement range**

### Exercise #3

Specify the measurement models for the following types of measurement:

1. Temperature – **additive model**
2. Neutron Coincidence Counter – **relative model because of counting**
3. Calorimeter – **either a mixed or additive model**
4. Pressure – **additive model**
5. Tank volume – **additive model, however, the systematic variance tends to relative for the regression parameter estimates, while the random variance is additive**
6. Density – **additive model**

## 7. Weight – additive model

### Exercise #4

Consider an analytical method for concentration involving dilutions, such as Davies-Gray Titration. Process measurements are as follows: two samples, two analysts and two measurements per sample.

1. Specify a reasonable model for this measurement scenario.
  - **Model is  $y_{ijk} = \mu(1 + \eta_i + \theta_j + \varepsilon_{ijk})$ , where  $\eta_i$  is the random effect for the  $i^{\text{th}}$  sample,  $\theta_j$  is the random effect for the  $j^{\text{th}}$  analyst and  $\varepsilon_{ijk}$  is the random effect for the  $i^{\text{th}}$  sample, the  $j^{\text{th}}$  analyst and the  $k^{\text{th}}$  measurement.**
2. What kind of effects are the samples and analysts?
  - **These are short-term systematic effects**
3. Are the sample and analyst effects different from random measurement effects?
  - **Yes, these effects are held constant for certain measurements**
4. What would a significant analyst variance or effect represent?
  - **This analyst might need additional training or coaching. Some investigation would be needed to find the problem. It could be the chemicals being used as opposed to preparation technique**
5. How could an analyst effect be used?
  - **As indicated in #4 above, this effect could be used to uncover issues or problems with one or more analyst's technique or with the chemicals used by the analysts.**

### Exercise #5

Suppose  $y_i = \mu(1 + \eta + \varepsilon_i)$ , where  $\eta$  is  $N(0, \sigma_\eta^2)$  and  $\varepsilon_i$  are iid  $N(0, \sigma_\varepsilon^2)$ .

Compute the following by using the defined model for  $y_i$ :

1.  $E(y_1) = \mu$
2.  $E(y_1 + y_2) = E(y_1) + E(y_2) = 2\mu$
3.  $E(y_1 - y_2) = E(y_1) - E(y_2) = 0$
4.  $E(\bar{y}) = n\mu/n = \mu$
5.  $V(y_1) = \mu^2(\sigma_\eta^2 + \sigma_\varepsilon^2)$
6.  $V(y_1 + y_2) = 4\mu^2\sigma_\eta^2 + 2\mu^2\sigma_\varepsilon^2$
7.  $V(y_1 - y_2) = 2\mu^2\sigma_\varepsilon^2$
8.  $V(\bar{y}) = \mu^2\sigma_\eta^2 + \mu^2\sigma_\varepsilon^2/n$
9. Are  $y_1$  and  $y_2$  independent?
  - a. **If  $y_1$  and  $y_2$  are independent, then  $V(y_1+y_2) = V(y_1) + V(y_2)$**

- b. The  $V(y_1) = \mu^2(\sigma_\eta^2 + \sigma_\varepsilon^2)$ , and similarly  $V(y_2) = \mu^2(\sigma_\eta^2 + \sigma_\varepsilon^2)$ . And  $V(y_1) + V(y_2) = 2\mu^2\sigma_\eta^2 + 2\mu^2\sigma_\varepsilon^2$
- c. From Exercise #5 Question 6,  $V(y_1 + y_2) = 4\mu^2\sigma_\eta^2 + 2\mu^2\sigma_\varepsilon^2$
- d. Therefore  $y_1$  and  $y_2$  are not independent. These measurements are correlated through the long-term systematic effect  $\eta$ .

10. What is  $\text{Cov}(y_1, y_2)$ ?

- a. Remember,  $V(y_1 + y_2) = V(y_1) + V(y_2) + 2\text{Cov}(y_1, y_2)$
- b. Substituting from above,  $4\mu^2\sigma_\eta^2 + 2\mu^2\sigma_\varepsilon^2 = 2\mu^2\sigma_\eta^2 + 2\mu^2\sigma_\varepsilon^2 + 2\text{Cov}(y_1, y_2)$
- c.  $2\text{Cov}(y_1, y_2) = 2\mu^2\sigma_\eta^2$
- d.  $\text{Cov}(y_1, y_2) = \mu^2\sigma_\eta^2$

### Exercise #6

Suppose  $y_i = \mu_i(1 + \eta + \varepsilon_i)$ , where  $\eta$  is  $N(0, \sigma_\eta^2)$  and  $\varepsilon_i$  are iid  $N(0, \sigma_\varepsilon^2)$ .

Compute and answer the following:

1.  $V(y_1 + \dots + y_{10}) = \sigma_\eta^2 (\sum_i \mu_i)^2 + \sigma_\varepsilon^2 \sum_i \mu_i^2$ , for  $i=1$  to  $10$
2. Discuss the differences in the affects of systematic and random variances on the variance for a sum of measurements.
  - **Systematic effects can propagate with a much larger effect. The coefficients are larger in magnitude for systematic effects as compared to random effects.**
3. In general, what type of variance is most important to control?
  - **Need to control the systematic variance**

# Exercises

## Measurement Models

---

### Session Objectives:

After the session the participants will:

1. Understand the calculations of variances for functions involving measurements
2. Understand the application to measurement models

### Estimated Time:

There are six (6) exercises in this module. The completion times are as follows:

1. Exercise #1 – 30 minutes
2. Exercise #2 – 20 minutes
3. Exercise #3 – 15 minutes
4. Exercise #4 – 20 minutes
5. Exercise #5 – 45 minutes
6. Exercise #6 – 30 minutes

These exercises will require 160 minutes or approximately 2.5 hours to complete.

### Materials Needed:

1. One computer with Microsoft Excel for each group of 4 to 5 students
2. The students must be familiar with the use of Excel
3. Pencil and paper
4. Spreadsheet support personnel

### Instructions:

1. There are six (6) exercises in this module
2. Students can work individually or in groups
3. The exercises are included in the presentation
4. Students will be requested to complete a particular exercise
5. Each exercise will then be discussed

### Exercise #1

Let  $x_1, \dots, x_n$  be independent, identically distributed (iid)  $N(\mu, \sigma^2)$ .

Compute the following:

1.  $E(\mathbf{x}_1 - \mathbf{x}_2) =$
2.  $E(\mathbf{x}_1 + 2\mathbf{x}_2 - \mathbf{x}_3 - \mathbf{x}_4 + 5) =$
3.  $E(\mathbf{x}_1 + \dots + \mathbf{x}_n) =$
4.  $E((\mathbf{x}_1 + \dots + \mathbf{x}_n)/n)$  or  $E(\bar{\mathbf{x}}) =$
5.  $V(\mathbf{x}_1 - 2\mathbf{x}_2 - 5) =$
6.  $V(\mathbf{x}_1 + \dots + \mathbf{x}_n) =$
7.  $V((\mathbf{x}_1 + \dots + \mathbf{x}_n)/n) = V(\bar{\mathbf{x}}) =$

### Exercise #2

Questions related to measurement models:

1. How are the model terms different between the additive and relative models?
2. How would a plot of the absolute differences look for an additive model?
3. How would a plot of the measurement values look for a relative model?
4. How would a plot of the relative differences look for a relative model?

### Exercise #3

Specify the measurement models for the following types of measurement:

1. Temperature –
2. Neutron Coincidence Counter –
3. Calorimeter –
4. Pressure –
5. Tank volume –
6. Density –
7. Weight –

#### Exercise #4

Consider an analytical method for concentration involving dilutions, such as Davies-Gray Titration. Process measurements are as follows: two samples, two analysts and two measurements per sample.

1. Specify a reasonable model for this measurement scenario.
2. What kind of effects are the samples and analysts?
3. Are the sample and analyst effects different from random measurement effects?
4. What would a significant analyst variance or effect represent?
5. How could an analyst effect be used?

#### Exercise #5

Suppose  $y_i = \mu(1 + \eta + \varepsilon_i)$ , where  $\eta$  is  $N(0, \sigma_\eta^2)$  and  $\varepsilon_i$  are iid  $N(0, \sigma_\varepsilon^2)$ .

Compute the following by using the defined model for  $y_i$ :

1.  $\mathbf{E}(\mathbf{y}_1) =$
2.  $\mathbf{E}(\mathbf{y}_1 + \mathbf{y}_2) = \mathbf{E}(\mathbf{y}_1) + \mathbf{E}(\mathbf{y}_2) =$
3.  $\mathbf{E}(\mathbf{y}_1 - \mathbf{y}_2) = \mathbf{E}(\mathbf{y}_1) - \mathbf{E}(\mathbf{y}_2) =$
4.  $\mathbf{E}(\bar{\mathbf{y}}) = \mathbf{n}\boldsymbol{\mu}/\mathbf{n} =$
5.  $\mathbf{V}(\mathbf{y}_1) =$
6.  $\mathbf{V}(\mathbf{y}_1 + \mathbf{y}_2) =$
7.  $\mathbf{V}(\mathbf{y}_1 - \mathbf{y}_2) =$
8.  $\mathbf{V}(\bar{\mathbf{y}}) =$
9. Are  $y_1$  and  $y_2$  independent?

10. What is  $\text{Cov}(y_1, y_2)$ ?

**Exercise #6**

Suppose  $y_i = \mu_i(1 + \eta + \varepsilon_i)$ , where  $\eta$  is  $N(0, \sigma_\eta^2)$  and  $\varepsilon_i$  are iid  $N(0, \sigma_\varepsilon^2)$ .

Compute and answer the following:

1.  $V(y_1 + \dots + y_{10}) =$
2. Discuss the differences in the effects of systematic and random variances on the variance for a sum of measurements.
3. In general, what type of variance is most important to control?



## **Module 3**

---

# **Measurement Models**

# Objectives

---

- **Review GUM concepts as they relate to measurement models**
- **Discuss the statistics used in describing measurement models**
- **Understand additive and relative measurement models and be able to establish the type of model for a particular measurement method**
- **Understand expectation and variance calculations associated with measurement models and apply them to some example measurement methods**

# Measurement Models and GUM

---

**GUM recommendations related to measurement models:**

- **In general, the use of measurement models results in Type A uncertainties, which are uncertainties derived by statistical methods.**
- **Uncertainties derived by statistical methods, such as measurement models, are characterized by estimated variances,  $s_i^2$ , and the appropriate degrees of freedom,  $\nu_i$ .**
- **GUM recommends that combined uncertainty is derived by adding the variance components and then expressing the combined uncertainty as a standard deviation or a one-sigma value. This is a direct result of using a statistical measurement model.**

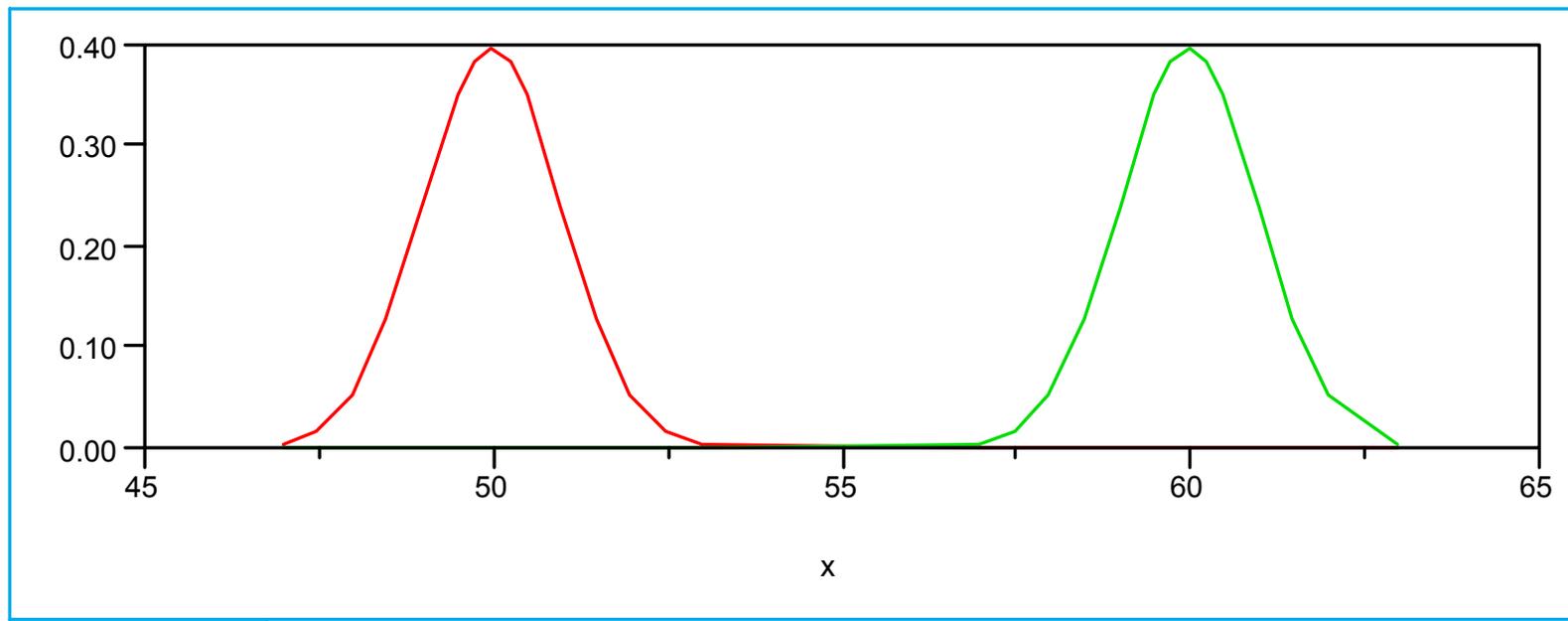
# Normal Distribution

---

- It is a bell-shaped, symmetric and continuous distribution
- A random variable,  $x$ , with a normal distribution can assume any value along a continuum of possible values
- Important uses of the Normal distribution are for hypothesis testing, the derivation of confidence intervals and the distribution of error terms for measurement models
- The expected value or mean ( $\mu$ ) represents the location or theoretical average of the distribution, while the variance ( $\sigma$ ) represents the spread of the distribution

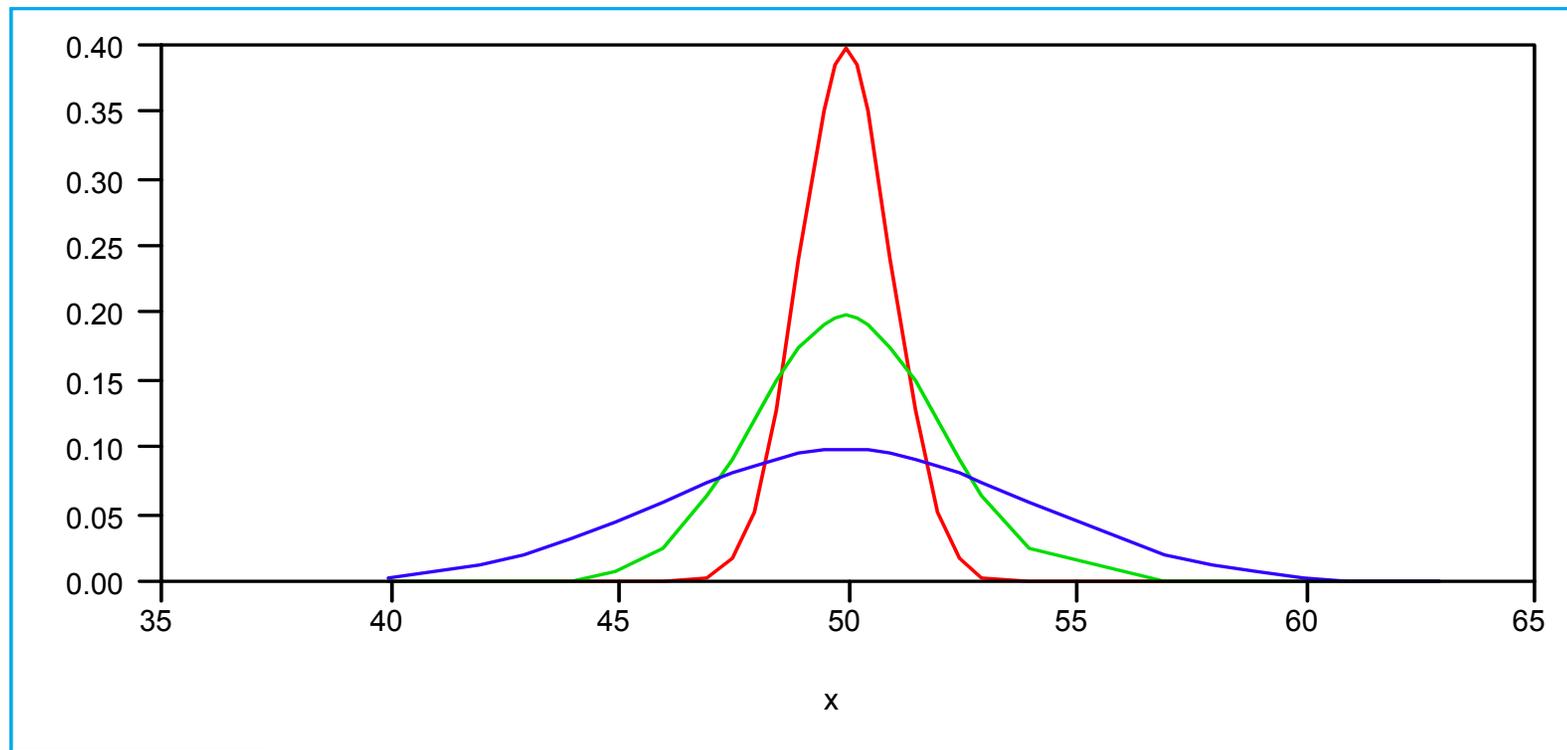
# Normal Distribution: Examples

- Two Normal distributions with different means, but the same standard deviation



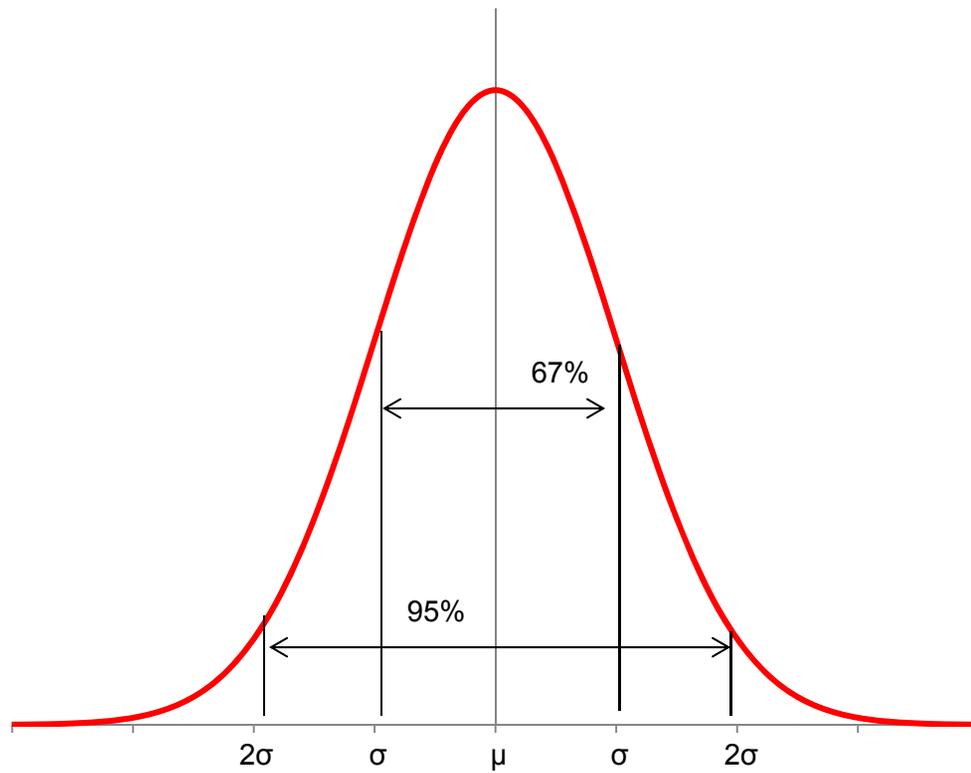
# Normal Distribution: Examples

- Three Normal distributions with the same mean, but different standard deviations



# Normal Distribution Properties

---



# Normal Distribution Properties

---

Expectation, Variance and Covariance

Let  $x \sim N(\mu_x, \sigma_x^2)$ , then

The expected value of  $x$  or  $E(x) = \mu_x$ , and

$$E(ax+b) = a\mu_x + b, \text{ where } a \text{ and } b \text{ are constants}$$

The variance of  $x$  or  $V(x) = \sigma_x^2$ , and

$$V(ax+b) = a^2\sigma_x^2$$

Let  $y \sim N(\mu_y, \sigma_y^2)$ , then

$$E(x+y) = E(x) + E(y) = \mu_x + \mu_y$$

If  $x$  and  $y$  are independent, then

$$V(x+y) = V(x) + V(y) = \sigma_x^2 + \sigma_y^2$$

# Normal Distribution Properties

---

Expectation, Variance and Covariance

If  $x$  and  $y$  are not independent, then

$V(x+y) = V(x) + V(y) + 2\text{Cov}(x,y)$ , where,

Covariance of  $x$  and  $y = \text{Cov}(x,y) = E(xy) - E(x)E(y)$

- The concept of covariance is related to systematic measurement effects
- An example of covariance will be discussed later in this module

# Normal Distribution Properties

---

## Standard Normal Distribution

- If  $x \sim N(\mu, \sigma^2)$ , that is,  $x$  is distributed as a normal random variable with mean  $\mu$  and variance  $\sigma^2$  and

$$Z = \frac{x - \mu}{\sigma}$$

then  $Z$  is said to have the standard normal distribution.

- Note that the mean of  $Z$  is zero and its standard deviation is 1.
- In statistical text books tables are available for  $Z$

# Normal Distribution Properties

---

One of the most important properties of the Normal distribution is as follows:

- Let  $x_1$  and  $x_2$  be independent and identically distributed (iid)  $N(\mu, \sigma^2)$ , then  $(x_1 + x_2)$  has a normal distribution with a mean of  $2\mu$  and variance of  $2\sigma^2$
- In other words, the sum of normally distributed random variables is also normally distributed
- In general, let  $x_1, \dots, x_n$  be iid  $N(\mu, \sigma^2)$ , then  $(a_1x_1 + \dots + a_nx_n) \sim N(\mu \sum_i a_i, \sigma^2 \sum_i a_i^2)$ , where  $a_1, \dots, a_n$  are constants

# Normal Distribution: Parameter Estimation

---

Estimation of  $\mu$  and  $\sigma^2$  parameters of the Normal distribution

- Let  $x_1, \dots, x_n$  be iid  $N(\mu, \sigma^2)$
- The parameter  $\mu$  represents the mean value or location of the distribution, while  $\sigma^2$  represents the variance or spread in the distribution
- As expected, the best point estimate of  $\mu$  is  $\bar{x}$  or  $\frac{1}{n} \sum_i x_i$
- The best point estimate of  $\sigma^2$  is  $s^2 = \frac{1}{n-1} \sum_i (x_i - \bar{x})^2$
- $\sigma$  is then estimated by  $s$  or  $+\sqrt{s^2}$

# Exercise #1

---

Let  $x_1, \dots, x_n$  be iid  $N(\mu, \sigma^2)$ .

Compute the following:

1.  $E(x_1 - x_2)$
2.  $E(x_1 + 2x_2 - x_3 - x_4 + 5)$
3.  $E(x_1 + \dots + x_n)$
4.  $E((x_1 + \dots + x_n)/n)$  or  $E(\bar{x})$
5.  $V(x_1 - 2x_2 - 5)$
6.  $V(x_1 + \dots + x_n)$
7.  $V((x_1 + \dots + x_n)/n)$  or  $V(\bar{x})$

# Measurement Models

---

- **Two main types:**
  - **Absolute**
    - Also called additive
    - Examples would be length, temperature, weight and density measurements
  - **Relative**
    - Also called multiplicative
    - Examples would be analytical methods that require dilutions, such as Davies-Gray Titration, and neutron coincidence counting
  - **Mixed Models also possible**
- **Measurement type determines appropriate model**
- **Data plots can assist with model determination**

# Additive or Absolute Model

---

Consider the following simple additive model with only a random effects term:

$$Y_{ij} = \mu_i + \varphi_{ij}$$

Where,

$Y_{ij}$  = the  $j^{\text{th}}$  measurement for  $\mu_i$

$\mu_i$  = true value for standard  $\mu_i$

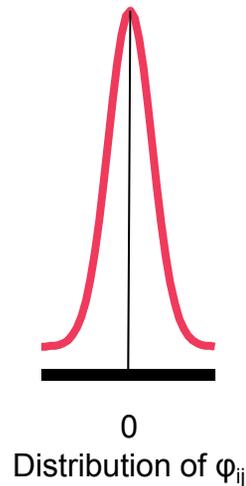
$\varphi_{ij}$  = random measurement effect for the  $j^{\text{th}}$  measurement for  $\mu_i$

The  $\varphi_{ij}$  are iid  $N(0, \sigma_\varphi^2)$ .

# Distribution of Model Error Effects

---

Distribution for additive random effects  $\varphi_{ij}$



**The variance term,  $\sigma_{\varphi}^2$  is unknown and must be estimated.**

**The units for this effect are in relative or percentage terms.**

# Additive Model: Length Measurements

---

Consider a model for length measurements using a tape measure.

The uncertainty associated with length measurements tends to be constant over the measurement range of the tape measure.

A reasonable model is as follows:

$$Y_{ij} = \mu_i + \varphi_{ij}$$

Where,

$Y_{ij}$  =  $j^{\text{th}}$  length measurement for  $\mu_i$

$\mu_i$  = true length for the  $i^{\text{th}}$  standard length

$\varphi_{ij}$  = random measurement effect for the  $j^{\text{th}}$  length measurement for  $\mu_i$ , ( $\varphi_{ij}$  are iid  $N(0, \sigma_\varphi^2)$ )

# Additive Model: Evaluation

---

In general, data plots are used to determine the nature or model associated with a particular measurement process.

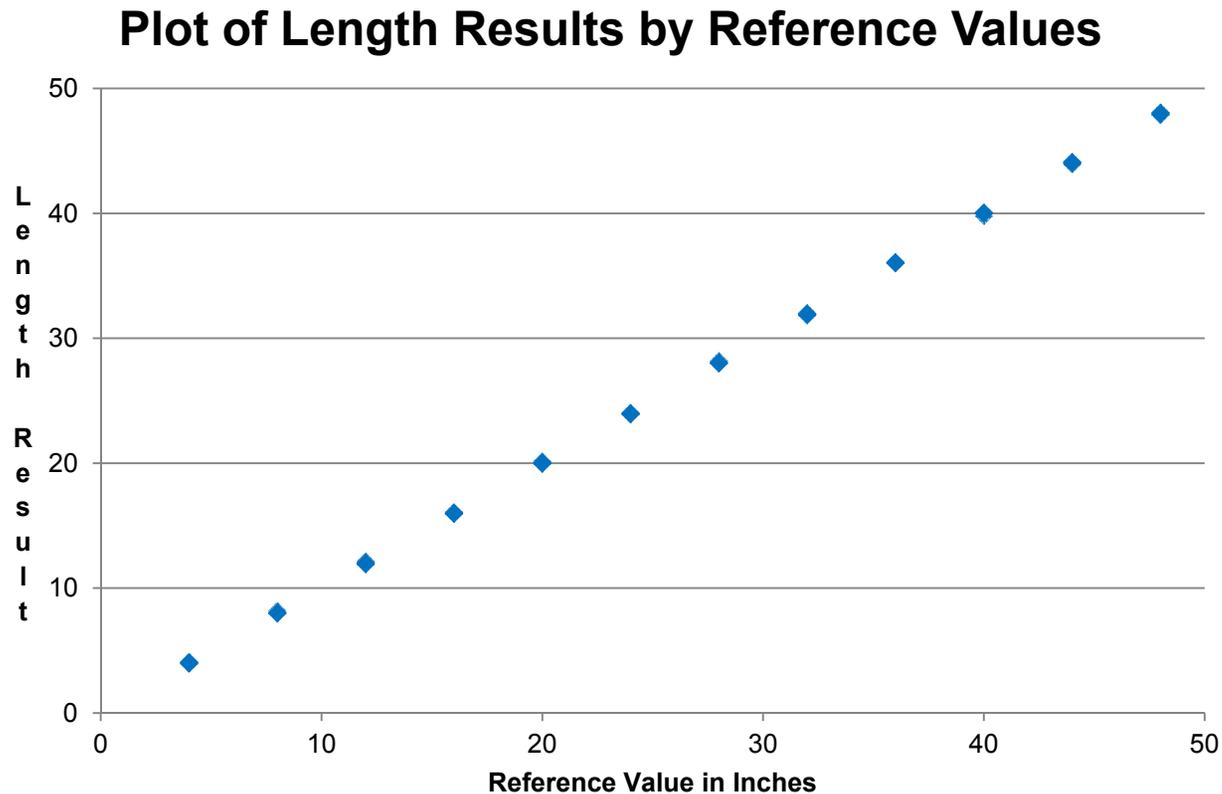
Two plots will be presented for evaluating the nature of weight measurements:

1. Plot of length measurements by the reference values
2. Plot of the absolute differences ( $Y_{ij} - \mu_i$ ) by the reference values

# Additive Model: Data Plots

---

Consider a plot of the length measurements by the reference values:



# Additive Model: Data Plots

---

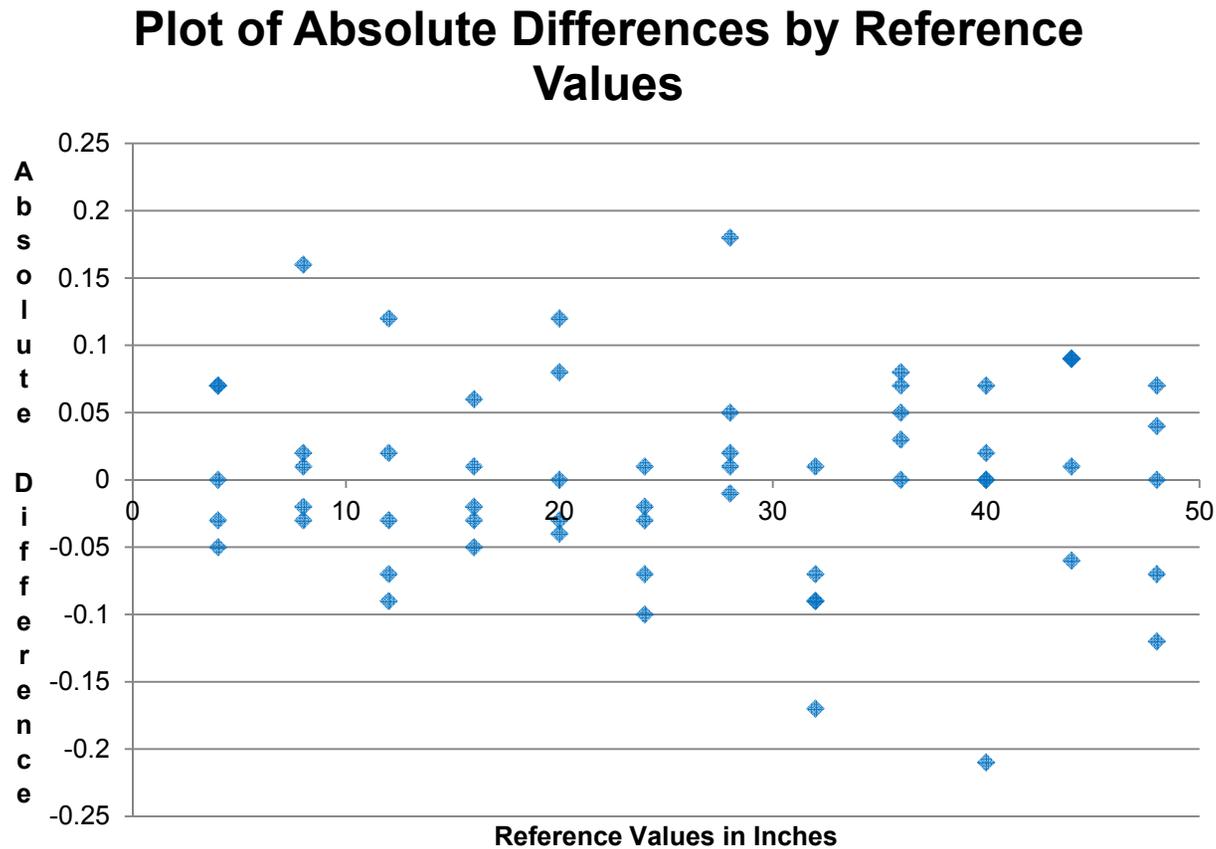
**In many cases, a plot of the length measurements by the reference values does not have enough resolution to evaluate the nature of the measurements.**

**However, this kind of plot does demonstrate the expected linear relationship between the length measurement and the reference values.**

**Now, consider the plot of the absolute differences by the reference values.**

# Additive Model: Data Plots

Data plot of the absolute differences  $(Y_{ij} - \mu_i)$  by the reference values:



# Additive Model: Conclusion

---

**A data plot of the absolute differences by the reference values is the best technique for evaluating the appropriateness of an additive model for a particular measurement method.**

**For an additive model, the variability of the absolute differences should be approximately constant over the measurement range of the method.**

# Additive Model

---

Depending on the situation, a more complex additive model may be needed. For example:

$$Y_{ijkl} = \mu_i + \theta_j + \xi_k + \varphi_{ijkl}$$

Where,

$Y_{ijkl}$  = measurement value

$\mu_i$  = true value for  $\mu_i$  (may not be a standard)

$\theta_j$  = systematic measurement effect for the  $j^{\text{th}}$  analyst

$\xi_k$  = systematic measurement effect for the  $k^{\text{th}}$  sample

$\varphi_{ijkl}$  = random measurement effect for the  $l^{\text{th}}$  measurement for  $\mu_i$ , analyst  $j$  and sample  $k$

The  $\theta_j$  are iid  $N(0, \sigma_\theta^2)$ , the  $\xi_k$  are iid  $N(0, \sigma_\xi^2)$ , and the  $\varphi_{ijkl}$  are iid  $N(0, \sigma_\varphi^2)$ . In addition, the  $\theta_j$ ,  $\xi_k$ , and  $\varphi_{ijkl}$  are independent.

# Multiplicative or Relative Model

---

Consider the following relative model with systematic and random effects terms:

$$Y_{ij} = \mu_i (1 + \eta + \varepsilon_{ij})$$

Where,

$Y_{ij}$  = the  $j^{\text{th}}$  measurement for  $\mu_i$

$\mu_i$  = true value for standard  $\mu_i$

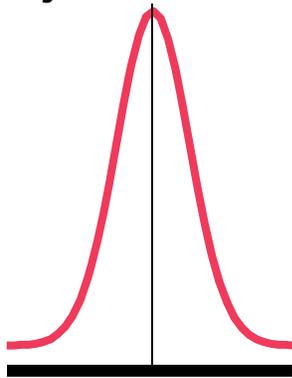
$\eta$  = systematic measurement effect for a single analyst

$\varepsilon_{ij}$  = random measurement effect for the  $j^{\text{th}}$  measurement for  $\mu_i$

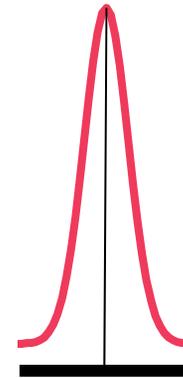
The  $\eta$  is  $N(0, \sigma_\eta^2)$  and the  $\varepsilon_{ij}$  are iid  $N(0, \sigma_\varepsilon^2)$ . In addition,  $\eta$  and the  $\varepsilon_{ij}$  are independent.

# Distribution of Model Error Effects

Distribution for relative random effects  $\eta$   
and  $\varepsilon_{ij}$



0  
Distribution of  $\eta$



0  
Distribution of  $\varepsilon_{ij}$

**The variance terms,  $\sigma_{\eta}^2$  and  $\sigma_{\varepsilon}^2$  are unknown and must be estimated.  
The units for these effects are in relative or percentage terms.**

# Relative Model: Davies-Gray Titration

---

Consider a relative model for Davies-Gray Uranium concentration measurements.

Davies-Gray involves dilutions and, because of this, the uncertainty in the concentration measurements is not constant over the measurement range of the method.

A reasonable model for the Davies-Gray method is as follows:

$$Y_{ij} = \mu_i \times (1 + \eta + \varepsilon_{ij})$$

# Relative Model: Davies-Gray Titration

---

Where,

$Y_{ij}$  =  $j^{\text{th}}$  concentration measurement for  $\mu_i$

$\mu_i$  = true concentration for standard  $\mu_i$

$\eta$  = systematic measurement effect due to a single analyst performing the method

$\varepsilon_{ij}$  = random measurement effect for the  $j^{\text{th}}$  concentration measurement of  $\mu_i$

The  $\eta$  effect is  $N(0, \sigma_\eta^2)$  and the  $\varepsilon_{ij}$  are iid  $N(0, \sigma_\varepsilon^2)$ . In addition,  $\eta$  and the  $\varepsilon_{ij}$  are independent.

# Relative Model: Evaluation

---

In general, data plots are used to determine the nature or model associated with a particular measurement process.

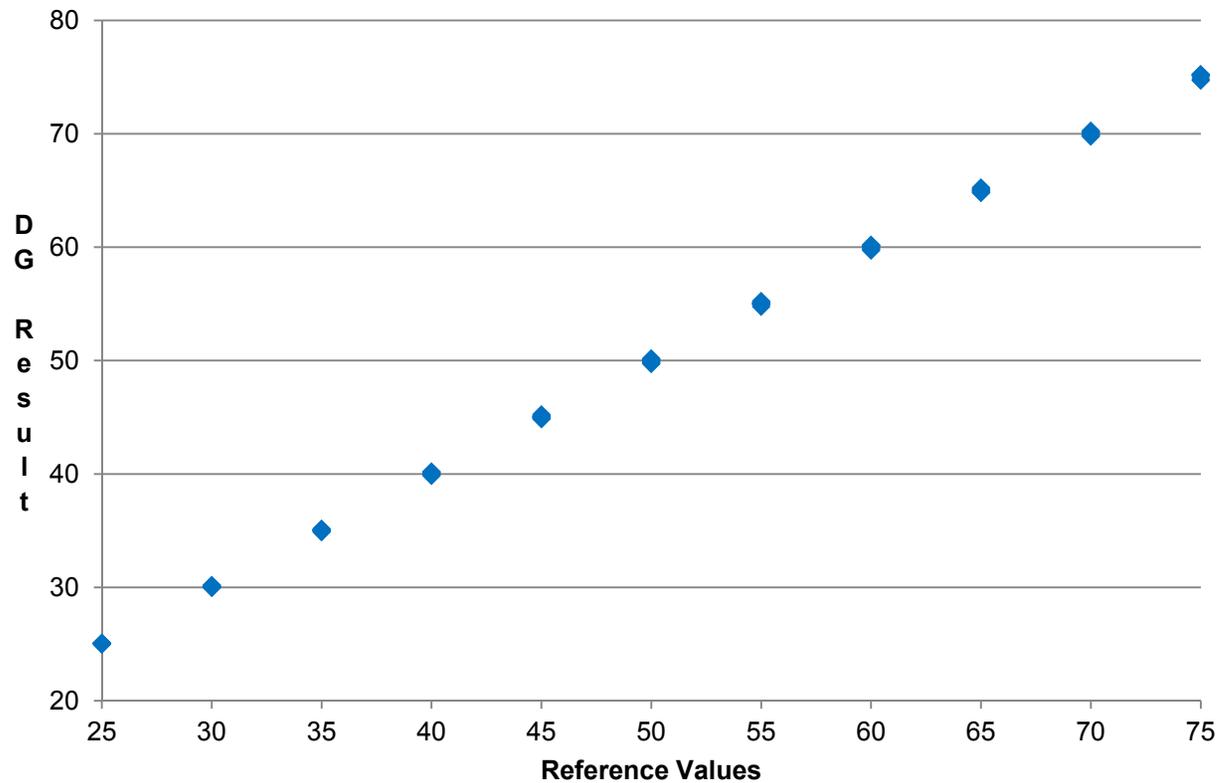
Three plots will be presented for evaluating the nature of Davies-Gray concentration measurements:

1. Plot of the concentration measurements by the concentration standards
2. Plot of the absolute differences  $(Y_{ij} - \mu_i)$  by the concentration standards
3. Plot of the relative differences  $(Y_{ij} - \mu_i)/\mu_i$  by the concentration standards

# Relative Model: Data Plots

Consider a plot of the concentration measurements by the concentration standards:

Plot of DG Result by Reference Values



# Relative Model: Data Plots

---

**A plot of the concentration measurements by the standard values does not have enough resolution to evaluate the nature of the measurement model.**

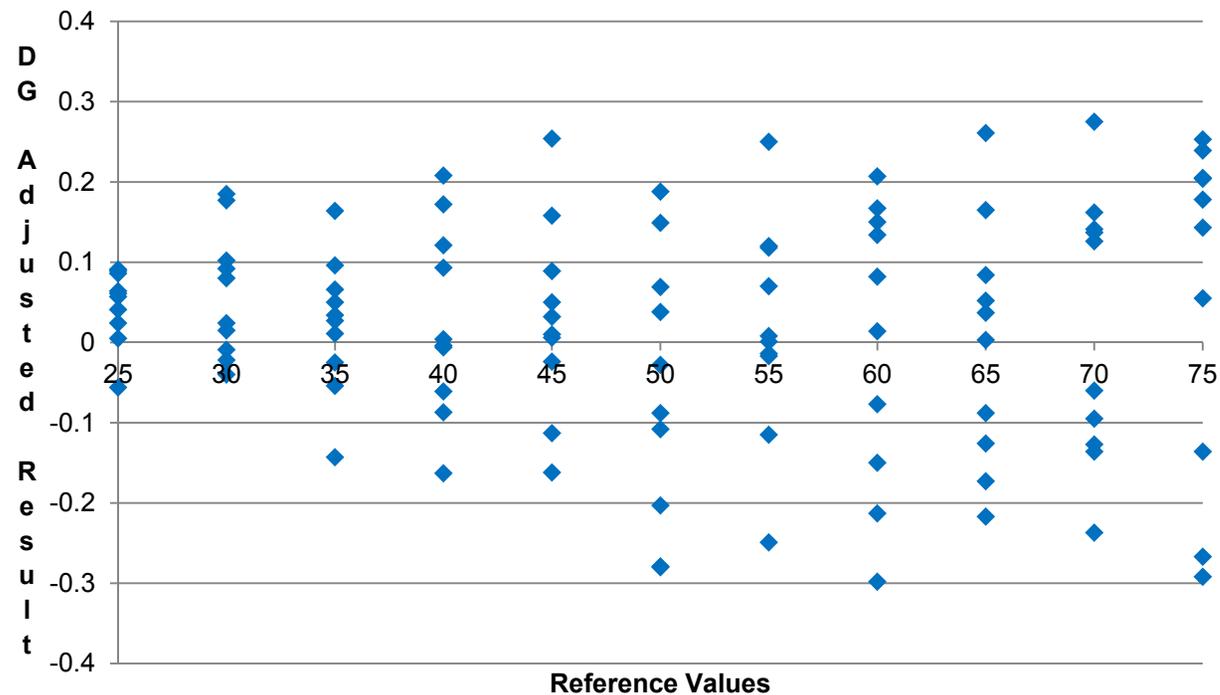
**However, this plot does demonstrate the expected linear relationship between the method results and the reference values.**

**Next, consider a plot of the absolute differences,  $(Y_{ij} - \mu_i)$ , by the standard values.**

# Relative Model: Data Plots

Data plot of the absolute differences,  $(Y_{ij} - \mu_i)$ , by the standard values:

Plot of Absolute Differences by the Reference Values



# Relative Model: Data Plots

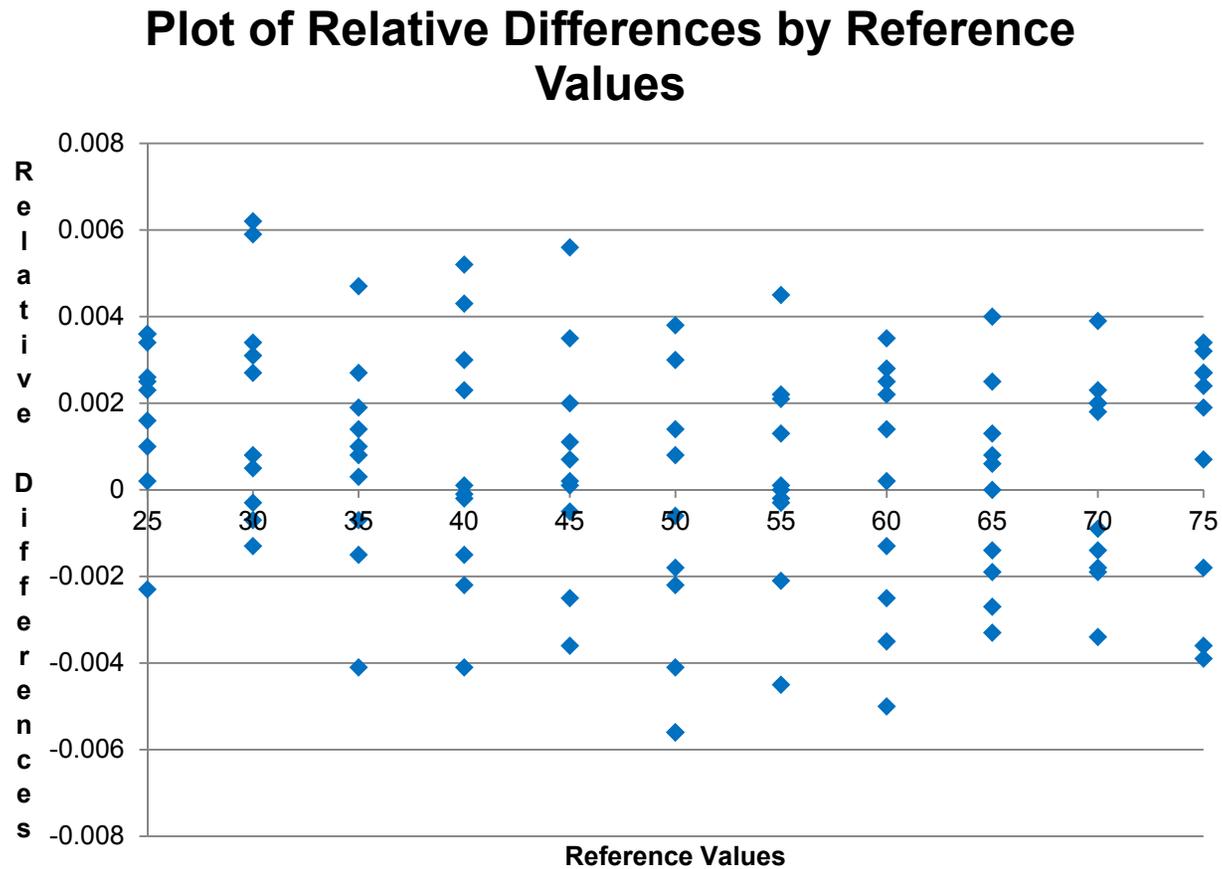
---

The data plot of the absolute differences,  $(Y_{ij} - \mu_i)$ , by the standard values shows the variability is not constant over the measurement range of the Davies-Gray method. The variability tends to increase as the standard values increase. This is the expected behavior for a relative model.

Finally, consider a plot of the relative differences,  $(Y_{ij} - \mu_i)/\mu_i$ , by the standard values.

# Relative Model: Data Plots

Data plot of the relative differences  $((Y_{ij}-\mu_i)/\mu_i)$  by the standard values:



# Relative Model: Conclusion

---

**A data plot of the relative differences by the reference values is the best technique for evaluating the appropriateness of a relative model for a particular measurement method.**

**For a relative model, the variability of the relative differences should be approximately constant over the measurement range of the method.**

# Relative Model

---

Again, depending on the situation, a more complex relative model may be needed. For example:

$$Y_{ijkl} = \mu_i (1 + \theta_j + \xi_k + \varphi_{ijkl}),$$

where the terms  $\theta_j$ ,  $\xi_k$  and  $\varphi_{ijkl}$  could be similar to the terms described for the additive model discussed earlier. The random effects terms used in the relative model would reflect the measurement situation being described or modeled.

# The Nature of a Measurement

---

- **The basis for a particular measurement is the assumed statistical model for that measurement**
- **A measurement is observed or realized as the result of an actual measurement method or process**
- **A measurement results when systematic and random effects associated with the measurement model are drawn or sampled from their respective Normal distributions**
- **The frequency with which an effect is sampled depends on the nature of the effect**

# The Nature of a Measurement

---

- **Systematic effects are sampled and held constant for the duration of the effect. For example, during the period of time that a certain standard is used, the systematic effect is sampled and held constant while the standard is in use. When the standard changes, then another systematic effect is sampled and held constant while the new standard is in use.**
- **Random effects are sampled for each measurement**
- **The actual values of the systematic and random effects are not known, but the measurement data provides information regarding the uncertainties associated with the systematic and random effects**

# Exercise #2

---

## Measurement Models

- 1. How are the model terms different between the additive and multiplicative models?**
- 2. How would a plot of the absolute differences look for an additive model?**
- 3. How would a plot of the measurement values look for a relative model?**
- 4. How would a plot of the relative differences look for a relative model?**

# Exercise #3

---

**Specify the measurement models for the following types of measurement:**

- **Temperature**
- **Neutron Coincidence Counter**
- **Calorimeter**
- **Pressure**
- **Tank volume**
- **Density**
- **Weight**

# Exercise #4

---

**Consider an analytical method for concentration involving dilutions, such as Davies-Gray Titration. Process measurements are as follows: two samples, two analysts, and two measurements per sample.**

- 1. Specify a reasonable model for this measurement scenario.**
- 2. What kind of effects are the samples and analysts?**
- 3. Are sample and analyst effects different from random measurement effects?**
- 4. What would a significant analyst variance or effect represent?**
- 5. How would an analyst effect be addressed?**

## Exercise #5

---

Suppose  $y_i = \mu(1 + \eta + \varepsilon_i)$  and  $\eta$  is  $N(0, \sigma_\eta^2)$  and  $\varepsilon_i$  are iid  $N(0, \sigma_\varepsilon^2)$ . Compute the following:

1.  $E(y_1)$
2.  $E(y_1 + y_2)$
3.  $E(y_1 - y_2)$
4.  $E(\bar{y})$
5.  $V(y_1)$
6.  $V(y_1 + y_2)$
7.  $V(y_1 - y_2)$
8.  $V(\bar{y})$

## Exercise #5 (cont'd)

---

9. Are  $y_1$  and  $y_2$  independent?

Is  $V(y_1 + y_2) = V(y_1) + V(y_2)$ ?

10. If not, what is  $\text{Cov}(y_1, y_2)$ ?

## Exercise #6

---

Suppose  $y_i = \mu_i(1 + \eta + \varepsilon_i)$  and  $\eta$  is  $N(0, \sigma_\eta^2)$  and  $\varepsilon_i$  are iid  $N(0, \sigma_\varepsilon^2)$ . Compute the following:

1.  $V(y_1 + \dots + y_{10})$ ?
2. Discuss the differences in the affects of systematic and random variances on the variance for a sum of measurements.
3. What type of variance is most important to control?

# Summary

---

- **Reviewed GUM concepts as they relate to measurement models**
- **Discussed the statistics used in describing measurement models**
- **Introduced additive and relative measurement models and discussed how to establish the type of model for a particular measurement method**
- **Introduced expectation and variance calculations associated with measurement models and applied them to some example measurement methods**



## **Module 4**

---

# **Introduction to Variance Propagation Techniques**

# Objectives

---

- **Understand the basic concepts of variance propagation**
- **Understand the propagation of random variances**
- **Understand the propagation of systematic variances**
- **Be able to use Excel for solving variance propagation problems**

# The GUM “Connection”

---

- **Recommendation INC-1 (1980) is an overview of an agreed-upon approach to measurement uncertainty evaluation**
- **INC-1 relied on the General Law of “Variance Propagation.” This law is based on partial derivatives of Taylor Series expansions for a given functional relationship**
- **The partial derivatives are called sensitivity coefficients**

# Variance Propagation

---

- **Often, measurement data are processed through multiplication, addition, or other functional manipulation to arrive at a derived number of more immediate interest.**
- **The values that are produced by these processing steps will be distributed in a way that is dependent on both the original distribution and the types of operations carried out.**

# Combining Random Variables (linear combinations)

---

The determination of the expected value and variance of linear combinations of random variables has been reviewed.

Specifically,

Let  $X$  and  $Y$  be random variables and let  $R = a \cdot X + b \cdot Y + c$ .

Then

$$E(R) = a \cdot E(X) + b \cdot E(Y) + c$$

And

$$V(R) = a^2 \cdot V(X) + b^2 \cdot V(Y) + 2 \cdot a \cdot b \cdot \text{Cov}(X, Y)$$

What if  $X$  and  $Y$  are uncorrelated?

Specifically, for  $R = X + Y$  or  $R = X - Y$ , if  $X$  and  $Y$  are uncorrelated, then

$$\sigma_R = \sqrt{\sigma_X^2 + \sigma_Y^2}$$

# Sum or Differences of Counts

---

A common application of this situation arises when counts resulting from a radioactive source must be corrected by subtracting an appropriate background count. If we assume equal counting times and note the independence of the two counts, then

$$\text{net counts} = \text{total counts} - \text{background counts}$$

Or

$$r = x - y$$

Let  $x = 1071$  and  $y = 521$ . Then  $r = 1071 - 521 = 550$ .

In addition, the estimators of the standard deviations of  $x$  and  $y$  are the square roots of the measured counts. Thus,  $\sigma_x$  is estimated by  $\sqrt{x}$  and  $\sigma_y$  is estimated by  $\sqrt{y}$ . Then,  $\sigma_r$  is estimated by

$$\sigma_r = \sqrt{\sigma_x^2 + \sigma_y^2} \rightarrow \hat{\sigma}_r = \sqrt{1071 + 521} = \sqrt{1592} = 39.9$$

# Multiplication or Division by a Constant

---

A familiar example of this case is the calculation of a counting rate. If  $x$  counts are recorded over a time  $t$ , then

$$\text{Count Rate} = r = x/t$$

Let  $x = 1120$  counts and  $t = 5$  s (assumed to be measured with very small uncertainty).

Then  $r = 1120 \text{ counts} / (5 \text{ s}) = 224 \text{ counts/s}$ .

The associated standard deviation (in counts per second) is, where it is noted that the estimated variance of  $x$  is 1120.

$$\sigma_r = \sqrt{\frac{\sigma_x^2}{t^2}} = \frac{\sigma_x}{t} \rightarrow \hat{\sigma}_r = \frac{\sqrt{1120}}{5} = 6.7$$

# Mean Value of Multiple Independent Counts

---

Suppose we have recorded  $n$  repeated counts from the same source for equal counting times. Let the results of these counts be designated  $x_1, x_2, \dots, x_n$  and let the sum be represented as

$$\text{SUM}_x = x_1 + x_2 + \dots + x_n$$

Then the variance of  $\text{SUM}_x$  (assuming that all of the counts  $x_i$  are independent) is given by

$$\sigma_{\text{SUM}_x}^2 = \sigma_{x_1}^2 + \sigma_{x_2}^2 + \dots + \sigma_{x_n}^2$$

And since  $\sigma_{x_i} = \sqrt{x_i}$  for each independent count,

$$\sigma_{\text{SUM}_x} = \sqrt{x_1 + x_2 + \dots + x_n}$$

# Mean Value of Multiple Independent Counts

---

Now calculate a sample mean from the  $n$  independent counts

$$\bar{x} = \frac{\text{SUM}_x}{n}$$

The standard deviation of the sample mean is given by

$$\sigma_{\bar{x}} = \frac{\sigma_{\text{SUM}_x}}{n} \Rightarrow \hat{\sigma}_{\bar{x}} = \frac{\sqrt{\text{SUM}_x}}{n} = \frac{\sqrt{n\bar{x}}}{n} = \sqrt{\frac{\bar{x}}{n}}$$

**A general conclusion is that, to improve the statistical uncertainty of a given measurement by a factor of 2, the number of counts must increase by a factor of 4.**

# A More General Case

---

What about the variance of a value  $r$  calculated as a general function of any number of random variables?

$$r = f(x, y, z, \dots)$$

The variance of  $r$  is estimated using a variance propagation formula that is based on a Taylor series expansion of the function  $f(x, y, z, \dots)$

$$\sigma_r^2 = \left(\frac{\partial f}{\partial x}\right)^2 \sigma_x^2 + \left(\frac{\partial f}{\partial y}\right)^2 \sigma_y^2 + \left(\frac{\partial f}{\partial z}\right)^2 \sigma_z^2 + \dots + 2\left(\frac{\partial f}{\partial x}\right)\left(\frac{\partial f}{\partial y}\right)\text{Cov}(x, y) + 2\left(\frac{\partial f}{\partial x}\right)\left(\frac{\partial f}{\partial z}\right)\text{Cov}(x, z) + \dots$$

It should be noted that not all of the variables  $x$ ,  $y$ ,  $z$ , etc will be correlated.

Also, if the variables  $x$ ,  $y$ ,  $z$ , ... are uncorrelated, then the covariance terms are zero and the variance of  $r$  becomes

$$\sigma_r^2 = \left(\frac{\partial f}{\partial x}\right)^2 \sigma_x^2 + \left(\frac{\partial f}{\partial y}\right)^2 \sigma_y^2 + \left(\frac{\partial f}{\partial z}\right)^2 \sigma_z^2 + \dots$$

# Product of Two Measurements

---

Consider a U235 gram amount determination that is calculated as follows:

$$G = V \times C, \text{ where}$$

$$G = {}^{235}\text{U} \text{ gram amount}$$

$$V = \text{Measured tank volume}$$

$$C = \text{Measured concentration from a sample}$$

$$\sigma_v = \text{Random uncertainty for volume}$$

$$\sigma_c = \text{Random uncertainty for concentration}$$

Assume additive models for both  $V$  and  $C$  and that  $V$  and  $C$  are not correlated.

What is the variance of  $G$ ?

# Product of Two Measurements

---

The partial derivatives are as follows:

$$\sigma_G^2 = \left(\frac{\partial G}{\partial V}\right)^2 \sigma_V^2 + \left(\frac{\partial G}{\partial C}\right)^2 \sigma_C^2 = C^2 \sigma_V^2 + V^2 \sigma_C^2$$

If  $\sigma_V$  and  $\sigma_C$  are relative uncertainties, then the variance of G is as follows:

$$\sigma_G^2 = C^2 V^2 \sigma_V^2 + V^2 C^2 \sigma_C^2 = (VC)^2 \sigma_V^2 + (VC)^2 \sigma_C^2 = G^2 \sigma_V^2 + G^2 \sigma_C^2$$

In practice, the terms  $\sigma_V^2$  and  $\sigma_C^2$  would be estimated by  $s_V^2$  and  $s_C^2$  .

# Sums of Products

---

Consider a U-235 gram amount determination that is calculated as follows:

$$G = V_1 C_1 + V_2 C_2 \quad , \text{ where,}$$

$G$  = U-235 gram amount

$V_i$  = measured volume for tank i

$C_i$  = measured concentration for tank i

$\sigma_{V_i}$  = volume random uncertainty for tank i

$\sigma_{\beta C}$  = concentration systematic uncertainty

$\sigma_C$  = concentration random uncertainty

Assume  $\sigma_{V_i}$ ,  $\sigma_{\beta C}$  and  $\sigma_C$  are relative uncertainties.

What is  $V(G)$ ?

# Sums of Products

---

Since the uncertainties are relative, the  $V(G)$  will be relative to the  $G_1$  and  $G_2$  gram amounts. The  $V(G)$  calculation is as follows:

$$\begin{aligned}\sigma_G^2 &= G_1^2 \sigma_{V1}^2 + G_1^2 \sigma_{\beta C}^2 + G_1^2 \sigma_C^2 + G_2^2 \sigma_{V2}^2 + G_2^2 \sigma_{\beta C}^2 + G_2^2 \sigma_C^2 + 2G_1 G_2 \sigma_{\beta C}^2 \\ &= G_1^2 \sigma_{V1}^2 + G_2^2 \sigma_{V2}^2 + (G_1^2 + G_2^2) \sigma_C^2 + (G_1^2 + G_2^2) \sigma_{\beta C}^2 + 2G_1 G_2 \sigma_{\beta C}^2 \\ &= G_1^2 \sigma_{V1}^2 + G_2^2 \sigma_{V2}^2 + (G_1^2 + G_2^2) \sigma_C^2 + (G_1 + G_2)^2 \sigma_{\beta C}^2\end{aligned}$$

Again, the terms  $\sigma_{V1}^2$ ,  $\sigma_{V2}^2$ ,  $\sigma_C^2$ , and  $\sigma_{\beta C}^2$  would be estimated by  $s_{V1}^2$ ,  $s_{V2}^2$ ,  $s_C^2$  and  $s_{\beta C}^2$ .

# Summary

---

- **Discussed the basic concepts of variance propagation**
- **Reviewed the propagation of random variances**
- **Reviewed the propagation of systematic variances**
- **Used Excel for solving variance propagation problems**

**Chinese Measurement Control Workshop**  
**Measurement Method Qualification Module**  
**Davies-Gray Concentration Measurements**  
**Exercise #5**

		<b>Result</b>	<b>Standard</b>	
	<b>Measurement</b>	<b>in</b>	<b>in</b>	<b>Relative</b>
<b>Sample ID</b>	<b>Date</b>	<b>mg/g</b>	<b>mg/g</b>	<b>Difference</b>
200158371	12-Jun-01	54.0506	54.0705	-0.0004
200158373	12-Jun-01	53.9417	54.0705	-0.0024
200158374	12-Jun-01	53.9998	54.0705	-0.0013
200158375	12-Jun-01	53.9956	54.0705	-0.0014
200161089	19-Jun-01	54.0748	54.0705	0.0001
200162439	19-Jun-01	54.1235	54.0705	0.001
200161086	19-Jun-01	53.9037	54.0705	-0.0031
200161088	19-Jun-01	54.2321	54.0705	0.003
200161092	19-Jun-01	54.2349	54.0705	0.003
200158379	20-Jun-01	54.1849	54.0705	0.0021
200163495	28-Jun-01	54.0767	54.0705	0.0001
200162441	28-Jun-01	54.0088	54.0705	-0.0011
200162458	23-Jul-01	54.26	54.0705	0.0035
200162460	25-Jul-01	54.1456	54.0705	0.0014
200162469	1-Aug-01	54.105	54.0705	0.0006
200162466	1-Aug-01	54.0617	54.0705	-0.0002
200162468	1-Aug-01	54.0518	54.0705	-0.0003
200162471	11-Aug-01	54.1523	54.0705	0.0015
200163507	20-Aug-01	54.1328	54.0705	0.0012

<b>Relative Differences for Analysis</b>								
-0.0004	0.0001	0.0021	0.0001	0.0035	0.0014	0.0006	0.0015	0.0012
-0.0024	0.001		-0.0011			-0.0002		
-0.0013	-0.0031					-0.0003		
-0.0014	0.003							
	0.003							

Anova: Single Factor

**SUMMARY**

<i>Groups</i>	<i>Count</i>	<i>Sum</i>	<i>Average</i>	<i>Variance</i>
Column 1	4	-0.0055	-0.001375	6.69E-07
Column 2	5	0.004	0.0008	6.36E-06
Column 3	1	0.0021	0.0021	#DIV/0!
Column 4	2	-0.001	-0.0005	7.2E-07
Column 5	1	0.0035	0.0035	#DIV/0!
Column 6	1	0.0014	0.0014	#DIV/0!
Column 7	3	0.0001	3.33333E-05	2.43E-07
Column 8	1	0.0015	0.0015	#DIV/0!
Column 9	1	0.0012	0.0012	#DIV/0!

<b>Uncertainty Estimates</b>	
Bias	0.038%
Systematic	0.068%
Random	0.169%

**ANOVA**

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	3.08E-05	8	3.84639E-06	1.343286	0.324694	3.071658
Within Groups	2.86E-05	10	2.86342E-06			
<b>Total</b>	<b>5.94E-05</b>	<b>18</b>	<b>3.30029E-06</b>			

Since Systematic Variance is not significant, then Random=	0.18%
The standard deviation of the relative differences =	0.18%

**Measurement Method Qualification**  
**Davies-Gray Concentration Measurements**  
**One-Way ANOVA Results**

<b>Sample ID</b>	<b>Measurement Date</b>	<b>Result in mg/g</b>	<b>Standard in mg/g</b>	<b>Relative Difference</b>
200158371	12-Jun-01	54.0506	54.0705	-0.0004
200158373	12-Jun-01	53.9417	54.0705	-0.0024
200158374	12-Jun-01	53.9998	54.0705	-0.0013
200158375	12-Jun-01	53.9956	54.0705	-0.0014
200161089	19-Jun-01	54.0748	54.0705	0.0001
200162439	19-Jun-01	54.1235	54.0705	0.001
200161086	19-Jun-01	53.9037	54.0705	-0.0031
200161088	19-Jun-01	54.2321	54.0705	0.003
200161092	19-Jun-01	54.2349	54.0705	0.003
200158379	20-Jun-01	54.1849	54.0705	0.0021
200163495	28-Jun-01	54.0767	54.0705	0.0001
200162441	28-Jun-01	54.0088	54.0705	-0.0011
200162458	23-Jul-01	54.26	54.0705	0.0035
200162460	25-Jul-01	54.1456	54.0705	0.0014
200162469	1-Aug-01	54.105	54.0705	0.0006
200162466	1-Aug-01	54.0617	54.0705	-0.0002
200162468	1-Aug-01	54.0518	54.0705	-0.0003
200162471	11-Aug-01	54.1523	54.0705	0.0015
200163507	20-Aug-01	54.1328	54.0705	0.0012

## Exercise

# Variance Propagation

---

### Session Objectives:

After the session the participants will be able to do the following:

1. Understand the basic concepts of variance propagation
2. Understand the propagation of random variances
3. Understand the propagation of systematic variances
4. Be able to use Excel to solve variance propagation problems

### Estimated Time:

There are two exercises in this module. The completion times are as follows:

1. Exercise #1 – 30 minutes
2. Exercise #2 – 15 minutes

A total of 45 minutes will be required to complete the exercises.

### Materials Needed:

1. One computer with Microsoft Excel for each group of four or five students
2. This problem can be solved with pencil and paper or with Excel
3. Students need to have a good working knowledge of Microsoft Excel
4. Spreadsheet support person

### Instructions:

1. Students should work in groups of four or five
2. The exercise information is presented in the Student Copy Excel spreadsheet for this module
3. Students will use Excel to perform the needed calculations
4. All results will be discussed

## Exercise #1

Background Information:

After Pu oxide has been calcined, the material is loaded into a mixer/blending device where the material is blended for a set amount of time. After blending, four random samples are taken and sent to the laboratory for analysis. The final Pu weight % value is based on the average of the four analyses. Four containers are loaded with 500g of Pu from the blender. The amount of Pu in each container is determined by weight and the Pu weight % measurement from the laboratory. The readability of the scale is 0.1g.

The total inventory of Pu is computed as follows:

$$G = \sum_{ij} W_{ij}C_{ij}, \text{ for } i=1 \text{ to } 5 \text{ and } j=1 \text{ to } 5, \text{ where,}$$

$G$  = Total Pu grams

$W_{ij}$  = PuO<sub>2</sub> weight for the  $i^{\text{th}}$  batch and  $j^{\text{th}}$  container

$C_{ij}$  = Pu weight % for the  $i^{\text{th}}$  batch and  $j^{\text{th}}$  container

$\sigma_W$  = PuO<sub>2</sub> weight random uncertainty = 0.02%

( $\sigma_W$  is derived as  $100 \times (0.1\text{g}/500\text{g}) = 0.02\%$ )

$\sigma_C$  = Pu weight percent random uncertainty = 0.25%

For each container, assume the  $W_{ij}$  are equal to 500g and the  $C_{ij}$  are equal to 85% or 0.85.

Use Excel and the information provided to answer the following questions:

1. What is  $G$ ? **10,625 grams**
2. What is the random variance portion of  $V(G)$ ?  **$0.18\text{g}^2$**
3. Is there a systematic variance? **Yes**
  - If so, what is the systematic variance portion of  $V(G)$ ?  **$35.28\text{g}^2$**
4. What is  $V(G)$ ?  **$35.46\text{g}^2$**
5. Total uncertainty is **5.95g**

## Exercise #2

Background Information:

Everything is the same as for Exercise #1. The only difference is that no samples are taken from the blender. One sample is taken from each container and sent to the laboratory for analysis. A single weight percent measurement along with a weight measurement is used to determine the Pu inventory for a particular container.

Use Excel and the information provided to answer the following questions:

1. What is  $G$ ? **10,625 grams**
2. What is the random variance portion of  $V(G)$ ?  **$28.40\text{g}^2$**
3. Is there a systematic variance? **No**
  - If so, what is the systematic variance portion of  $V(G)$ ? **NA**
4. What is  $V(G)$ ?  **$28.40\text{g}^2$**
5. What is the total uncertainty? **5.33g**

<b>Variance Propagation Module</b>	
<b>Exercise #2 - One Sample from each Container</b>	
<b>Scale Uncertainty</b>	0.0002
<b>Weight % Uncertainty</b>	0.0025
<b>Number of batches</b>	5
<b>Number of containers</b>	5
<b>Pu Oxide in one container</b>	500
<b>Weight % for each container</b>	0.85
<b>Samples analyzed</b>	1
<b>Pu in one container</b>	425
<b>Total Pu</b>	10,625
<b>Systematic Variance</b>	0.00
<b>Systematic Uncertainty</b>	0.00
<b>Random Variance</b>	28.40
<b>Random Uncertainty</b>	5.33
<b>Total Variance</b>	28.40
<b>Total Uncertainty</b>	5.33

Weight and weight % applied to each container

# Exercise

## Variance Propagation

---

### Session Objectives:

After the session the participants will be able to do the following:

1. Understand the basic concepts of variance propagation
2. Understand the propagation of random variances
3. Understand the propagation of systematic variances
4. Be able to use Excel to solve variance propagation problems

### Estimated Time:

There are two exercises in this module. The completion times are as follows:

1. Exercise #1 – 30 minutes
2. Exercise #2 – 15 minutes

A total of 45 minutes will be required to complete the exercises.

### Materials Needed:

1. One computer with Microsoft Excel for each group of four or five students
2. This problem can be solved with pencil and paper or with Excel
3. Students need to have a good working knowledge of Microsoft Excel
4. Spreadsheet support person

### Instructions:

1. Students should work in groups of four or five
2. The exercise information is presented in the Student Copy Excel spreadsheet for this module
3. Students will use Excel to perform the needed calculations
4. All results will be discussed

## Exercise #1

Background Information:

After Pu oxide has been calcined, the material is loaded into a mixer/blending device where the material is blended for a set amount of time. After blending, four random samples are taken and sent to the laboratory for analysis. The final Pu weight % value is based on the average of the four analyses. Four containers are loaded with 500g of Pu from the blender. The amount of Pu in each container is determined by weight and the Pu weight % measurement from the laboratory. The readability of the scale is 0.1g.

The total inventory of Pu is computed as follows:

$$G = \sum_{ij} W_{ij}C_{ij}, \text{ for } i=1 \text{ to } 5 \text{ and } j=1 \text{ to } 5, \text{ where,}$$

$G$  = Total Pu grams

$W_{ij}$  = PuO<sub>2</sub> weight for the  $i^{\text{th}}$  batch and  $j^{\text{th}}$  container

$C_{ij}$  = Pu weight % for the  $i^{\text{th}}$  batch and  $j^{\text{th}}$  container

$\sigma_W$  = PuO<sub>2</sub> weight random uncertainty = 0.02%

( $\sigma_W$  is derived as  $100 \times (0.1\text{g}/500\text{g}) = 0.02\%$ )

$\sigma_C$  = Pu weight percent random uncertainty = 0.25%

For each container, assume the  $W_{ij}$  are equal to 500g and the  $C_{ij}$  are equal to 85% or 0.85.

Use Excel and the information provided to answer the following questions:

1. What is  $G$ ?
2. What is the random variance portion of  $V(G)$ ?
3. Is there a systematic variance?
  - If so, what is the systematic variance portion of  $V(G)$ ?
4. What is  $V(G)$ ?
5. Total uncertainty is

## Exercise #2

Background Information:

Everything is the same as for Exercise #1. The only difference is that no samples are taken from the blender. One sample is taken from each container and sent to the laboratory for analysis. A single weight percent measurement along with a weight measurement is used to determine the Pu inventory for a particular container.

Use Excel and the information provided to answer the following questions:

1. What is  $G$ ?
2. What is the random variance portion of  $V(G)$ ?
3. Is there a systematic variance?
  - If so, what is the systematic variance portion of  $V(G)$ ?
4. What is  $V(G)$ ?
5. What is the total uncertainty?

<b>Variance Propagation Module</b>	
<b>Exercise #1 - Average of 4 Samples from each Blender Batch</b>	
<b>Scale Uncertainty</b>	0.0002
<b>Weight % Uncertainty</b>	0.0025
<b>Number of batches</b>	5
<b>Number of containers</b>	5
<b>Pu Oxide in one container</b>	500
<b>Weight % for each container</b>	0.85
<b>Samples analyzed</b>	4
<b>Pu in one container</b>	425
<b>Total Pu</b>	
<b>Systematic Variance</b>	
<b>Systematic Uncertainty</b>	
<b>Random Variance</b>	
<b>Random Uncertainty</b>	
<b>Total Variance</b>	
<b>Total Uncertainty</b>	

**Chinese Measurement Control Workshop**  
**Measurement Method Qualification Module**  
**Davies-Gray Concentration Measurements**  
**Exercise #5**

		<b>Result</b>	<b>Standard</b>	
	<b>Measurement</b>	<b>in</b>	<b>in</b>	<b>Relative</b>
<b>Sample ID</b>	<b>Date</b>	<b>mg/g</b>	<b>mg/g</b>	<b>Difference</b>
200158371	12-Jun-01	54.0506	54.0705	-0.0004
200158373	12-Jun-01	53.9417	54.0705	-0.0024
200158374	12-Jun-01	53.9998	54.0705	-0.0013
200158375	12-Jun-01	53.9956	54.0705	-0.0014
200161089	19-Jun-01	54.0748	54.0705	0.0001
200162439	19-Jun-01	54.1235	54.0705	0.001
200161086	19-Jun-01	53.9037	54.0705	-0.0031
200161088	19-Jun-01	54.2321	54.0705	0.003
200161092	19-Jun-01	54.2349	54.0705	0.003
200158379	20-Jun-01	54.1849	54.0705	0.0021
200163495	28-Jun-01	54.0767	54.0705	0.0001
200162441	28-Jun-01	54.0088	54.0705	-0.0011
200162458	23-Jul-01	54.26	54.0705	0.0035
200162460	25-Jul-01	54.1456	54.0705	0.0014
200162469	1-Aug-01	54.105	54.0705	0.0006
200162466	1-Aug-01	54.0617	54.0705	-0.0002
200162468	1-Aug-01	54.0518	54.0705	-0.0003
200162471	11-Aug-01	54.1523	54.0705	0.0015
200163507	20-Aug-01	54.1328	54.0705	0.0012

<b>Relative Differences for Analysis</b>								
-0.0004	0.0001	0.0021	0.0001	0.0035	0.0014	0.0006	0.0015	0.0012
-0.0024	0.001		-0.0011			-0.0002		
-0.0013	-0.0031					-0.0003		
-0.0014	0.003							
	0.003							

Anova: Single Factor

**SUMMARY**

<i>Groups</i>	<i>Count</i>	<i>Sum</i>	<i>Average</i>	<i>Variance</i>
Column 1	4	-0.0055	-0.001375	6.69E-07
Column 2	5	0.004	0.0008	6.36E-06
Column 3	1	0.0021	0.0021	#DIV/0!
Column 4	2	-0.001	-0.0005	7.2E-07
Column 5	1	0.0035	0.0035	#DIV/0!
Column 6	1	0.0014	0.0014	#DIV/0!
Column 7	3	0.0001	3.33333E-05	2.43E-07
Column 8	1	0.0015	0.0015	#DIV/0!
Column 9	1	0.0012	0.0012	#DIV/0!

<b>Uncertainty Estimates</b>	
Bias	0.038%
Systematic	0.068%
Random	0.169%

**ANOVA**

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	3.08E-05	8	3.84639E-06	1.343286	0.324694	3.071658
Within Groups	2.86E-05	10	2.86342E-06			
<b>Total</b>	<b>5.94E-05</b>	<b>18</b>	<b>3.30029E-06</b>			

Since Systematic Variance is not significant, then Random=	0.18%
The standard deviation of the relative differences =	0.18%

**Measurement Method Qualification**  
**Davies-Gray Concentration Measurements**  
**One-Way ANOVA Results**

<b>Sample ID</b>	<b>Measurement Date</b>	<b>Result in mg/g</b>	<b>Standard in mg/g</b>	<b>Relative Difference</b>
200158371	12-Jun-01	54.0506	54.0705	-0.0004
200158373	12-Jun-01	53.9417	54.0705	-0.0024
200158374	12-Jun-01	53.9998	54.0705	-0.0013
200158375	12-Jun-01	53.9956	54.0705	-0.0014
200161089	19-Jun-01	54.0748	54.0705	0.0001
200162439	19-Jun-01	54.1235	54.0705	0.001
200161086	19-Jun-01	53.9037	54.0705	-0.0031
200161088	19-Jun-01	54.2321	54.0705	0.003
200161092	19-Jun-01	54.2349	54.0705	0.003
200158379	20-Jun-01	54.1849	54.0705	0.0021
200163495	28-Jun-01	54.0767	54.0705	0.0001
200162441	28-Jun-01	54.0088	54.0705	-0.0011
200162458	23-Jul-01	54.26	54.0705	0.0035
200162460	25-Jul-01	54.1456	54.0705	0.0014
200162469	1-Aug-01	54.105	54.0705	0.0006
200162466	1-Aug-01	54.0617	54.0705	-0.0002
200162468	1-Aug-01	54.0518	54.0705	-0.0003
200162471	11-Aug-01	54.1523	54.0705	0.0015
200163507	20-Aug-01	54.1328	54.0705	0.0012

Name: Lu  
 Method: Davies Gray U

Sample	Reported R Value	Known K Value	R - K Difference	Std. Dev. of Known	(R-K)/SD Normalized	((R-K)/SD)^2 Variance
1	24.900	25.000		0.0330		
2	10.006	10.000		0.0150		
3	10.008	10.020		0.0150		
4	25.010	25.000		0.0330		
5	25.001	25.000		0.0330		
6	24.985	25.000		0.0330		
7	2.005	2.000		0.0040		
8	10.022	10.000		0.0150		
9	10.006	10.020		0.0150		

Total =  $\Sigma(R-K)/SD =$  \_\_\_\_\_  
 Sum of Squares =  $\Sigma((R-K)/SD)^2 =$  \_\_\_\_\_  
 SUM = Absolute value of Total FF =  $SS/N =$  \_\_\_\_\_  
 SUM =  $TT = \Sigma(SUM(ABS)N^{.5} =$  \_\_\_\_\_  
 N = 9

If TT is greater than  $T(N)^*$ , then the bias is significantly greater than zero  
 If FF is greater than  $F(N)^{**}$ , then the Std. Dev. Is significantly greater than one.  
 N is the number of analyses in the current quality control program.

BIAS IS: Significant \_\_\_\_\_ Not Significant \_\_\_\_\_  
 STD DEV. IS: Significant \_\_\_\_\_ Not Significant \_\_\_\_\_

\* t-Table value for  $(\alpha=0.1)/2$  and 60 df = 1.67  
 \*\* F Table Value at the 90% CI for df 60 & 9 = 1.74

Standards	Concentration mgU/gSol	Method RSD	Method SD
1	2.000	0.20%	0.004
2	10.000	0.15%	0.015
3	10.020	0.15%	0.015
4	25.000	0.13%	0.033

# Module 6. Proficiency Testing & Sample Exchange



## Module 6

### Proficiency Training & Testing Program & Sample Exchange Programs

#### Learning Objectives

- Demonstrate method for qualifying lab personnel
- Understand the statistical criteria for qualification
- Study an example of data collected in testing program
- Illustrate how sequential testing can expedite training
- Review US DOE proficiency testing program (sample exchange)

Module 6 - 2

#### Department of Energy Order Training Plan Requirements

- Training: Each facility shall have a documented plan for the training of measurement personnel. It shall specify training, qualification, and requalification requirements for each measurement method
- Qualification program shall ensure measurement personnel demonstrate acceptable levels of proficiency before performing measurements, and are re-qualified according to requirements in the training plan
- For destructive analysis of nuclear material, this proficiency shall be demonstrated, at a minimum, once per day for each method used that day

Module 6 - 3

#### Elements of Training Program

- Academic training: completion of high school or above, depending on responsibility required for the job
- Applicable experience
- On-the-job training in an analytical chemistry laboratory
- Special courses: seminars, factory instrumentation classes, or company training courses, shall be used to update and improve skills

Module 6 - 4

#### Statistical Criteria for Testing

- QC program's method standard deviation for each standard is used to normalize the trainee's difference between the measured & known values
- A modified student's t-test is used to compare the trainee's absolute average bias with the table value at 90% confidence interval with 60 degrees of freedom
- The trainee's and method's average random errors are compared using an F test
- Testing is done at the 90% confidence level for testing the trainee's bias and reproducibility
  - 60 degrees of freedom for t-test value of 1.67 and
  - 60 and 9 degrees of freedom for F-test value of 1.74 are used as the critical limits for their bias and precision.

Module 6 - 5

#### Overview of Training Program

- Method is demonstrated to Analyst
- Procedure is read & applied
- Known standards are run until confident
- Testing involves analyzing 9 unknowns over 3 days
- Testing data evaluated against method's uncertainty

Module 6 - 6

# Module 6. Proficiency Testing & Sample Exchange

## T&T Evaluation Form: Record trainee's measurands of unknown QC standards

Name: George		Method: Davies & Gray U				
Sample	Reported R Value	Known K Value	R - K Difference	Std. Dev. of Known	(R-K)/SD Normalized	
1	1.992					
2	10.006					
3	10.008					
4	25.010					
5	25.001					
6	24.985					
7	2.005					
8	10.000					
9	10.006					
Sum of Squares=			Total =	$\sum(R-K)/SD=$		
SUM=	Absolute value of Total FF =		TT=	$\sum((R-K)/SD)^2=$		
SUM=				SS/N=		
				ABS(SUM)/N <sup>2</sup> =		

If TT is greater than T(N)\*, then the bias is significantly greater than zero  
 If FF is greater than F(N)\*\*, then the Std. Dev. is significantly greater than one.  
 N is the number of analyses in the current quality control program.  
 BIAS IS: Significant Not Significant  
 STD DEV. IS: Significant Not Significant  
 \* t-Table value for (α= 0.1)/2 and 60 df = 1.67  
 \*\* F Table Value at the 90% CI for df 60 & 9 =1.74

Module 6 - 7

## QC Standards Used for Training & Testing

U Standards	Standard Uncertainty (U)	Relative Standard U
Known	Std Dev	% Std Dev
2.000	0.0040	0.20%
10.000	0.0120	0.12%
10.010	0.0120	0.12%
25.000	0.0250	0.10%

Module 6

Module 6 - 8

## T&T Data Evaluation Form: + known values & their standard uncertainties

Name: George		Method: Davies & Gray U				
Sample	Reported R Value	Known K Value	R - K Difference	Std. Dev. of Known	(R-K)/SD Normalized	
1	1.992	2.000		0.004		
2	10.006	10.000		0.012		
3	10.008	10.010		0.012		
4	25.010	25.000		0.025		
5	25.001	25.000		0.025		
6	24.985	25.000		0.025		
7	2.005	2.000		0.004		
8	10.000	10.010		0.012		
9	10.006	10.000		0.012		
Sum of Squares=			Total =	$\sum(R-K)/SD=$		
SUM=	Absolute value of Total FF =		TT=	$\sum((R-K)/SD)^2=$		
SUM=				SS/N=		
				ABS(SUM)/N <sup>2</sup> =		

If TT is greater than T(N)\*, then the bias is significantly greater than zero  
 If FF is greater than F(N)\*\*, then the Std. Dev. is significantly greater than one.  
 N is the number of analyses in the current quality control program.  
 BIAS IS: Significant Not Significant  
 STD DEV. IS: Significant Not Significant  
 \* t-Table value for (α= 0.1)/2 and 60 df = 1.67  
 \*\* F Table Value at the 90% CI for df 60 & 9 =1.74

Module 6 - 9

## T&T Data Evaluation Form: Reported – known values = bias (difference)

Name: George		Method: Davies & Gray U		Bias		
Sample	Reported R Value	Known K Value	R - K Difference	Std. Dev. of Known	(R-K)/SD Normalized	
1	1.992	2.000	-0.008	0.0040	0.0040	
2	10.006	10.000	0.006	0.0120	0.0120	
3	10.008	10.010	-0.002	0.0120	0.0120	
4	25.010	25.000	0.010	0.0250	0.0250	
5	25.001	25.000	0.001	0.0250	0.0250	
6	24.985	25.000	-0.015	0.0250	0.0250	
7	2.005	2.000	0.005	0.0040	0.0040	
8	10.000	10.010	-0.010	0.0120	0.0120	
9	10.006	10.000	0.006	0.0120	0.0120	
Sum of Squares=			Total =	$\sum(R-K)/SD=$		
SUM=	Absolute value of Total FF =		TT=	$\sum((R-K)/SD)^2=$		
SUM=				SS/N=		
				ABS(SUM)/N <sup>2</sup> =		

If TT is greater than T(N)\*, then the bias is significantly greater than zero  
 If FF is greater than F(N)\*\*, then the Std. Dev. is significantly greater than one.  
 N is the number of analyses in the current quality control program.  
 BIAS IS: Significant Not Significant  
 STD DEV. IS: Significant Not Significant  
 \* t-Table value for (α= 0.1)/2 and 60 df = 1.67  
 \*\* F Table Value at the 90% CI for df 60 & 9 =1.74

Module 6 - 10

## T&T Data Evaluation Form: Bias values normalized by dividing by SD of U Stds.

Name: George		Method: Davies & Gray U			Bias in Std. Deviations	
Sample	Reported R Value	Known K Value	R - K Difference	Std. Dev. of Known	(R-K)/SD Normalized	
1	1.992	2.000	-0.008	0.0040	-2.00	
2	10.006	10.000	0.006	0.0120	0.50	
3	10.008	10.010	-0.002	0.0120	-0.17	
4	25.010	25.000	0.010	0.0250	0.40	
5	25.001	25.000	0.001	0.0250	0.04	
6	24.985	25.000	-0.015	0.0250	-0.60	
7	2.005	2.000	0.005	0.0040	1.25	
8	10.000	10.010	-0.010	0.0120	-0.83	
9	10.006	10.000	0.006	0.0120	0.50	
Sum of Squares=			Total =	$\sum(R-K)/SD=$		
SUM=	Absolute value of Total FF =		TT=	$\sum((R-K)/SD)^2=$		
SUM=				SS/N=		
				ABS(SUM)/N <sup>2</sup> =		

If TT is greater than T(N)\*, then the bias is significantly greater than zero  
 If FF is greater than F(N)\*\*, then the Std. Dev. is significantly greater than one.  
 N is the number of analyses in the current quality control program.  
 BIAS IS: Significant Not Significant  
 STD DEV. IS: Significant Not Significant  
 \* t-Table value for (α= 0.1)/2 and 60 df = 1.67  
 \*\* F Table Value at the 90% CI for df 60 & 9 =1.74

Module 6 - 11

## T&T Data Evaluation Form: Bias t-tested & variance ratio F tested (Pass)

Name: Lu		Method: Davies Gray U				
Sample	Reported R Value	Known K Value	R - K Difference	Std. Dev. of Known	(R-K)/SD Normalized	
1	24.900	25.000	-0.100	0.0330	-3.03	
2	10.006	10.000	0.006	0.0150	0.40	
3	10.008	10.020	-0.012	0.0150	-0.80	
4	25.010	25.000	0.010	0.0330	0.30	
5	25.001	25.000	0.001	0.0330	0.03	
6	24.985	25.000	-0.015	0.0330	-0.45	
7	2.005	2.000	0.005	0.0040	1.25	
8	10.022	10.000	0.022	0.0150	1.46	
9	10.006	10.020	-0.014	0.0150	-0.93	
Sum of Squares=			Total =	$\sum(R-K)/SD=$		
SUM=	Absolute value of Total FF =		TT=	$\sum((R-K)/SD)^2=$		
SUM=				SS/N=		
				ABS(SUM)/N <sup>2</sup> =		

Technician is considered qualified  
 If TT is greater than T(N)\*, then the bias is significantly greater than zero  
 If FF is greater than F(N)\*\*, then the Std. Dev. is significantly greater than one.  
 N is the number of analyses in the current quality control program.  
 BIAS IS: Significant Not Significant  
 STD DEV. IS: Significant Not Significant  
 \* t-Table value for (α= 0.1)/2 and 60 df = 1.67  
 \*\* F Table Value at the 90% CI for df 60 & 9 =1.74

Module 6 - 12

# Module 6. Proficiency Testing & Sample Exchange

Name: **George**  
 Method: **Davies & Gray U**

Sample	Reported R Value	Known K Value	R - K Difference	Std. Dev. of Known	(R-K)/SD Normalized
1	7.992	2.000	-0.008	0.0040	-2.00
2	10.006	10.000	0.006	0.0120	0.50
3	10.008	10.010	-0.002	0.0120	-0.17
4	25.010	25.000	0.010	0.0250	0.40
5	25.001	25.000	0.001	0.0250	0.04
6	24.985	25.000	-0.015	0.0250	-0.60
7	1.990	2.000	-0.010	0.0040	-2.50
8	9.988	10.010	-0.022	0.0120	-1.83
9	10.006	10.000	0.006	0.0120	0.50

Sum of Squares =  $\sum(R-K)^2 = -5.66$   
 Absolute value of Total FF =  $\sum|(R-K)/SD| = 14.65$   
 SS/N =  $1.63$   
 ABS(SUM)/N =  $1.89$

**Technician must retest before qualified.**  
 If TT is greater than T(N)\*, then the bias is significantly greater than zero  
 If FF is greater than F(N)\*\*, then the Std. Dev. is significantly greater than one.  
 N is the number of analyses in the current quality control program.

BIAS IS: Significant **X** Not Significant  
 STD DEV. IS: Significant Not Significant **X**

\* t-Table value for  $(\alpha = 0.1)/2$  and 60 df = 1.67  
 \*\* F Table Value at the 90% CI for df 60 & 9 = 1.74

Module 6 - 13

## T&T Qualification Exercise

### Calculate: Use your calculator to solve

Name: **Lu**  
 Method: **Davies Gray U**

Sample	Reported R Value	Known K Value	R - K Difference	Std. Dev. of Known	(R-K)/SD Normalized	((R-K)/SD) <sup>2</sup> Variance
1	24.990	25.000	-0.010	0.0330	-0.30	0.09
2	10.006	10.000	0.006	0.0150	0.40	0.16
3	10.008	10.020	-0.012	0.0150	-0.80	0.64
4	25.010	25.000	0.010	0.0330	0.30	0.09
5	25.001	25.000	0.001	0.0330	0.03	0.00
6	24.985	25.000	-0.015	0.0330	-0.45	0.21
7	2.005	2.000	0.005	0.0040	1.25	1.56
8	10.022	10.000	0.022	0.0150	1.47	2.15
9	10.006	10.020	-0.014	0.0150	-0.93	0.87

Sum of Squares =  $\sum(R-K)^2 = 14.87$   
 Absolute value of Total FF =  $\sum|(R-K)/SD| = 14.65$   
 SS/N =  $1.65$   
 ABS(SUM)/N =  $0.59$

N = 9

If TT is greater than T(N)\*, then the bias is significantly greater than zero  
 If FF is greater than F(N)\*\*, then the Std. Dev. is significantly greater than one.  
 N is the number of analyses in the current quality control program.

BIAS IS: Significant Not Significant  
 STD DEV. IS: Significant Not Significant

Module 6 - 14

## Completed T&T Exercise Worksheet

Completed Work Sheet      Instructor's Notes

Name: **Lu**  
 Method: **Davies Gray U**

Sample	Reported R Value	Known K Value	R - K Difference	Std. Dev. of Known	(R-K)/SD Normalized	((R-K)/SD) <sup>2</sup> Variance
1	24.990	25.000	-0.010	0.0330	-0.30	0.09
2	10.006	10.000	0.006	0.0150	0.40	0.16
3	10.008	10.020	-0.012	0.0150	-0.80	0.64
4	25.010	25.000	0.010	0.0330	0.30	0.09
5	25.001	25.000	0.001	0.0330	0.03	0.00
6	24.985	25.000	-0.015	0.0330	-0.45	0.21
7	2.005	2.000	0.005	0.0040	1.25	1.56
8	10.022	10.000	0.022	0.0150	1.47	2.15
9	10.006	10.020	-0.014	0.0150	-0.93	0.87

Sum of Squares =  $\sum(R-K)^2 = 14.87$   
 Absolute value of Total FF =  $\sum|(R-K)/SD| = 14.65$   
 SS/N =  $1.65$   
 ABS(SUM)/N =  $0.59$

N = 9

If TT is greater than T(N)\*, then the bias is significantly greater than zero  
 If FF is greater than F(N)\*\*, then the Std. Dev. is significantly greater than one.  
 N is the number of analyses in the current quality control program.

BIAS IS: Significant Not Significant **X**  
 STD DEV. IS: Significant Not Significant **X**

\* t-Table value for  $(\alpha = 0.1)/2$  and 60 df = 1.67  
 \*\* F Table Value at the 90% CI for df 60 & 9 = 1.74

Module 6 - 15

## Performance Testing Required Before Qualification Attained

- Technician qualified if his t and F values are less than the statistical limits established (*slide 5*)
- Technician must re-test if either value exceeds the limits
- If a manual system is used in the testing program, significant time can lapse between the time the trainee submits his testing data and the time it is evaluated and returned to management
- An automated program can be used to evaluate testing data and greatly reduce the training and testing time

Module 6 - 16

## Sequential Tests of Trainee Precision and Accuracy-1

- Why Sequential Testing?
  - A sequential test can be more efficient (in terms of number of required tests) than a preset number of samples
- When is a Sequential Test Preferred over a preset number of samples?
  - If the technician precision and accuracy is generally much better or much worse than the acceptable levels of precision and accuracy, a sequential test generally is preferred to a preset number of samples, because an early decision is likely
  - If a decision cannot be easily and quickly made between successive stages (measurements), then a preset number of samples is preferable

Module 6 - 17

## Sequential Tests of Trainee Precision and Accuracy-2

- Preset number of samples
  - A preset number of measurements must be completed. Then a rule is applied to decide between a hypothesis (A) that the technician has acceptable precision and accuracy and a hypothesis (B) that the technician does not have acceptable precision or accuracy
- Sequential Test
  - The sample size is not preset. The sample size varies from application to application. After each measurement a rule is defined to decide whether (A) that the technician has acceptable precision and accuracy, a hypothesis (B) that the technician does not have acceptable precision or accuracy, or (C) insufficient information exists to make a determination between (A) and (B)

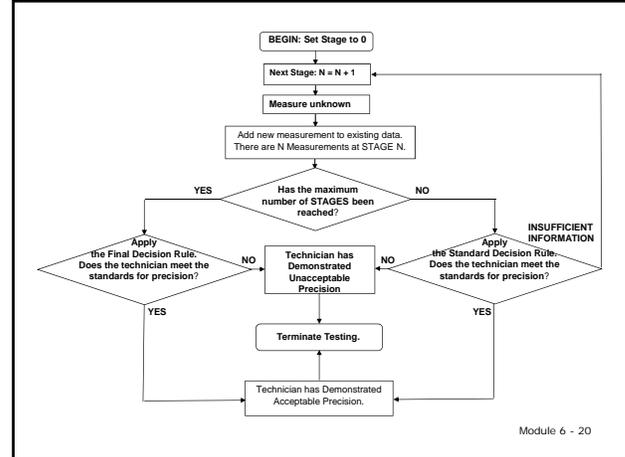
Module 6 - 18

# Module 6. Proficiency Testing & Sample Exchange

## Sequential Tests of Trainee Precision and Accuracy-3

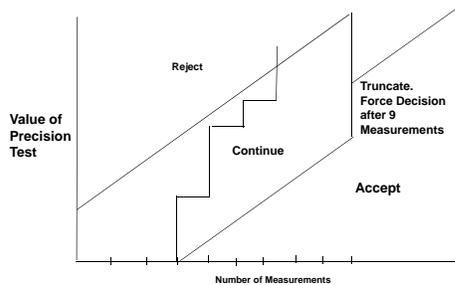
- Can a sequential test fail to terminate?
  - No, but the number of measurement could be very large in some of the applications
  - This is not an issue with a truncated sequential test. A truncated sequential test is forced to terminate after a preset maximum
- What is the technical basis for the technician accuracy and precision tests?
  - The technician accuracy and precision tests are based on a truncated sequential probability ratio tests (SPRT). An SPRT minimizes the expected sample size under the null and alternative hypotheses for stated probabilities of false positives and false negatives

Module 6 - 19



Module 6 - 20

## Graphical Procedure for Sequential Testing



Module 6 - 21

## Current T&T Program

- Training and practice is the same
- A computer program evaluates the testing data as it is collected
- If a value exceeds a critical limit they must start over
- If the trainee demonstrates excellent results on the first 6 samples they qualify
- This improvement significantly reduces training time and allows the lab to use the trainee to provide analytical support sooner

Module 6 - 22

## Training & Testing Program Summary

- Trainees must perform multiple measurements within specified bias and precision limits to demonstrate their measurement proficiency
- Manual testing systems often delay qualifying trainees and waste time in qualifying them to make routine laboratory measurements
- Automated evaluation of testing data using sequential testing enhances the training and testing qualification process

Module 6 - 23

## Summary

- Demonstrated method for qualifying lab personnel
- Described the statistical criteria for qualification
- Reviewed an example of data collected in testing program
- Illustrated how sequential testing can expedite training

Module 6 - 24

# Module 6. Proficiency Testing & Sample Exchange



## Module 6

### Proficiency Training & Testing Program

#### Learning Objectives

- Demonstrate method for qualifying lab personnel
- Understand the statistical criteria for qualification
- Study an example of data collected in testing program
- Illustrate how sequential testing can expedite training

Module 6 - 2

#### Department of Energy Order Training Plan Requirements

- Training: Each facility shall have a documented plan for the training of measurement personnel. It shall specify training, qualification, and requalification requirements for each measurement method
- Qualification program shall ensure measurement personnel demonstrate acceptable levels of proficiency before performing measurements, and are re-qualified according to requirements in the training plan
- For destructive analysis of nuclear material, this proficiency shall be demonstrated, at a minimum, once per day for each method used that day

Module 6 - 3

#### Elements of Training Program

- Academic training: completion of high school or above, depending on responsibility required for the job
- Applicable experience
- On-the-job training in an analytical chemistry laboratory
- Special courses: seminars, factory instrumentation classes, or company training courses, shall be used to update and improve skills

Module 6 - 4

#### Statistical Criteria for Testing

- QC program's method standard deviation for each standard is used to normalize the trainee's difference between the measured & known values
- A modified student's t-test is used to compare the trainee's absolute average bias with the table value at 90% confidence interval with 60 degrees of freedom
- The trainee's and method's average random errors are compared using an F test
- Testing is done at the 90% confidence level for testing the trainee's bias and reproducibility
  - 60 degrees of freedom for t-test value of 1.67 and
  - 60 and 9 degrees of freedom for F-test value of 1.74 are used as the critical limits for their bias and precision.

Module 6 - 5

#### Overview of Training Program

- Method is demonstrated to Analyst
- Procedure is read & applied
- Known standards are run until confident
- Testing involves analyzing 9 unknowns over 3 days
- Testing data evaluated against method's uncertainty

Module 6 - 6

# Module 6. Proficiency Testing & Sample Exchange

## T&T Evaluation Form: Record trainee's measurands of unknown QC standards

Name: George		Method: Davies & Gray U				
Sample	Reported R Value	Known K Value	R - K Difference	Std. Dev. of Known	(R-K)/SD Normalized	
1	1.992					
2	10.006					
3	10.008					
4	25.010					
5	25.001					
6	24.985					
7	2.005					
8	10.000					
9	10.006					
Sum of Squares=			Total =	$\sum(R-K)/SD=$		
SUM=	Absolute value of Total FF =		TT=	$\sum((R-K)/SD)^2=$		
SUM=				SS/N=		
				ABS(SUM)/N =		

If TT is greater than T(N)\*, then the bias is significantly greater than zero  
 If FF is greater than F(N)\*\*, then the Std. Dev. is significantly greater than one.  
 N is the number of analyses in the current quality control program.  
 BIAS IS: Significant Not Significant  
 STD DEV. IS: Significant Not Significant  
 \* t-Table value for  $(\alpha=0.1)/2$  and 60 df = 1.67  
 \*\* F Table Value at the 90% CI for df 60 & 9 = 1.74

Module 6 - 7

## QC Standards Used for Training & Testing

U Standards	Standard Uncertainty (U)	Relative Standard U
Known	Std Dev	% Std Dev
2.000	0.0040	0.20%
10.000	0.0120	0.12%
10.010	0.0120	0.12%
25.000	0.0250	0.10%

Module 6

Module 6 - 8

## T&T Data Evaluation Form: + known values & their standard uncertainties

Name: George		Method: Davies & Gray U				
Sample	Reported R Value	Known K Value	R - K Difference	Std. Dev. of Known	(R-K)/SD Normalized	
1	1.992	2.000		0.004		
2	10.006	10.000		0.012		
3	10.008	10.010		0.012		
4	25.010	25.000		0.025		
5	25.001	25.000		0.025		
6	24.985	25.000		0.025		
7	2.005	2.000		0.004		
8	10.000	10.010		0.012		
9	10.006	10.000		0.012		
Sum of Squares=			Total =	$\sum(R-K)/SD=$		
SUM=	Absolute value of Total FF =		TT=	$\sum((R-K)/SD)^2=$		
SUM=				SS/N=		
				ABS(SUM)/N =		

If TT is greater than T(N)\*, then the bias is significantly greater than zero  
 If FF is greater than F(N)\*\*, then the Std. Dev. is significantly greater than one.  
 N is the number of analyses in the current quality control program.  
 BIAS IS: Significant Not Significant  
 STD DEV. IS: Significant Not Significant  
 \* t-Table value for  $(\alpha=0.1)/2$  and 60 df = 1.67  
 \*\* F Table Value at the 90% CI for df 60 & 9 = 1.74

Module 6 - 9

## T&T Data Evaluation Form: Reported - known values = bias (difference)

Name: George		Method: Davies & Gray U		Bias		
Sample	Reported R Value	Known K Value	R - K Difference	Std. Dev. of Known	(R-K)/SD Normalized	
1	1.992	2.000	-0.008	0.0040	0.0040	
2	10.006	10.000	0.006	0.0120	0.0120	
3	10.008	10.010	-0.002	0.0120	0.0120	
4	25.010	25.000	0.010	0.0250	0.0250	
5	25.001	25.000	0.001	0.0250	0.0250	
6	24.985	25.000	-0.015	0.0250	0.0250	
7	2.005	2.000	0.005	0.0040	0.0040	
8	10.000	10.010	-0.010	0.0120	0.0120	
9	10.006	10.000	0.006	0.0120	0.0120	
Sum of Squares=			Total =	$\sum(R-K)/SD=$		
SUM=	Absolute value of Total FF =		TT=	$\sum((R-K)/SD)^2=$		
SUM=				SS/N=		
				ABS(SUM)/N =		

If TT is greater than T(N)\*, then the bias is significantly greater than zero  
 If FF is greater than F(N)\*\*, then the Std. Dev. is significantly greater than one.  
 N is the number of analyses in the current quality control program.  
 BIAS IS: Significant Not Significant  
 STD DEV. IS: Significant Not Significant  
 \* t-Table value for  $(\alpha=0.1)/2$  and 60 df = 1.67  
 \*\* F Table Value at the 90% CI for df 60 & 9 = 1.74

Module 6 - 10

## T&T Data Evaluation Form: Bias values normalized by dividing by SD of U Stds.

Name: George		Method: Davies & Gray U			Bias in Std. Deviations	
Sample	Reported R Value	Known K Value	R - K Difference	Std. Dev. of Known	(R-K)/SD Normalized	
1	1.992	2.000	-0.008	0.0040	-2.00	
2	10.006	10.000	0.006	0.0120	0.50	
3	10.008	10.010	-0.002	0.0120	-0.17	
4	25.010	25.000	0.010	0.0250	0.40	
5	25.001	25.000	0.001	0.0250	0.04	
6	24.985	25.000	-0.015	0.0250	-0.60	
7	2.005	2.000	0.005	0.0040	1.25	
8	10.000	10.010	-0.010	0.0120	-0.83	
9	10.006	10.000	0.006	0.0120	0.50	
Sum of Squares=			Total =	$\sum(R-K)/SD=$		
SUM=	Absolute value of Total FF =		TT=	$\sum((R-K)/SD)^2=$		
SUM=				SS/N=		
				ABS(SUM)/N =		

If TT is greater than T(N)\*, then the bias is significantly greater than zero  
 If FF is greater than F(N)\*\*, then the Std. Dev. is significantly greater than one.  
 N is the number of analyses in the current quality control program.  
 BIAS IS: Significant Not Significant  
 STD DEV. IS: Significant Not Significant  
 \* t-Table value for  $(\alpha=0.1)/2$  and 60 df = 1.67  
 \*\* F Table Value at the 90% CI for df 60 & 9 = 1.74

Module 6 - 11

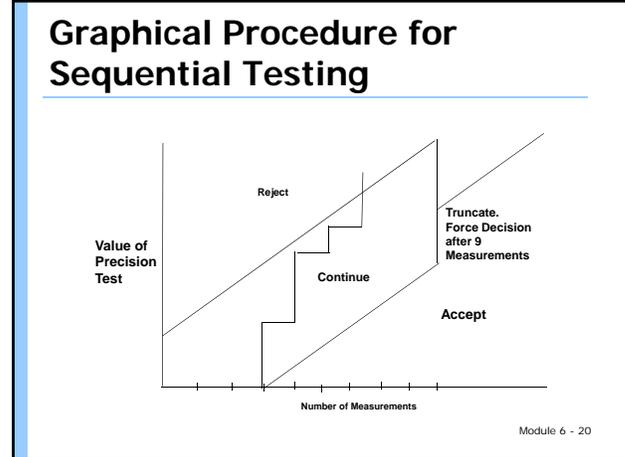
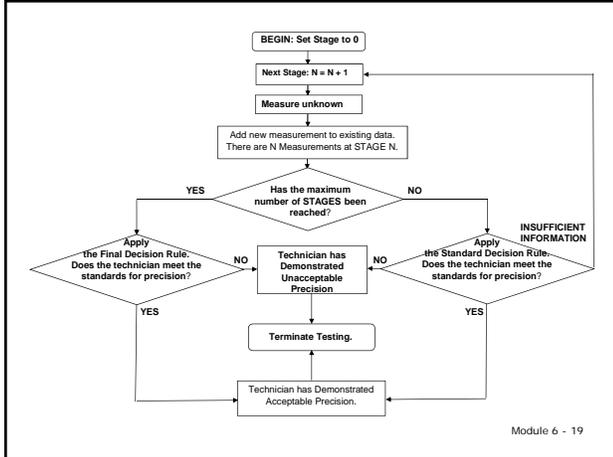
Name: George		Method: Davies & Gray U				
Sample	Reported R Value	Known K Value	R - K Difference	Std. Dev. of Known	(R-K)/SD Normalized	
1	1.992	2.000	-0.008	0.0040	-2.00	
2	10.006	10.000	0.006	0.0120	0.50	
3	10.008	10.010	-0.002	0.0120	-0.17	
4	25.010	25.000	0.010	0.0250	0.40	
5	25.001	25.000	0.001	0.0250	0.04	
6	24.985	25.000	-0.015	0.0250	-0.60	
7	2.005	2.000	0.005	0.0040	1.25	
8	10.000	10.010	-0.010	0.0120	-0.83	
9	10.006	10.000	0.006	0.0120	0.50	
Sum of Squares=			Total =	$\sum(R-K)/SD=$		
SUM=	Absolute value of Total FF =		TT=	$\sum((R-K)/SD)^2=$		
SUM=				SS/N=		
				ABS(SUM)/N =		

Technician must retest before qualified.  
 If TT is greater than T(N)\*, then the bias is significantly greater than zero  
 If FF is greater than F(N)\*\*, then the Std. Dev. is significantly greater than one.  
 N is the number of analyses in the current quality control program.  
 BIAS IS: Significant Not Significant  
 STD DEV. IS: Significant Not Significant  
 \* t-Table value for  $(\alpha=0.1)/2$  and 60 df = 1.67  
 \*\* F Table Value at the 90% CI for df 60 & 9 = 1.74

Module 6 - 12



# Module 6. Proficiency Testing & Sample Exchange



## Current T&T Program

- Training and practice is the same
- A computer program evaluates the testing data as it is collected
- If a value exceeds a critical limit they must start over
- If the trainee demonstrates excellent results on the first 6 samples they qualify
- This improvement significantly reduces training time and allows the lab to use the trainee to provide analytical support sooner

Module 6 - 21

## Training & Testing Program Summary

- Trainees must perform multiple measurements within specified bias and precision limits to demonstrate their measurement proficiency
- Manual testing systems often delay qualifying trainees and waste time in qualifying them to make routine laboratory measurements
- Automated evaluation of testing data using sequential testing enhances the training and testing qualification process

Module 6 - 22

## Summary

- Demonstrated method for qualifying lab personnel
- Described the statistical criteria for qualification
- Reviewed an example of data collected in testing program
- Illustrated how sequential testing can expedite training

Module 6 - 23

## Technician Training and Testing Results Evaluation Exercise:

Evaluate the data below as follows:

1. Subtract the known value from the reported value and record in column R-K
2. Divide these values by the corresponding Standard Deviation (SD) and record in the last column.
3. Sum the values in column (R-K)/SD and record in first cell below the column as  $\Sigma (R-K)/SD=$  below.
4. Square each value in the (R-K)/SD column and sum and record them as  $\Sigma((R-K)/SD)^2=$  below.
5. Divide the total from line 4 above by 9, which is the number of test samples and record as SS/N.
6. Divide the absolute value in step 3 above by the square root of 9 and record as  $(ABS)SUM(ABS)N^{.5}=$
7. Test average bias ( $(ABS)SUM(ABS)N^{.5}=$ ) to see if it is less the t-table value of 1.67 and Pass or Fail.
8. Test the precision (SS/N) to if it is less the F-table value of 1.74 and Pass or Fail.

Name: Lu

Method: Davies Gray U

Sample	Reported R Value	Known K Value	R - K Difference	Std. Dev. of Known	(R-K)/SD Normalized	((R-K)/SD)^2 Variance
1	24.900	25.000		0.0330		
2	10.006	10.000		0.0150		
3	10.008	10.020		0.0150		
4	25.010	25.000		0.0330		
5	25.001	25.000		0.0330		
6	24.985	25.000		0.0330		
7	2.005	2.000		0.0040		
8	10.022	10.000		0.0015		
9	10.006	10.020		0.0015		

		Total =	$\Sigma(R-K)/SD=$	
	Sum of Squares=		$\Sigma((R-K)/SD)^2=$	
SUM=	Absolute value of Total FF =		SS/N=	
SUM=		TT=	$(ABS)SUM/N^{.5}=          $	
		N= 9		

If TT is greater than T(N)\*, then the bias is significantly greater than zero  
 If FF is greater than F (N)\*\*, then the Std. Dev. Is significantly greater than one.  
 N is the number of analyses in the current quality control program.

BIAS IS: Significant            Not Significant             
 STD DEV. IS: Significant            Not Significant           

\* t-Table value for  $(\alpha= 0.1)/2$  and 60 df = 1.67  
 \*\* F Table Value at the 90% CI for df 60 & 9 =1.74

Standards	mgU/gSol Concentration	Method RSD	Method SD
1	2.000	0.20%	0.004
2	10.000	0.15%	0.015
3	10.020	0.15%	0.015
4	25.000	0.13%	0.033



## Technician Training and Testing Results Evaluation Exercise:

Evaluate the data below as follows:

1. Subtract the known value from the reported value and record in column R-K
2. Divide these values by the corresponding Standard Deviation (SD) and record in the last column.
3. Sum the values in column (R-K)/SD and record in first cell below the column as  $\Sigma (R-K)/SD=$  below.
4. Square each value in the (R-K)/SD column and sum and record them as  $\Sigma((R-K)/SD)^2=$  below.
5. Divide the total from line 4 above by 9, which is the number of test samples and record as SS/N.
6. Divide the absolute value in step 3 above by the square root of 9 and record as  $(ABS)SUM(ABS)N^{.5}= $$$
7. Test average bias ( $(ABS)SUM(ABS)N^{.5}= $$$ ) to see if it is less the t-table value of 1.67 and Pass or Fail.
8. Test the precision (SS/N) to if it is less the F-table value of 1.74 and Pass or Fail.

Name: Lu

Method: Davies Gray U

Sample	Reported R Value	Known K Value	R - K Difference	Std. Dev. of Known	(R-K)/SD Normalized	((R-K)/SD)^2 Variance
1	24.900	25.000		0.0330		
2	10.006	10.000		0.0150		
3	10.008	10.020		0.0150		
4	25.010	25.000		0.0330		
5	25.001	25.000		0.0330		
6	24.985	25.000		0.0330		
7	2.005	2.000		0.0040		
8	10.022	10.000		0.0015		
9	10.006	10.020		0.0015		
Total =				$\Sigma(R-K)/SD=$		
Sum of Squares=				$\Sigma((R-K)/SD)^2=$		
SUM=	Absolute value of Total FF =			SS/N=		
SUM=	TT=			$(ABS)SUM/N^{.5}=$		
N= 9						

If TT is greater than  $T(N)^*$ , then the bias is significantly greater than zero

If FF is greater than  $F(N)^{**}$ , then the Std. Dev. Is significantly greater than one.

N is the number of analyses in the current quality control program.

BIAS IS: Significant \_\_\_\_\_ Not Significant \_\_\_\_\_

STD DEV. IS: Significant \_\_\_\_\_ Not Significant \_\_\_\_\_

\* t-Table value for  $(\alpha=0.1)/2$  and 60 df = 1.67

\*\* F Table Value at the 90% CI for df 60 & 9 =1.74

Standards	mgU/gSol Concentration	Method RSD	Method SD
1	2.000	0.20%	0.004
2	10.000	0.15%	0.015
3	10.020	0.15%	0.015
4	25.000	0.13%	0.033





## **Module 7**

---

# **Sampling Variability Solids and Oxides**

# Objectives

---

- **Understand the issues with sampling**
- **Understand the activities that can be done to minimize the problems of heterogeneity within a batch of material**
- **Be able to apply correct sampling principles, analyses, tools, and techniques**
- **Be able to use Excel functions and the ANOVA capability to evaluate sampling data**

# Sampling Variability

---

- **Batch of material resulting from some process**
- **Material needs to be sampled**
- **Material is not homogeneous**
- **How do you sample this material?**

# Population versus Sample

---

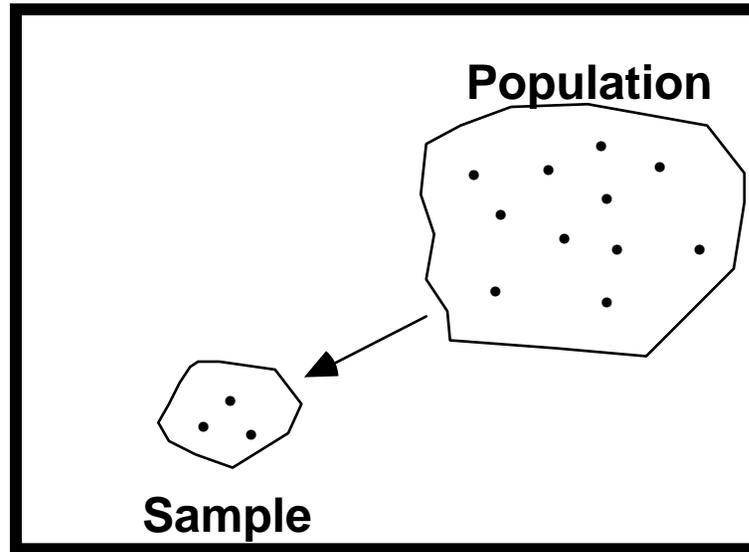
- A population is the totality of those entities about which we desire to establish a certain property or characteristic.
  - Examples
    - Number of TIDs improperly applied on containers in a particular vault.
    - The number of containers in the correct location in a particular vault.

# Population versus Sample

---

- A sample of a population is a part of that population. It is a group of observations taken from a population.
- The objective of sampling is to obtain samples that are representative of the population from which they are drawn.

# Types of Samples



A simple random sample of size  $n$  is one in which every possible sample of size  $n$  has the same probability of being selected.

A convenience sample is one that is chosen simply by taking observations that are easily or inexpensively obtained.

Which approach do you think is more likely to meet our objective for sampling?

# Goal of Good Sampling

---

**The goal of good sampling is to follow a sampling protocol that produces a sample whose chemical or physical measurements of interest are:**

1. Representative of the entire lot

The key is random sampling which enables an unbiased estimate and an estimate of the precision

2. As consistent as possible with other samples that would be obtained if the entire sampling protocol could be repeated

# Representative and Consistent Samples

---

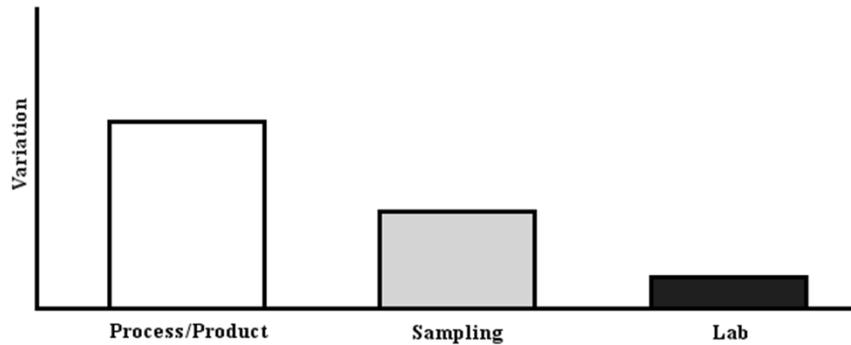
- Getting representative samples requires using physical sampling techniques that have as little bias as possible (Accuracy)
- Getting consistent samples means reducing sampling-to-sampling variation (Precision)
- Accuracy and precision (reproducibility) should be agreed upon by the customer and supplier
- Sampling errors can lead to unnecessary process changes, the analysis of additional samples, or the release of off-spec material

# Examples of Good Sampling Practices

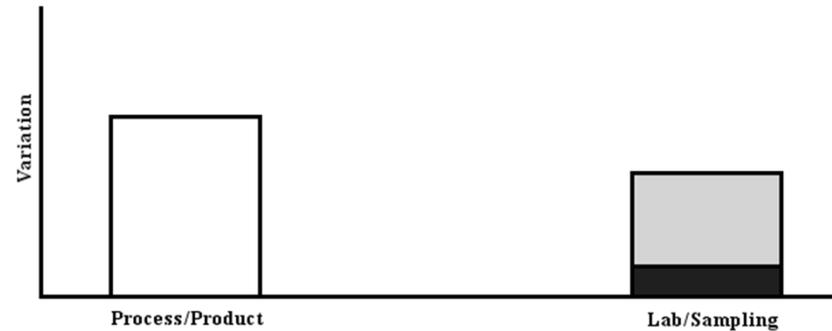
---

- Mixing and grinding the material before sampling
- Compositing sampling increments to form the sample
- Using a container that will not react with the sample
- Proper handling of samples
- Sampling method must preserve the integrity of the sample

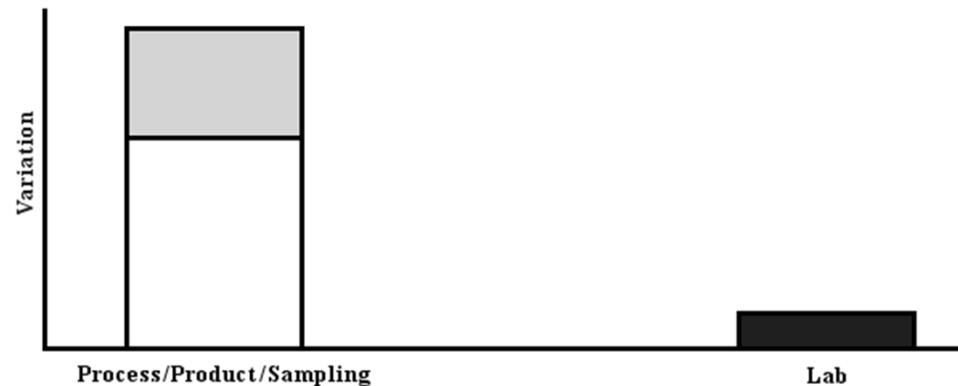
# Proper Separation of Variation



Process, sampling, and lab variation separated



Sampling and lab variation not separated.



Sampling and process variation not separated

# Material Variation

---

- **Error 1: Fundamental Error (FE)**

Heterogeneity of solids is influenced by particle size, shape, density, chemical composition, and other physical properties. This error is usually large for solids and negligible for liquids and gases.

- **Error 2: Grouping and Segregation Error**

Heterogeneity caused by the spatial distribution of the constituents and shape of the lot. Many solids are known to settle or stratify. Sampling from the bottom versus the top can generate different samples.

# Process Variation

---

- **Error 3: Long-range non-periodic heterogeneity fluctuation**
- Processes change over time, sometimes in short intervals and sometimes over a longer time span. Samples taken at different times can produce different results. Should determine trends and how they behave.
- **Error 4: Long-range periodic heterogeneity fluctuation**

Processes can experience periodic changes over time. For example, the process may be effected by day and night temperature cycles. Systematic sampling that has the same frequency as the cycles will not reveal the entire variation of the process and produce biased results.

# Tools and Techniques

---

- **Error 5: Delimitation error**

Nonrandom samples, such as judgmental and spot samples, are useful but probability and random samples are fundamental to obtaining unbiased estimates. A delimitation error occurs when not every part of the lot has an equal chance of being in the sample. For example, scooping off the top of a large solid pile can produce samples with misleading results.

- **Error 6: Extraction Error**

An extraction error occurs when a sample that has been identified cannot be obtained. Extraction error is typically due to the equipment used. For example, in sampling a tank, a thief probe may produce an extraction error because it may not be able to extract material at the very bottom.

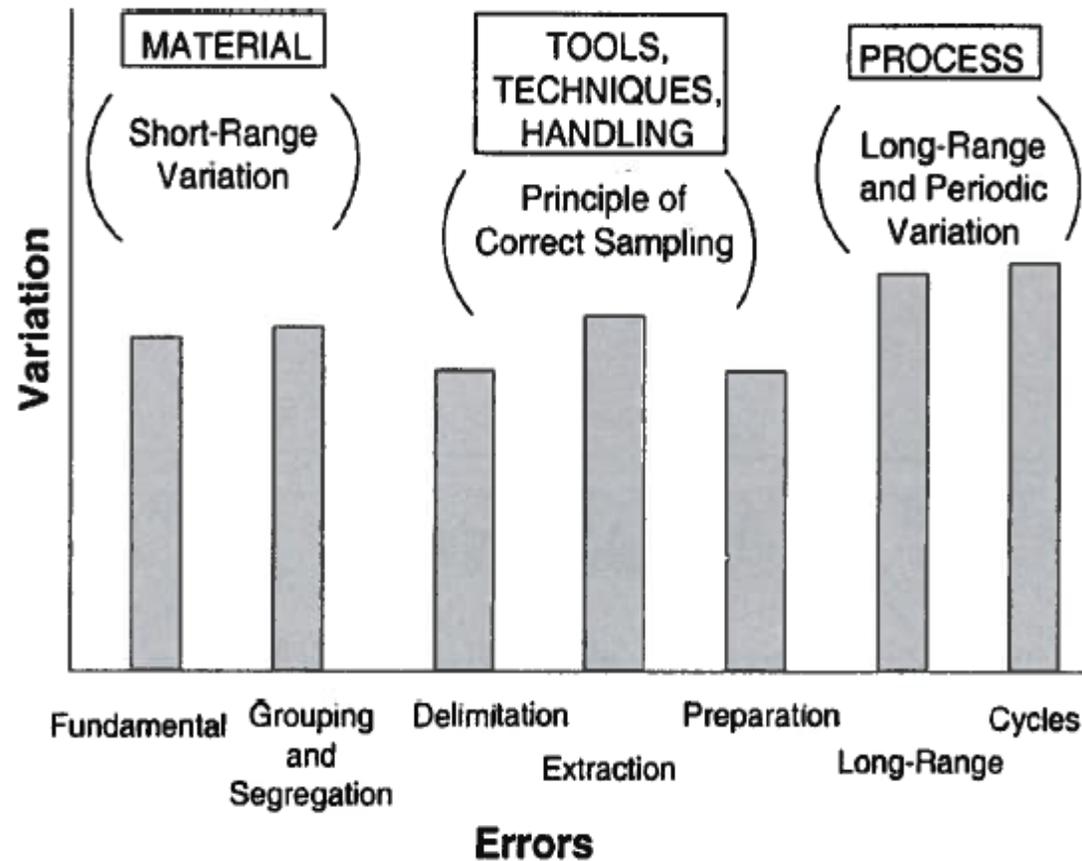
# Sample Handling

---

- **Error 7: Sample handling, sample integrity, or sample preservation**

Samples can change between the time they are taken and the time they were analyzed.

# Error Sources



Example bar graph of variation vs. errors for sampling.  
(Actual variation depends on the situation.)

# Heterogeneity

---

## **Heterogeneous:**

Consisting of dissimilar ingredients or constituents “not all the same” “not uniform throughout” or “different.”

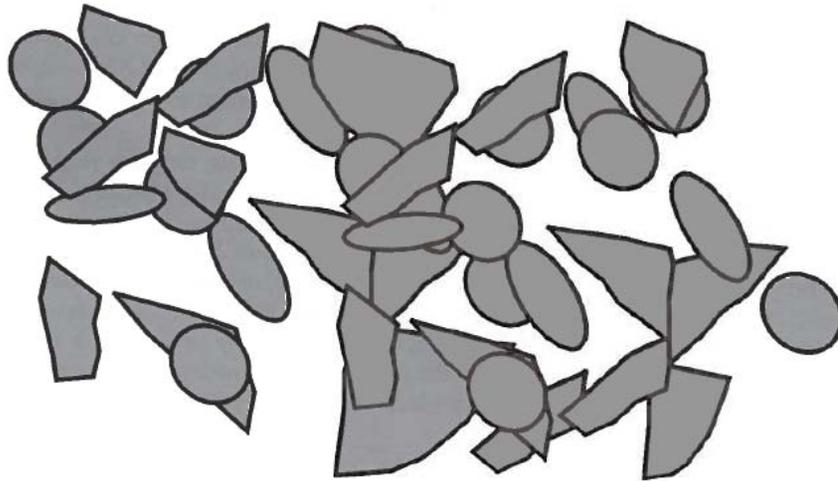
There are two types of material heterogeneity: constituent and distribution.

1. Constituent heterogeneity (CH): Differences in constitution or make-up of material (particles or molecules)
2. Distribution heterogeneity (DH): How the material is distributed or mixed due to density, particle size, etc.

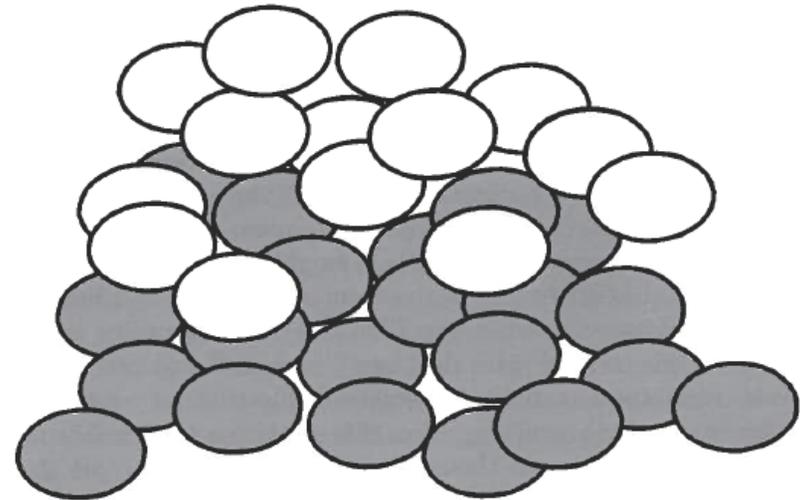
*Both give rise to sampling error.*

# Illustrations of Heterogeneity

---



Constitution heterogeneity (CH). The particles are not uniform.



Distribution heterogeneity (DH) for solids. The particles are not distributed uniformly.

# Fundamental Error

---

**Fundamental Error is the** difference between the sample amount and the lot content relative to the lot as a whole.

- Reduce the Fundamental Error: With random sampling, increasing the quantity of material in the sample-> Reduced Variability
- Decreasing the individual particle size of material (e.g., By Grinding) in the lot before sampling-> Reduced Variability

*Must preserve the integrity of the samples so that the components of interest are not changed*

## **Sample Size:**

- Statisticians think of the number of units in the sample
- Chemists think of mass, weight, or volume of the sample

# Reducing the Fundamental Error

---

In statistical sampling, under independence it is well known that:

$$\sigma_{\bar{x}} = \frac{\sigma_{Population}}{\sqrt{n}}$$

- For a fixed particle size, increasing the number of units in the sample is comparable to increasing the sample weight of a chemical sample.
- For a fixed sample weight, decreasing the particle size of material in the lot before sampling has the effect of increasing the number of sampling units.

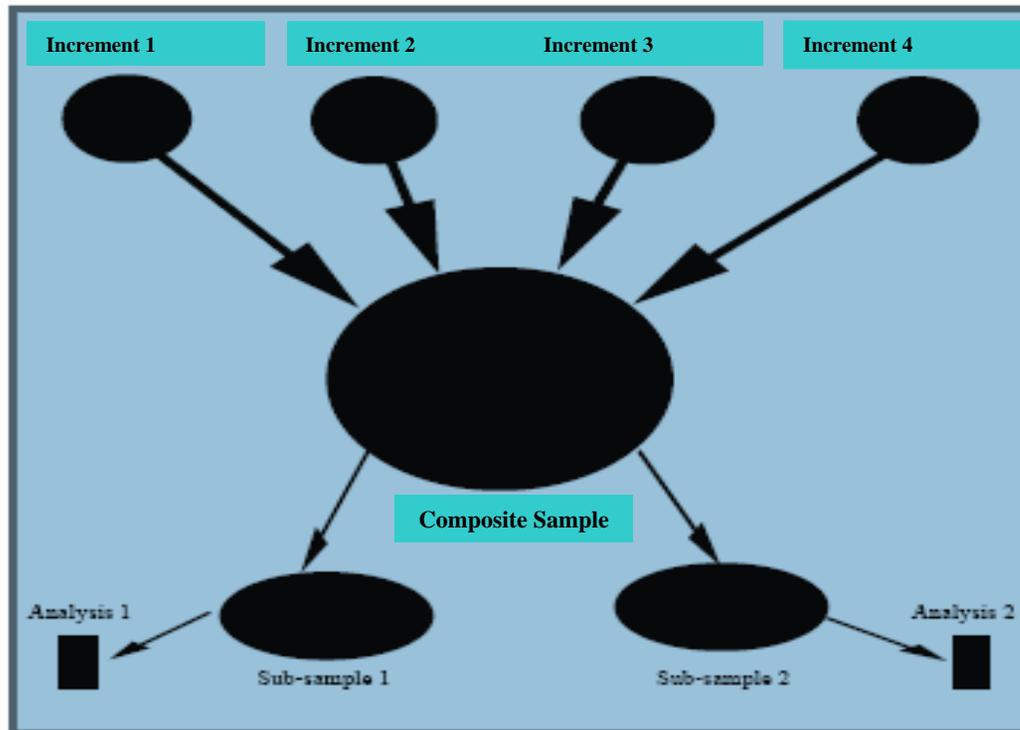
# Reducing Segregation Error

---

- To reduce the effect of segregation, we should mix the entire lot if possible. Other alternatives are necessary for large immobile lots (e.g., waste piles, ship cargo)
- Solid particles that differ in size, density, and shape are susceptible to poor mixing. After mixing, solid granules may re-segregate during handling and storage.
- Mixing studies could be performed to measure the effectiveness of mixing over time and space.
- Good practice is to take small increments randomly and combine (composite) them to get a sample when estimating the average.

# Composite Sampling

In compositing, drawing the sample and the physical mixing procedure may change the physical characteristics of the material (e.g.: the particle size distribution could change).



- Useful for reducing cost when the samples (increments) being combined are similar.
- Compositing is not useful when looking for hot spots or segregating material.
- Have sufficient material from each increment for discrete samples to be analyzed.

# Correct Sampling

---

- Increase the mass of the total physical sample
- Collect several random increments from the lot and combine them to form the sample
- For solids sampling, grind the particles in the lot before sampling
- Mix the lot before sampling

# Correct Sampling for Bulk Solids

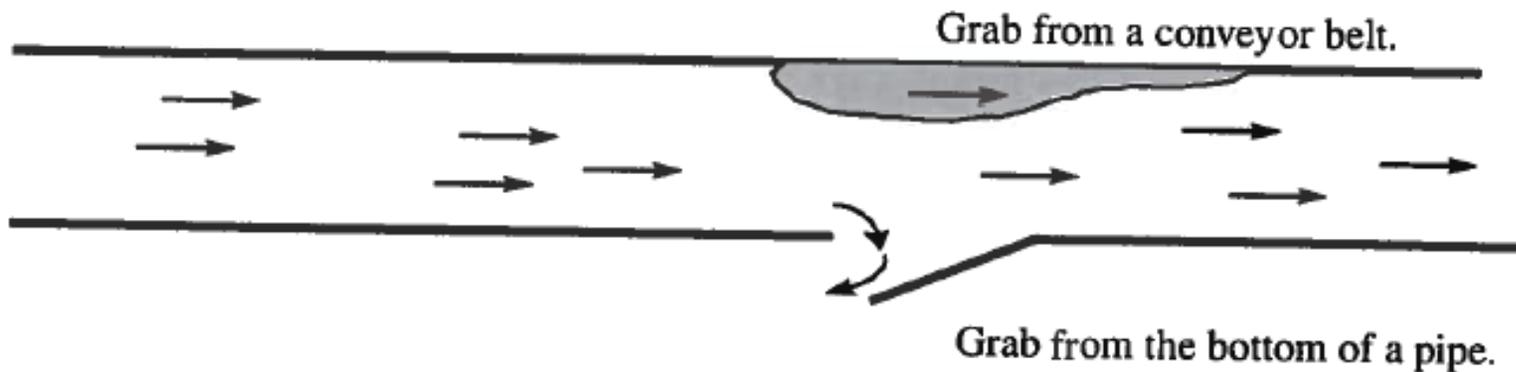
---

## Guiding principals for random sampling of heterogeneous material

- Every part of the lot has an equal chance of being in the sample.
- Define and physically obtain the sample.
- In Grab Sampling, certain parts of the lot have no chance of being in the sample.
- The integrity of the sample is preserved during and after sampling. Between the time it is taken and analyzed, oxidation, abrasion, and evaporation may take place.
  - Contamination (Clean your device after every use)
  - Loss
  - Mistakes (Use proper labeling)

# Correct Sampling or Not?

---

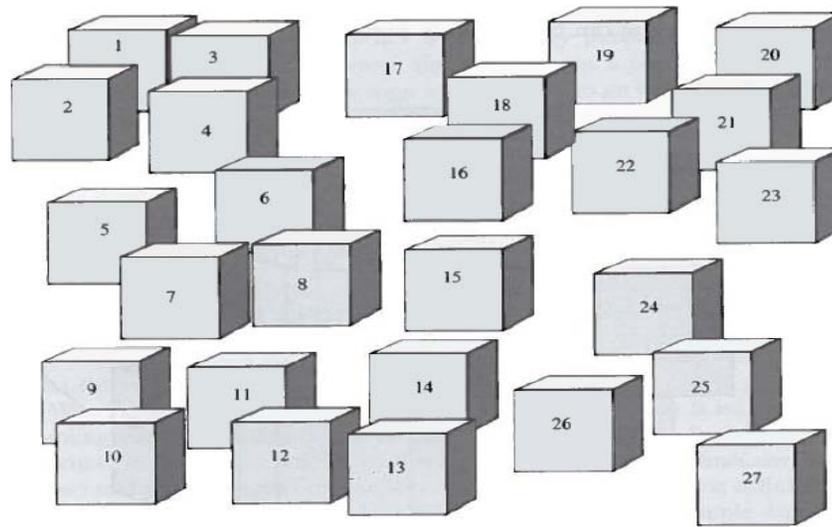


Examples of grab sampling from the side of a conveyor belt or from the bottom of a pipe.

# Zero Dimensional Sampling

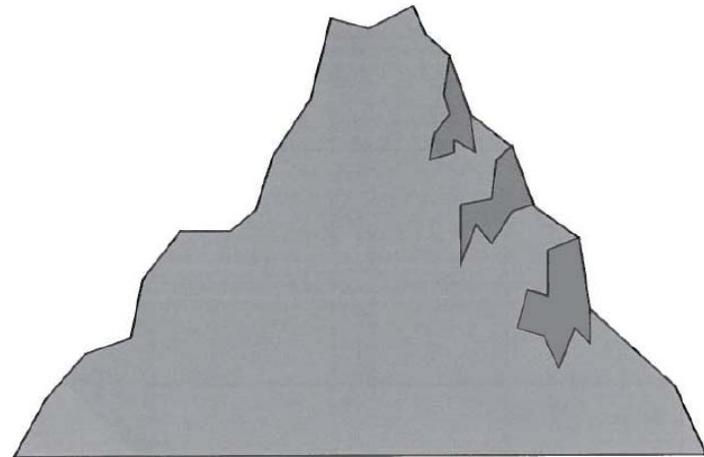
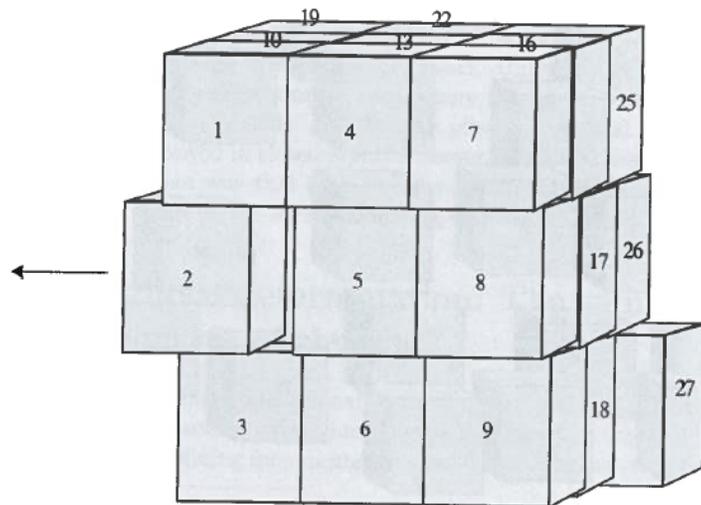
---

- Blocks numbered individually.
- All blocks are accessible.
- Every part of the lot has an equal chance of being in the sample.
- No difficulty extracting randomly selected blocks.
- No sample handling issues.



# Three Dimensional Sampling

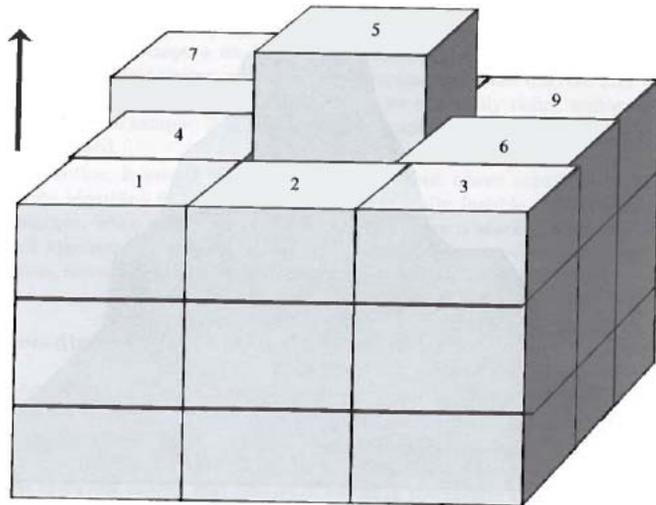
- The 27 blocks are numbered as before.
- Selected blocks may be in the middle or bottom layers.
- Pulling out the blocks could be a major problem for a larger number of stacked blocks.



A pile of solid particles. Mound could collapse as soon as sampling starts.

# Two Dimensional Sampling

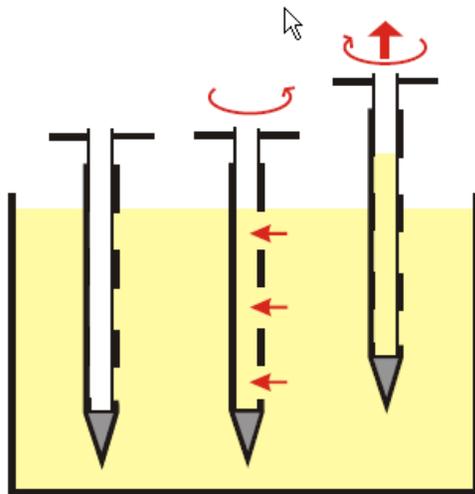
- 27 blocks arranged in 9 numbered stacks. Now there are 9 rather than 27 sampling units.
- The sampling unit is a vertical stack of three blocks.
- Vertical sampling core should be a cylinder ensuring an equal amount of material from the top, middle and bottom.



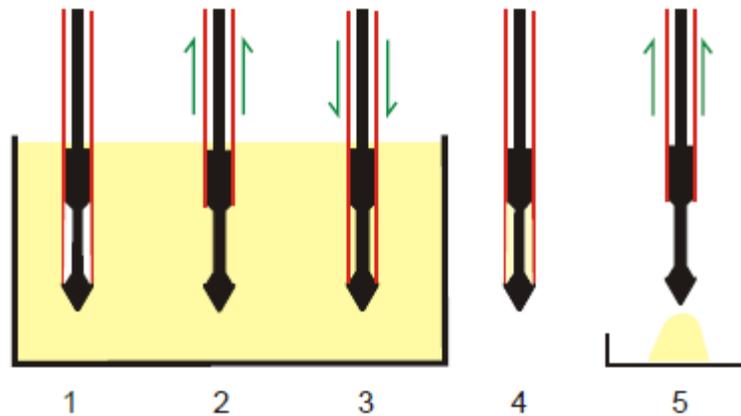
Thief probe for solids sampling.

# Slot Sampler/Powder Thief

- Designed for volume sampling of several points



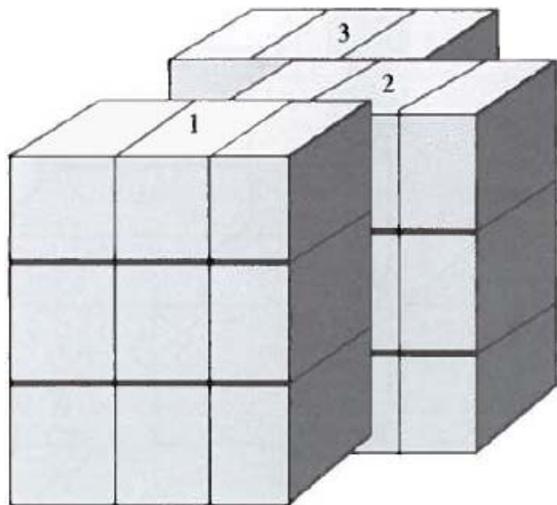
Multi-Level Sampling



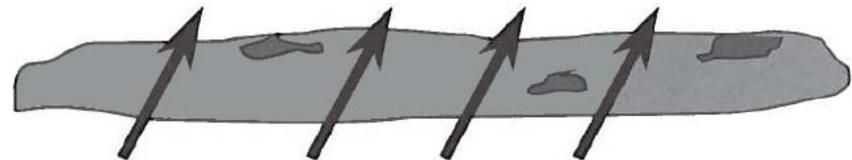
Single Level Sampling

# One Dimensional Sampling

- Frequently, one dimensional sampling is practical in sampling solids.
- Group in 2 dimensions and sample across the 3<sup>rd</sup> dimension.
- Defining the sampling unit as 9 blocks in a plane giving 3 consecutive stacks of 3



27 blocks arranged in 3 numbered planes

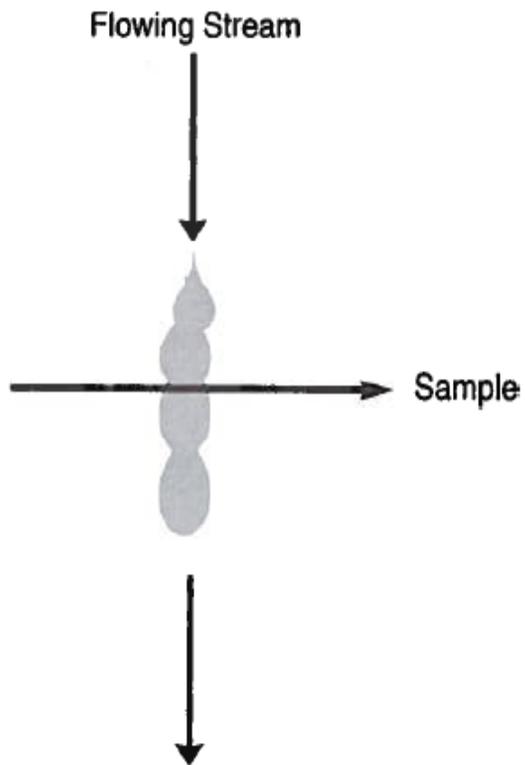


Slicing across a fairly flat pile. May be prone to extraction error, but can be minimized by using a proper tool.

# One vs. Three Dimensional Sampling

---

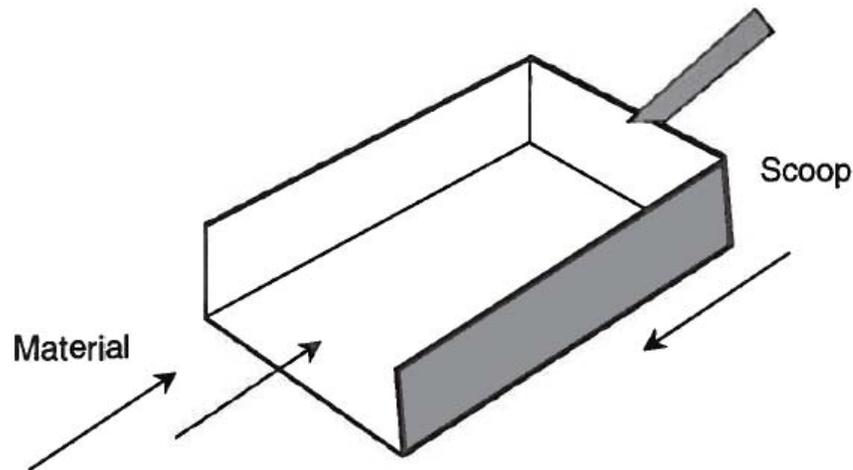
- May not be able to take a one-dimensional slice across a three dimensional lot because the material may be in a container.
- Taking a cross-stream sample from a flowing stream before it becomes a stationary lot. Could be material moving along a conveyer belt.



# Extracting the Sample

---

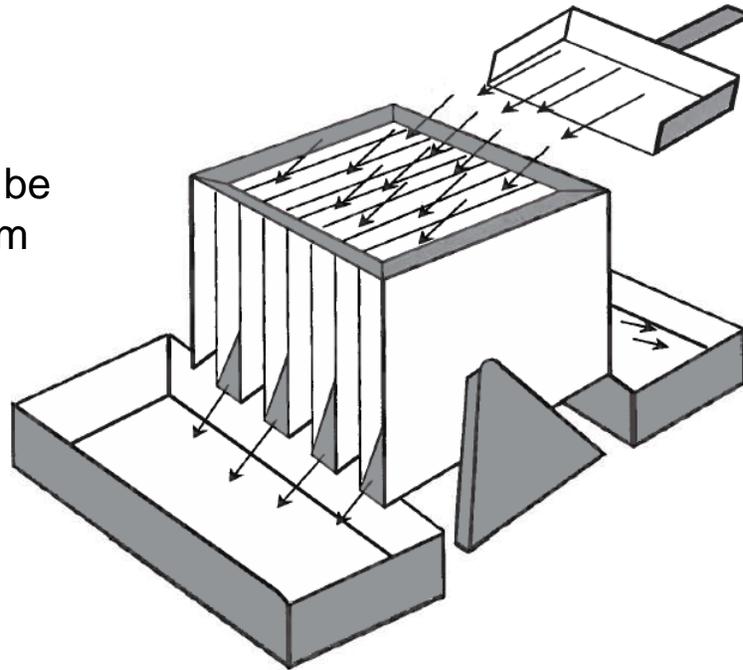
- The error in slicing across a pile can be minimized if the proper sampling tool is used.
- Must be large enough to hold all the material in the slice.
- Should have sides perpendicular to the bottom.
- Should be cleaned between samples.



# Extracting the Sample (continued)

**Typical riffle splitter (rifflers)** - Riffles are used for mixing and subsampling solid particles. Roughly half of the material is collected in each pan. The procedure can be repeated to get sub-samples by randomly selecting one of the pans. Spinning riffles that generally produce better samples are also used.

The sample must be chosen at random



# Spinning Riffler

By attaching a sieve to the top of the hopper, samples can be obtained which are representative of the initial sample while excluding all particles larger than the selected sieve size.



# Exercises – Process Stability Over Time

---

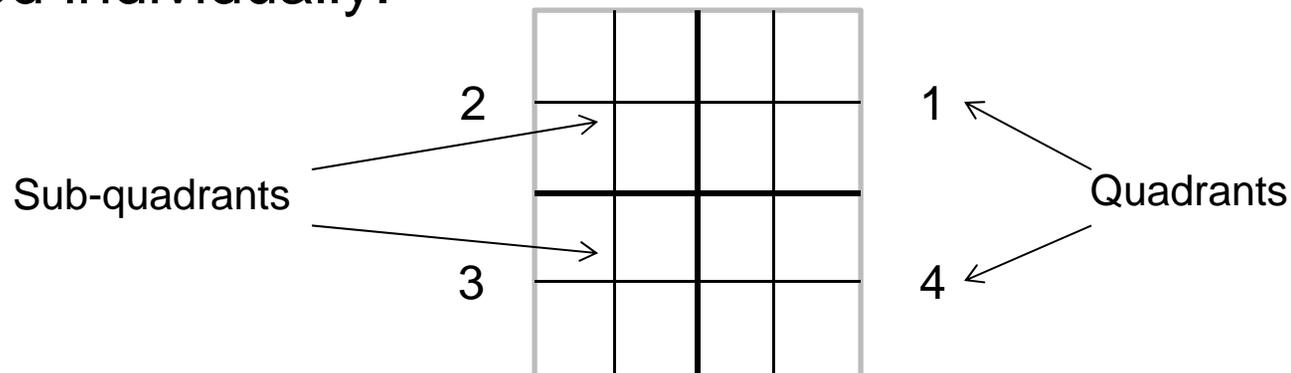
**Goal – Sample batches to determine if the process is consistently mixing/blending product. This will be done by taking random samples from multiple batches and statistically analyzing the results. Three different exercises will be used for evaluating batch differences and for estimating sampling variability.**

- Exercise #1 - Determine if several batches of material are consistent from a weight percent perspective from data set 1
- Exercise #2 - Determine if several batches of material are consistent from a weight percent perspective from data set 2
- Exercise #3 - Estimate the sampling and random measurement uncertainties for the batches of material based on weight percent data set 3

# Exercise #1

Background and Sampling approach:

Four oxide samples are taken from a large tray of calcined material after manually mixing the material for a set period of time. The tray is divided into four quadrants and each quadrant is divided into four equal sub-quadrants. For each quadrant, a random sub-quadrant is chosen and sampled. The four samples are sent to the laboratory and are analyzed individually.



# Exercise #1

---

Discussion topics and questions related to exercise:

1. Discuss methods for manually mixing the material.
2. How should the material be distributed prior to sampling?
3. Discuss methods for obtaining the four samples.
4. Bring up the Student Worksheet for Exercise #1.
5. Following the instructor's lead, use the Excel one-way ANOVA to determine if several batches of material are consistent from a weight percent perspective.
6. What is the result of the ANOVA evaluation?
7. What is the estimate for the weight percent random uncertainty?

# Exercise #2

---

Instructor led analysis of sampling results:

1. Bring up the Student Worksheet for Exercise #2.
2. Use the Excel one-way ANOVA to determine if several batches of material are consistent from a weight percent perspective.
3. What is the result of the ANOVA evaluation?
4. What is the estimate for the weight percent random uncertainty?

# Exercise #3

---

Discussion topics and Questions:

1. Bring up the Student Worksheet for Exercise #3. The instructor will briefly discuss the data for this exercise.
2. Following the instructor's lead, the students will use the Excel AVERAGE, DEVSQ and SUM functions to estimate the sampling and random uncertainties for the batches of material based on weight percent.
3. What is the estimate for the weight percent sampling uncertainty?
4. What is the estimate for the weight percent random uncertainty?

# Summary

---

- **Reviewed the issues with sampling**
- **Discussed the activities that can be done to minimize the problems of heterogeneity within a batch of material**
- **Discussed the application of correct sampling principles, analyses, tools, and techniques**
- **Used Excel functions and the ANOVA capability to evaluate sampling data**



## **Module 8**

---

# **Control Charts and Measurement Control**

# Objectives

---

- **Identify the purpose of control charts**
- **Identify the six elements of control charts and their purpose**
- **Discuss and analyze example control charts**
- **Discuss control charts and measurement control**
- **Discuss and analyze control charts from actual measurement systems**

# Purpose of Control Charts

---

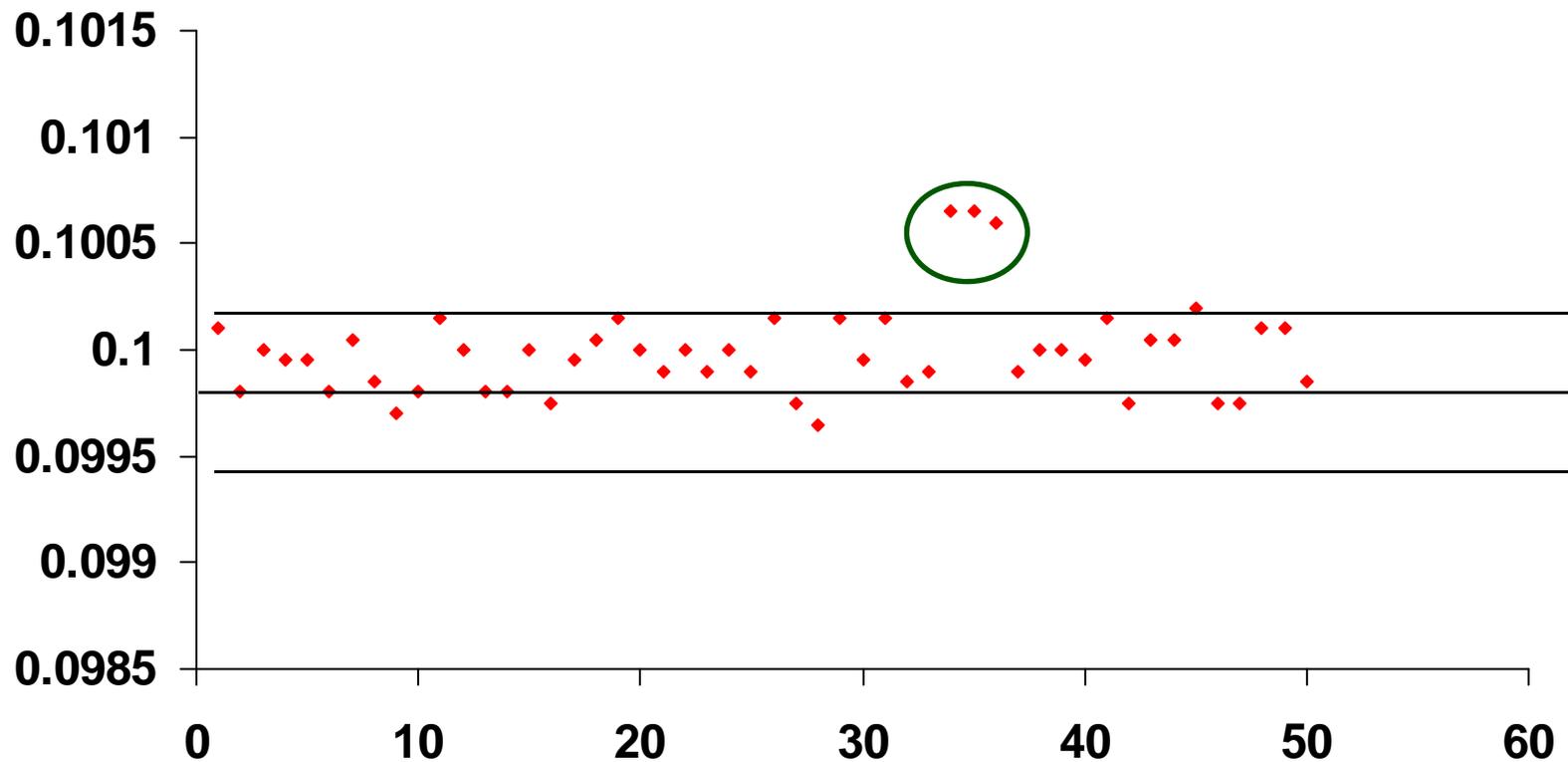
- **To obtain a clear picture of the performance of the process**
  - **Method**
  - **Inventory**
- **To indicate if process is under control and, if not, to indicate extent of departure from control**
- **To indicate capability of process when system is in control**

# Reasons for Monitoring Control Charts

---

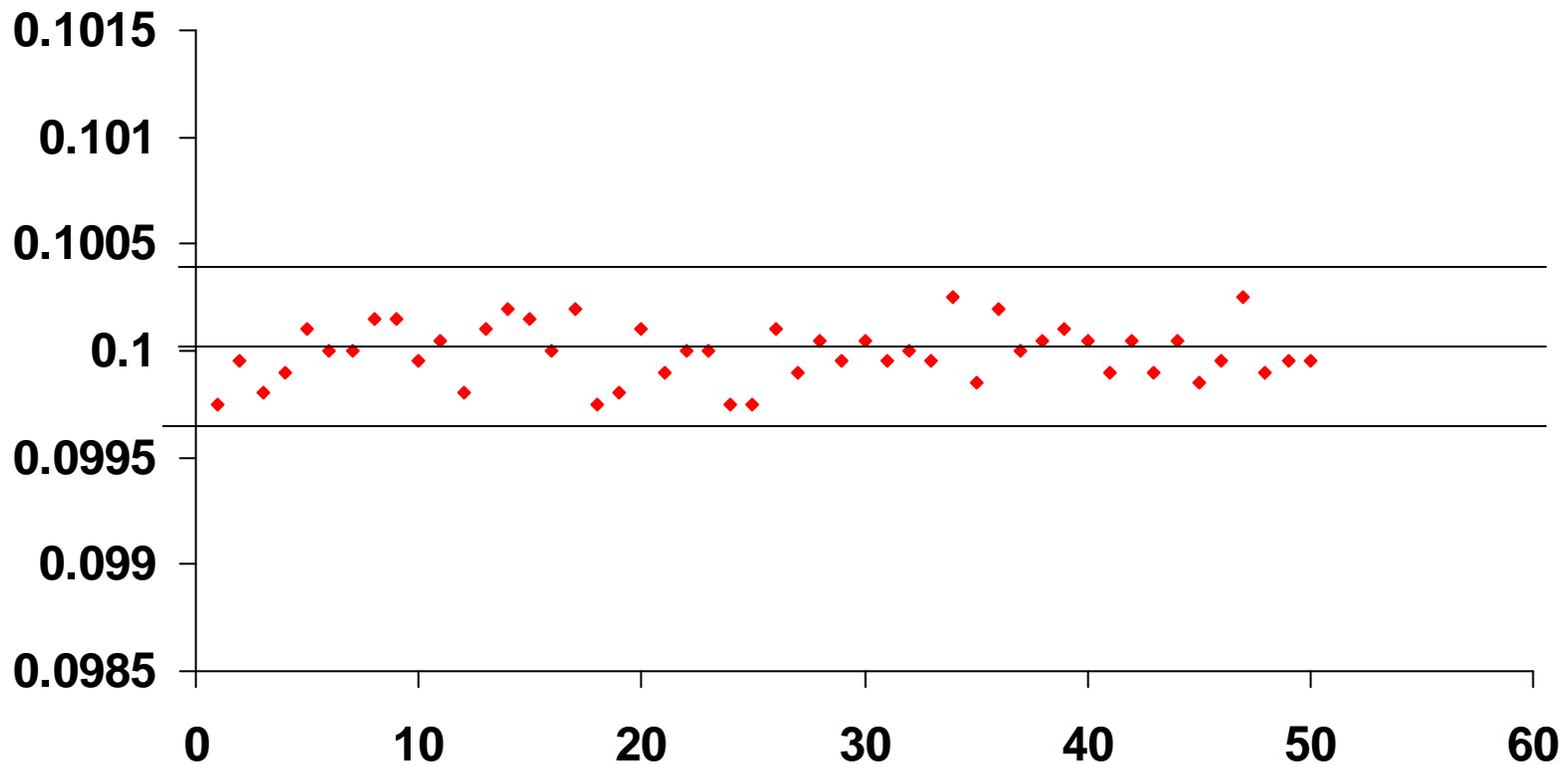
- 1. Assure stability**
- 2. Quantify quality**
- 3. Measure improvement**

# 1. To Assure Measurement Process Stability



## 2. To Determine Measurement Quality

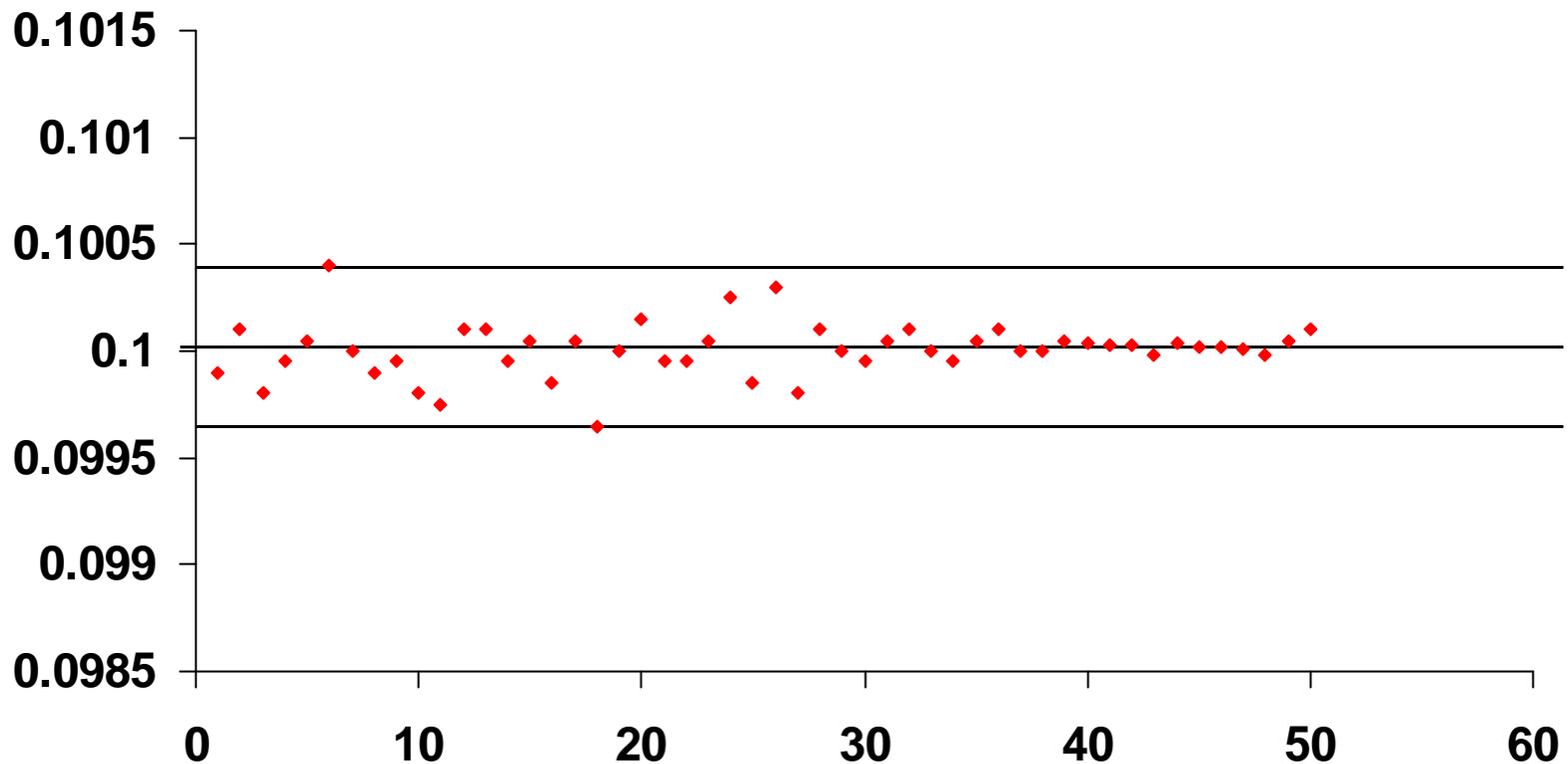
---



**Mean is 0.1 Standard deviation is  $\approx$ .0002**

### 3. To Provide a Process for Measuring Improvement

---



# Construction of a Control Chart

---

- **Order is of the greatest importance:**
  - **Data points must be plotted in the order (by date or time) in which they are taken**
- **Control limits are usually at the mean  $\pm 2$ -sigma or  $\pm 3$ -sigma units apart**

# Construction of a Control Chart

---

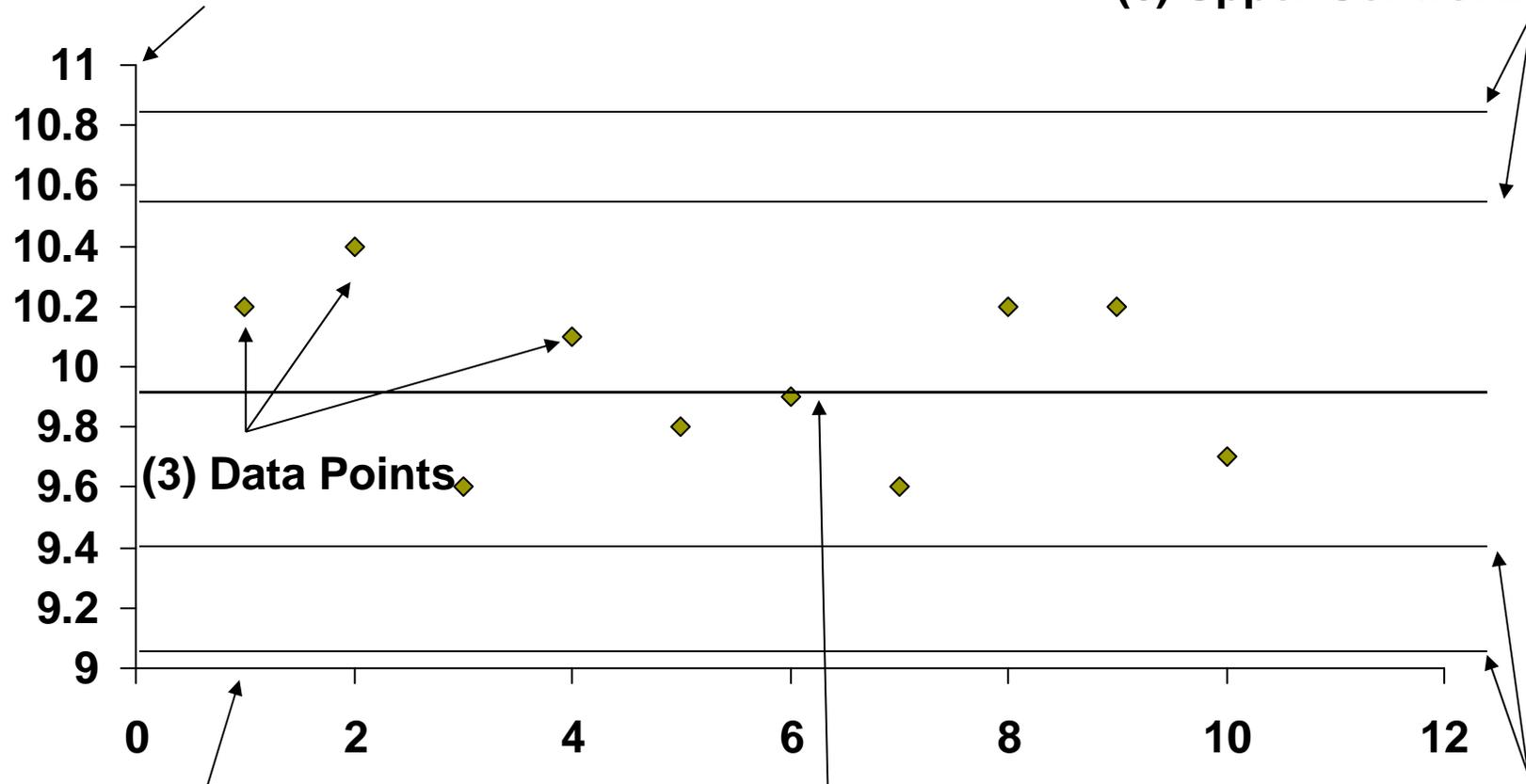
**Center Line could be any of the following:**

- **A target value**
- **Standard value**
- **Overall mean computed from the data points after specified time period**

# Six Elements of a Control Chart

(2) Measured Value Axis

(6) Upper Control Limits

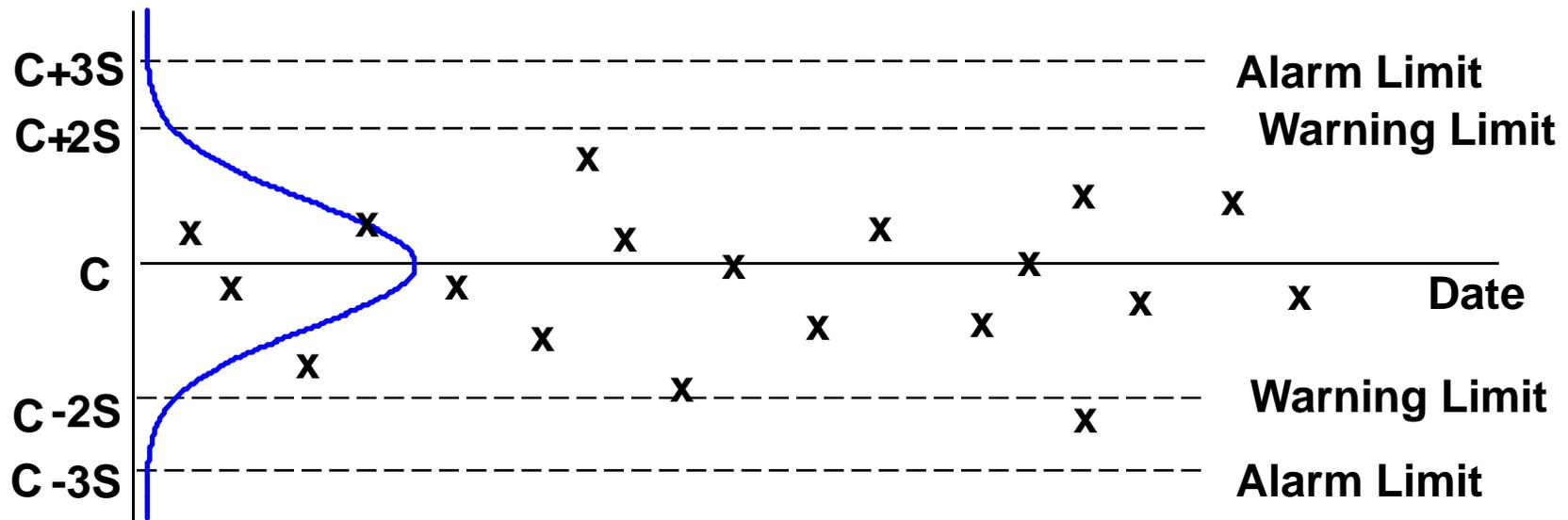


(1) Time Axis

(4) Reference Value Line

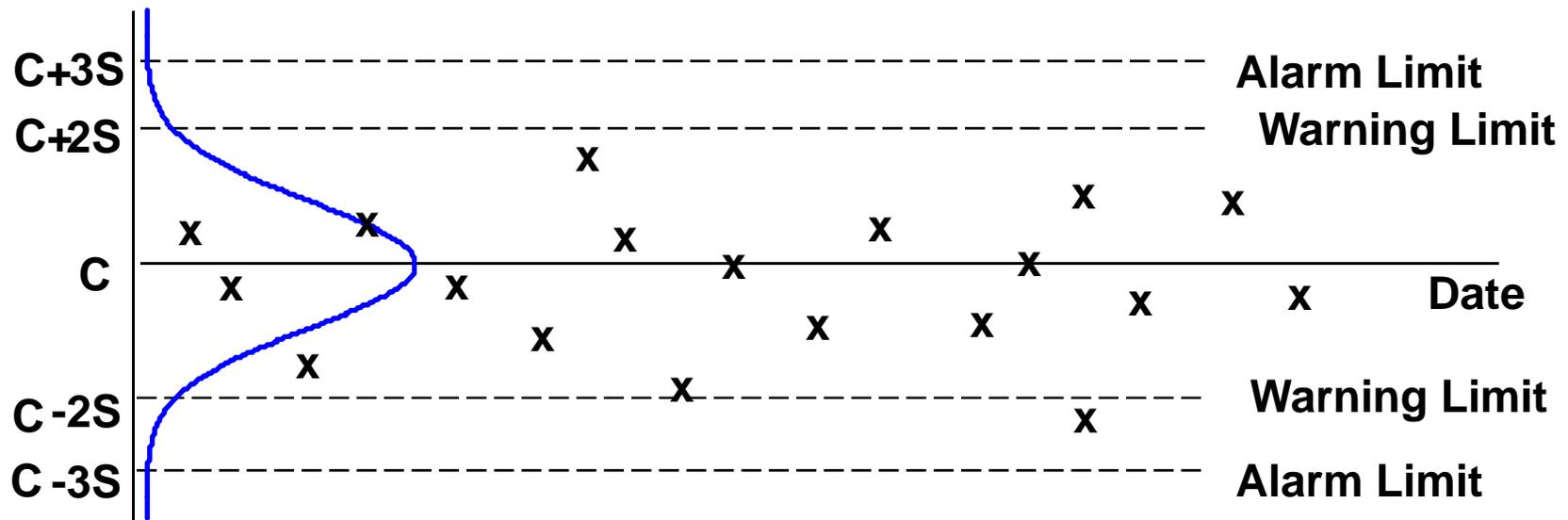
(5) Lower Control Limits

# Control Charts Simplified



- Centerline  $C$  would generally be based on a known or estimated target value  $T$
- $(\bar{X} - T)$  is called bias (or “systematic error”)
- Variability about  $\bar{X}$  indicates “random errors”

# Control Charts Simplified



- Generally, 95% of the measurement control data should fall between  $C \pm 2s$
- Generally, 99.7% of the measurement control data should fall between  $C \pm 3s$

# Analyzing Control Charts

---

- **Trends**
  - **Trends in data are non-random occurrences**
- **Outlier**
  - **An outlier is an observation that is so far removed from the remaining data that it suggests either of the following:**
    - **A mistake in measurement occurred**
    - **It came from a different population**

# Indications of Potential Problems

---

- **One point outside the 3s line**
- **Two out of three points outside the 2s line**
- **Eight consecutive points all above or below the centerline**
- **Six consecutive points trending upward or downward**

# Indications of Potential Problems

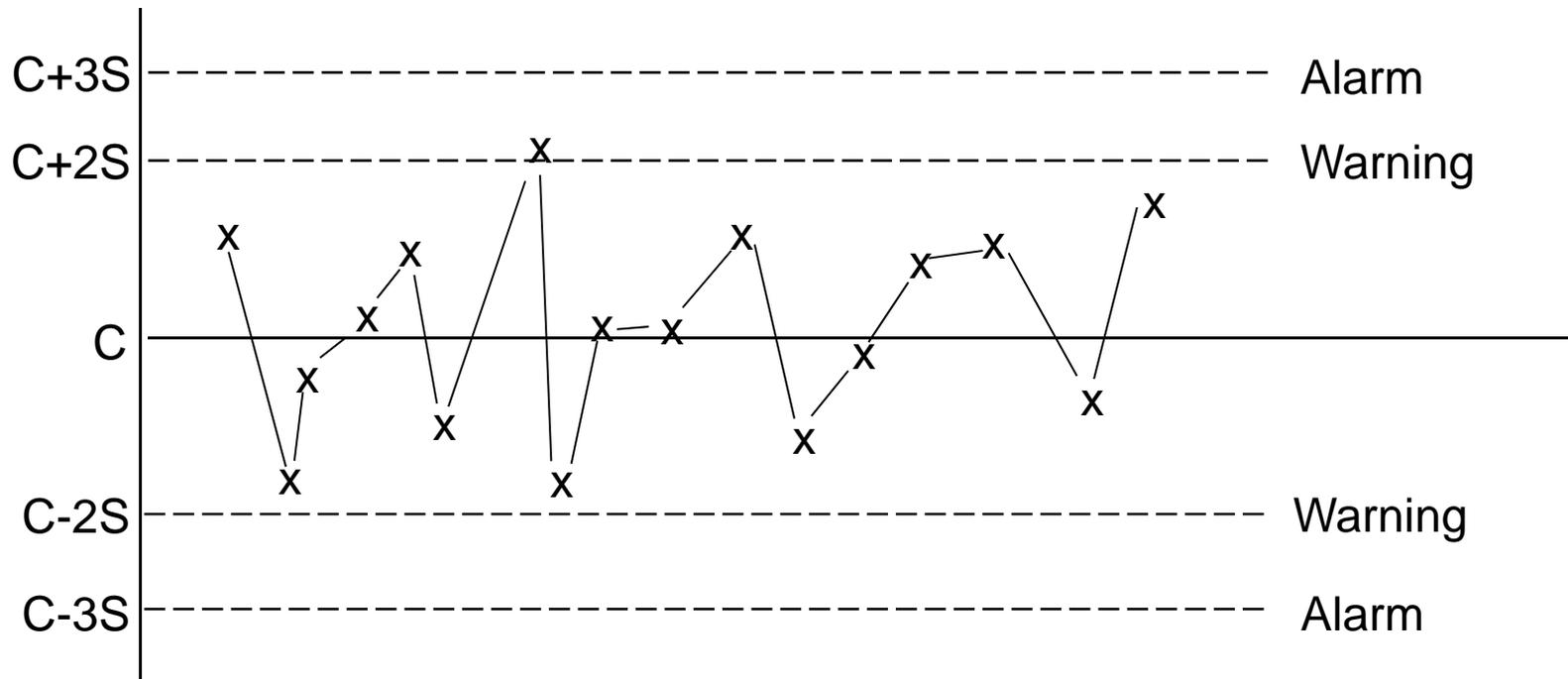
---

- **Fifteen consecutive points alternating above and below the centerline**

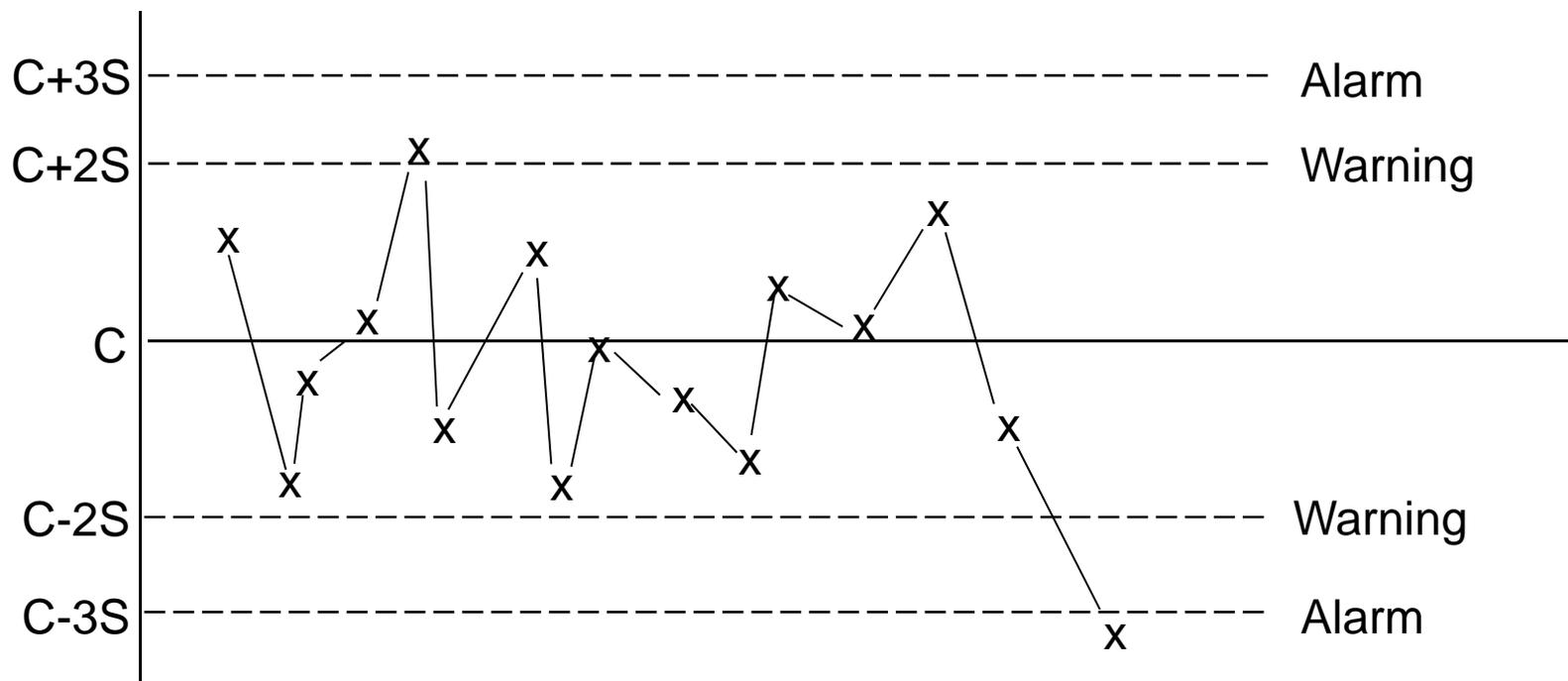
**Each situation is a possible indication of an out-of-control process**

**A measurement control program should adopt rules to identify out-of-control situations**

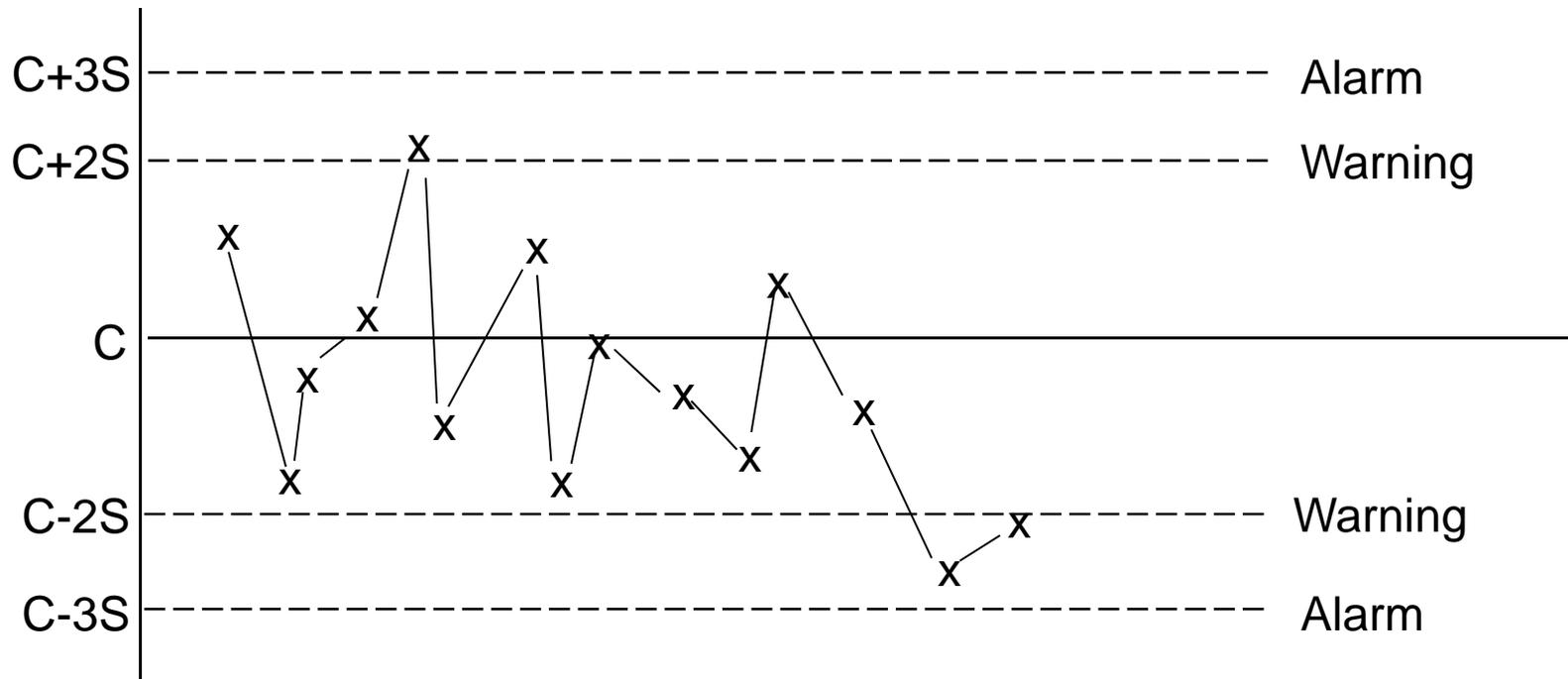
# Control Chart Example



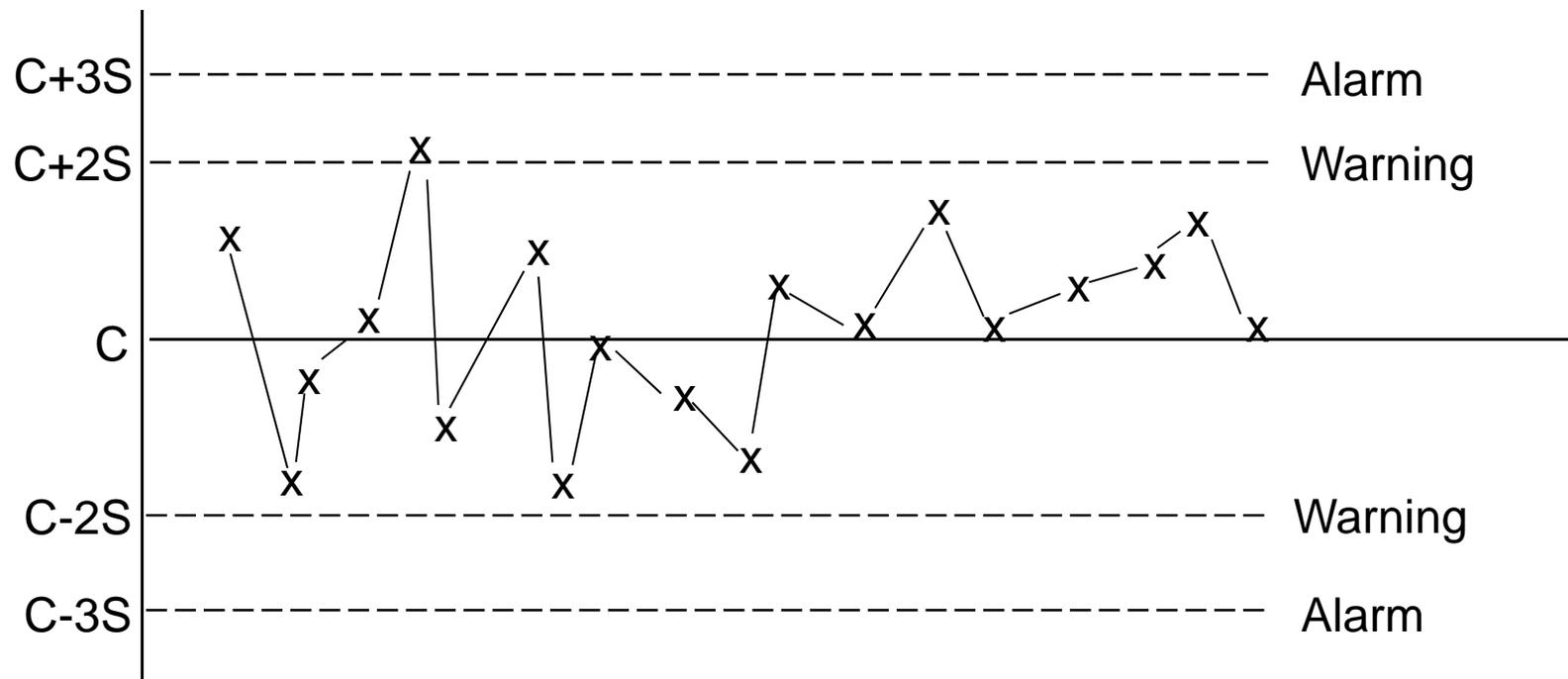
# Control Chart Example



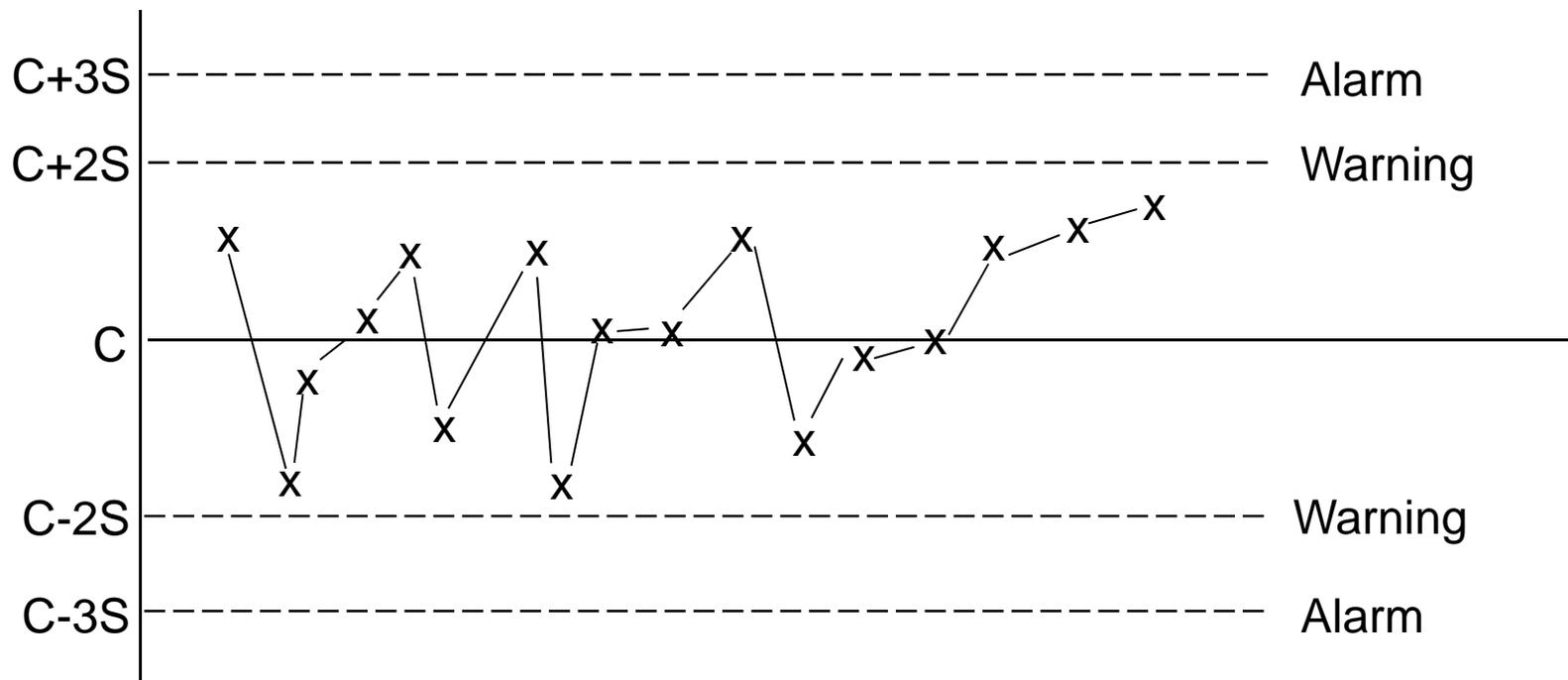
# Control Chart Example



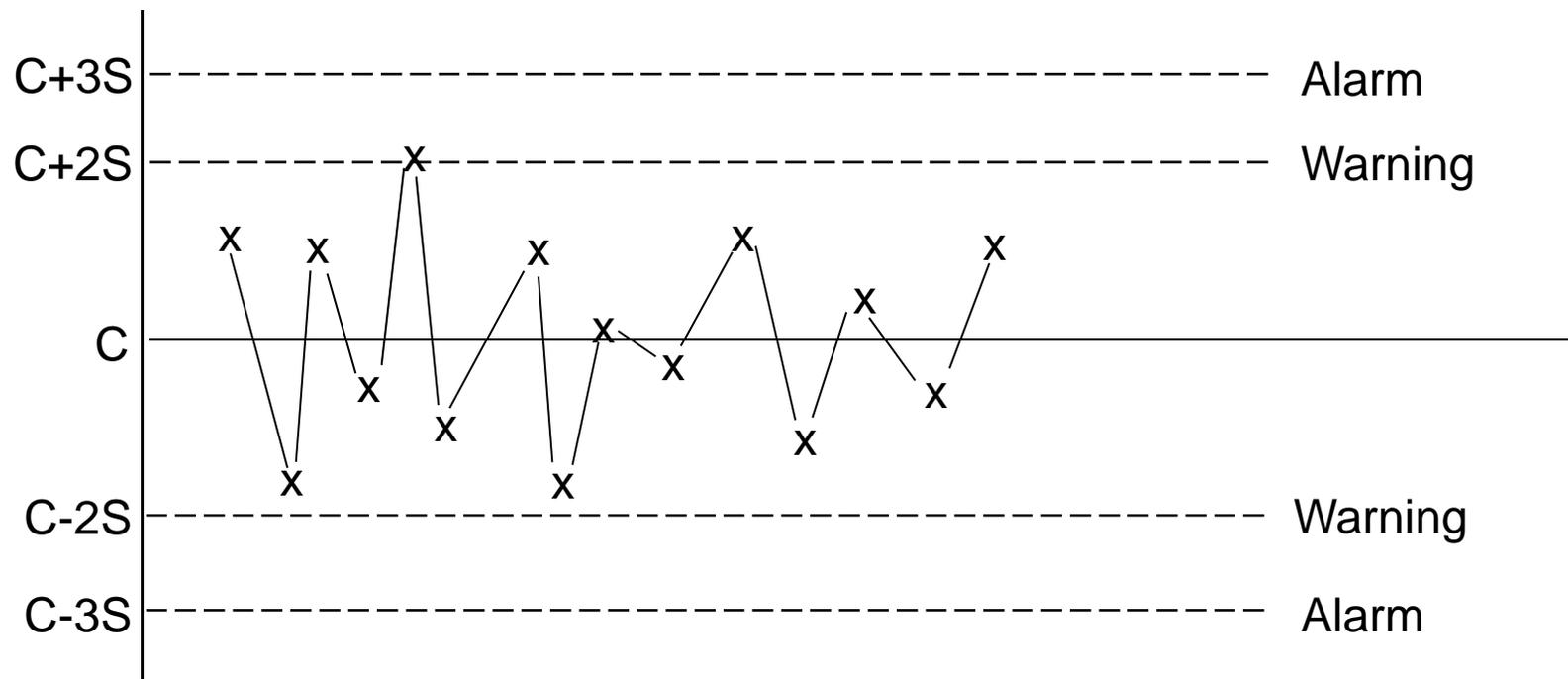
# Control Chart Example



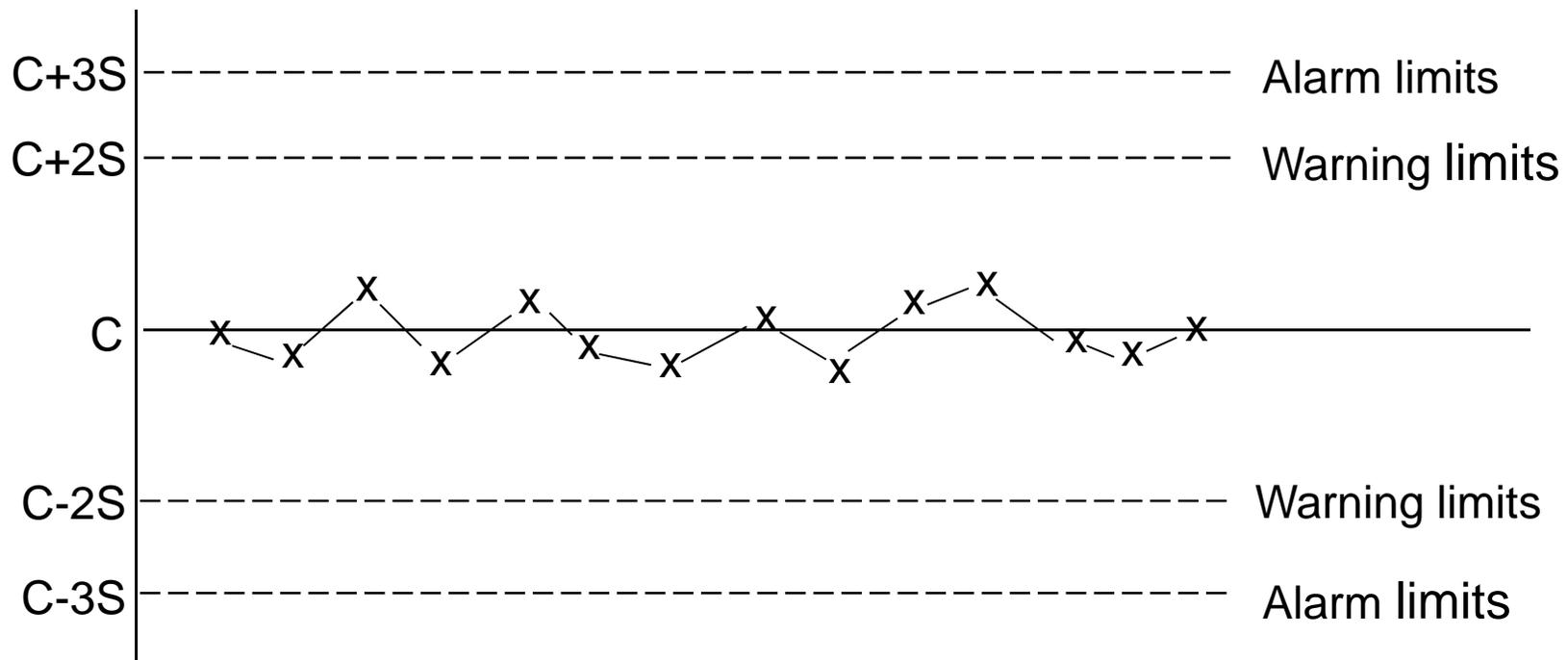
# Control Chart Example



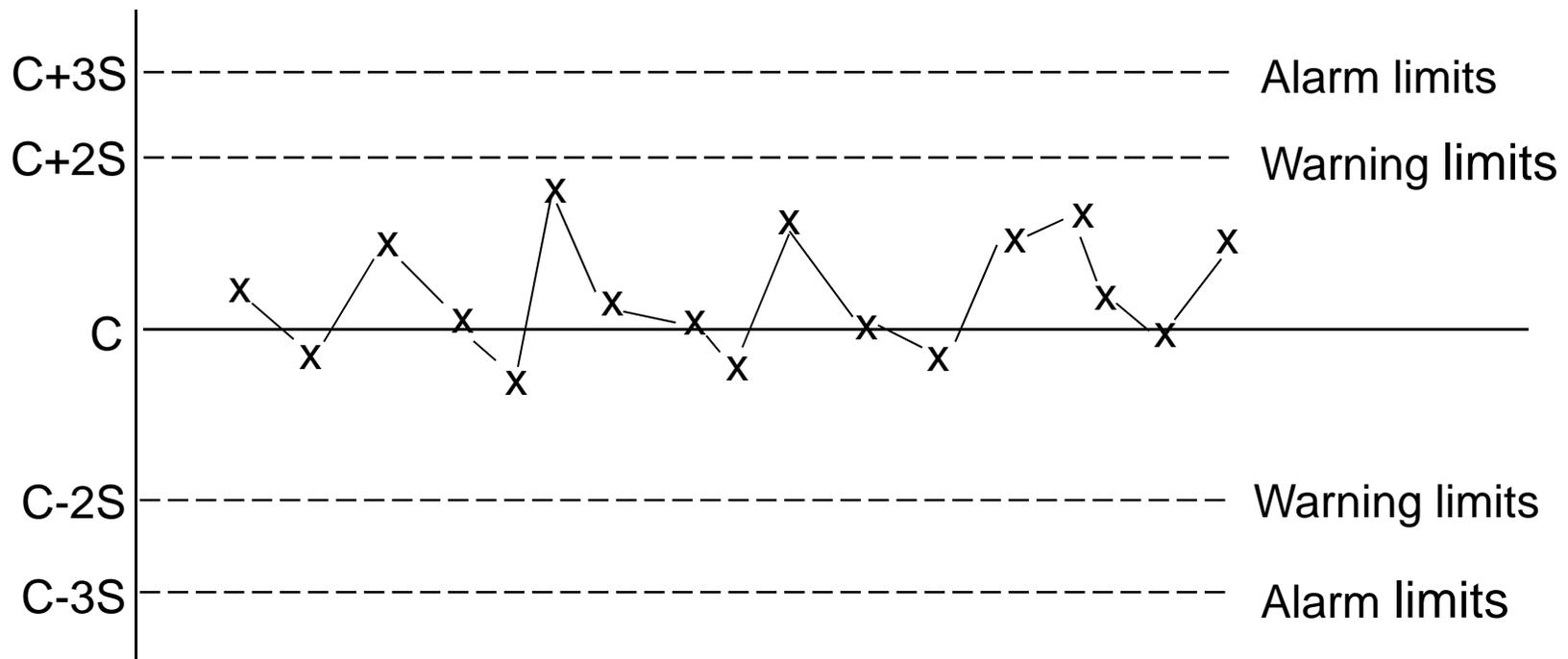
# Control Chart Example



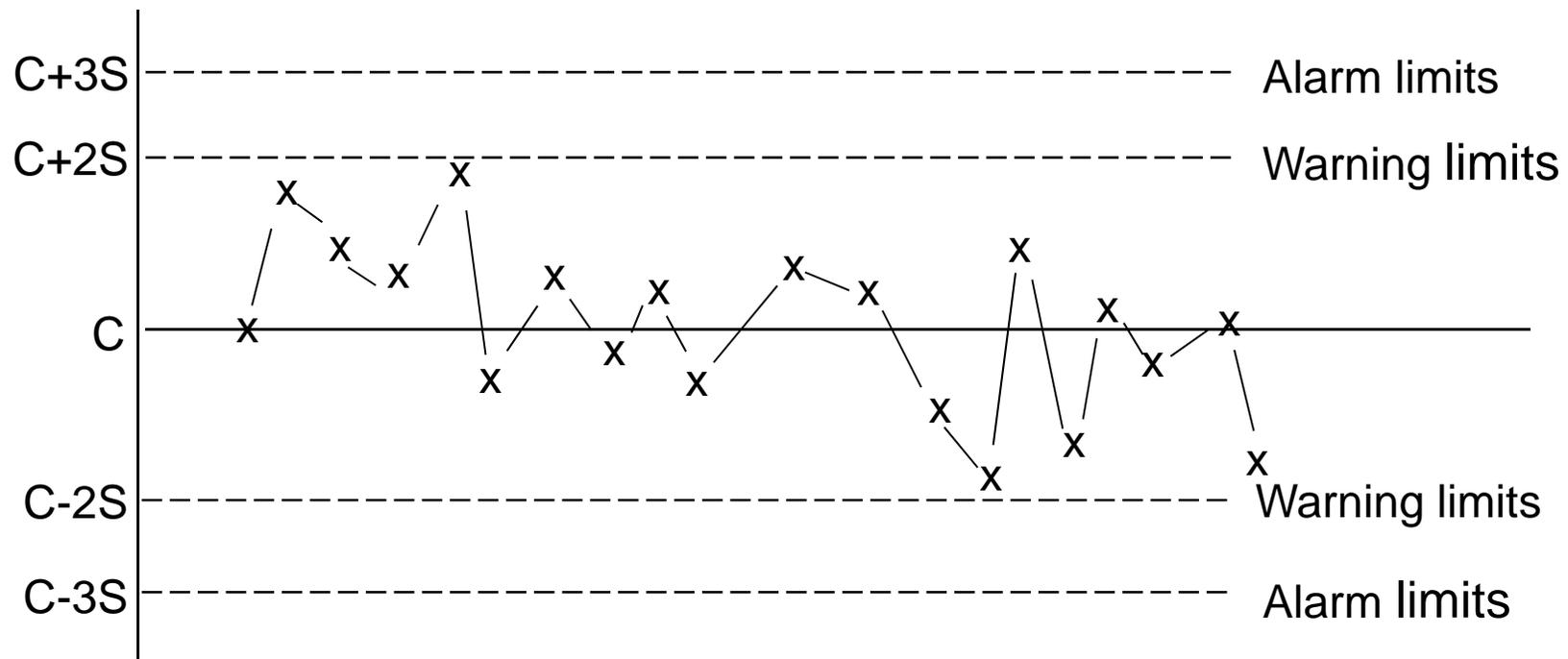
# Other Potential Problems



# Other Potential Problems



# Other Potential Problems



# Excluding Data and Outliers

---

- **When data is analyzed, examine the data for “special causes” or “assignable causes” that are used to exclude data that does not belong**
  - **For example, a review of raw data for an analytical result identified a significant weighing error**

# Excluding Data and Outliers

---

- **When analyzing data, one or more data points do not seem to “belong” and could be considered outliers**
- **Tests for outliers exist**
  - **Visual picture may serve as an indicator but formal tests should be applied**
  - **Statistical Tests (e.g., Grubbs’ T Test)**

## **Part 2**

---

# **Measurement Control Process and Control Charts**

# Measurement Control Process

---

- **The purpose of measurement control is to ensure the quality of a measurement**
- **This results in a measured value and an uncertainty for that value**
- **Sample or process measurements involve the determination of an unknown value**
- **Without measurement control, a measured value has very little, if any, meaning**

# Measurement Control Process

---

- **Quality control (QC) measurements must be made along with the process sample measurements**
- **This process cannot guarantee that process measurements are always correct**
- **However, if**
  - **the QC measurements are done the same way as the process measurements**
  - and**
  - **the QC samples are in control**

**Then there is a high level of assurance that the process measurements are valid and meaningful**

# Measurement Control Process

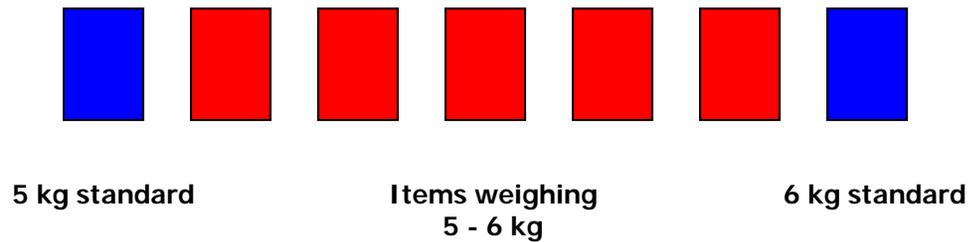
---

- **Process sample measurements should be bracketed or contained within QC sample measurements**
- **The measurement process should proceed as follows:**
  1. **Make an opening QC measurement**
  2. **If QC is in control, then proceed**
  3. **Make one or more process measurements**
  4. **Make a closing QC measurement**
  5. **If QC is in control, accept process measurements**
  6. **If more process measurements are required, then return to step 3**

# Measurement Control Process

---

**Bracket measurements of items with those of standards of similar weight**



**Standards within limits → accept measurements**

# Control Limits and Control Charts

---

- **Measurement control limits are derived and documented in the Method Qualification Report**
- **Control Limits are calculated at the 2 and 3 sigma levels**
  - **The 2 sigma limits are warning limits**
  - **The 3 sigma limits are alarm limits**
- **Control chart center line is set to zero or to the appropriate reference or historical value**
- **For additive models, limits are expressed in the same units as the measurement**
- **For multiplicative models, limits are expressed in relative or percent relative terms**

# Control Limits and Control Charts

---

- **Control limits can be calculated with or without bias corrections**
- **Control charts should be developed for each method**
- **In some cases, a particular method may have several control charts**
- **These charts are a critical tool for measurement control**

# Measurement Control Process

---

- **A control chart can be used to monitor the state of a measurement system**
- **A measurement system is considered out-of-control when**
  - **2 out of 3 consecutive QC results are outside warning limits**
  - or
  - **1 QC result is outside of alarm limits**
- **A measurement system declared as out-of-control cannot be used for accountability measurements**
- **Actions must be taken to resolve the out-of-control condition**

# Measurement Control Process

---

- **The measurement system must demonstrate in-control capability before measurements can resume**
- **This capability is demonstrated by having**
  - **3 consecutive QC results within warning limits**
  - and
  - **a result on each side of the center line**
- **If an opening QC measurement is out-of-control, then process measurements cannot proceed until the measurement system is shown to be in-control**
- **If a closing QC measurement is out-of-control, then all process measurements since the last opening QC must be re-measured**

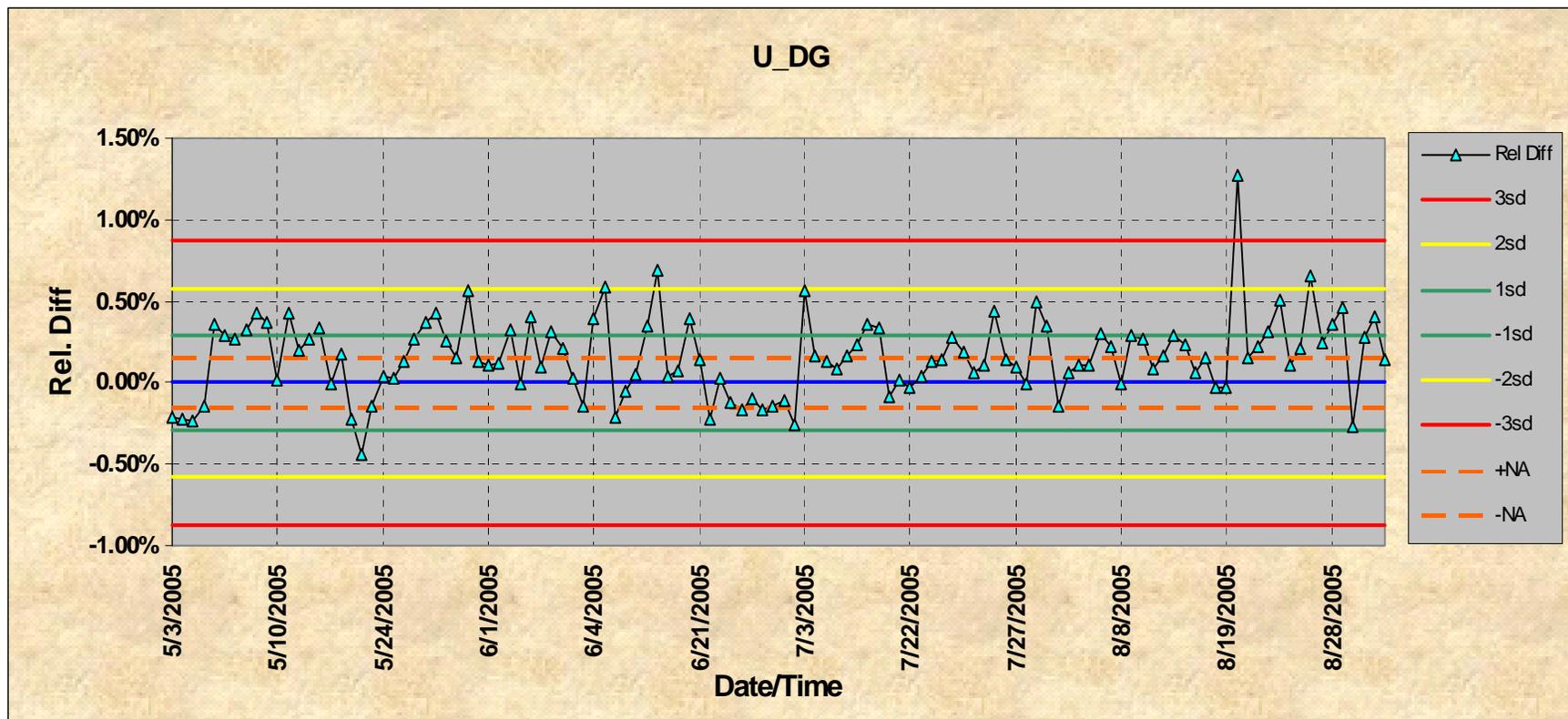
# Measurement Control Process

## Discussion Topics

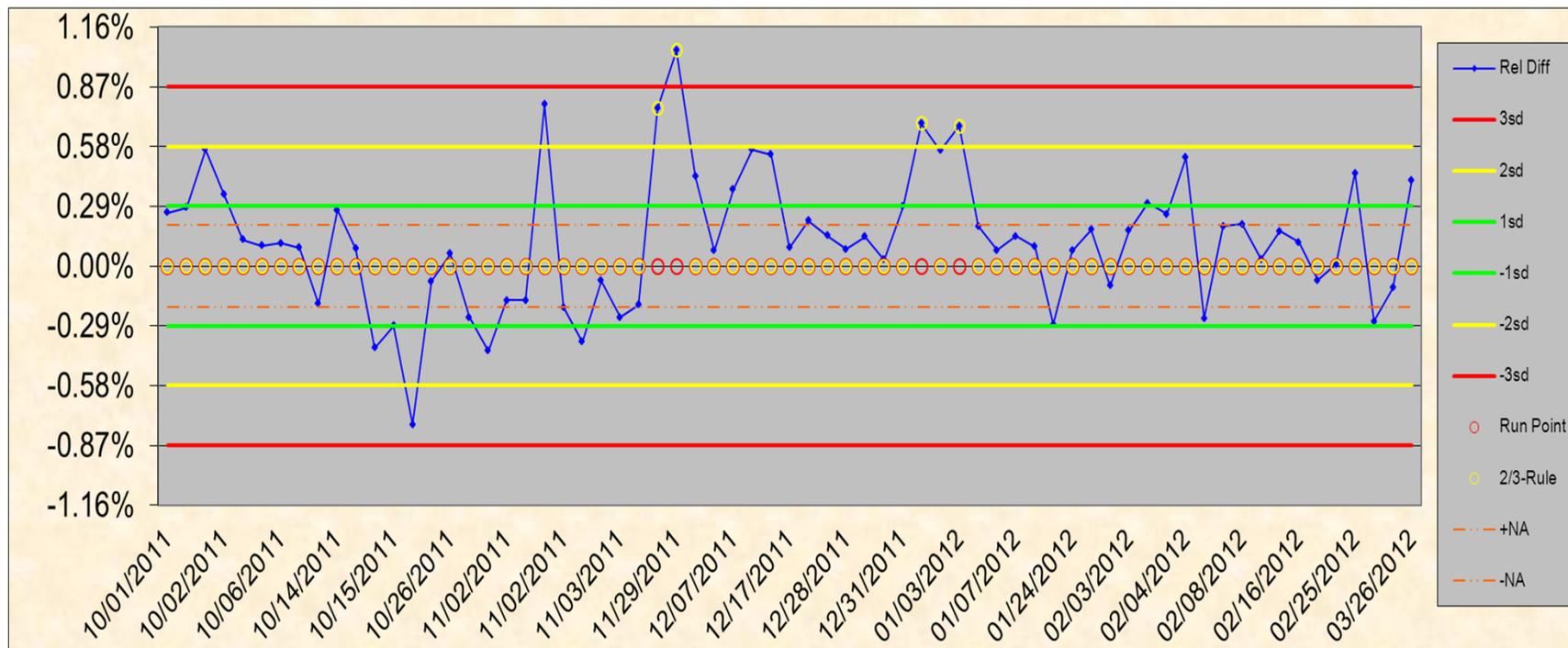
---

- 1. What has happened if an opening QC is out-of-control?**
- 2. How can a closing QC be out-of-control?**
- 3. What action should be taken if an opening QC value exceeds a warning limit?**
- 4. When can a closing QC also be an opening QC?**
- 5. Discuss strategies for bracketing process measurements.**
- 6. In an out-of-control situation, are re-measurements always feasible?**

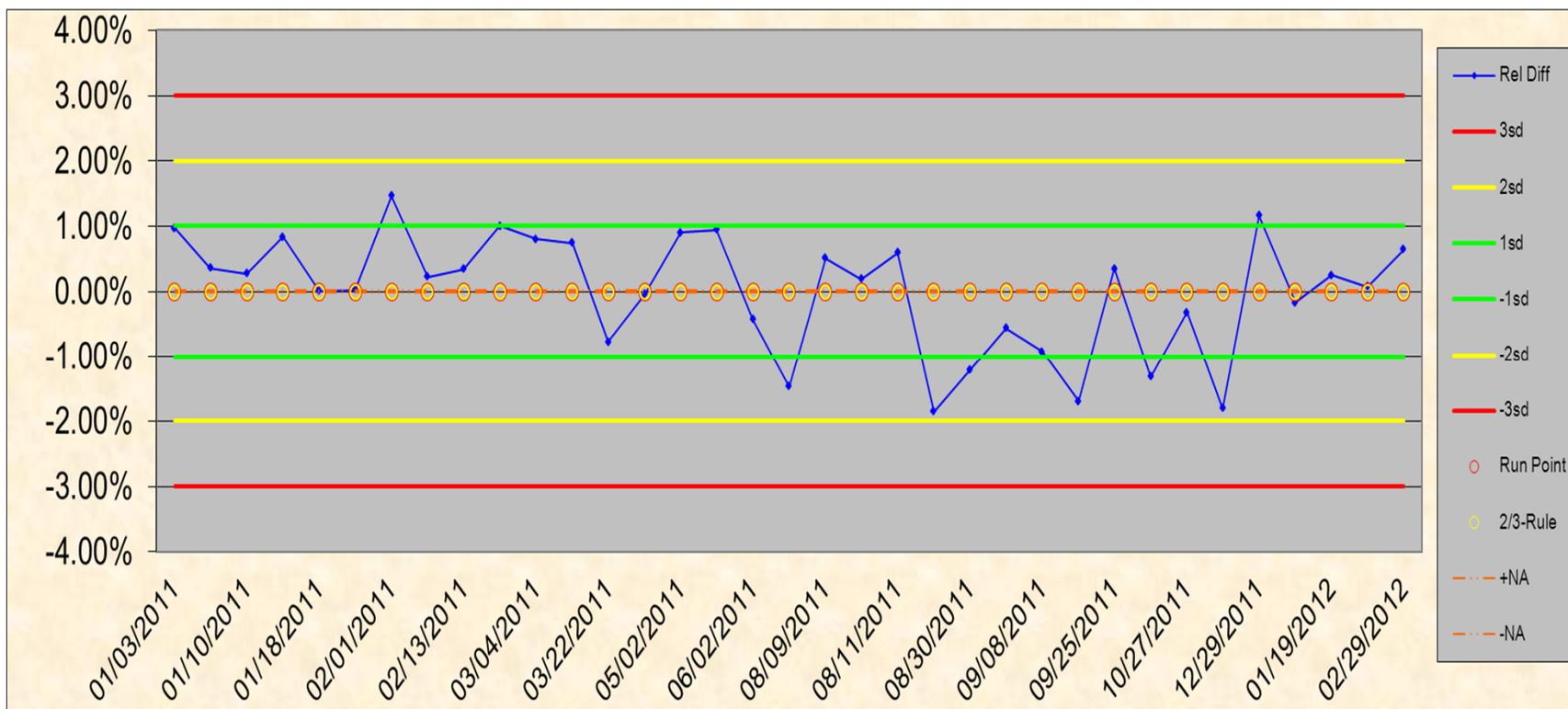
# Davies-Gray U Concentration



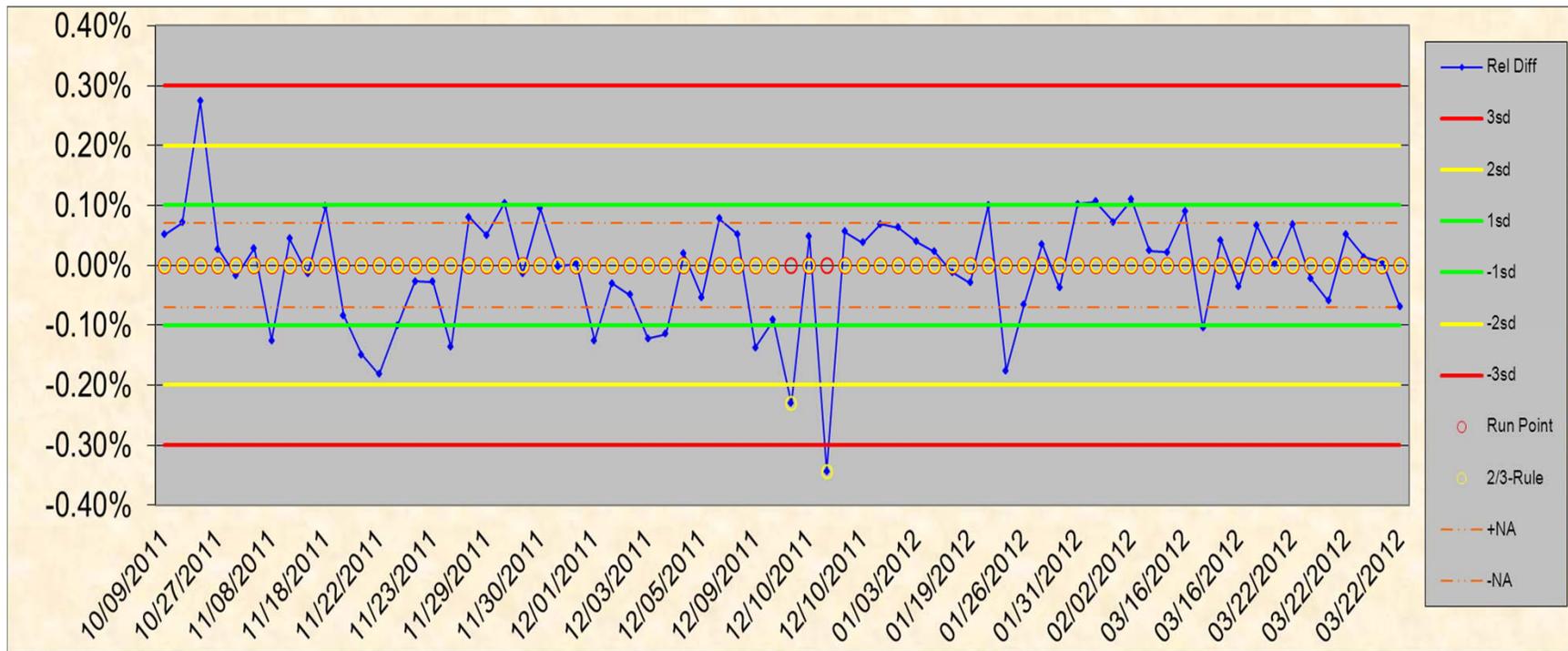
# Davies-Gray U Concentration



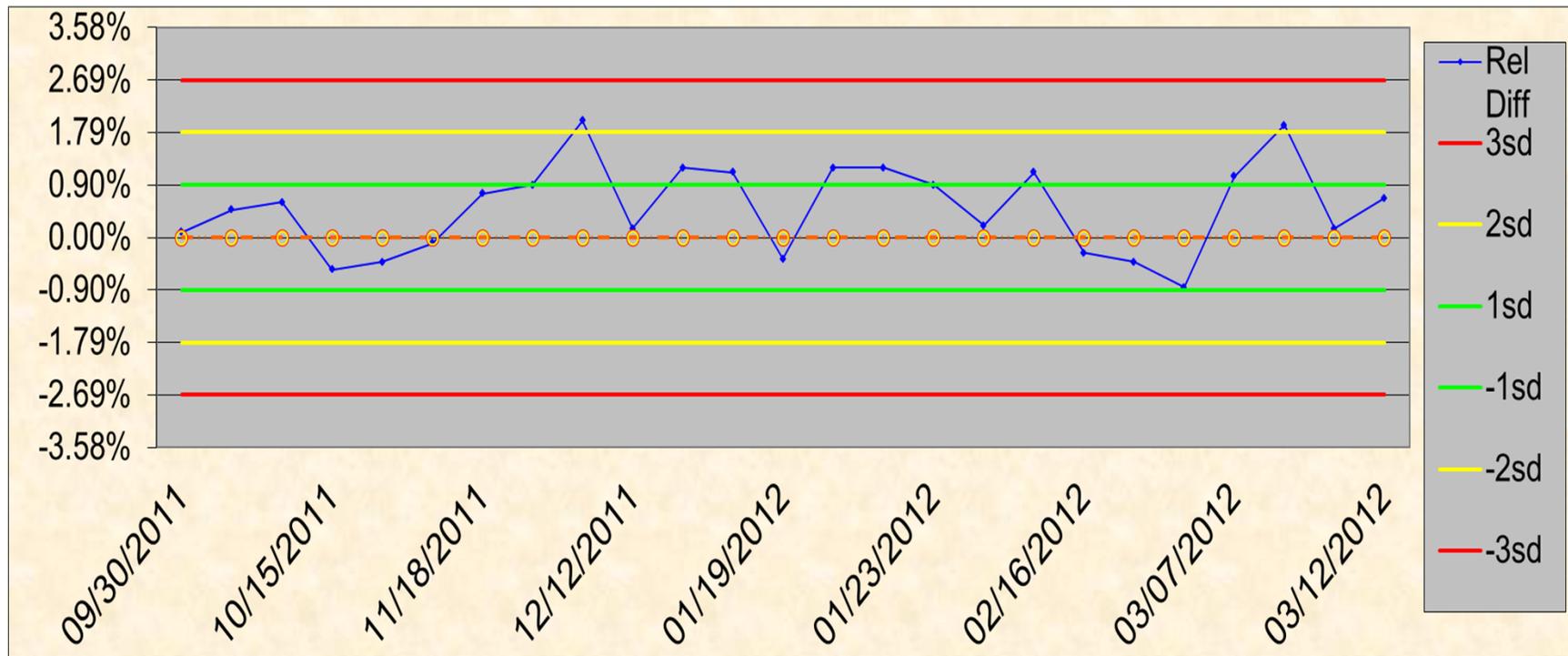
# Pu IDMS : Pu Concentration



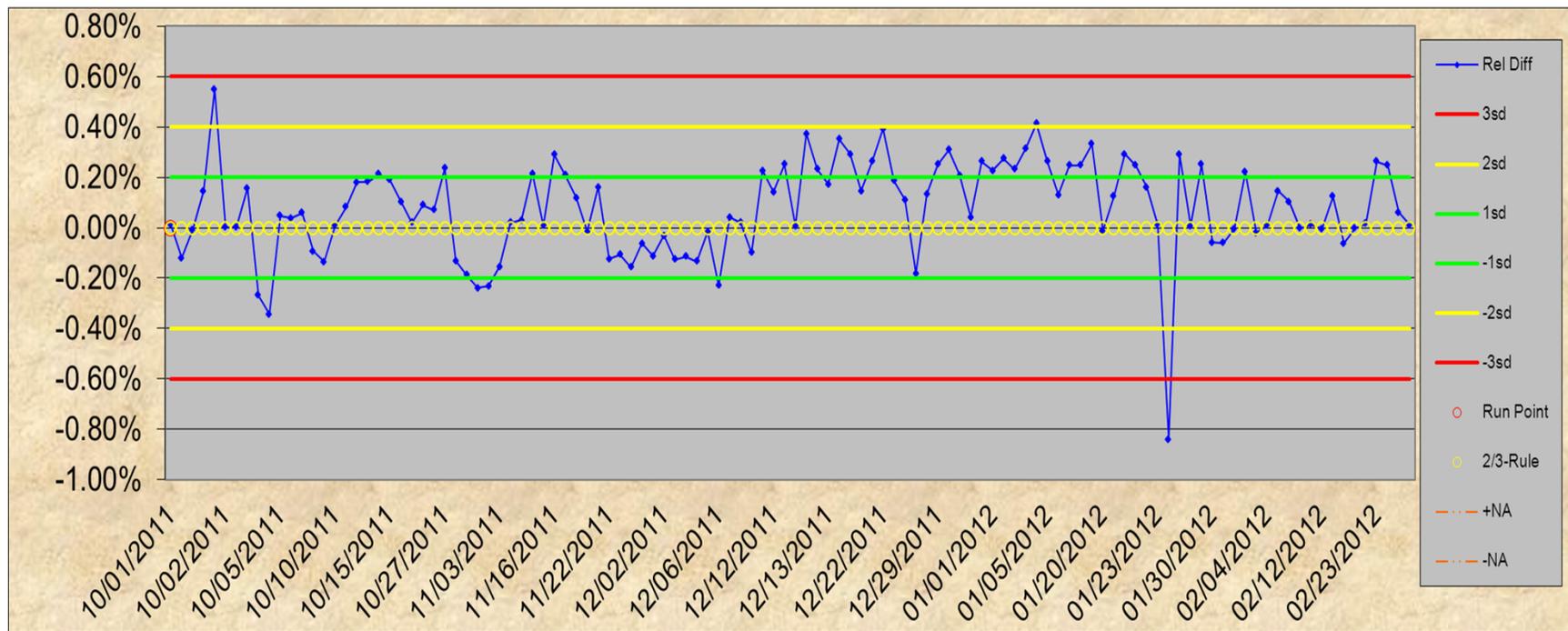
# Mass Spec Pu Isotopics



# U IDMS : U Concentration



# Mass Spec U-235 Isotopic



# Runs Rule Criteria Applied

---

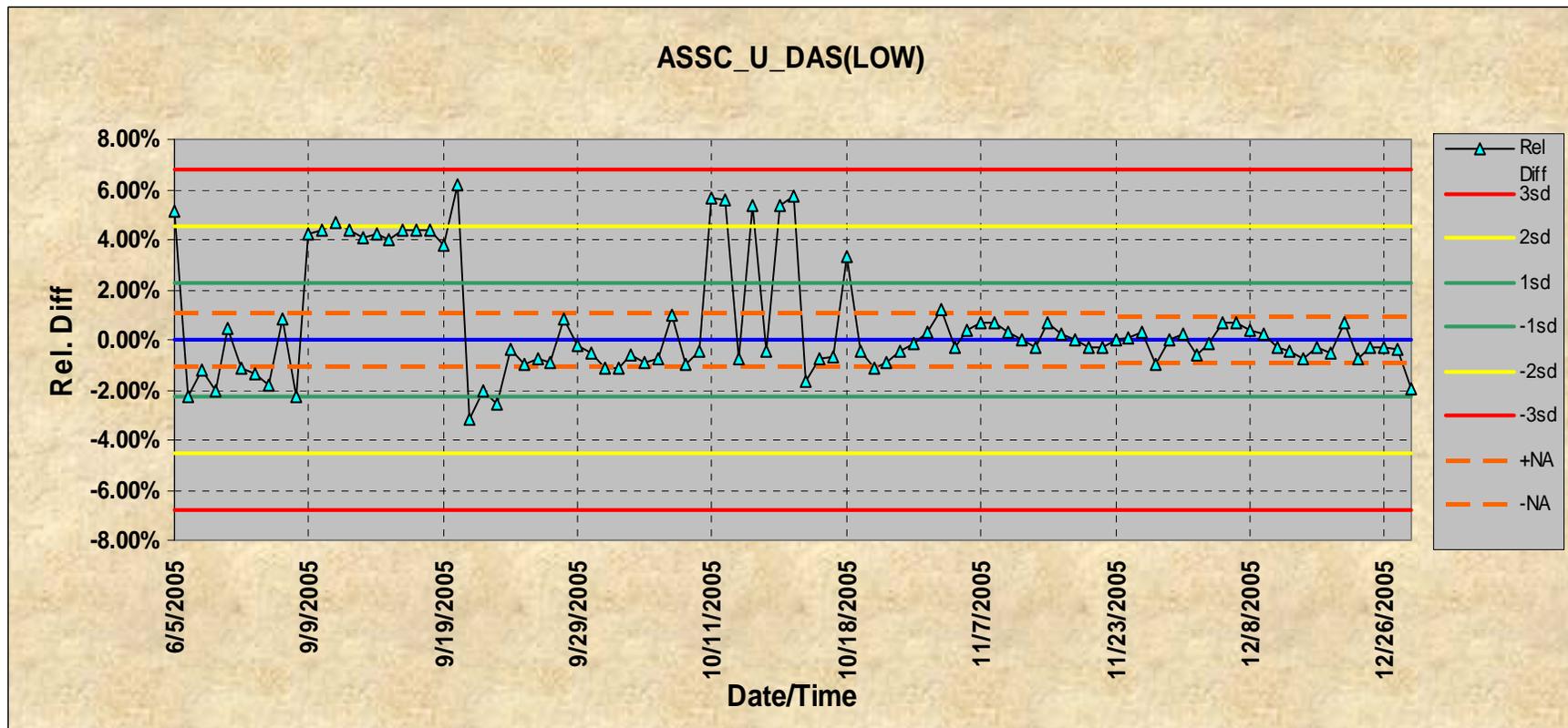
- **A runs rule is designed to detect an abrupt or slow change to a measurement system that results in a consistent bias**
- **This bias would result in QC measurements that are consistently high or low**
- **A runs rule violation, considered an “adverse condition,” occurs when 8 consecutive QC values are on the same side of the control chart center line**
- **An adverse condition is handled as follows:**
  1. **Investigate, and if possible, correct the adverse condition**
    - **An acceptable action is to continue with measurements while monitoring the system**
  2. **Document the adverse condition and any corrective actions taken**

# Runs Rule Criteria – Discussion Topics

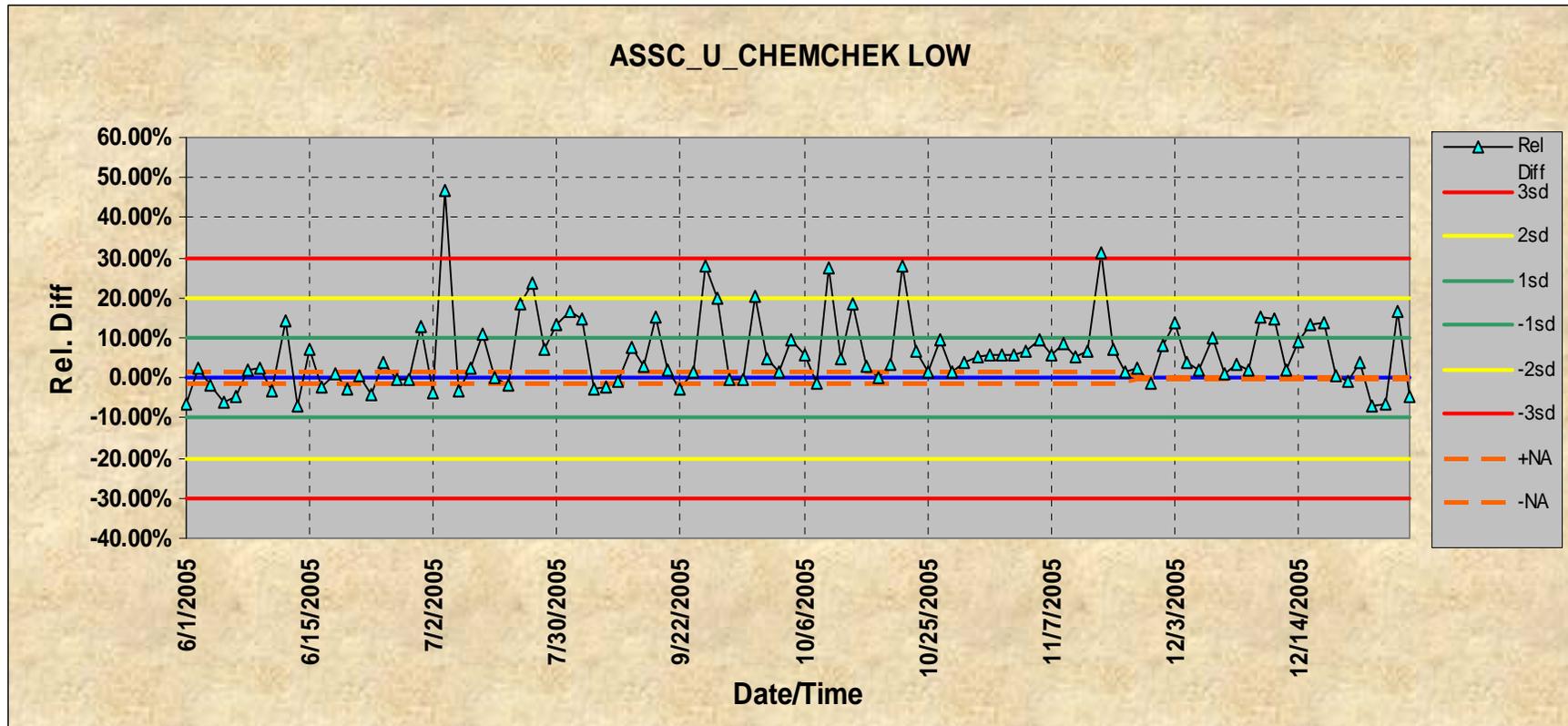
---

- 1. Could a method runs rule problem affect actual process samples?**
- 2. What should be done if 5 consecutive QC values show a constant bias?**

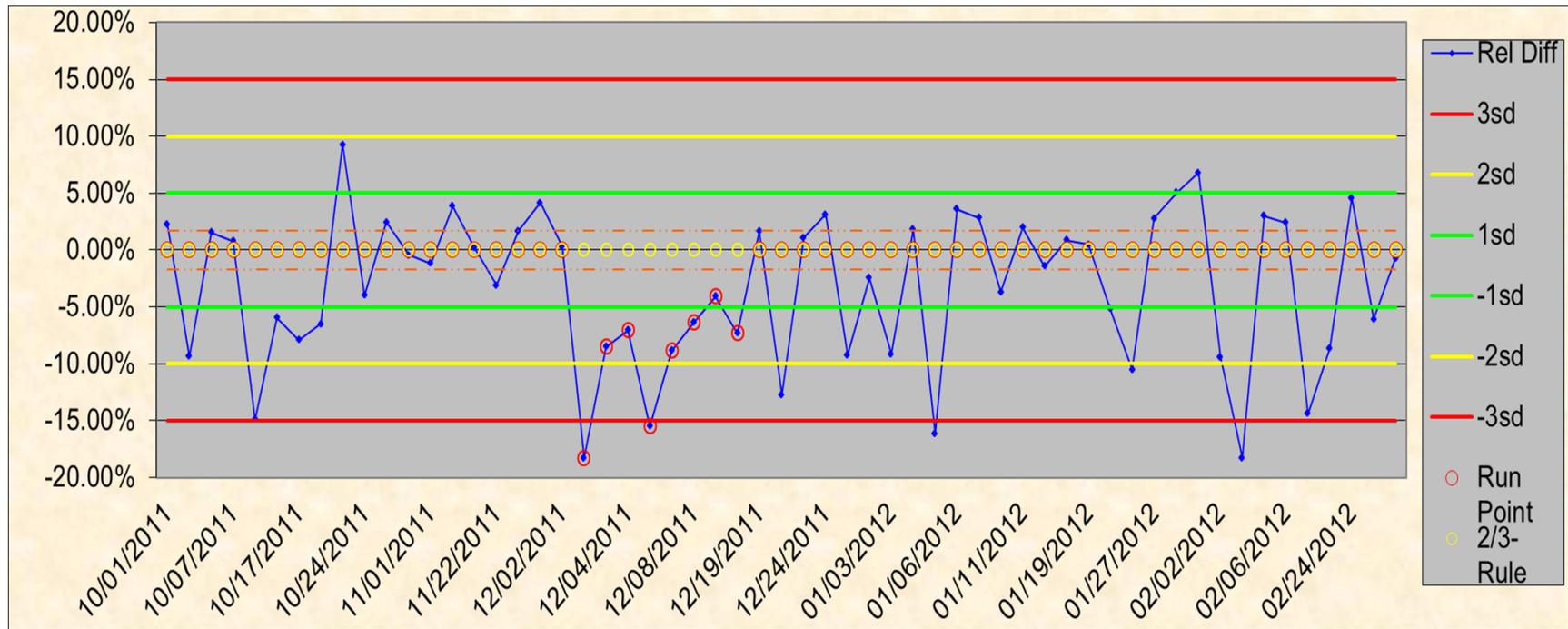
# Diode Array U Concentration



# ChemChek : Low U Concentration



# Pu TEVA : Low Concentration



# Lesson Summary

---

- **Identified the purpose of control charts**
- **Identified the six elements of control charts and their purpose**
- **Discussed and analyzed control charts**
- **Discussed control charts and measurement control**
- **Discussed and analyzed control charts from actual measurement systems**



## **Module 9**

---

# **Performance Calibration Modeling and Data Analysis**

# Objectives

---

- 1. Understand the function of a calibration model**
- 2. Understand the concept of calibration equation**
- 3. Understand the concept of regression analysis and the prediction equation**
- 4. Understand the use of regression analysis for calibration uncertainty**
- 5. Understand the concept of measurement uncertainty in calibration equations**

# Objective 1

---

**Identify the function of a  
calibration model**

# General Calibration Relationship

---

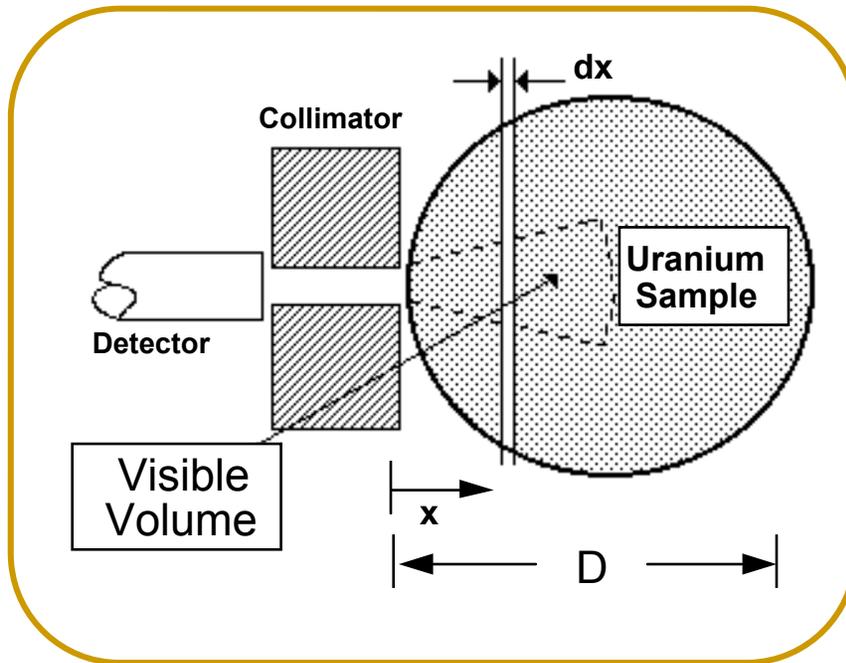
**Calibration is a process that defines the relationship between two variables or measures:**

**Input Variable (x)  
(Measurement Standard)**

**Output Variable (y)  
(Instrument Response)**

# Enrichment Meter Theory

- The Infinite Sample Enrichment Relation**



$$dR = \varepsilon E_w S dm_U \exp(-\mu\rho x) \exp(-\mu_c\rho_c t_c)$$

$$dm_U = A \rho_U dx$$

$\varepsilon$  = detection efficiency at the assay energy

$E_w$  = uranium enrichment (weight per cent)

$A$  = collimator channel area

$S$  = specific activity of the 185.7-keV  $\gamma$  ray

$\mu_c\rho_c$  = linear absorption coefficient of the container at the assay energy

$\mu\rho$  = linear absorption coefficient of the uranium (U) material and matrix (m) at the assay energy

$t_c$  = single wall thickness of the sample container

$$\mu\rho = \mu_U\rho_U + \mu_m\rho_m$$

$R$  = measured 186-keV count rate

$$= \varepsilon E_w S A \rho_U \exp(-\mu_c\rho_c t_c) \int_0^D \exp(-\mu\rho x) dx$$

Weight enrichment,

$$E_w = \left[ \frac{\mu_U}{\varepsilon S A} \right] R \left[ \frac{F \exp(\mu_c\rho_c t_c)}{1 - \exp(-\mu\rho D)} \right]$$

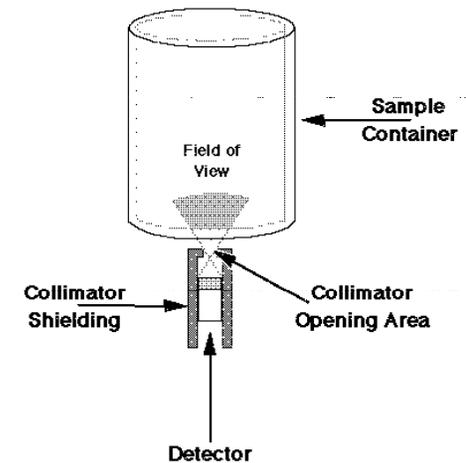
$$F = 1 + (\mu_m\rho_m / \mu_U\rho_U)$$

# Enrichment Meter Setup

**Assume you have nationally traceable reference standards**

**Your goal is to utilize these standards to generate a calibration curve for a portable enrichment meter using vendor software**

Schematic of Enrichment Measurement



Reference Standards

# Reference Standards

---

- **Internationally traceable standards**
- **Designed specifically for conducting enrichment meter measurements for uranium**
- **Five unique standards that can be used to generate a calibration curve**

Sample ID	Enrichment (wt.%)	Fill Height (mm)	U <sub>3</sub> O <sub>8</sub> mass (g)	<sup>235</sup> U mass (g)	RSD (%)
NBS-031	0.317	20.8	200.10	0.536	0.140
NBS-071	0.712	20.8	200.10	1.205	0.140
NBS-194	1.942	20.8	200.10	3.287	0.140
NBS-295	2.949	20.8	200.10	4.992	0.140
NBS-446	4.462	15.8	200.10	7.552	0.140

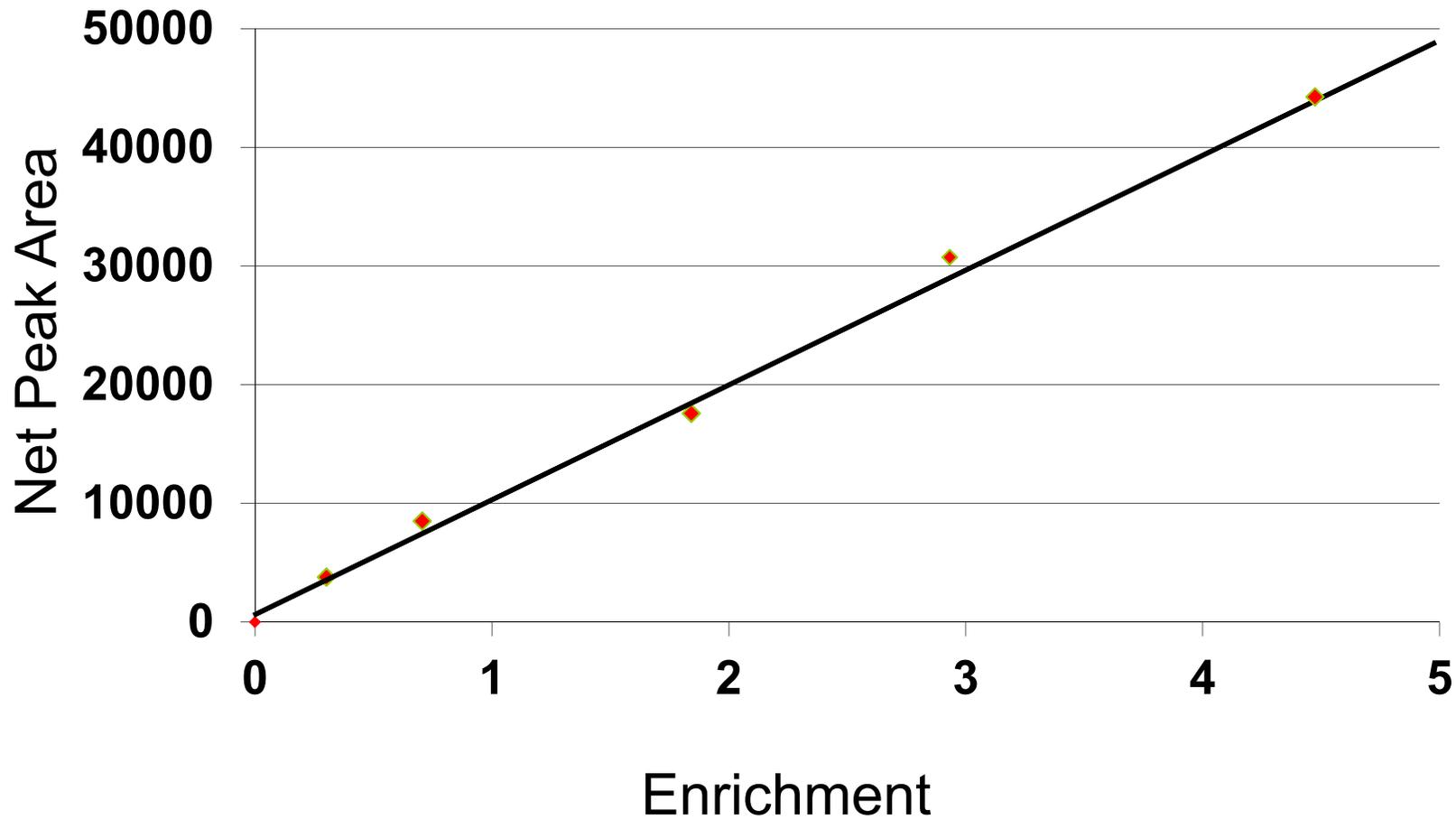
# Calibration Model

---

**An expression describing the calibration relationship**

- **Graph**
- **Equation**
- **Table**

# Net Peak Area vs. Enrichment

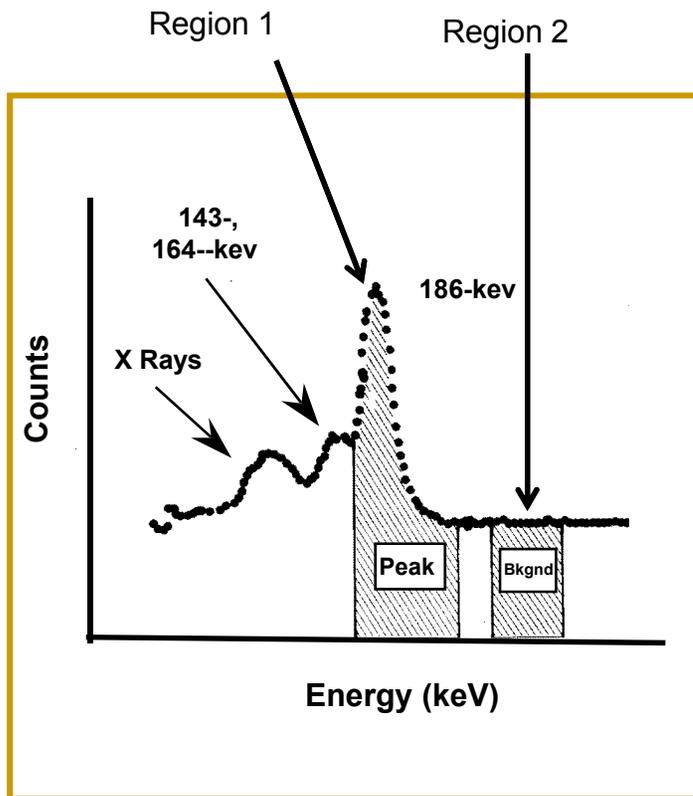


# Objective 2

---

**Identify the concept of calibration  
equation**

# The Calibration Method – Original



Region 1 = 130 to 210 keV  
Region 2 = 230 to 310 keV

Enrichment is estimated using the following formula

$$I = a A - b B$$

where  $I$  is the calculated enrichment,  $a$  and  $b$  are constants and  $A$  is the counts in Region 1 and  $B$  is the counts in Region 2

## The Calibration Method – Original (cont'd)

---

Given the relationship between the count is the two regions and the known enrichments

$$I_1 = a A(I_1) - b B(I_1)$$

$$I_2 = a A(I_2) - b B(I_2)$$

We can solve for a and b

$$a = \frac{I_1 \cdot B(I_2) - I_2 \cdot B(I_1)}{D}$$

$$b = \frac{I_1 \cdot A(I_2) - I_2 \cdot A(I_1)}{D}$$

$$D = A(I_1) \cdot B(I_2) - A(I_2) \cdot B(I_1)$$

## The Calibration Method – Original (cont'd)

- If the standards have values of 10.0% and 0.72% with net peak areas provided below

Enrichment (% <sup>235</sup> U)	A (counts)	B (counts)
I <sub>1</sub> = 10.0	80125	9790
I <sub>2</sub> = 0.72	18146	10902

then

$$a = \frac{I_1 \cdot B(I_2) - I_2 \cdot B(I_1)}{D}$$

$$b = \frac{I_1 \cdot A(I_2) - I_2 \cdot A(I_1)}{D}$$

$$D = A(I_1) \cdot B(I_2) - A(I_2) \cdot B(I_1)$$

# ASTM C 1514 Calibration Method

---

- Utilizes certified reference materials
- Geometry specified
- Precision for the net peak area is 1/10<sup>th</sup> the required method uncertainty
- Measurement parameters should be documented
- Three reference standards recommended for low resolution detector

$$E = A \times R_1 + B \times R_2$$

Where:

E = measured enrichment

A = Scaling constant for region 1

B = Scaling constant for region 2

R<sub>1</sub> = Count rate (c/s) in 185.7 keV region

R<sub>2</sub> = Count rate (c/s) in the Compton background region

# Measurement Value

---

**When attempting to find a measured value, the input and output variables from the calibration process are switched.**

**The input variable is now the instrument response, and the output is the measurement value obtained from the calibration curve.**

**Input Variable (y)  
(Instrument Response)**

**Output Variable (x)  
(Measured Value)**

# Measurement of Unknown Sample

---

Measurement of an unknown sample with the same container type and matrix give the following result

$$I = (1.47 \times 10^{-4})(45\ 090) - (1.78 \times 10^{-4})(10\ 100) \\ = 4.8\% .$$

Where 45,090 are the counts in A (or  $R_1$ ) and 10,100 are the counts in B (or  $R_2$ ).

**Note:** No measurement uncertainty reported yet.

# Objective 3

---

**Identify the concept of regression analysis**

# Regression Analysis

---

**Regression analysis is a method of determining the regression line (or equation) expressing a relationship between two variables**

# Deriving the Equation for the Measurement Relationship

---

**Original Equation:**

$$I = a A - b B$$

**or for ASTM C1514**

$$E = A \times R_1 + B \times R_2$$

**Where the values for the constants for a (or A) and b (or B) are derived from solving a simultaneous equation (see slide 12)**

# Deriving the Equation for the Measurement Relationship

---

- **The calibration constants and the uncertainty in the calibration constants are determined by performing multiple measurements of primary reference standards with known errors**
- **Vendor software provides estimates of this relationship for this specific measurement method**
- **The result of the calibration is provided by the software**

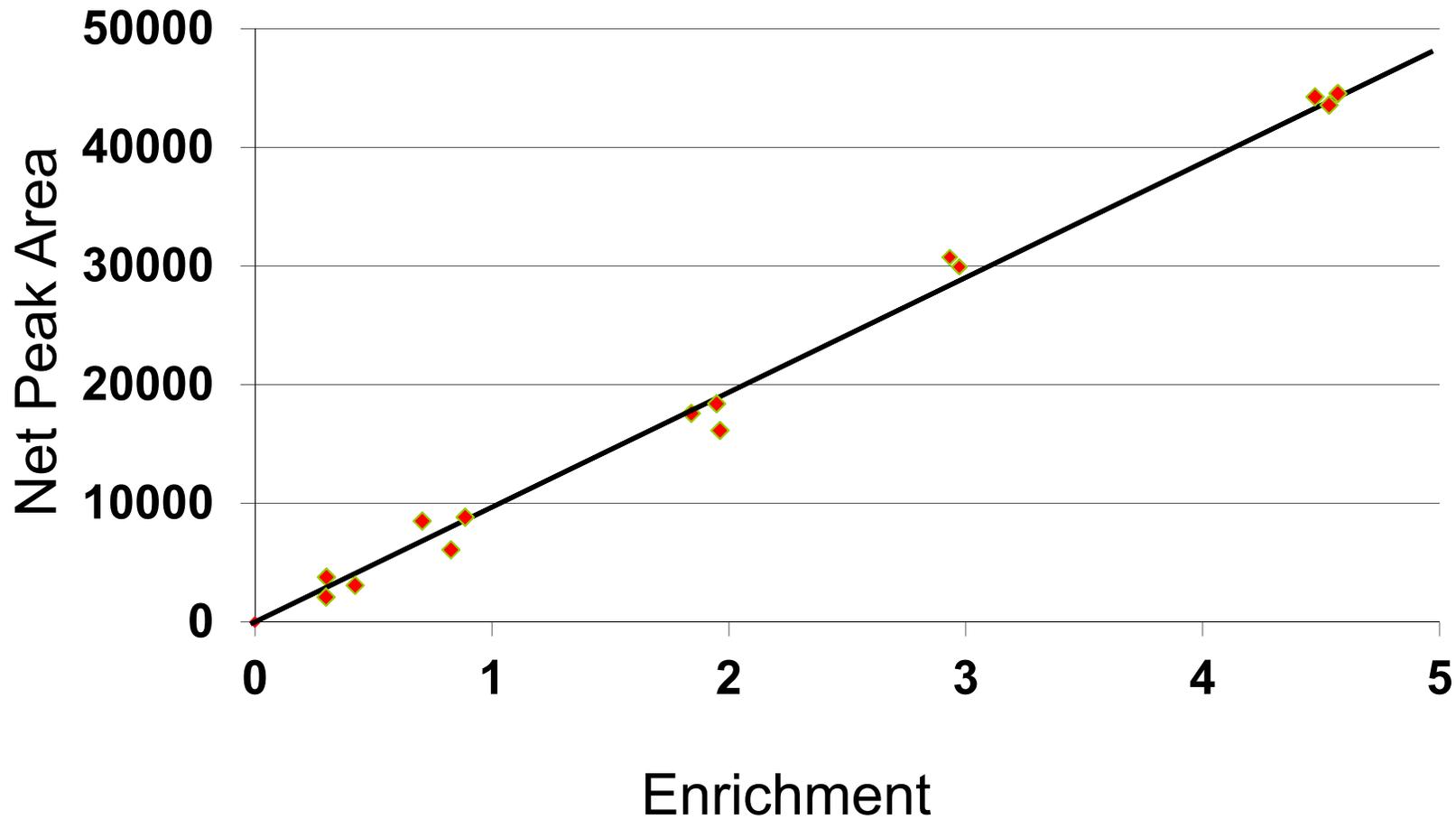
**This will be the prediction equation**

# Objective 4

---

**Identify the use of regression analysis for calibration uncertainty**

# Repeated Calibration with Error

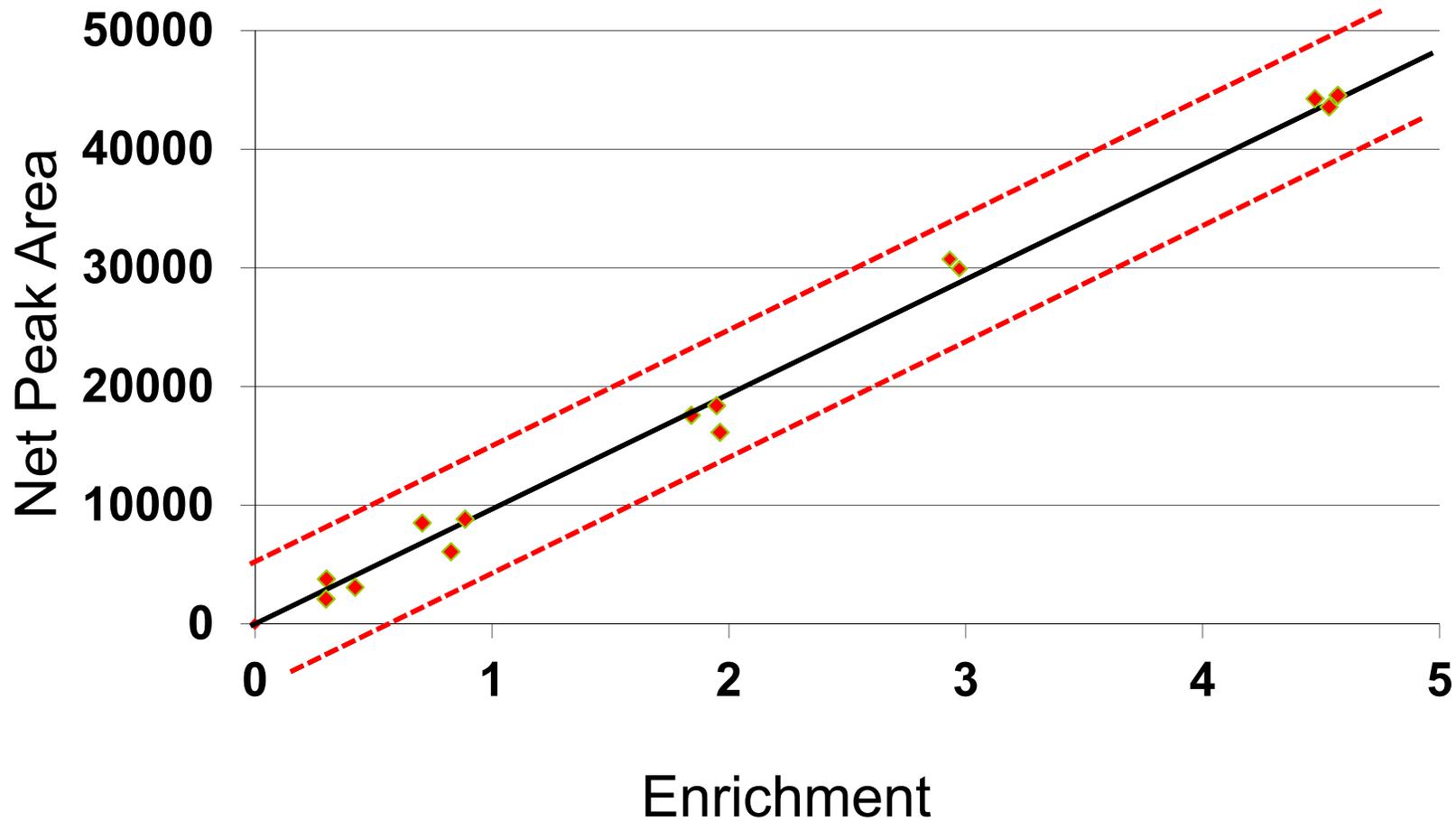


# Objective 5

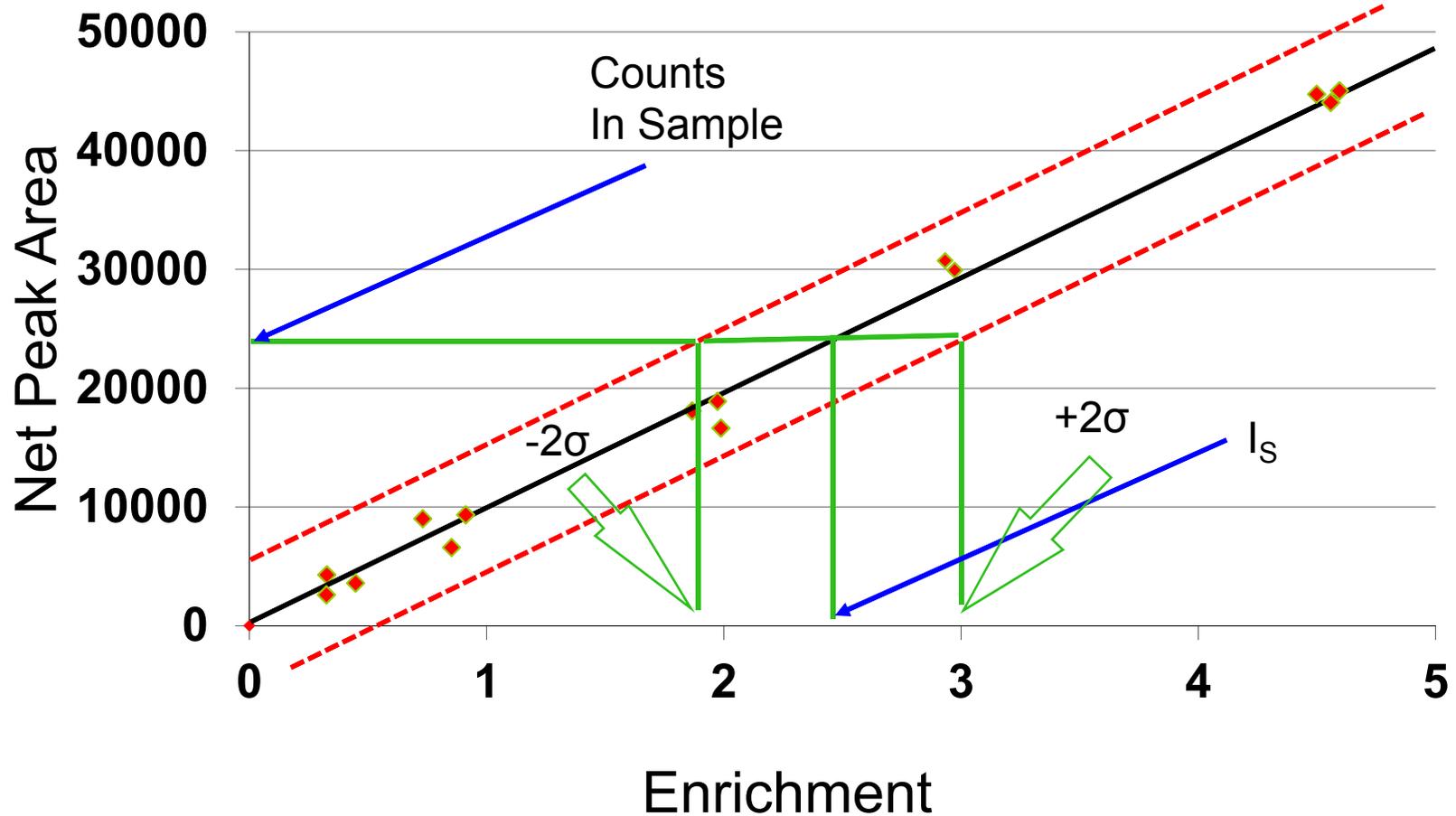
---

**Identify the concept of measurement uncertainty in calibration equations**

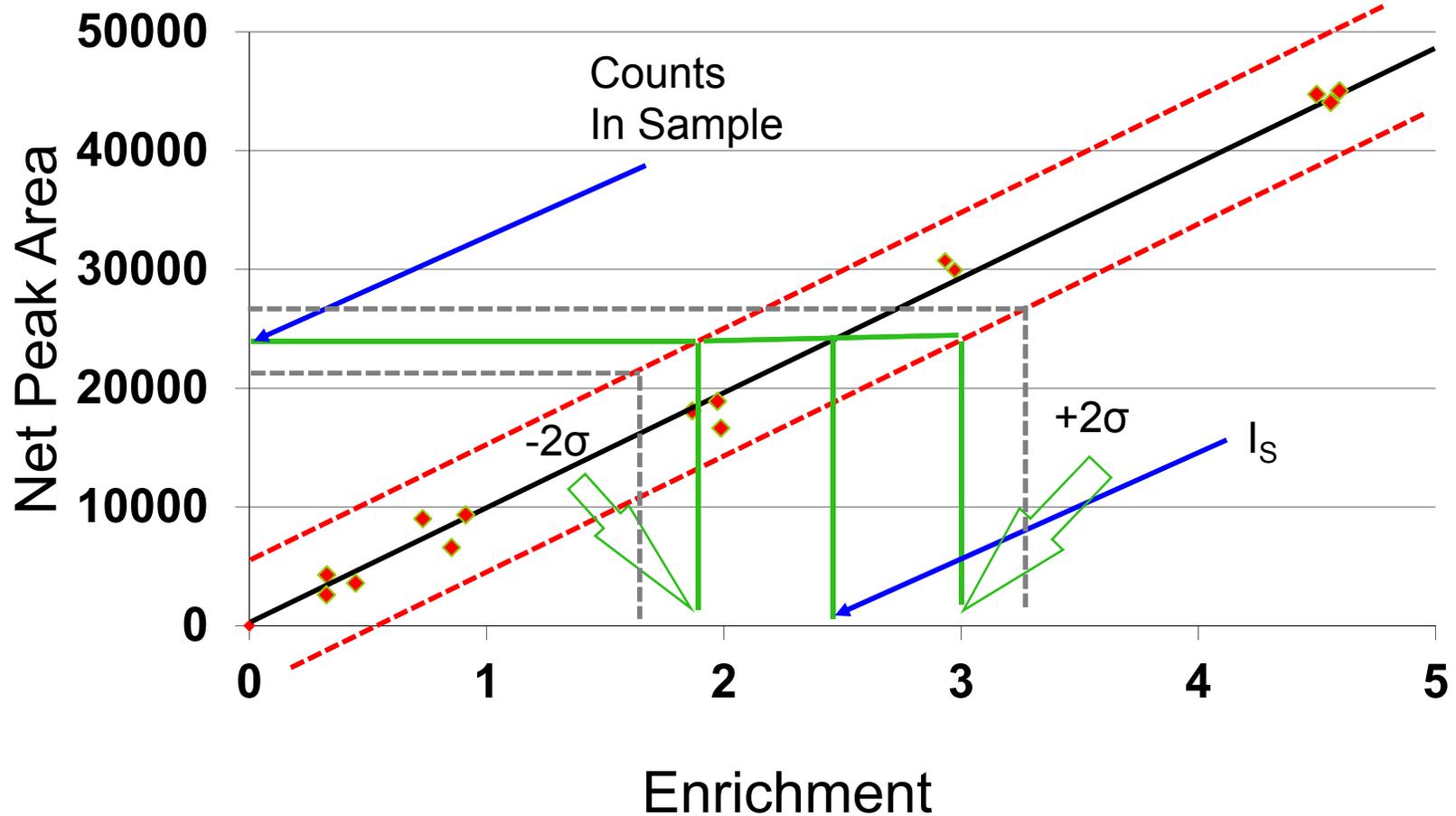
# Regression Line With 95% Confidence Limits



# Enrichment Confidence Limits due to Calibration Equation Uncertainty



# Measurement Error: Calibration Error



# Prediction Equation

---

- **Calibration equation is used to establish a relationship between two variables Net Peak Area and Enrichment**
- **Enrichment values were given by primary reference standards**
- **Net Peak Area measured using the gamma detector**
- **Calibration equation must be rearranged so that Enrichment can be computed from a calculated net peak area**

**This will be the prediction equation**

# Exercise #1:

---

- 1. Students will utilize the Inspector Mutli-Channel Analyzer and low resolution scintillation detector to generate a calibration curve using the NBS-031 and NBS-446 reference standards for a single measurement of 300 seconds**
- 2. Students will repeat step one to generate a calibration curve for two additional 300 second measurements for the same standards**
- 3. Students will add three measurements for the NBS-194 standard and evaluate the change in calibration coefficients and uncertainty**

# Derivation of Systematic and Random Uncertainties

---

**Variance propagation methods can be used to derive the systematic and random uncertainties associated with the use of the prediction equation. These uncertainties can then be incorporated into administrative controls for determining if the shipper's values can be confirmed.**

# Determination of Systematic and Random Uncertainties

---

- **For this method the random uncertainty should be within what is expected for counting statistics**
- **Systematic uncertainties result from variations in the prediction equation, wall thickness, matrix, geometry, etc**
- **Compare slope and intercept of prediction equation (or calibration curve) for the groups**

# Method Uncertainties

---

- The estimated uncertainty for the measured enrichment is:

$$\sigma = \sqrt{\frac{A^2 R_1 + B^2 \times R_2}{t}}$$

- where

**A and B are scaling constants**

**R<sub>1</sub> is the counts for the 185.7 keV region**

**R<sub>2</sub> is the counts for the background region**

**t is the count time in seconds**

# Method Uncertainties (cont'd)

- The estimated uncertainty for the scaling constants is:

$$A = \frac{\sum_{i=1}^n \left( \frac{E_i \times R_{1i}}{\sigma_{E_i}^2} \right) \times \sum_{i=1}^n \left( \frac{R_{2i}^2}{\sigma_{E_i}^2} \right) - \sum_{i=1}^n \left( \frac{E_i \times R_{2i}}{\sigma_{E_i}^2} \right) \times \sum_{i=1}^n \left( \frac{R_{1i} \times R_{2i}}{\sigma_{E_i}^2} \right)}{\sum_{i=1}^n \left( \frac{R_{1i}^2}{\sigma_{E_i}^2} \right) \times \sum_{i=1}^n \left( \frac{R_{2i}^2}{\sigma_{E_i}^2} \right) - \sum_{i=1}^n \left( \frac{R_{1i} \times R_{2i}}{\sigma_{E_i}^2} \right)^2} \quad (\text{A2.2})$$

$$B = \frac{\sum_{i=1}^n \left( \frac{E_i \times R_{2i}}{\sigma_{E_i}^2} \right) \times \sum_{i=1}^n \left( \frac{R_{1i}^2}{\sigma_{E_i}^2} \right) - \sum_{i=1}^n \left( \frac{E_i \times R_{1i}}{\sigma_{E_i}^2} \right) \times \sum_{i=1}^n \left( \frac{R_{1i} \times R_{2i}}{\sigma_{E_i}^2} \right)}{\sum_{i=1}^n \left( \frac{R_{1i}^2}{\sigma_{E_i}^2} \right) \times \sum_{i=1}^n \left( \frac{R_{2i}^2}{\sigma_{E_i}^2} \right) - \sum_{i=1}^n \left( \frac{R_{1i} \times R_{2i}}{\sigma_{E_i}^2} \right)^2} \quad (\text{A2.3})$$

where  $E_i$  is the enrichment of the standard,  $\sigma_E$  is the uncertainty in the reference standard enrichment and  $n$  is the number of measurements

# Calibration Equations

---

## Calibration equations are not always linear

- **NDA calibration equations may be second order (quadratic) or even third order (cubic)**
- **Some tank calibrations may be segmented depending on the construction of the tank and a residual heel in the tank**

# Calibration Equations

---

## Calibration equations are not always linear

- **Data analyses done by a statistician after consultation with the engineer**
- **Higher order calibration equations are beyond the scope of this course**
- **Other corrections may be required**

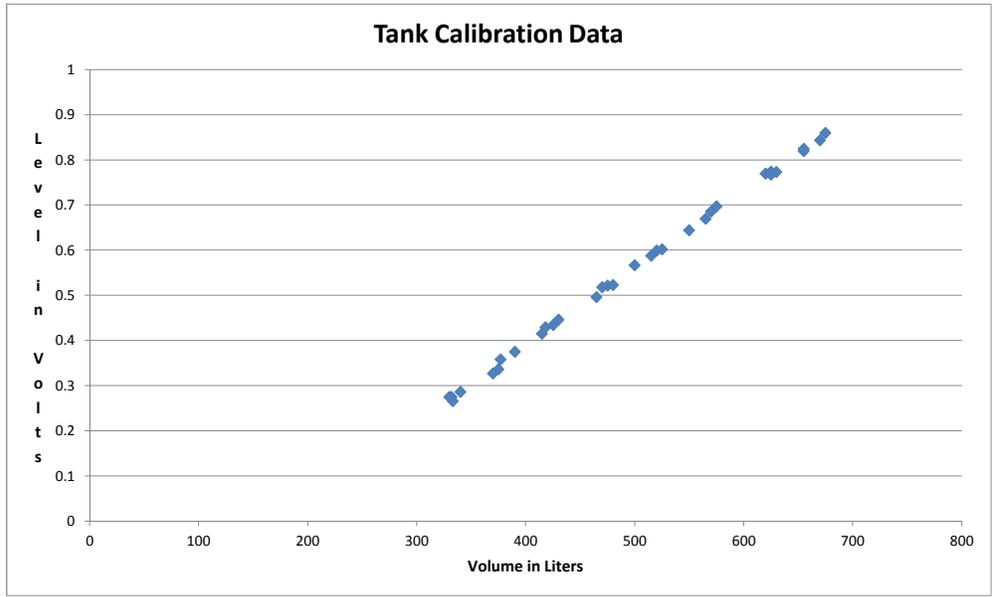
# Lesson Summary

---

- 1. Discussed the function of a calibration model**
- 2. Reviewed the concept of calibration equation**
- 3. Reviewed the concept of regression analysis and the prediction equation**
- 4. Reviewed the use of vendor software to evaluate the uncertainty due to the calibration approach**
- 5. Discussed the concept of measurement uncertainty in calibration equations**

Chinese Measurement Control Workshop  
Calibration Module  
Exercise #1

Volume	Level
Liters	Volts
330	0.275
332	0.275
333	0.266
340	0.286
370	0.327
375	0.336
377	0.358
390	0.375
415	0.415
418	0.429
425	0.434
430	0.446
465	0.496
470	0.518
475	0.522
480	0.523
500	0.567
515	0.588
520	0.599
525	0.602
550	0.644
565	0.67
570	0.686
575	0.697
620	0.77
625	0.774
625	0.768
630	0.773
655	0.82
655	0.825
670	0.844
675	0.86



Volume Prediction Uncertainties			
		Systematic Uncertainty	Random Uncertainty
Volume in Liters	Level in Volts	in liters	in liters
347.1	0.300	1.0	3.5
523.1	0.600	0.6	3.5
699.1	0.900	1.3	3.5

Regression Level Uncertainty =	0.006
Simulation Level Uncertainty =	0.005

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.999531276
R Square	0.999062771
Adjusted R Squar	0.99903153
Standard Error	0.00592418
Observations	32

ANOVA					
	df	SS	MS	F	Significance F
Regression	1	1.122341123	1.122341123	31979.26031	5.46558E-47
Residual	30	0.001052877	3.50959E-05		
Total	31	1.123394			

	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%
Intercept	-0.291675604	0.0048504	-60.13434409	7.77611E-33	-0.301581442	-0.281769766	-0.301581442	-0.281769766
X Variable 1	0.001704504	9.53156E-06	178.8274596	5.46558E-47	0.001685038	0.00172397	0.001685038	0.00172397

Cov(b0,b1)= -4.51E-08

**Chinese Measurement Control Workshop**  
**Calibration Module**  
**Exercise #1**

Volume	Level
Liters	Volts
330	0.28
332	0.28
333	0.27
340	0.29
370	0.33
375	0.34
377	0.36
390	0.37
415	0.42
418	0.43
425	0.43
430	0.45
465	0.5
470	0.52
475	0.52
480	0.52
500	0.57
515	0.59
520	0.6
525	0.6
550	0.64
565	0.67
570	0.69
575	0.7
620	0.77
625	0.77
625	0.77
630	0.77
655	0.82
655	0.82
670	0.84
675	0.86

<b>Predicted Volumes and Uncertainties</b>		
		<b>Systematic Uncertainty</b>
<b>Volume in Liters</b>	<b>Level in Volts</b>	<b>in liters</b>
	0.300	
	0.600	
	0.900	

**Regression Level Uncertainty =**

Simulation Level Uncertainty =	0.005
--------------------------------	-------

<b>Random Uncertainty</b>
<b>in liters</b>

# Exercise

## Calibration Module

---

### **Session Objectives:**

After the session the participants will be able to do the following:

1. Understand the function of a calibration model
2. Understand the concept of a calibration equation
3. Understand the concept of regression analysis and the prediction equation
4. Understand the use of regression analysis for calibration uncertainty
5. Understand the concept of measurement uncertainty in calibration and prediction equations
6. Understand the derivation of the prediction equation random and systematic uncertainties

### **Estimated Time:**

60 minutes to complete Exercise #1

### **Materials Needed:**

1. One computer with Microsoft Excel for each group of four or five students
2. Excel needs to have the Stat Package add-in loaded
3. Students need to have a good working knowledge of Microsoft Excel
4. Spreadsheet support person

### **Instructions:**

1. Students should work in groups of four or five
2. The tank calibration data will be supplied to the students in an Excel spreadsheet
3. Students will use the Excel Regression and other functions to compute uncertainties
4. The exercise will be instructor led
5. Discussion will occur at each step in the exercise emphasizing session objectives

## Exercise #1

The students, with instructor assistance, will complete the following activities:

1. Use the Excel Scatter Plot to produce a plot of the tank calibration data
2. Use the Regression Analysis function to estimate the calibration equation parameters, the parameter uncertainties and the residual mean square or variance
  - **The Intercept = -0.29 and the  $V(\text{Intercept}) = 0.0049^2$**
  - **The Slope = 0.0017 and the  $V(\text{Slope}) = (9.53\text{E-}6)^2$**
  - **The Cov(Intercept, Slope) = -4.51E-8 (not from Excel Regression Analysis)**
  - **The Residual Mean Square (RMS) = 3.51E-5 Volts<sup>2</sup>**
3. Invert the calibration equation to derive the prediction equation
  - **Prediction equation or Volume = (Level + 0.29) / 0.0017**
4. Use variance propagation techniques to compute the systematic and random uncertainties for the prediction equation for level values of 0.3, 0.6 and 0.9 volts.
  - **At 0.3 Volts: Predicted Volume = 347 L, Systematic Uncertainty = 1.0 L**
  - **At 0.6 Volts: Predicted Volume = 523 L, Systematic Uncertainty = 0.6 L**
  - **At 0.9 Volts: Predicted Volume = 699 L, Systematic Uncertainty = 1.3 L**
  - **Over Entire Voltage Range: Random Uncertainty = 3.5 L**

# Exercise

## Calibration Module

---

### Session Objectives:

After the session the participants will be able to do the following:

1. Understand the function of a calibration model
2. Understand the concept of a calibration equation
3. Understand the concept of regression analysis and the prediction equation
4. Understand the use of regression analysis for calibration uncertainty
5. Understand the concept of measurement uncertainty in calibration and prediction equations
6. Understand the derivation of the prediction equation random and systematic uncertainties

### Estimated Time:

60 minutes to complete Exercise #1

### Materials Needed:

1. One computer with Microsoft Excel for each group of four or five students
2. Excel needs to have the Stat Package add-in loaded
3. Students need to have a good working knowledge of Microsoft Excel
4. Spreadsheet support person

### Instructions:

1. Students should work in groups of four or five
2. The tank calibration data will be supplied to the students in an Excel spreadsheet
3. Students will use the Excel Regression and other functions to compute uncertainties
4. The exercise will be instructor led
5. Discussion will occur at each step in the exercise emphasizing session objectives

## **Exercise #1**

The students, with instructor assistance, will complete the following activities:

1. Use the Excel Scatter Plot to produce a plot of the tank calibration data
2. Use the Regression Analysis function to estimate the calibration equation parameters, the parameter uncertainties and the residual mean square or variance
3. Invert the calibration equation to derive the prediction equation
4. Use variance propagation techniques to compute the systematic and random uncertainties for the prediction equation for level values of 0.3, 0.6 and 0.9 volts.

	A	B	C	D	E	F	G
1	<b>Chinese Measurement Control Workshop</b>						
2	<b>Thermometer Calibration Data: Temperature and Liquid Height Information</b>						
3							
4	Height	Temp					
5	7.5	0.0					
6	9.0	0.0					
7	7.5	0.0					
8	8.5	0.0					
9	7.0	0.0					
10	10.0	25.0					
11	10.5	25.0					
12	10.0	25.0					
13	9.5	25.0					
14	10.5	25.0					
15	16.0	75.0					
16	16.5	75.0					
17	15.5	75.0					
18	16.0	75.0					
19	15.5	75.0					
20	19.0	100.0					
21	19.5	100.0					
22	18.0	100.0					
23	18.5	100.0					
24	20.0	100.0					
25							
26	<b>Temperature Prediction Uncertainties</b>						
27		<b>Uncertainty</b>	<b>Height</b>				
28	<b>Systematic Uncertainty =</b>	2.44	9.0				
29	<b>Systematic Uncertainty =</b>	4.05	15.0				
30	<b>Systematic Uncertainty =</b>	5.47	20.0				
31	<b>Random Uncertainty =</b>	5.85					

<i>Regression Statistics</i>	
Multiple R	0.990274481
R Square	0.980643547
Adjusted R Square	0.979568189
Standard Error	0.655637942
Observations	20

ANOVA			
	<i>df</i>	<i>SS</i>	<i>MS</i>
Regression	1	392	392
Residual	18	7.7375	0.42986111
Total	19	399.7375	

	<i>Coefficients</i>	<i>Standard Error</i>	<i>t Stat</i>
Intercept	7.625	0.236393622	32.2555234
X Variable 1	0.112	0.003708848	30.1980538

Cov(7.625, 0.112) = -6.88E-04

	H	I	J	K	L
1					
2					
3					
4					
5					
6					
7					
8					
9					
10					
11					
12					
13					
14					
15	<i>F</i>	<i>Significance F</i>			
16	911.9224556	7.13713E-17			
17					
18					
19					
20	<i>P-value</i>	<i>Lower 95%</i>	<i>Upper 95%</i>	<i>Lower 95.0%</i>	<i>Upper 95.0%</i>
21	2.22413E-17	7.12835543	8.12164457	7.12835543	8.12164457
22	7.13713E-17	0.104207999	0.119792001	0.104207999	0.119792001
23					
24					
25					
26					
27					
28					
29					
30					
31					

## **Balance Exercise**

---

### **Analytical Balance Precision, Accuracy and Uncertainty Determination Exercise**

#### **Exercise Objectives:**

1. Determine the variation in making weight measurements
2. Determine estimates of precision due to the variation between analysts and balances
3. Estimate the uncertainty of weight measurements at different levels over the weighing range.
4. Learn the importance of knowing the variable included in measurement precision estimates.

#### **Estimated Time:**

+1.00 hours completing exercise

+0.45 hours in large group discussion

1.75 hours total

#### **Materials needed:**

1. Four Laptop computers
2. Four zip or flash drives for use in transferring data between teams
3. Work sheets for each person and the certificate with the calibration values & uncertainties.
4. One barometer with calibration certificate or manufacturer specifications **in both Chinese and English**
5. One thermometer with readability to tenth of a degree (0.1C) must have calibration certificate or manufacturers specification.
6. Humidity meter with calibration certificate or manufacturer specifications **in both Chinese and English**
7. Four analytical balances (four places minimum)
8. Four sets of calibrated E2 mass standards (1-100 gram sets) with calibration certificates
9. Four sets of tweezers or tongs for handling weights.
10. At least 24 pair of cotton or insulated gloves.
11. Flip chart or dry board and colored markers
12. A printer for at least one of the computers to print out the results of the exercises.

## **Instructions:**

### **Exercise 1a (Repeatability)**

#### **Perform the following steps.**

1. On a team work sheet record the environmental conditions; weight ID, weight's conventional value & uncertainty from the calibration report, date and the name of each team member.
  2. Make sure the balance is level.
  3. Exercise the balance by placing a 100 g weight on the pan and removing it 3 times using tweezers.  
**Keep hands off the weights!**
  4. Zero the balance.
  5. Using tweezers, place the 100 g weight on center of the pan.
  6. Record the first stable reading.
  7. Remove the weight using tweezers.
  8. Repeat steps 4 through 7 nine more times. Do not Zero.
  9. Use the Excel spread sheet to record your data and calculate the average bias ( $U_b$ ), standard deviation ( $U_{sd}$ ), the standard's standard deviation ( $U_{std}$ ), uncertainty & relative uncertainty.
  10. Print 5 copies of the spreadsheet after you have accurately input the correct information.
  11. Give copies to the other teams and instructors, after your team has studied them.
- 

#### **Discussion Questions:**

1. How do the bias, standard deviation and uncertainty estimates differ between team members?
2. What is the largest source of uncertainty that is used to calculate the uncertainty of weight measurements made by your balance?
3. Did the uncertainty of the standard contribute significantly to the total uncertainty?
4. How much of the total uncertainty was contributed by the standard used?
5. This balance will be used in another exercise to calibrate pipettes.
6. Is it fit for that purpose? Why?

## Exercise 1b (Intermediate Precision)

This exercise uses all of the measurements made by each team to compute an **intermediate precision estimate**. All conditions have been held constant, except for the operators. The average and standard deviation of all the data are calculated in the last column of the Excel spreadsheet and an uncertainty estimate has been calculated and reported in the bottom line.

### Discussion Questions:

1. Is the team estimate different than the estimates of the individuals?
2. What is the major source of uncertainty in this exercise?
3. Save a copy of your Excel spreadsheet and change the uncertainty of each weight by multiplying it by 3 and recalculate the uncertainty estimates.
4. What affect did this have on the total uncertainty?
5. How can the uncertainties be reduced in Weighing?

## **Exercise 1c (Reproducibility)**

This exercise requires each team to get copies of the other teams exercise and use the information to determine the best estimate of uncertainty for weight measurements made by anyone in the class on any of the balances. Be ready to discuss how you determined the estimate with the rest of the class.

### **Discussion Questions:**

1. After reviewing the precision data and uncertainty estimates from all teams, which team has the smallest uncertainty? .
  2. Is there a significant difference in the uncertainty estimates of the various balances?
  3. Is there a significant difference in biases calculated for each of the balances?
- 

### **Summary Points for Exercises 1a through 1c:**

1. The exercises should demonstrate that the more variables a measurement system has, the larger the uncertainty estimate. Was this the case for this exercise?
2. Standards used for calibration and validation must have uncertainties  $< 1/3$  of the measurement instrument's uncertainty. Did the standards used for this exercise have small uncertainties?
3. Reproducibility conditions must be stated to have a meaningful estimate of the random error associated with weight measurements.

## Exercise 2

### Balance Linearity Testing and Uncertainty Estimations

This exercise involves testing the linearity of a balance at 5 points over the range and using the data to estimate the uncertainty of measurements made at the different ranges. Have one person from your team make 10 measurements with each of the 5 weights provided.

1. Record your name, the date & time, environmental conditions, balance and weight information. This includes the certificate conventional weight and uncertainty for each standard
2. Zero the balance then, place the 1 g weight in the center of the pan, record the first stable reading,
3. Remove, then weigh the 10 g weight, record,
4. Remove, then weigh the 50 g weight, record,
5. Remove, then weigh the 100 weight, record,
6. Remove, and then weigh the 150 combined weights.
7. Repeat steps 2 – 6 nine more times. Only zero the balance before weighing the series of 5 weights.
8. Then use the Exercise 2 Excel spreadsheet to calculate estimates of uncertainty at each level.
9. Print 5 copies of the spreadsheet after you have accurately input the correct information.

#### Discussion Questions:

1. How do the relative uncertainties differ for each level?
2. How do you characterize the linearity error of the balance? Is it significant?
3. What uncertainty error would you assign for weight measurements made with your balance?
4. Will the balance contribute significantly in weight measurements made for accountability?

**Balance Exercise 1a Repeatability Test & Uncertainty Estimates  
Balance Exercise 1b Intermediate Precision & Uncertainty Estimate**

1	Name:						Intermediate Precision Group's Total
2	Date/time						
3	Barometric Pressure=		Humidity=		Temp=		
4	Balance ID=		Model =				
5	Weight mass	100 g	100 g	100 g	100 g	100 g	
6	Weight ID						
7	Wt Certificate Conventional Mass						
8	Wt Certificate Uncertainty						
9							
10	Weighing 1						
11	Weighing 2						
12	Weighing 3						
13	Weighing 4						
14	Weighing 5						
15	Weighing 6						
16	Weighing 7						
17	Weighing 8						
18	Weighing 9						
19	Weighing 10						
20	<b>Average =</b>						
21	<b>Standard Deviation (U<sub>sd</sub>)=</b>						
22	Certificate Conventional Wt=						
23	Bias = Ave Wt – Certificate Wt						
24	<b>Bias Uncertainty (U<sub>b</sub>) = B/2=</b>						
25	<b>U of standard=(U<sub>std</sub>)</b>						
26	Square Root of 3 =						
27	<b>(U<sub>std</sub>) Certificate U/(3)<sup>.5</sup></b>						
28	Combined Unc <sup>**</sup> =						
29	Expanded U = U <sub>c</sub> x 2						
30	<b>Bias in mg</b>						
31	<b>Repeatability in mg</b>						
32	<b>U in mg ( U*1000)</b>						
33	<b>U in %</b>						
	<sup>**</sup> U <sub>c</sub> = $(U_{sd}^2 + U_{std}^2 + (B/2)^2)^{.5}$						

### Balance Linearity Test Exercise 2

1	Name:					
2	Date/time					
3	Barometric Pressure=		Humidity=		Temperature=	
4	Balance ID=		Model =			
5	Weight mass	1 g	10 g	50 g	100 g	150 g
6	Weight ID					
7	Wt Certificate Conventional Mass					
8	Wt Certificate Uncertainty					
9						
10	Weighing 1					
11	Weighing 2					
12	Weighing 3					
13	Weighing 4					
14	Weighing 5					
15	Weighing 6					
16	Weighing 7					
17	Weighing 8					
18	Weighing 9					
19	Weighing 10					
20	<b>Average =</b>					
21	<b>Standard Deviation (Usd)=</b>					
22	Certificate Conventional Wt=					
23	Bias = Ave Wt. - Conventional. Wt.					
24	<b>Bias Uncertainty (Ub) = B/2=</b>					
25	<b>Uncertainty of standard(s)*=(Us)</b>					
26	Square Root of 3 =					
27	<b>(Ustd) Certificate <math>U/(3)^{.5}</math></b>					
28	Combined Unc** =					
29	Expanded U = Uc x 2					
30	** Uc= $(Usd^2+Ustd^2+(B/2)^2)^{.5}$					
31	<b>Bias in mg</b>					
32	<b>Repeatability in mg</b>					
33	<b>U in mg ( U*1000)</b>					
34	<b>U in %</b>					

Revision 06-13-2012

Calibration Certificate Values for Weights done in 2011 by Troemner for 50 & 100 g Weights and SRS Standard Lab for 1 and 10 g weights.

**Weight Set      Mass      Marking      Conventional Wt      Uncertainty  
K = 2      Tolerance  
mg**

<b>*</b>	<b>1 g</b>	<b>1</b>	<b>1.00002</b>	<b>g</b>	<b>0.0045</b>	<b>0.054</b>
	<b>10 g</b>	<b>10</b>	<b>10.00001</b>	<b>g</b>	<b>0.015</b>	<b>0.074</b>
	<b>50 g</b>	<b>*</b>	<b>49.98410</b>	<b>g</b>	<b>0.12</b>	<b>0.12</b>
	<b>100 g</b>	<b>*</b>	<b>99.97173</b>	<b>g</b>	<b>0.45</b>	<b>0.25</b>
	<b>50 + 100 g</b>	<b>*</b>	<b>149.95583</b>	<b>g</b>	<b>0.466</b>	<b>0.277</b>

<b>A</b>	<b>1 g</b>	<b>A</b>	<b>1.00003</b>	<b>g</b>	<b>0.0045</b>	<b>0.054</b>
	<b>10 g</b>	<b>A</b>	<b>10.00004</b>	<b>g</b>	<b>0.015</b>	<b>0.074</b>
	<b>50 g</b>	<b>**</b>	<b>49.99996</b>	<b>g</b>	<b>0.12</b>	<b>0.12</b>
	<b>100 g</b>	<b>**</b>	<b>99.95392</b>	<b>g</b>	<b>0.45</b>	<b>0.25</b>
	<b>50 + 100 g</b>	<b>**</b>	<b>149.95389</b>	<b>g</b>	<b>0.466</b>	<b>0.277</b>

<b>B</b>	<b>1 g</b>	<b>B</b>	<b>1.00015</b>	<b>g</b>	<b>0.0045</b>	<b>0.054</b>
	<b>10 g</b>	<b>B</b>	<b>10.00149</b>	<b>g</b>	<b>0.015</b>	<b>0.074</b>
	<b>50 g</b>	<b>***</b>	<b>50.00058</b>	<b>g</b>	<b>0.12</b>	<b>0.12</b>
	<b>100 g</b>	<b>***</b>	<b>99.92643</b>	<b>g</b>	<b>0.45</b>	<b>0.25</b>
	<b>50 + 100 g</b>	<b>***</b>	<b>149.92700</b>	<b>g</b>	<b>0.466</b>	<b>0.277</b>

<b>C</b>	<b>1 g</b>	<b>C</b>	<b>1.00001</b>	<b>g</b>	<b>0.0045</b>	<b>0.054</b>
	<b>10 g</b>	<b>C</b>	<b>10.00009</b>	<b>g</b>	<b>0.015</b>	<b>0.074</b>
	<b>50 g</b>	<b>****</b>	<b>49.99816</b>	<b>g</b>	<b>0.12</b>	<b>0.12</b>
	<b>100 g</b>	<b>****</b>	<b>99.99340</b>	<b>g</b>	<b>0.45</b>	<b>0.25</b>
	<b>50 + 100 g</b>	<b>****</b>	<b>149.99156</b>	<b>g</b>	<b>0.466</b>	<b>0.277</b>

**Environment Conditions are in the Original Calibration Reports**

# Exercise 1

## Balance Module Exercise

---

### Session Objectives:

After the session the participants will be able to do the following:

1. To see measurements are comparisons of unknowns to reference standards.
2. To understand measurements have uncertainty.
3. To understand that reference standards also have uncertainty.
4. To understand measurements need uncertainty estimates with specified confidence intervals to have value.

### Estimated Time:

+. 5	hours completing exercise
+. 5	hours in large group discussion
.	hours total

### Materials need:

1. Work Sheets for each participant
2. Class Workbook with slides
3. Tables showing scale & weight classes (copies included in 3 page work sheet)
4. Pen or pencil
5. Calculators may be used, but are not required

### Instructions:

1. Write your name on the worksheet.

There are four classes of accuracy for weighing equipment. There are 7 classes of OIML weights. The lowest class weight is M3 and is usually the least expensive. It also has the highest uncertainty. List the accuracy class and choose the appropriate class of weights having uncertainties “fit for purpose” to test the accuracy of each of the 10 weighing instruments listed below.

You may refer to the tables given below for help in determining your answers to the 10 questions below. Fill in the blanks.

1. What class would a bathroom scale be if it has a 150 kg capacity and reads to 0.1 kg? \_\_\_\_\_ and could be calibrated with a \_\_\_\_\_ Class weight.
2. What is the accuracy class of a 4-place analytical balance that has a 200 g capacity and reads to 0.1 mg? Class \_\_\_\_\_ and could be calibrated with a \_\_\_\_\_ Class weight.
3. What is the accuracy class of a scale in the chemical make up area of a plant that has a 500 kg capacity and reads to 0.5 kg? Class \_\_\_\_\_ and could be calibrated with a \_\_\_\_\_ Class weight.
4. What is the accuracy class of an industrial scale that has a 2500 kg capacity and reads to 0.1 kg? Class \_\_\_\_\_ and could be calibrated with a \_\_\_\_\_ Class weight.
5. What is the accuracy class of a top loading balance that has a 15 kg capacity and reads to 1 mg and is used in a production line? Class \_\_\_\_\_ and could be calibrated with a \_\_\_\_\_ Class weight.
6. What is the accuracy class of a truck scale that has a capacity of 25000 kg and reads to 1 kg? Class \_\_\_\_\_ and could be calibrated with a \_\_\_\_\_ Class weight.
7. What is the accuracy class of a scale in the store that has a capacity of 10 kg and reads to 100 g? Class \_\_\_\_\_ and could be calibrated with a \_\_\_\_\_ Class weight.
8. What is the accuracy class of a Jeweler's 500 g capacity scale that reads to 0.1 g? Class \_\_\_\_\_ and could be calibrated with a \_\_\_\_\_ Class weight.
9. What is the accuracy class of a student's top loading balance that has a 1000 g capacity and has 10 mg readability? Class \_\_\_\_\_ and could be calibrated with a \_\_\_\_\_ Class weight.
10. What is the accuracy class of a microbalance that reads to 1  $\mu\text{g}$  with a 5-gram capacity? Class \_\_\_\_\_ and could be calibrated with a \_\_\_\_\_ Class weight.

Information on the classes of balances and weights are listed below.



## Metric Weight Tolerances - OIML

The table below is a listing of the tolerances of various classes of masses. The weight value can deviate above or below the nominal value by the tolerance defined. To determine the tolerance of a mass, look at the denomination or nominal value of the weight and the appropriate class you need.

		International Organization of Legal Metrology Recommendation R111*						
Denomination Metric	E1	E2	F1	F2	M1	M2	M3	Denomination Metric
	mg	mg	mg	mg	mg	mg	mg	
5000 kg			25 000	80 000	250 000	800 000	2 500 000	5000 kg
3000 kg								3000 kg
2000 kg			10 000	30 000	100 000	300 000	1 000 000	2000 kg
1000 kg		1 600	5 000	16 000	50 000	160 000	500 000	1000 kg
500 kg		800	2 500	8 000	25 000	80 000	250 000	500 kg
300 kg								300 kg
200 kg		300	1 000	3 000	10 000	30 000	100 000	200 kg
100 kg		160	500	1 600	5 000	16 000	50 000	100 kg
50 kg	25	80	250	800	2 500	8 000	25 000	50 kg
30 kg								30 kg
25 kg								25 kg
20 kg	10	30	100	300	1 000	3 000	10 000	20 kg
10 kg	5.0	16	50	160	500	1 600	5 000	10 kg
5 kg	2.5	8.0	25	80	250	800	2 500	5 kg
3 kg								3 kg
2 kg	1.0	3.0	10	30	100	300	1 000	2 kg
1 kg	0.5	1.6	5.0	16	50	160	500	1 kg
500 g	0.25	0.8	2.5	8.0	25	80	250	500 g
300 g								300 g
200 g	0.10	0.3	1.0	3.0	10	30	100	200 g
100 g	0.05	0.16	0.5	1.6	5.0	16	50	100 g
50 g	0.03	0.10	0.30	1.0	3.0	10	30	50 g
30 g								30 g
20 g	0.025	0.08	0.25	0.8	2.5	8.0	25	20 g
10 g	0.020	0.06	0.20	0.6	2.0	6.0	20	10 g
5 g	0.016	0.05	0.16	0.5	1.6	5.0	16	5 g
3 g								3 g
2 g	0.012	0.04	0.12	0.4	1.2	4.0	12	2 g
1 g	0.010	0.03	0.10	0.3	1.0	3.0	10	1 g
500 mg	0.008	0.025	0.08	0.25	0.8	2.5		500 mg
300 mg								300 mg
200 mg	0.006	0.020	0.06	0.20	0.6	2.0		200 mg
100 mg	0.005	0.016	0.05	0.16	0.5	1.6		100 mg
50 mg	0.004	0.012	0.04	0.12	0.4			50 mg
30 mg								30 mg
20 mg	0.003	0.010	0.03	0.10	0.3			20 mg
10 mg	0.003	0.008	0.025	0.08	0.25			10 mg
5 mg	0.003	0.006	0.020	0.06	0.20			5 mg
3 mg								3 mg
2 mg	0.003	0.006	0.020	0.06	0.20			2 mg
1 mg	0.003	0.006	0.020	0.06	0.20			1 mg
0.5 mg								0.5 mg
0.3 mg								0.3 mg
0.2 mg								0.2 mg
0.1 mg								0.1 mg
0.05 mg								0.05 mg

\* OIML – International Recommendation R111 replaces International Recommendation numbers 1, 2, 20, 52.

<i>Class</i>	<i>Value of the Verification Scale Division</i>	<i>Number of Scale Divisions (n)</i>	
		<i>Minimum</i>	<i>Maximum</i>
<b><i>SI Units</i></b>			
<b><i>I</i></b>	<b><i>Equal to or greater than 1 mg</i></b>	<b><i>50 000</i></b>	<b><i>20 000 000</i></b>
<b><i>II</i></b>	<b><i>1 to 50 mg, inclusive</i></b>	<b><i>100</i></b>	<b><i>100 000</i></b>
	<b><i>Equal to or greater than 100 mg</i></b>	<b><i>5 000</i></b>	<b><i>100 000</i></b>
<b><i>III</i></b>	<b><i>0.1 to 2 g inclusive</i></b>	<b><i>100</i></b>	<b><i>10 000</i></b>
	<b><i>Equal to or greater than 5 g</i></b>	<b><i>500</i></b>	<b><i>10 000</i></b>
<b><i>IIII</i></b>	<b><i>Equal to or greater than 5 g</i></b>	<b><i>100</i></b>	<b><i>1 200</i></b>

## Balance Module Exercise:

Fill in the blank. You may refer to your copy of the slides used in the “Balance Measurement Control Program Module” in determining your answers.

There are four classes of accuracy for weighing equipment. There are 7 classes of OIML weights. The lowest class weight is M3 and is usually the least expensive. It also has the highest uncertainty. List the accuracy class and choose the appropriate class of weights having uncertainties “fit for purpose” to test the accuracy of each of the 10 weighing instruments listed below.

1. What class would a bathroom scale be if it has a 150 kg capacity and reads to 0.1 kg? III and could be calibrated with a M3 Class weight.
2. What class would a 4-place analytical balance be if it has a 200 g capacity and reads to 0.1 mg? I and could be calibrated with a E2 Class weight.
3. What class is a scale in the chemical make up area of a plant that has a 500 kg capacity and reads to 0.5 kg III and could be calibrated with a M3 Class weight?
4. What Class is an industrial scale that has a 3000 kg capacity and reads to 0.5 kg? III and could be calibrated with a M2 Class weight.
5. What class is a top loading balance that has a 15 kg capacity and reads to 1 mg and is used in a production line? I and could be calibrated with a F1 Class weight.
6. What class is a truck scale that has a capacity of 25000 kg and reads to 1 kg? II and could be calibrated with a M1 Class weight.
7. What class is a scale in the store that has a capacity of 10 kg and reads to 100 g? III and could be calibrated with a M3 Class weight.
8. What class is a Jeweler’s 500 g capacity scale that reads to 0.1 g? III and could be calibrated with a F1 Class weight.
9. What class is a student’s top loading balance that has a 1000 g capacity and has 10 mg readability? II and could be calibrated with a F1 Class weight.
10. What class is a microbalance that reads to 1  $\mu\text{g}$  with a 5-gram capacity? I and could be calibrated with a E2 Class weight.

**Balance Exercise 1a Repeatability Test Uncertainty Estimates**  
**Balance Exercise 1b Intermediate Precision Uncertainty Estimate**

姓名 : Name						中间 Intermediate
日期/时间 : Date/Time						精度 Precision
气压 : Barometric Pressure		湿度= Humidity		温度= Temp		
天平 ID= Balance ID		型号= Model				总计 Total
砝码质量 Weight Mass	100 g	100 g	100 g	100 g	100 g	100 g
砝码ID Weight ID						
砝码证书常规质量 Wt Certificate Conventional Mass						
砝码证书不确定性 Wt Certificate Uncertainty						
称重 (Weighing) 1						###
称重 (Weighing) 2						###
称重 (Weighing) 3						###
称重 (Weighing) 4						###
称重 (Weighing) 5						###
称重 (Weighing) 6						###
称重 (Weighing) 7						###
称重 (Weighing) 8						###
称重 (Weighing) 9						###
称重 (Weighing) 10						###
平均 = Average	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!
标准偏移 (Usd)= Standard Deviation	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!
证书常规重量 = Certificate Conventional Wt.						0.000000
偏差 = 平均重量 - 证书重量 Bias = Avg Wt - Convent. Wt.	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!
偏差不确定性 (Ub) = B/2= Bias Uncertainty	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!
标样不确定性 =(Ustd) Uncertainty of Standard(s)	0.000000					
3 的均方根 = Square Root of 3	1.73	1.73	1.73	1.73	1.73	1.73
(标样不确定性) 证书 U/(3)^.5 (Ustd)Certificate U/(3)^.5	0.000000	#VALUE!	#VALUE!	#VALUE!	#VALUE!	#VALUE!
合并 Unc** = Combined Unc**	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!
扩展不确定性= Uc x 2 Expanded U	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!
偏差(mg) Bias in mg	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!
可重复性(mg) Repeatability in mg	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!
不确定性mg ( U*1000) U in mg	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!
不确定性 % U in %	#####	#####	#####	#####	#####	#DIV/0!

\*\* Uc= (Usd^2+Ustd^2+(B/2)^2)^.5

Calibration Certificate Values for Weights Done in 2011 by Troemner for 50 100 g Weights and SRS Standard's Lab for 1 and 10 g weights.

Weight Set	Mass	Marking	Conventional Wt	Uncertainty K = 2	Tolerance mg
*	1 g	1	1.00002	g 0.0045	0.054
	10 g	10	10.00001	g 0.015	0.074
	50 g	*	49.98410	g 0.12	0.12
	100 g	*	99.97173	g 0.45	0.25
	50 + 100 g	*	149.95583	g 0.466	0.277

A	1 g	A	1.00003	g 0.0045	0.054
	10 g	A	10.00004	g 0.015	0.074
	50 g	**	49.99996	g 0.12	0.12
	100 g	**	99.95392	g 0.45	0.25
	50 + 100 g	**	149.95389	g 0.466	0.277

B	1 g	B	1.00015	g 0.0045	0.054
	10 g	B	10.00149	g 0.015	0.074
	50 g	***	50.00058	g 0.12	0.12
	100 g	***	99.92643	g 0.45	0.25
	50 + 100 g	***	149.92700	g 0.466	0.277

C	1 g	C	1.00001	g 0.0045	0.054
	10 g	C	10.00009	g 0.015	0.074
	50 g	****	49.99816	g 0.12	0.12
	100 g	****	99.99340	g 0.45	0.25
	50 + 100 g	****	149.99156	g 0.466	0.277

Environment Conditions are in the Original Calibration Reports



## Module 10

### Balance Measurement Control Program

#### Objectives

- Review the elements of a MCP for scales or balances
- Discuss the classes of balances & mass standards
- Exercise on classes of balances and weights
- Review method for determining weighing uncertainty
- Discuss the Savannah River site balance calibration/verification program
- Discuss sources and types of error in weighing

Module 10 - 2

#### Balance MCP Elements

- Selection of appropriate equipment & standards
- Training personnel in care and use of equipment
- Controls to verify balances are in control before use
- Procedures for verification prior to use
  - Test the range of use (maximum & minimum if <75%)
  - May use calibrated artifact or appropriate mass standard
  - Repeat validation if environmental conditions are changing
  - Good to end weighing sequence with check standard
- Data collection and control charting: use computers
- Statistical procedures for evaluating control data
  - Periodic updating of uncertainty estimates & control limits

Module 10 - 3

#### Good Weight Measurements Require:

- Choosing the appropriate weighing equipment
- Choosing appropriate mass standards
- Proper handling and use of standards & balances
- Routine calibration/verification
- Administrative procedures for measurement control
- Verify balance is "in control" before measuring unknowns using appropriate check standards
- Reliable uncertainty estimates for weighing systems

Module 10 - 4

### PREREQUISITE ACTIONS

- Balances should be located and used per manufacturer's recommendations
- Good Balance Operating Conditions & Practices
  1. Limit traffic in area
  2. Located by solid wall
  3. Avoid vents/windows to stable temperature
  4. Stay away from motors
  5. Locate balance on stable surface
  6. Balance plugged in and energized
  7. Clean and debris free

### Environmental Considerations



Module 10 - 5

### Factors that influence weight readings

- Design
- Installation
- Staff & Procedures
- Standards
- Facility (Environment/Location)
- Method of Use

Module 10 - 6

### Four classes of scales and balances Parameters for Accuracy Classes

Class	Value of the Verification Scale Division	Number of Scale Divisions (n)	
		Minimum	Maximum
<i>SI Units</i>			
<i>I</i>	<i>equal to or greater than 1 mg</i>	<i>50 000</i>	<i>20 000 000</i>
<i>II</i>	<i>1 to 50 mg, inclusive</i>	<i>100</i>	<i>100 000</i>
	<i>equal to or greater than 100 mg</i>	<i>5 000</i>	<i>100 000</i>
<i>III</i>	<i>0.1 to 2 g inclusive</i>	<i>100</i>	<i>10 000</i>
	<i>equal to or greater than 5 g</i>	<i>500</i>	<i>10 000</i>
<i>III</i>	<i>equal to or greater than 5 g</i>	<i>100</i>	<i>1 200</i>

Module 10 - 7

### OIML Weight Classes

- **Class E1** weights - intended for use in metrology laboratories as primary reference standards where the stability of the environment and careful handling are assured
  - Although very stable, one-piece construction Class E1 weights have no method of adjustment and are not suitable for general laboratory use
- **Class E2** Can be used as a reference standard in calibrating other weights and
  - Also appropriate for calibrating high precision analytical balances with a readability as low as 0.1 mg to 0.01 mg

Module 10 - 8

## OIML Weight Classes (continued)

- Class F1 weights - appropriate for calibrating high-precision top loading balances with readability as low as 0.01 g to 0.001 g
  - can also be used to calibrate Class F2 weights
- Class F2 weights can be used to calibrate weighing instruments for important commercial transactions like gold and precious stones.
  - For calibration of semi-analytical balances & student use
  - They can also be used to calibrate Class M2 weights

Module 10 - 9

## OIML Weight Classes *cont'd*

- Class M1 weights are used to:
  - validate M2 weights and
  - validate class III balances
- Class M2 weights are used to:
  - validate M3 weights and
  - validate accuracy class III balances
  - They are brass weights most commonly used for educational purposes
- Class M3 weights are used on weighing class III instruments.
- M Class weights are economical weights for general laboratory, industrial, commercial, technical and educational use

Module 10 - 10

## Background

### ISO/IEC 17025, "General Requirements of the Competence of Testing and Calibration Laboratories"

1. States that a calibration or testing laboratory shall have, and shall apply, a procedure to estimate the uncertainty of measurement for all calibrations/measurements
2. Requires calibration reports shall contain the measurement results and measurement uncertainty statement and
3. Requires measurement results be traceable to a national standard through an unbroken chain of calibrations or comparisons, each having a stated uncertainty

Module 10 - 11

## NISTIR 6919 Overview

- Recommended Guide for Determining and Reporting Uncertainties for Balances and Scales
  - Chapter 1 gives purpose and background
  - Chapter 2 presents general concepts & GUM 8 step method
  - Chapters 3, 4 and 5 address specific processes.
    - Each chapter addresses some special issues that are typically encountered in those calibration processes
    - Instructions are provided for the most appropriate method of calculating a reasonable uncertainty for a weighing device in each situation
  - Chapter 6 contains sample calculations and includes the rationale that might be used in calculating and evaluating the resulting uncertainties

Module 10 - 12

## NISTIR6919 (continued)

This guide provides the necessary tools to:

- evaluate the calibration process being used
- identify uncertainty contributors for the measurements made
- quantify the impact of the uncertainty contributors on the measurement results
- combine the uncertainty contributions in a standardized manner
- obtain and evaluate an expanded uncertainty, and
- report the measurement results with a properly computed, properly documented, uncertainty statement

Module 10 - 13

## Eight Basic Steps in Determining Measurement Uncertainty Estimates

1. **Specify** the process and equation:
2. **Identify** and characterize the uncertainty sources
3. **Quantify** the resulting uncertainty components
4. **Convert** the influences of the uncertainty components on the measurement to standard deviation equivalents
5. **Calculate** the combined standard uncertainty ( $u_c$ )
6. **Calculate** the expanded uncertainty ( $U$ )
7. **Evaluate**  $U$  for appropriateness
8. **Report** the uncertainty

Module 10 - 14

## Uncertainty Sources

- The calibration engineer must be capable of identifying those measurement influences that affect the measurement result and be able to estimate how each influence affects the balance or scale indication (Type B error sources)
- These estimated quantities are then combined according to a documented procedure and reported as the uncertainty of the balance or scale calibration process

Module 10 - 15

## Sources of Uncertainty in Weighing

1. Uncertainty or tolerance of the applied load
2. Repeatability of the weighing system
3. Readability
4. Reproducibility of the weighing system, and
5. Effects of:
  - temperature changes
  - drafts or wind
  - off center loading
  - indicator drift
  - electrical noise and variation
  - vibration

*Note: This list is not all inclusive*

Module 10 - 16

## Savannah River Site Balance Calibration Program

- Savannah River Standards Laboratory
  - Accredited to Requirements of ISO 17025
  - Calibrates over 500 scales & balances on site
  - Calibrates over 5000 mass standards
  - Most balance calibrations are done on site in place
  - Most balance are calibrated when received & when moved
  - Most balances are calibrated annually. Some quarterly

Module 10 - 17

## Balance Calibration/Validation

- All calibration/validation tests report both “As Found” and “As Left” conditions.
- Many analytical 5 place analytical balances have built in calibration systems.
  - (Balances with this feature are recommended)
  - These balances compensate for local gravity & elevation in force compensation weighing systems
  - Many of these balances have auto calibration features, which will recalibrate the balance when the room temperature change by 1° C
  - These built in calibration feature do not nullify the calibration/verification done by the standards organization

Module 10 - 18

## Typical Balance Calibration Overview

- Perform visual inspections & verify functionality
- Exercise balance high range weight and determine if the “load” test is within the QA limits.
- Measure the respective test weights at the high, mid, low & sensitivity points after zeroing balance.
- Repeat 4 more times to test reproducibility
- Perform corner loading test
- Evaluate automated Calibration Report Analyses
- **As needed adjust and/or calibrate balance per manufacturer’s procedure. Repeat “As Left” Calibration verification tests as needed.**

Module 10 - 19

## Calibration/Verification Includes:

- Record environmental conditions at time of test.
- Function Testing includes:
  - Verify the balance has been energized and is working properly. NOTE: The balance should be turned on for at least 30 minutes before starting the performance testing.
  - The display is readable and complete.
  - The zero feature is verified by depressing the tare bar and observing zero on the display.

	Environmental Conditions		
	Before	After	Average
Temp (C)	24	26	25
Humidity (%)	37	39	38

Module 10 - 20

## Calibration/Verification Includes: (continued)

- The load function is tested:
  - first by placing the full capacity test weight on the scale twice to exercise the balance and observing the value after zeroing between loading the weighing pan.
  - The balance is zeroed and the high range weight is weighed 3 more times and the results record in the "Span Load Test" blocks. If the average value does not fall within QA precision tolerance the balance fails the load test.

High Wt	Span Load Test
1	9999.983
2	9999.999
3	10000.032
Ave =	10000.005

Module 10 - 21

## SRS Calibration Worksheet

- Shaded area's are for input from calibration personnel
- The program has built in tables that contain:
  - QA test limits
  - Sensitivity limits
  - Maintenance SD
  - Available Weight sets
  - Uncertainties of each Weight
- Time required is < 1 hour
- All evaluations are built in.
- Graphs are produced
- Minimum quantities that can be weighed are listed based on uncertainties.
- Method exceeds ISO 17025 requirements.

SRS Method

Analyst Information		Visual Inspection Parameters		
Calibrator Initials		Damaged	Pass/Fail	
Calibrator ID #		Complete	Pass/Fail	
Date		Clean	Pass/Fail	
Balance Information		Level	Pass/Fail	
Function Tests				
Location		Power	Pass/Fail	
Unique ID Number		Display	Pass/Fail	
Manufacturer	Mettler	Zeroing	Pass/Fail	
MODEL #	PK4001	Load Test	#DIV/0!	
Confidence Level	2-Digit	Cornerloading Test (g)		
QA Limit (%)	0.1000	Position	Reading	
Sen. Limit (g)	0.00000	Top		
1 Std. Maint. SD	0.02000	Right		
Wt. Set Selection	SL-9999SET	Bottom		
		Left		
Environmental Conditions				
Span Load Test		Before	After	
High Wt		Temp (C)	Average	
1		Humidity (%)	#DIV/0!	
2			#DIV/0!	
3				
Ave =	#DIV/0!			
MEASUREMENTS (in grams)				
Stacking Information	High Wt(s)	Mid Wt(s)	Low Wt.	Sensitivity Wt.
High Weights(g)	500	300	50	5
10000				
No stacking				
Mid-Weights(g)				
5000				
No stacking				

Module 10 - 22

## Calibration/Verification Includes: (continued)

- Typical Balance Calibration Overview:
  - Measure the respective test weights at the high, mid, low & sensitivity points after zeroing balance.
  - Repeat 4 more times to test reproducibility

Stacking Information	MEASUREMENTS (in grams)			
	High Wt(s)	Mid Wt(s)	Low Wt.	Sensitivity Wt.
High Weights(g)	10000	5000	2000	200
10000	10000.000	5000.032	2000.013	200.001
No stacking	10000.000	5000.032	2000.013	200.002
Mid-Weights(g)	9999.998	5000.033	2000.013	200.002
5000	9999.999	5000.034	2000.015	200.003
No stacking	10000.001	5000.032	2000.014	200.002

Module 10 - 23

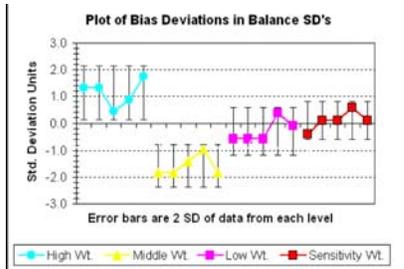
## Statistical Evaluation of the performance testing data

Statistics				
	High Wt(s)	Mid Wt(s)	Low Wt.	Minimal Wt.
AVERAGE	9999.9996	5000.0326	2000.0136	200.002000
Bias (abs)	0.0026	-0.0036	-0.0006	0.000180
% Bias	0.0000	-0.0001	0.0000	0.000090
% RSD	0.0000	0.0000	0.0000	0.000354
SD(abs)	0.0011	0.0009	0.0009	0.000707
Max SD	0.0023	0.0022	0.0020	0.002001
Calculated t	Not Significant	Not Significant	Not Significant	Not Significant
Pooled Abs. Std. Dev., 16 df =		0.00092	Tab. Chi Sq =	32.0
Tabled t, 16 df (99% Conf.) =		2.921	Cal. Chi Sq =	3.4
Tabled F, 2, 16 df (99% Conf.) =		6.23	F Statistic =	Not Significant

Module 10 - 24

## Graph Showing Variation of Deviations

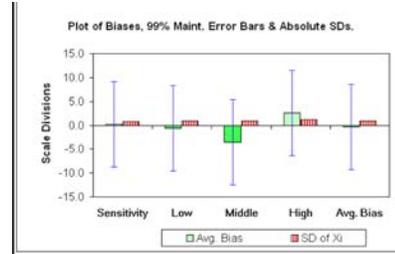
- Data plots of the deviations over the balance's range show all results were within  $\pm 3$  SD



Module 10 - 25

## Graph of Biases, Stdev's & Error Bars

- Results of tests over the balance's range show the balance performs with specified control limits



Module 10 - 26

## Results of Corner Load Tests

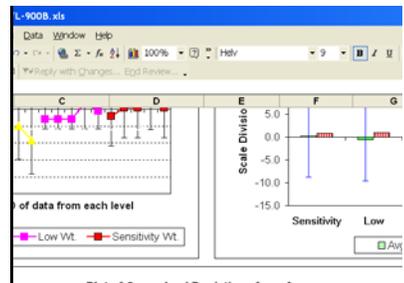
- The deviation of each measurement from the average of the mid range weight is divided by the greater of the maintenance SD or the pooled SD of all the measurements or the maintenance SD plus the RSS of the weight(s) uncertainty.
- The balance fails corner loading if any deviation from the average reading in the center is  $> 3$  SD. The next slide shows this balance failed the corner loading tests.

Cornerloading(g)	5000
Position	Reading
Top	5000.024
Right	5000.042
Bottom	5000.044
Left	5000.024

Module 10 - 27

## Results of Corner Load Tests

- Plot shows corner loading errors outside of control limits. A warning will be given on the report.



Module 10 - 28

## Illustration of Final Evaluation of Tests

- The evaluation below shows there may be a corner loading problem.
  - This is not uncommon, so a label should be attached that states "CENTER ALL OBJECTS"
- The evaluation provides the minimum quantities that can be weighed to stay within given control limits

ACCEPTANCE CRITERIA	
Summary:	Balance passes QA Limits
Linearity(Bias)	Balance passes
Precision (SD)	Balance passes
Corner Loading	WARNING: Balance failed corner loading test. Attach limited calibration sticker stating CENTER ALL OBJECTS.
Disposition	May need corner loading and/or linearity adjustment.
	30.0 grams minimum quantity that can be weighed to maintain QA Test Limits with 99.7% confidence
	3.0 grams minimum quantity that can be weighed to maintain 3 Standard Deviation Limits @ 0.1% Tolerance per USP

Module 10 - 29

## Random & Systematic Errors in Weight Measurement

- VIM Definitions of these types of error will be studied
- At the end of this module weighing exercises will be conducted to collect data that will be used to estimate errors affecting precision and accuracy errors in weighing
- Also these errors will be determined over the operating range on an analytical balance

Module 10 - 30

## Measurement Precision VIM 2.19 (3.13)

Precision is closeness of agreement between indications or measured quantity values obtained by replicate measurements on the same or similar objects under specified conditions

NOTE 1 - Measurement precision is usually expressed numerically by measures of imprecision, such as standard deviation, variance, or coefficient of variation under the specified conditions of measurement

NOTE 2 - The 'specified conditions' can be, for example,

- repeatability conditions of measurement
- intermediate precision conditions of measurement, or
- reproducibility conditions of measurement (see ISO 5725-3:1994)

Module 10 - 31

## Random Measurement Error VIM 2.19 (3.13)

Random error is a component of measurement error that in replicate measurements varies in an unpredictable manner

NOTE 1 - A reference quantity value for a random measurement error is the average that would ensue from an infinite number of replicate measurements of the same measurand

NOTE 2 - Random measurement errors of a set of replicate measurements form a distribution that can be summarized by its expectation, which is generally assumed to be zero, and its variance

NOTE 3 - Random measurement error equals measurement error minus systematic measurement error

Module 10 - 32

## 2.20 repeatability condition of measurement

- condition of measurement, out of a set of conditions that includes the same measurement procedure, same operators, same measuring system, same operating conditions and same location, and replicate measurements on the same or similar objects over a short period of time
  - NOTE 1 A condition of measurement is a repeatability condition only with respect to a specified set of repeatability conditions.

Module 10 - 33

## Intermediate Precision Condition VIM 2.22

Condition of measurement, out of a set of conditions that includes the same measurement procedure, same location, and replicate measurements on the same or similar objects over an extended period of time, but may include other conditions involving changes

NOTE 1 - The changes can include new calibrations, calibrators, operators, and measuring systems

NOTE 2 - A specification for the conditions should contain the conditions changed and unchanged, to the extent practical

Module 10 - 34

## Summary

- Reviewed the elements of a MCP for scales or balances
- Discussed the classes of balances & mass standards
- Completed and Exercise on classes of Balances & Standards
- Reviewed method for determining weighing uncertainty
- Discussed the Savannah River site balance calibration/verification program
- Discussed sources and types of error in weighing

Module 10 - 35

## Reproducibility Condition of Measurement VIM 2.24 (3.7, Note 2)

Condition of measurement, out of a set of conditions that includes different locations, operators, measuring systems, and replicate measurements on the same or similar objects

NOTE 1 - The different measuring systems may use different measurement procedures.

NOTE 2 - A specification should give the conditions to the extent practical

Module 10 - 36

## **Instrumental Bias** VIM 4.20 (5.25)

---

Average of replicate indications minus a reference quantity value

Module 10 - 37

## **Balance Exercise Objectives:**

---

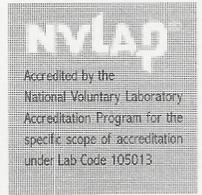
- **Determine uncertainty estimates for a balance**
  - By using technical information from specifications
  - By experiment using calibrated weights
- **Evaluate balance accuracy and precision errors (exercise)**
- **Determine what effect multiple operators and balances will have on random error estimates in weight measurements**

Module 10 - 38





Henry Troemner LLC



# Calibration Certificate

201 Wolf Drive • P.O. Box 87 • Thorofare, NJ 08086-0087 • Phone: 856-686-1600 • Fax: 856-686-1601 • www.troemner.com • e-mail: troemner@troemner.com

Page 1 of 1

**Weight**

Certificate Number : JOEWTS-1  
Date of Calibration : 09-SEP-2011  
Next Due Date : 09-SEP-2012

End user

Troemner Inc  
201 Wolf Drive  
Thorofare NJ 08086

Description of Weights: ASTM E617-97 Class 1

Order Number : 0060800  
Construction : One Piece  
Material : Stainless Steel(O/P)

Date Received : N/A  
Date of Issue : 09-SEP-2011  
Weight Range : 50g,100g  
ID# :

Environmental Condition at Time of Test  
Temperature: 22.22°C

Pressure: 756.49 mm Hg

Relative Humidity: 48%

**Pertinent Information**

This calibration also meets specifications as outlined in ISO 9001, ISO/IEC 17025, ANSI/NCSL Z540-1-1994. Weights listed in the calibration report have been compared to reference standards that are directly traceable a National Standard under Test No. 822-275872. Uncertainty is the standard deviation associated with the results of the measurement that characterizes the dispersion of the values that could reasonably be attributed to the measureand. The uncertainty is calculated in accordance with NIST Tech Note 1297 using a coverage factor of k=2 (k=2 defines the interval having a level of confidence of approximately 95%). Uncertainty does not include possible effects of magnetism. Conventional mass is defined as a weight taken at 20°C with a reference density of 8.0g\*cm-3 and balanced in air density of 0.00120g\*cm-3.  
**Notes:** \* - indicates duplicate weights **F** - indicates failed As Found **X** - indicates weight out of tolerance not adjustable **N** - indicates new weight added

**Calibration Data**

Nominal Mass Value	Notes	Serial No.	Conventional Mass Value As Found	Mass Value As Left	Uncertainty	Tolerance
100g	*XF		99.971726 g		0.044 mg	0.250 mg
100g	2XF		99.953924 g		0.044 mg	0.250 mg
100g	3XF		99.926428 g		0.044 mg	0.250 mg
100g	4XF		99.934047 g		0.044 mg	0.250 mg
50g	*XF		49.984100 g		0.024 mg	0.120 mg
50g	2XF		49.999962 g		0.024 mg	0.120 mg
50g	3XF		50.000575 g		0.024 mg	0.120 mg
50g	4XF		49.998157 g		0.024 mg	0.120 mg

**Addendum:**

**Approved Signatory**

**Joseph Moran, Metrology Manager**

**Person Performing Work**

**Annemarie Love**

This certificate of calibration shall not be reproduced except in full, without the written approval of Henry Troemner, LLC. This certificate of calibration must not be used by the customer to claim product endorsement by NIST/NVLAP or any agency of the U.S. government.

日期： Date				
时间： Time				
气温 - Air Temperature				
水温 - Water Temperature				
气压 - Barometric Pressure				
湿度 - Humidity				
移液管ID - Pipette ID				
姓名： Name				
	分析员-1 Analyst 1	分析员-2 Analyst 2	分析员-3 Analyst 3	分析员-4 Analyst 4
重量 1 Weight 1				
重量 2 Weight 2				
重量 3 Weight 3				
重量 4 Weight 4				
重量 5 Weight 5				
重量 6 Weight 6				
重量 7 Weight 7				
重量 8 Weight 8				
重量 9 Weight 9				
重量 10 Weight 10				
平均 - Average	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!
标准偏差 - Std. Deviation	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!
Z系数 - Z-Factor				
体积 (Z x 平均重量) - Volume (Z x Avg. Wt.)	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!
体积，微升 (µL) - Volume in micro liters (µL)	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!
标准偏差 x Z = +/- ml 称称体积 -	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!
Nominal Volume	1000	1000	1000	1000
计算体积，µL - Calculated Volume in µL	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!
偏差 (不准确) Bias (inaccuracy)	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!
(±7-8.0µL) 体积容差 = Volume Tolerance	8	8	8	8
标准偏差 ml x 1000= SD in µL (±7-1.5 µL 标准偏差容差)	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!
SD Tolerance	1.5	1.5	1.5	1.5
如果标准偏差和偏差小于容差，则通过 Pass if SD & Bias < Tolerances	Pass	Fail	Fail	Fail
Uc = (Usd^2+(B/2)^2)^.5	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!

扩展 U = Uc*2 Expanded	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!
相对 % 不确定性 Relative % Uncertainty	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!
	偏差和精度小组平均评价 TEAM AVERAGE EVALUATION OF BIAS & PRECISION			
平均 = Average	#DIV/0!	###	###	###
标准偏差 - Standard Deviation	#DIV/0!	###	###	###
Z 系数 - Z Factor	#DIV/0!	###	###	###
体积 (Z x 平均值) - Volume (Z x Avg. Wt.)	#DIV/0!	###	###	###
体积, 微升 (µL) - Volume in micro liters (µL)	#DIV/0!	###	###	###
标准偏差 x Z*1000 = µL SD x Z*1000 = µL	#DIV/0!	###	###	###
偏差 (µL) Bias	#DIV/0!	###	###	###
$Uc = (U_{sd}^2 + (B/2)^2)^{.5}$	#DIV/0!	###	###	###
扩展不确定性 = Uc*2 Expanded U = Uc*2	#DIV/0!	###	###	###
相对 % 不确定性 Relative % Uncertainty	#DIV/0!	###	###	###
如果标准偏移和偏差小于容差, 则通过 Pass if SD & Bias < Tolerances		###	###	###

Sheet Password = CIAE  
工作单密码=CIAE



# Module 11

---

## **Analytical Chemistry Laboratory Measurement Control Programs**

# Objectives

---

- **Understand laboratory measurements must have uncertainty estimates for accountability of NM**
- **Review MCP technical & administrative components of ANSI N15.51**
- **Discuss laboratory techniques for estimating error**
- **Discuss uses of measurement control data**
- ***Intro to Laboratory Information Management Systems (LIMS)* and review LIMS MCP output for D&G U method**

# Measurement Quality Must Be Known

---

Dr. John Keenan Taylor in QA of Chemical Measurements

- “Quantitative measurements are always estimates of the value of the measure and involve some level of uncertainty.
- The measurements must be made so that the limits of uncertainty can be assigned within a stated probability.
- Without such an assignment, no logical use can be made of the data.
- To achieve this, measurements must be made in such a way as to provide statistical predictability.”

# **Publications on Laboratory QA & QC**

---

- **ANSI N15.51-2012 “Methods of Nuclear Material Control—Measurement Control Program—Analytical Chemistry Laboratory”**
- **“Quantifying Uncertainty in Analytical Measurements, ISBN 0-948926-08-2, Eurachem English Publication 1995**
- **CITAC Guide 1 "International Guide to Quality in Analytical Chemistry--An Aid to Accreditation," ISBN 0948926 09 0 English First Edition 1995.**
- **\*IAEA STR – 368 “International Target Values for Measurement Uncertainties in Safeguarding Nuclear Materials”, Vienna, November 2010 (ITVs)**

# Analytical Chemistry Laboratory MCP

---

- Purpose is to provide reliable measurements for nuclear materials accountability and process control that are fit for purpose
- Has technical and administrative aspects that addresses the basic elements of a MCP that were discussed earlier
- Requires the utilization of a LIMS to facilitate and provide consistency in operation of the laboratory in every aspect of sample handling, personnel qualification, proper procedures, method selection & qualification, QC for the measurements, reporting, accountability, records, sample management, etc.

# MCP Technical Aspects: Methods

---

- A measurement control program provides assurance that data produced from a measurement system are acceptable for meeting established measurement performance requirements.
- For the measurement control program to have any value, it must generate data that represents (or reflects) the quality of measurements performed on process materials.
- Thus, one first selects a measurement method to meet the desired level of performance, and then uses a measurement control program to verify (or detect the lack of) such performance, both initially and on a continuing basis.

# MCP Technical Aspects: Methods cont.

---

- **A method selected should contains the following characteristics:**
  - **technically sound;**
  - **specific for the property being measured;**
  - **free from interferences (or be correctable for interferences);**
  - **have an acceptable measurement range for the property being measured;**
  - **capable of producing data that will meet established precision and accuracy requirements.**
- **Target values define the required level of performance of each analytical chemistry laboratory measurement. The IAEA has developed target values for the measurement of nuclear materials**
  - **For individual facilities, the performance-level requirements may exceed or be less than the target values depending on their needs and requirements. These target values provide estimates of the capability that could reasonably and realistically be expected from industrial-type laboratories on a routine basis.**

# MCP Technical Aspects: Documentation

- Document the measurement control program, including descriptions of the statistical tests performed and the minimum acceptable limits
- Measurement and measurement control methods are formally qualified and validated as adequate for their intended use
- Define a standards program to include
  - Preparation of control standards
  - Determination of standards' values and uncertainties
  - Documentation of traceability, storage, and calibration of instruments

# MCP Technical Aspects: Controls

---

- **Define:**
  - **Limits for measurement control**
  - **Specify the corrective actions and responses to violations of the control limits:**
    - **Responses should provide not only recovery but**
    - **Also either re-measurement of samples or**
    - **Assurance that sample results made just prior to the response condition were acceptable;**
- **Define conditions for quantifying method performance**
  - **Bias and precision in order to determine measurement uncertainty and to adjust control limits;**

# MCP Technical Aspects – Monitoring

---

- **Collect measurement control data and evaluate it statistically**
- **Prepare and issue periodic reports on measurement performance**
- **Review and adjust control limits to reflect the current performance of measurement systems on a routine basis, if corrective action is not indicated**
- **Monitor and document data from inter-laboratory comparison programs**

## **MCP Technical Aspects – Monitoring cont.**

- **Monitor performance of specifically identified laboratory measurement system components, e.g.,**
  - **Analyst, equipment, standard, etc.**
  - **Require documentation of all performance & corrective actions**
- **Train, qualify, and re-qualify analysts, and other personnel associated with measurements, using objective testing methods**
- **Define a replicate sampling program in order to assure that measurement of the replicate samples is performed in the same manner as measurement of the original (routine) samples**

# **MCP Administration**

---

- **Define Organization and Management Program to:**
  - provide for detection and correction of adverse changes;
  - maintain the desired level of performance for all measurements conducted in the laboratory;
  - quantify the uncertainty associated with each reported measurement;
  - quantify the performance of the measurement system.
- **Train, qualify, and re-qualify analysts, and other personnel associated with measurements, using objective testing methods**
- **Review and audit shall consist of a comprehensive examination and evaluation of all aspects of the program.**

# **MCP Administration** continued

---

- **Documentation is required to ensure a clear understanding of the organization, policies, responsibilities, and procedures, and to enable the review and confirmation of measurement performance (by audit) in a timely manner.**
- **All procedures shall be controlled and formally reviewed for clarity, consistency, and adequacy before approval. A formal review shall be performed periodically thereafter to ensure that the procedures are still adequate and appropriate.**
- **Deficiencies and corrective actions**
  - **A facility shall develop a program to promptly detect, correct, and document adverse conditions that affect quality of data. These adverse conditions are sometimes called deficiencies and include failures, defects, errors, deviations from specific requirements, and other conditions that adversely affect quality.**

# Measurement Quality Parameters

---

- **Accuracy\***
- **Precision\***
- **Cost**
- **Turn around time, and**
- **Back-up capability limitations**

**\* Most often required by regulators and/or Government Orders.**

# Regulations for Measurement Control Vary in USA

---

## The Environmental Protection Agency:

- is prescriptive in the measurement controls that it requires.
  - Establishes “Data Quality Objectives” for laboratory assays
  - Specifies methods, MCs and sample handling requirements for the laboratories analyzing samples for their programs
- DOE and Nuclear Regulatory Agency require MCPs that comply with its orders, standards and are in harmony with national and international Standards.
  - The contractors have latitude in how they meet requirements.

# Accuracy Definition

---

- **Accuracy of measurement is closeness of the agreement between the result of a measurement and a *reference value* of the analyte**
  - **"Accuracy" is a qualitative concept**
  - **The term "precision" should not be used for "accuracy"**

# Precision Definitions

---

**Precision is the closeness of agreement between independent test results obtained under stipulated conditions**

- Precision depends only on the distribution of random errors and does not relate to the true value or specified value
- The measure of precision is usually expressed in terms of imprecision and computed as a standard deviation of the test results
- **Less precision is reflected by a larger standard deviation**
- Quantitative measures of precision depend critically on the stipulated conditions
  - **Repeatability and reproducibility conditions are particular sets of extreme stipulated conditions**

# Uncertainty of Measurement

---

- **Characterizes the dispersion of the values that could reasonably be attributed to assay**
- **Defined by standard deviation or confidence interval width**
- **Comprises many components**
  - **From assumed probability distributions: knowledge based**
  - **From statistical distribution of a series of measurements**
- **Measurement is the best estimate of the value of the assay and that all components of uncertainty, including those arising from systematic effects, such as components associated with corrections and reference standards contribute to the dispersion**

# Precision Estimates for a Lab Method

---

SOURCE OF PRECISION ESTIMATE	RELATIVE STANDARD DEVIATION
Chemist's Value for Method	<u>2%</u>
Monthly QC Report	<u>4%</u>
Yearly QC Report	<u>6%</u>

- Which is the correct estimate of the method's Precision?

# Chemical Analysis Process With Calibration & QC Functions

## “Duplicate the Process”

- QC samples should have the same matrix as plant samples
  - If not add matrix if required
  - Or run a blank through analysis
- Analysis may require sub sampling. Treat QC the same
- Intermediate steps may be required before measurement
- Calibration of method should be done with RM or WRM
- Use appropriate factors
- Calculate & Report results

## Flow Chart of Analysis

Sample	QC Matrix
Sub Sample	Matrix
Digestion	Blank
Extraction	
Derivatization	Spike Sample
Separation	
Measurement	Calibration RM
Calculation of Result	Factors
Reporting of Result	

# MC Techniques & Parameter Estimated

---

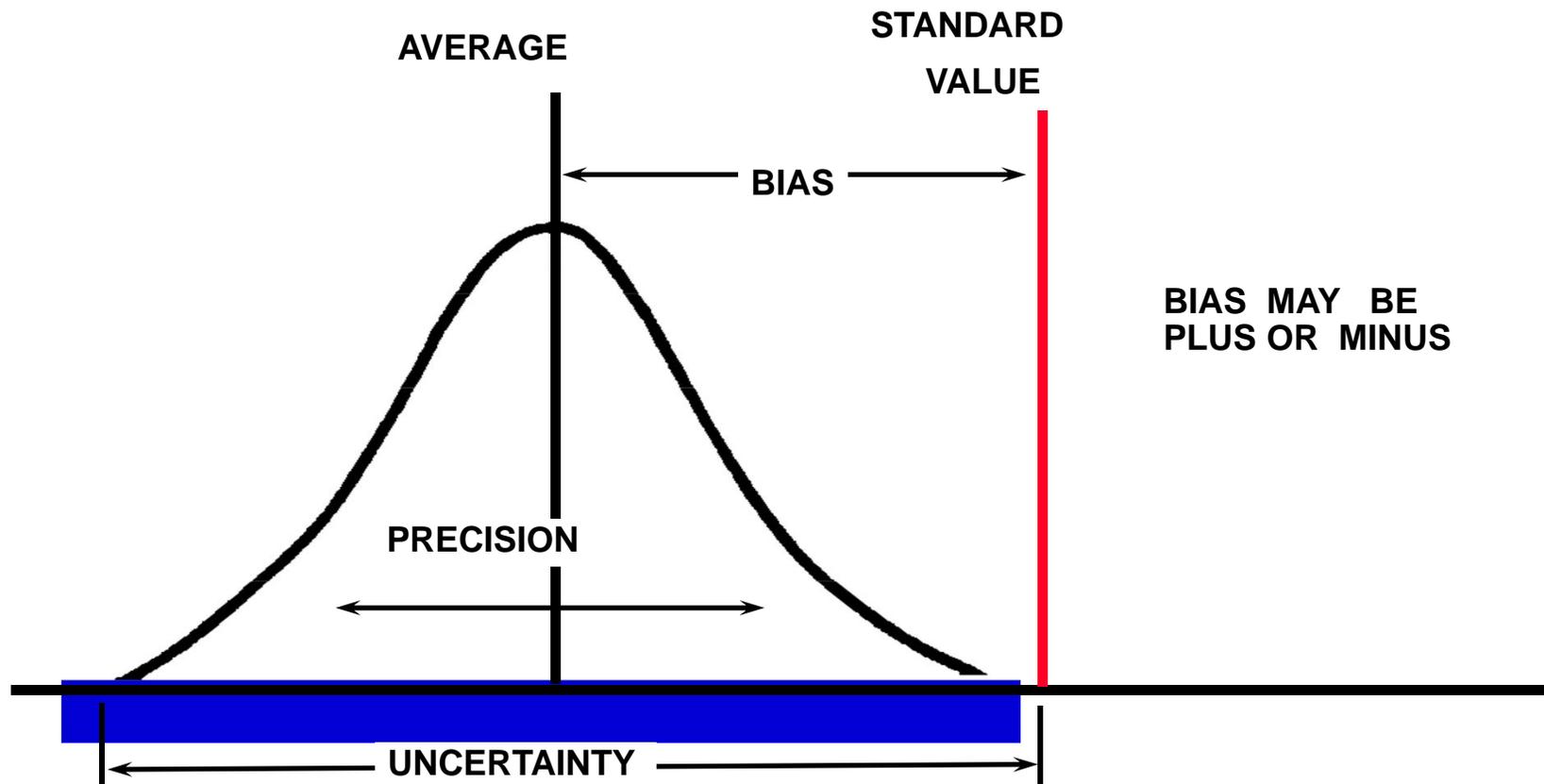
## Measurement Control Technique Accuracy Precision

1. Bench or check standards	Yes	Yes
2. Blind standards	Yes	Yes
3. Split samples	No	Yes*
4. Replicate measurements	No	Yes
5. Inter-laboratory comparisons	Yes	Yes*
6. Quality control charts	No**	Yes
7. <u>Spike of known concentration</u>	Yes	Yes*

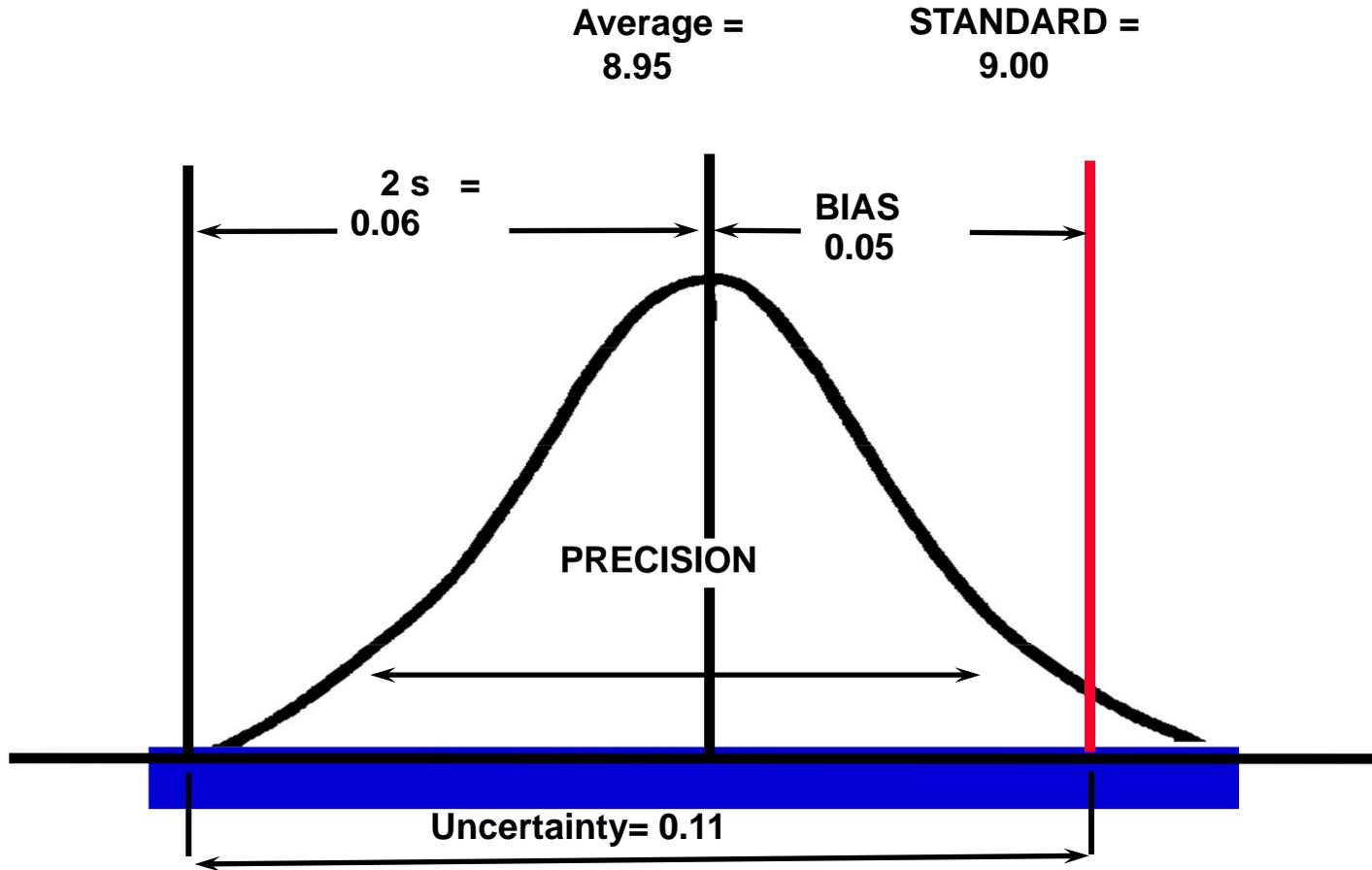
\* Yes, if several analyses on different samples over time.

\*\*No for QC Charts comparing current data with historic data.  
(Yes , if plotted against a known value)

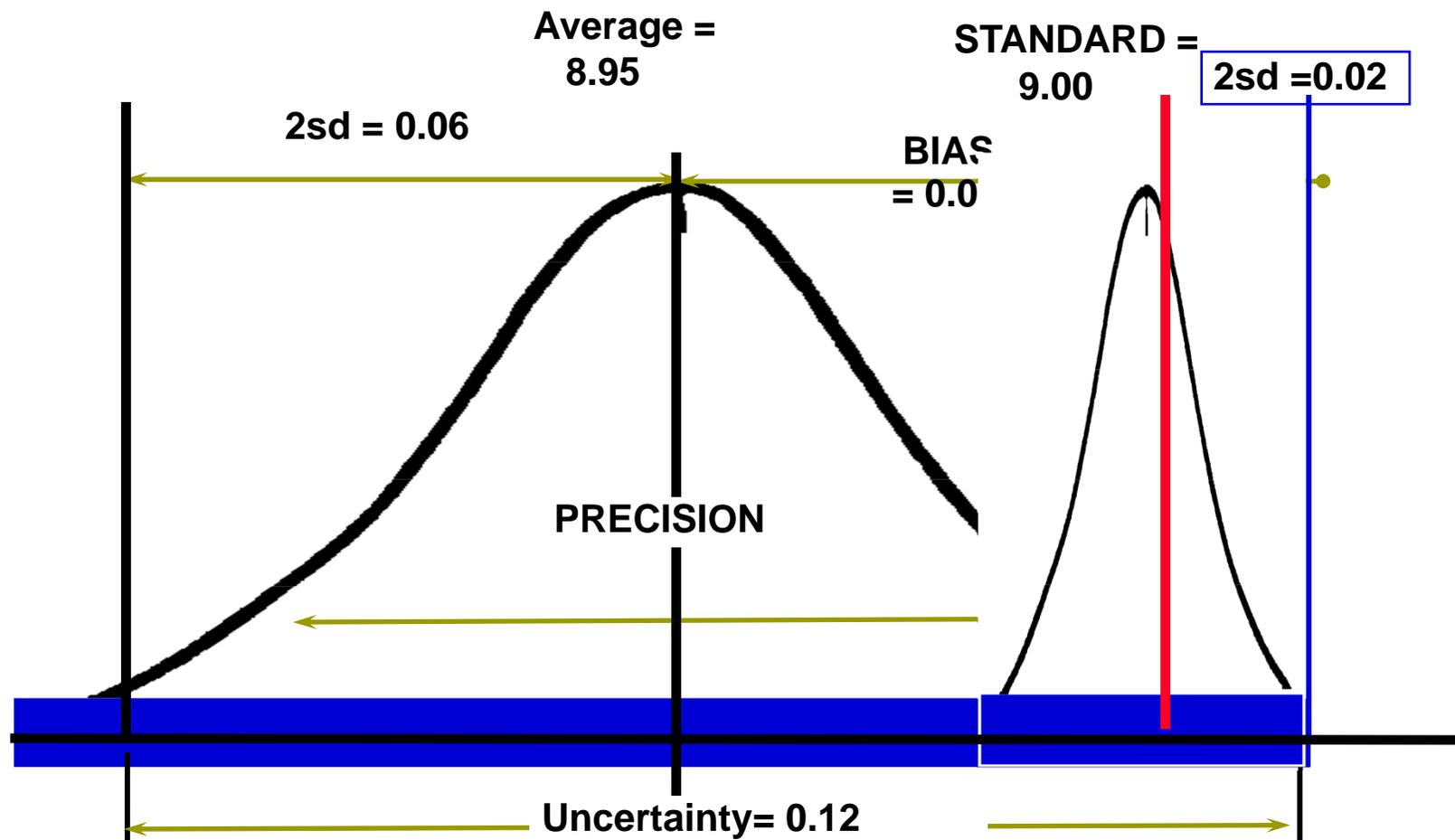
# Relationships of Bias, Precision & Uncertainty in a pH Measurement



# pH Measurement Bias, Precision & Uncertainty



# pH Measurement Uncertainty includes the Uncertainty of the Standard ( $2s = .02$ )



# Physical Measurement & Error models

---

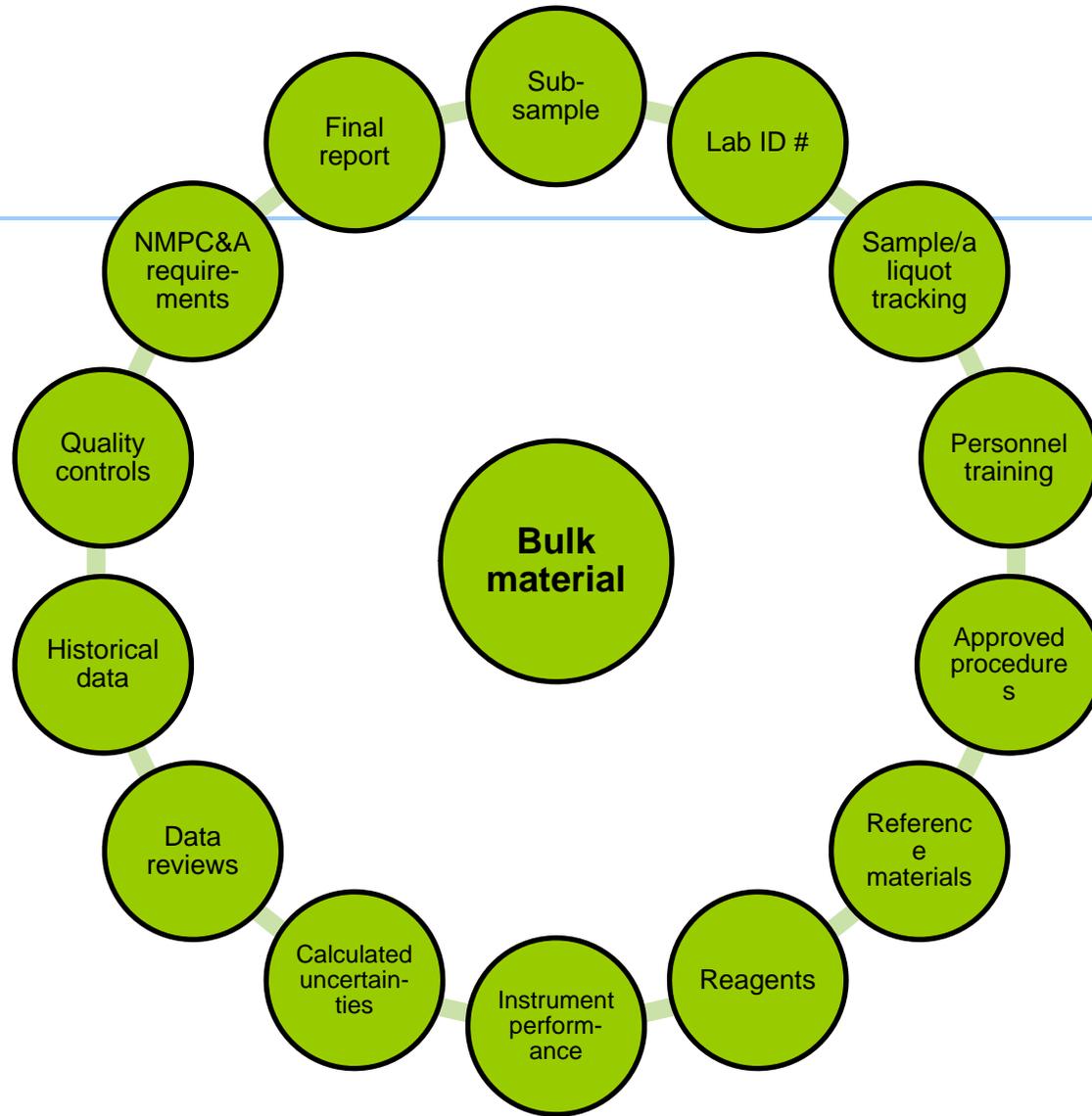
- **Modeling a Measurement Process**
  - **Controlling a measurement process effectively depends on understanding that process thoroughly**
  - **A thorough understanding, in turn, is gained by determining the significant factors that affect the measurement process and their relationship to the quality of measurement produced**
- **This relationship usually is expressed in a model**
- **In general, a measurement process is described by both a physical and a measurement error model**
- **The GUM method begins with a mathematical formula for the measurement in developing estimates of measurement uncertainty**

# Laboratory Information Management Systems (LIMS)

---

- **Essential in 21<sup>st</sup> Century to coordinate all the elements of a measurement control program in providing measurements (fit for purpose) for the accountability and control of nuclear materials and the needed statistics for calculating limits of error.**
- **LIMS have evolved over the years from home grown programs to commercially available systems that can be customized to the specific characteristics of individual laboratories.**
- **An overview of the information needed for a reliable measurements for a bulk material will be reviewed.**
- **A LIMS evaluation of D&G U QC data is presented.**

# LIMS



**Circle of information associated with the bulk material**

# Information Associated With Bulk Nuclear Material (Another View)

---

- Sub-sample
- Lab ID #
- Sample/aliquot tracking
- Personnel training
- Approved procedures
- Reference materials and Reagents
- Quality controls and Instrument performance
- Calculated uncertainties
- Data reviews
- Historical data
- NMPC&A requirements
- Final report

# The LIMS is the interface to all of the laboratory information produced and associated with the bulk material

---

- **Samples**
  - Identities and source batch controls (could be for insider protection and security reasons lab personnel do not need the source identity, except for their own created batches and respective analyses)
  - Keeps quantity, material type, and other necessary characteristics for proper handling with safety and security
  - Tracks locations (lab/room/bin/etc.)
  - Tracks lab processing and tracking (splitting, sub-sampling, salvage for recycle, waste disposal, etc.)
- **Analyses**
  - Elemental, isotopic and impurity measurements
  - Identification and approval of method, instrument and analyst
  - Mean results from multiple aliquots and uncertainties
  - Data processing for reporting and historical retention of data
- **QA/QC**
  - Traceability of reference materials used for calibrations and controls (known and blinds)
  - Monitoring with control charts for response to anomalous conditions

# **LIMS** (continued)

---

- **There are multiple commercial LIMS packages available for purchase**
- **Knowing your laboratory processes and what your needs and requirements are is essential when purchasing a LIMS package**
  - **Every analytical lab operates in a unique way**
  - **The LIMS package must be configured for your requirements and your instruments**
  - **The vendor will help with the initial installation but it is up to the lab to configure the details for successful implementation**
- **For a uranium standards laboratory a LIMS is essential for the defensibility of the measurements you make and the data you produce**

# LIMS (continued)

---

- **ORNL is currently considering LIMS vendors for their Nuclear Analytical and Isotopics Laboratories**  
**They include:**
  - **STARLIMS®**
  - **LABVANTAGE®**
  - **LabWare, Inc.**
  - **Thermo Scientific SampleManager LIMS**

# LIMS Provide Measurement Control

---

- **Use of a computerized information management system allows management to build in control mechanisms for measurement methods**
- **Limits are set to actually “STOP WORK” when the analysis of the QC sample fails to meet acceptance criteria. Examples will be discussed**
- **LIMS also can provide QC charts for quick evaluation of the measurement process over specified time intervals**
- **QC data can be used to evaluate the many variables in the measurement process & for requalification**

# Types of Cases in LIMS & how they are handled

---

- **LIMS compares the result with the reference value. The method status is flagged with 'Active' or 'Locked'**
- **If the result is within or equal to the  $\pm 2$  standard deviation (sd) limits, it is a **Case 1** result, the method is in control and active**
- **If the result is greater than 2 sd and less than equal to 3 sd limits, it is a **Case 2** result. It indicates that the method may be going out of control**
- **If the previous QCS was a Case 1, samples can be analyzed and data entered into the LIMS system**

# Types of Cases in LIMS & how they are handled

(continued)

---

- If two consecutive QCs analyzed on the method are designated **Case 2**, LIMS locks-out the method. No one can use the method until a Case 1 result is entered
- If the result is between 3 and 6 sd limits, it is a **Case 3** “Out-of-Control”. The method is “Locked”
- Results greater than 6 sd limits is a **Case 4** “Outlier” and the method is “Locked”

# Special Events

---

- Run Event
  - Any pattern of eight (8) consecutive points that lie on the same side of the control chart center line or no-action band if implemented (runs rule).
    - *No-action bands: Statistically-derived bands used to expand the target value of an analytical method control chart so that measurement control results falling within these bands do not count towards a runs rule violation*
- Two out of three event
- Two out of three consecutive points are outside the warning limits
- Evaluate for non-random data patterns and trends

# Statistics Used

% Relative difference

% rel Stdev of RD

Quoted Uncertainty at 1-sigma

Total uncertainty

#8-Run 2 of 3 Warn

Event #8-Run 2 of 3 Pts

Method	Case (1)	Case (2)	Case (3)	N (total)	LIMS +/-1sd	% Bias	% rel Stdev	Total	#8-Run s	#8-Run 2 of 3 Pts	Warn Pts
Previous 6 Months <i>Deuterium Oxide</i>	15			15	5.95%	2.16%	4.93%	5.38%			
Current evaluation Deuterium Oxide	41			41	5.95%	-1.68%	2.88%	3.34%			
Annual Evaluation <i>Deuterium Oxide</i>	50			50	5.95%	-0.77%	3.81%	3.89%			

## Summarized Information

---

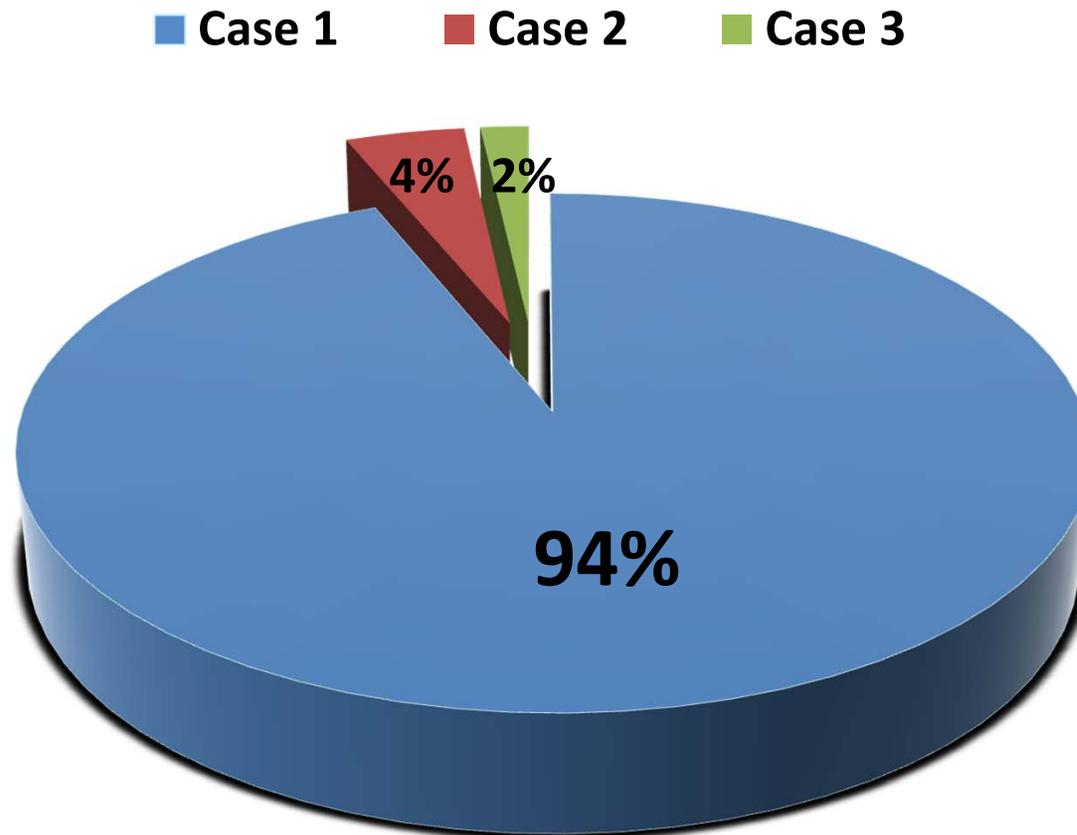
- 16 Available Accountability methods
- 4 Inactive methods
- 12 Active Methods

# Summary of the MC&A QC Data (12 -16 methods)

6 Months		14 Months	
◆ 953 data points		❖ 2859 data points	
◆ 894 case 1' s		❖ 2686 case 1' s	
◆ 42 case 2' s		❖ 125 case 2' s	
◆ 17 case 3' s		❖ 48 case 3' s	
◆ Monthly Average ~160		■ Monthly Average ~ 204	

# Chart for Cases (6 and 14 months)

---



# Davies & Gray U Method Uncertainty

---

- **Current method uncertainty**
  - **0.29% at 1-sigma**
  - **International Target Value (ITV) 0.1% for random and systematic.**

# Customer Support

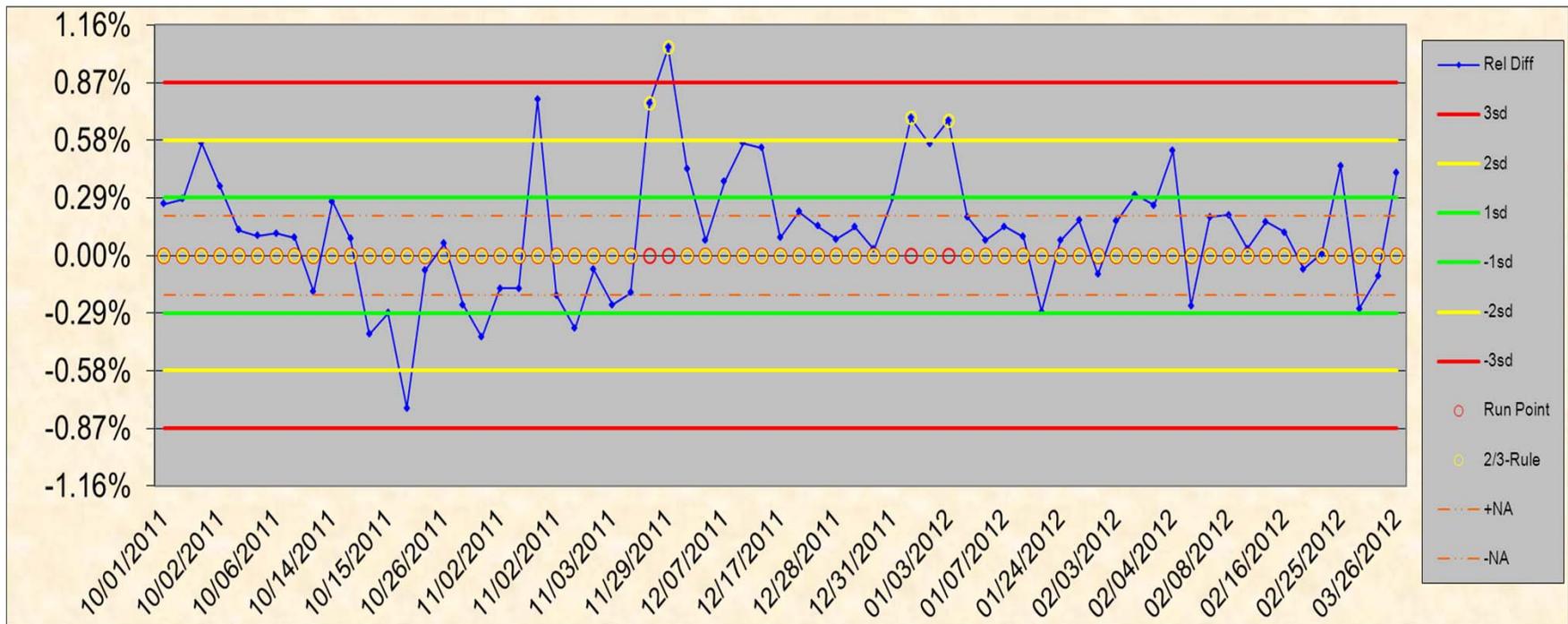
---

- **Customer**
  - **5 production processes**
- **Active participant in the NBL SME program**
- **Internal lab support**
- **MC&A for accountable measurements**

# Statistics for Uranium by Davies and Gray

Method	Case (1)	Case (2)	Case (3)	N (total)	LIMS +/-1sd	Bias	Stdev	Total	#8-Run Events	#8-Run Pts	2 of 3 Events	2 of 3 Warn Pts
Davies-Gray (previous data)	114	4	1	119	0.29%	-0.02%	0.33%	0.33%	4	40	0	0
Davies-Gray (6 months)	61	5	1	67	0.29%	0.13%	0.33%	0.35%	0	0	2	4
Davies-Gray (14 months)	198	15	3	216	0.29%	0.09%	0.36%	0.37%	3	47	4	8

# Control Chart for U by Davies and Gray (6 months)



# Real Time Estimate of Measurement Uncertainty for an Analytical Method

---

- **Analysis of the QC data provides an estimate of the measurement process variation that should include all the variables of the process:**
  - **Environmental: Temperature, Humidity & Barometric Pressure**
  - **Operators/Analysts**
  - **Instruments & sample preparation**
  - **Standards and reagents**
  - **Other (vibration, time of day, etc.)**
- **Uncertainty of the standard(s)(goal  $<1/4$  of method)**
- **Other major sources (drift?)**
- **Combine by RSS for standard estimate of uncertainty**
- **Multiply by appropriate K value (2 for 95% CI)**

# Precision Estimates for a Lab Method

---

- Chemist estimated repeatability of method on one day
- Monthly QC Report estimated intermediate reproducibility over a set of operators, standards, operating conditions, etc. over a month
- Year's QCs captured all variations in operators, standards, operating conditions, etc. It best estimates the total variation that could be expected in Assays. Reproducibility over a year

The correct estimate of the method's PRECISION depends on the assumptions!

<b>SOURCE OF PRECISION ESTIMATE</b>	<b>RELATIVE STANDARD DEVIATION</b>
<b>Chemist's Value for Method</b>	<b>2%</b>
<b>Monthly QC Report</b>	<b>4%</b>
<b>Yearly QC Report</b>	<b>6%</b>

# Summary

---

- **Understand laboratory measurements must have uncertainty estimates for accountability of NM**
- **Reviewed MCP technical & administrative components of ANSI N15.51**
- **Discussed laboratory techniques for estimating error**
- **Discussed uses of measurement control data**
- ***Introduced Laboratory Information Management Systems (LIMS)* and reviewed LIMS MCP output for D&G U method**



Exercise:

# Pipette Calibration

# Objectives

- Learn the Sources of Error in Volume determinations
- Determine the variation within and between operators
- Estimate the uncertainty of volumetric measurements
- Compare calculated uncertainty estimates with manufacturer's specifications.
- 1000 $\mu$ L Tolerances = Accuracy  $\pm 0.8\%$  or  $\pm 8.0 \mu\text{L}$   
Precision  $\pm 0.15\%$  or  $\pm 1.5 \mu\text{L}$

# Validation of Accuracy and Precision

- Precision is an agreement between replicate measurements
  - Precision is quantified by imprecision
  - High precision, i.e. small imprecision means very little variation between repeated measurements
- Accuracy
  - It is possible to be very consistent, but consistently wrong
  - Inaccuracy is the numerical difference between the mean of a set of replicate measurements and the reference or target value

## Gravimetric Pipette Calibration Exercise:

- On the data sheet record, name, date and time, water temperature, room temperature, humidity and barometric pressure
- Procedure:
  1. Install a new tip on the pipette
  2. Tare the balance with a glass flask containing H<sub>2</sub>O
  3. Fill pipette with deionized water or equivalent
  4. Dispense water into flask
  5. Record the weight of the flask
  6. Repeat steps 2 through 5 nine more times
  7. Calculate the average, standard deviation & volume
  8. Compare results to manufacturer's specifications.

Discussion topics for Improving testing:  
PROPER PIPETTING TECHNIQUES & TIPS

Technique –

- Most end users have a tendency to believe that the volume delivery is completely dependent on the setting of the micrometer dial
- Obviously, this is not the case, since many factors associated with pipettes come into play

# PROPER PIPETTING TIPS -1

## Tips - Use Manufacturers' Tips

### Temperature –

- The volume delivery performance specifications of pipettes have been referenced by most manufacturers at room temperature which is defined as 20-25°C. Any deviation from this specification can affect the amount of liquid dispensed due to the expansion or contraction of the internal components
- Temperature is probably the most important factor that influences pipette performance. In fact, the density of water in a gravimetric analysis is calculated as a function of temperature

## PROPER PIPETTING TIPS -2

### Equilibration Time –

- It is recommended that the tip, the pipette, the liquid being transferred, and the transfer container itself all be allowed to equilibrate to the same temperature
- This is done to lessen the effects of thermal expansion which can dramatically impact the delivered volume

## PROPER PIPETTING TIPS -3

### Thermal Conductance –

- Thermal energy can be transferred from the operator's hand to the air within the pipette (dead air) or even to the internal components themselves
- This can have a dramatic impact on the amount of liquid dispensed due to the effects of expansion and/or contraction
- To lessen this effect, it is recommended that some type of thermally insulated gloves like latex or cloth be worn

# PROPER PIPETTING TIPS -4

## Position –

- Pipettes should be held vertical during the aspiration of liquids, however, some end users often hold pipettes at many different angles during a pipetting interval
- Holding a pipette 30° off vertical can cause as much as 0.7% more liquid to be aspirated due to the impact of hydrostatic pressure
- Always store pipettes in an upright position when not in use

## PROPER PIPETTING TIPS -5

### Pre-Wetting/Pre-Rinsing Tips –

- Failing to pre-wet tips can cause inconsistency between samples since liquid in the initial samples adhere to the inside surfaces of the pipette tip, but liquid from later samples does not
- Also, if a new volume is dialed in on the pipette's micrometer, you will receive better results at the new volume by taking the old tip off and placing a new one on the shaft before you commence pipetting

## PROPER PIPETTING TIPS -6

### Immersion Depth –

- The pipette tip should only be inserted into the vessel containing the liquid to be transferred about 1-3mm
- If the tip is immersed beyond this, the results could be erroneously high. This is due to the fact that liquid could adhere to the tip and be transferred along with the aliquot in the tip
- If the tip is not immersed far enough then air could be drawn into the tip which could yield results that are incorrect on the low end

# PROPER PIPETTING TIPS -7

## Release of Plunger –

- It is recommended that a smooth, consistent pipetting rhythm be employed since it helps to increase both accuracy and precision
- After the liquid has been aspirated into the tip, the pipette should be placed against the wall of the receiving vessel and the plunger slowly depressed. This will help all of the liquid in the tip to be dispensed
- After a pause of about 1 second, depress the plunger to the bottom or blowout position (if equipped) and remove the pipette from the sidewall by utilizing either a sliding action up the wall or a brief movement away from the wall (called “touching off”)

# Repeat the Exercise Using the techniques discussed.

## Procedure:

1. Install a new tip on the pipette
2. Tare the balance with a glass flask containing H<sub>2</sub>O
3. Fill pipette with deionized water or equivalent
4. Slowly dispense water into flask
5. Record the first stable weight of the flask plus aliquot
6. Repeat steps 2 through 5 nine more times
7. Calculate the average, standard deviation, volume & bias
8. Compare results to manufacturer's specifications
9. Compare the first and second results
10. With your team measurements recalculate the same values
11. Determine the addition error caused by different operators

# Gravimetric Pipette Calibration/Validation

Given a certain mass of water with a known specific gravity, its volume can then be predicted

- Most common calibration method
- Physical Model:  $V = (X_i + e) * Z$ - factor
- Z-factor: Conversion factor ( $\mu\text{L}/\text{mg}$ ) incorporating the density of water when buoyed in air as a function of temperature and pressure.
  - $Z\text{-factor} = (1/(\rho_w - \rho_a)) * (1 - (\rho_a / \rho_b))$
  - $\rho_w$  = density of water
  - $\rho_a$  = density of air
  - $\rho_b$  = density of weights

## ISO 8655 gravimetric method

- Given a certain mass of water with a known specific gravity, its volume can then be predicted
- Weighing vessel: Never plastics!!!!
- Thermometer: Uncertainty of  $< 0,2 \text{ }^{\circ}\text{C}$
- Hygrometer: Uncertainty of  $< 10\%$
- Barometer: Uncertainty of  $< 0,5 \text{ kPa}$

# Z-Factor Values

## Converting Wt. to Volume

- Look up corresponding Z-factor for water temperature
- Multiple the average of the 10 aliquots of water
- Subtract this value from 1,000 ml to determine the bias
- Is it within the +/- 8.0  $\mu\text{L}$  tolerance for 1 ml?

TEMP ACTUAL °C	Z-FACTOR
20.0	1.0029
20.5	1.0030
21.0	1.0031
21.5	1.0032
22.0	1.0033
22.5	1.0034
23.0	1.0035
23.5	1.0036
24.0	1.0038
24.5	1.0039

# Discussion Topics

- What variables contributed to the volume uncertainty?
- How was the standard deviation affected by more operators?
- What affect did additional measurements have on the average volume?
- How do your bias and precision estimates compare to the manufacturer's specification?
- What uncertainty value would you assign to the volumes delivered by your pipette?
- What Uncertainty would you assign to any 1 ml volume dispensed by any person in the room?

# Summary

- There are many variables that affect the uncertainty of volumes, using the gravimetric method
- Training and a comprehensive procedure help minimize variation in volume measurements
- Uncertainty estimates should also include the assumptions made in their determination
- The user of the volume measurements must determine the limit of error that is “fit for purpose”

## Pipette Calibration/Validation Exercise

---

### Exercise Objectives:

After the session the participants will be able to do the following:

1. Explain the sources of error in pipette volume measurements
2. Discuss the variation within and between operators
3. Estimate the uncertainty of volumetric measurements
4. Compare calculated uncertainty estimates with manufacturer's specifications.  
1000 $\mu$ L tolerances = Accuracy  $\pm 0.8\%$  or  $\pm 8.0 \mu\text{L}$   
Precision  $\pm 0.15\%$  or  $\pm 1.5 \mu\text{L}$

### Estimated Time:

- +1.50 hours completing exercise
- +0.50 hours in large group discussion
- 2.00 hours total

### Materials needed:

1. Four laptop computers
2. Work sheets for each person
3. One barometer with calibration certificate or manufacturer specifications
4. Two thermometers with readability to tenth of a degree (0.1C) **must have calibration certificates or manufacturers specifications in both English and Chinese.** One must be able to be used to read the temperature of water.
5. Humidity meter with calibration certificate or manufacturer specifications **in both English and Chinese**
6. Four 1 ml fixed volume air displaced pipettes. (Calibration certificates NOT Required)
7. Four boxes of disposable tips from the manufacturer of the pipettes
8. Two liters of distilled water
9. Five 50 ml glass volumetric flask
10. Four 250 ml bottles
11. Flip chart or dry board and colored markers

### Instructions:

**On your work sheet record: your name, date, time, water temperature, room temperature, humidity and barometric pressure and the uncertainty or tolerance of each instrument.**

#### Procedure:

1. **Install a new tip on the pipette**
2. **Tare the balance with a glass flask containing H<sub>2</sub>O**
3. **Fill pipette with deionized water or equivalent**
4. **Dispense water into flask**
5. **Record the weight of the dispensed volume of water.**
6. **Repeat steps b through e 9 more times for a total of 10 dispensing**

7. Calculate the average weight of the water, & the standard deviation.

## **VALUE FOR Z ( $\mu\text{L}/\text{MG}$ ), AS A FUNCTION OF TEMPERATURE AND PRESSURE, FOR DISTILLED WATER AT 1 ATM.**

TEMP °C	ACTUAL Z-FACTOR	TEMP °C	ACTUAL Z-FACTOR	TEMP °C	ACTUAL Z-FACTOR
15.0	1.0020	20.0	1.0029	25.0	1.0040
15.5	1.0020	20.5	1.0030	25.5	1.0041
16.0	1.0021	21.0	1.0031	26.0	1.0043
16.5	1.0022	21.5	1.0032	26.5	1.0044
17.0	1.0023	22.0	1.0033	27.0	1.0045
17.5	1.0024	22.5	1.0034	27.5	1.0047
18.0	1.0025	23.0	1.0035	28.0	1.0048
18.5	1.0026	23.5	1.0036	28.5	1.0050
19.0	1.0027	24.0	1.0038	29.0	1.0051
19.5	1.0028	24.5	1.0039	29.5	1.0052
				30.0	1.0054

### Converting Wt. to Volume

1. Look up corresponding Z-factor for water temperature.
2. Multiple the average weight of the 10 aliquots of water by the Z factor.
3. Subtract this value from 1,000 ml to determine the bias.
4. Is it within the +/- 8.0- $\mu\text{L}$  tolerances for 1 ml?
5. Is the standard deviation within the +/- 1.5  $\mu\text{L}$  Discussion Topics
6. Combine all of the data from the team and repeat the calculations

### Discussion Questions

1. What variables contributed to the volume uncertainty?
2. How did more operators affect the standard deviation?
3. What affect did additional measurements have on the average volume?
4. How do your bias and precision estimates compare to the manufacturer's specification?
5. What uncertainty value would you assign to the volumes delivered by your pipette?
6. What uncertainty would you assign to any 1 ml volume dispensed by any person in the room?

### Summary

1. There are many variables that affect the uncertainty of volumes, using the gravimetric method.
2. Training and a comprehensive procedure help minimize variation in volume measurements.
3. Uncertainty estimates should also include the assumptions made in their determination.
4. The user of the volume measurements must determine the limit of error that is "fit for purpose"

Date		Group:			Tolerance
Air Temperature=					
Water Temperature=					
Barometric Pressure=					
Humidity=					
Pipette ID=					
Name:					
	Analyst-1	Analyst-2	Analyst-3	Analyst-4	Analyst-5
1 weight					
2 weight					
3 weight					
4 weight					
5 weight					
6 weight					
7 weight					
8 weight					
9 weight					
10 weight					
Average =					
Standard Deviation=					
Z-Factor =					
Volume (Z x Ave Wt.) =					
Volume in micro liters (µL)=					
SD x Z = +/- ml					
SD ml x 1000= SD in µL					
Nominal Volume=					
Calculated Volume in µL=					
Bias (inaccuracy)					
(+/-8.0µL) Volume Tolerance =					
(+/- 1.5 µL SD Tolerance)					
Pass if SD & Bias<Tolerances					
$Uc = (Usd^2+(B/2)^2)^{.5}$					
Expanded U = $Uc*2$					
Relative % Uncertainty					
	<b>TEAM AVERAGE EVALUATION OF BIAS &amp;PRECISION</b>				
Average =					
Standard Deviation=					
Z-Factor =					
Volume (Z x Ave Wt.) =					
Volume in micro liters (µL)=					
SD x Z*1000 = µL					
Bias					
$Uc = (Usd^2+(B/2)^2)^{.5}$					
Expanded U = $Uc*2$					
Relative % Uncertainty					

## Part 2 of the Exercise: Repeat with more detailed instructions and tips for accurate Pipetting;

### Discussion topics for Improving testing:

#### PROPER PIPETTING TECHNIQUES & TIPS

##### TECHNIQUES –

1. Most end users have a tendency to believe that the volume delivery is completely dependent on the setting of the micrometer dial.
2. Obviously, this is not the case, since many factors associated with pipettes come into play.

##### TIPS –

1. Use Manufacturers' Tips

##### Temperature

1. The volume delivery performance specifications of pipettes have been referenced by most manufacturers at room temperature, which is defined as 20-25°C. Any deviation from this specification can affect the amount of liquid dispensed due to the expansion or contraction of the internal components.
2. Temperature is probably the most important factor that influences pipette performance. In fact, the density of water in a gravimetric analysis is calculated as a function of temperature.

##### Equilibration Time

1. It is recommended that the tip, the pipette, the liquid being transferred, and the transfer container itself all be allowed to equilibrate to the same temperature.
2. This is done to lessen the effects of thermal expansion, which can dramatically impact the delivered volume.

##### Thermal Conductance

1. Thermal energy can be transferred from the operator's hand to the air within the pipette (dead air) or even to the internal components themselves.
2. This can have a dramatic impact on the amount of liquid dispensed due to the effects of expansion and/or contraction.
3. To lessen this effect, it is recommended that some type of thermally insulated gloves like latex or cloth be worn.

##### Position

1. Pipettes should be held vertical during the aspiration of liquids; however, some end users often hold pipettes at many different angles during a pipetting interval.
2. Holding a pipette 30° off vertical can cause as much as 0.7% more liquid to be aspirated due to the impact of hydrostatic pressure.
3. Always store pipettes in an upright position when not in use.

##### Pre-Wetting/Pre-Rinsing Tips

1. Failing to pre-wet tips can cause inconsistency between samples since liquid in the initial samples adhere to the inside surfaces of the pipette tip, but liquid from later samples does not.
2. Also, if a new volume is dialed in on the pipette's micrometer, you will receive better results at the new volume by taking the old tip off and placing a new one on the shaft before you commence pipetting.

##### Immersion Depth

1. The pipette tip should only be inserted into the vessel containing the liquid to be transferred about 1-3mm.
2. If the tip is immersed beyond this, the results could be erroneously high. This is due to the fact that liquid could adhere to the tip and be transferred along with the aliquot in the tip.
3. If the tip is not immersed far enough then air could be drawn into the tip that could yield results that are incorrect on the low end.

### **Release of Plunger –**

1. It is recommended that a smooth, consistent pipetting rhythm be employed since it helps to increase both accuracy and precision.
2. After the liquid has been aspirated into the tip, the pipette should be placed against the wall of the receiving vessel and the plunger slowly depressed. This will help all of the liquid in the tip to be dispensed.
3. After a pause of about 1 second, depress the plunger to the bottom or blowout position (if equipped) and remove the pipette from the sidewall by utilizing either a sliding action up the wall or a brief movement away from the wall (called “touching off”).

**Repeat the exercise using the techniques given above and discussed.**

### ● **Procedure:**

1. Install a new tip on the pipette
2. Tare the balance with a glass flask containing H<sub>2</sub>O
3. Fill pipette with deionized water or equivalent
4. Slowly dispense water into flask
5. Record the first stable weight of the flask plus aliquot
6. Repeat steps 2 through 5 nine more times
7. Calculate the average, standard deviation, volume & bias
8. Compare results to manufacturer’s specifications.
9. Compare your first and second results with each other, then
10. With all of your team measurements recalculate the same values
11. How can you determine the addition error caused by different operators?

### **Gravimetric Pipette Calibration/Validation**

12. Second validation of a pipette’s volume and operator’s precision using the “tips and techniques” listed above to reduce operator variation in the use of the pipette to dispense volume measurements. Use another copy of the worksheet for the second attempt to validate the calibration of a pipette and calculate the uncertainty of volume measurements made with the pipette in the laboratory.
13. Discuss the results of the second exercise.

Date		Group:			Tolerance
Air Temperature=					
Water Temperature=					
Barometric Pressure=					
Humidity=					
Pipette ID=					
Name:					
	Analyst-1	Analyst-2	Analyst-3	Analyst-4	Analyst-5
1 weight					
2 weight					
3 weight					
4 weight					
5 weight					
6 weight					
7 weight					
8 weight					
9 weight					
10 weight					
Average =					
Standard Deviation=					
Z-Factor =					
Volume (Z x Ave Wt.) =					
Volume in micro liters (µL)=					
SD x Z = +/- ml					
SD ml x 1000= SD in µL					
Nominal Volume=					
Calculated Volume in µL=					
Bias (inaccuracy)					
(+/-8.0µL) Volume Tolerance =					
(+/- 1.5 µL SD Tolerance)					
Pass if SD & Bias<Tolerances					
$Uc = (Usd^2+(B/2)^2)^{.5}$					
Expanded U = Uc*2					
Relative % Uncertainty					
	<b>TEAM AVERAGE EVALUATION OF BIAS &amp;PRECISION</b>				
Average =					
Standard Deviation=					
Z-Factor =					
Volume (Z x Ave Wt.) =					
Volume in micro liters (µL)=					
SD x Z*1000 = µL					
Bias					
$Uc = (Usd^2+(B/2)^2)^{.5}$					
Expanded U = Uc*2					
Relative % Uncertainty					



## Module 12

### Case Study: Uranium Working Standards Preparation

#### Objectives

---

- Understand how to produce a standard that has an uncertainty of  $1/3$  or less of the uncertainty of the measurement it is meant to control
- Review a case study on the production of a Uranium Nitrate Solution to use as working calibration material (WRM) that is traceable to a Certified Reference Material.
- Review the statistical tests used in assigning a concentration value with associated estimate of the uncertainty of the WRM that is traceable to the CRM.

Module 12 - 2

## **Introduction:**

---

- **Over 3000 years ago King Solomon wrote “Differing weights and differing measures -- The Lord detests them both.” Proverbs 20:10**
- **Civilization has recognized the need for standards for millenniums and governments have established special organizations to maintain & regulate them**
- **The nuclear industry has its standards & regulations which which apply to the measurements needed for MC&A, as well as production and safety.**
- **Uranium standards are expensive, but can be produced locally at a significant cost savings and still be traceable to CRMs if done correctly.**

Module 12 - 3

## **Overview**

---

- **Personal Experience in Standards Preparation**
- **Data Quality Objectives**
  - **Measurement Methods Uncertainties**
  - **Available standards**
- **Uranyl nitrate stock solution preparation**
- **Characterization Methods and Laboratories**
- **Data Collection**
- **Statistical tests used in evaluation characterization of the traceable stock solution**
- **Assigned Concentrations & Uncertainties**

Module 12 - 4

## Work Experience

---

- **Chemist at nuclear fuels reprocessing plant**
- **Qualified by Chemist training & testing program**
- **Research Chemist in Standards Lab**
  - Prepared U and Pu solution standards for QC programs
  - Safeguards Analytical Laboratory Evaluation (SALE) program
  - Managed Chemist & Analysts training program & QC program
- **Ran Standards Lab for commercial nuclear fuels reprocessing**
  - Prepared U standards for calibration, QC & Training & Testing
  - Prepare 300 liters of U solution stock solution for AGNS
- **Savannah River Site –Analytical Services**
  - Used AGNS stock U solution for QC programs
  - Worked on PuO<sub>2</sub> standards for NDA MCPs

Module 12 - 5

## Standards & Data Quality Objectives

---

- **Standard or Certified Reference Material (SRM or CRM)**
- **Working Reference Material (WRM)**
- **Working Calibration and Test Material (WCTM)**
- **Reference Calibration and Test Material (RCTM)**
- **Data Quality Objectives**
  - Uncertainty of methods to be calibrated & monitored
  - Target Uncertainty of measurement methods
- **Available standards**
  - NBS SRM-960 normal uranium metal with known purity
  - Impurity standards for emission spectroscopy
  - Used NUREG-0253 special LANL publication as procedure
- **Target Value Uncertainty of Standard is <1/3 of Method Uncertainty**

Module 12 - 6

## WCTM Characteristics

---

- Should be stable over extended storage periods
- Closely match the material routinely measured
- Have an uncertainty consistent with its intended use
- It should be convenient to use
- It should be economical

Module 12 - 7

## Certified Reference Materials Uranium metal, Isotopic & Impurity U oxides

---

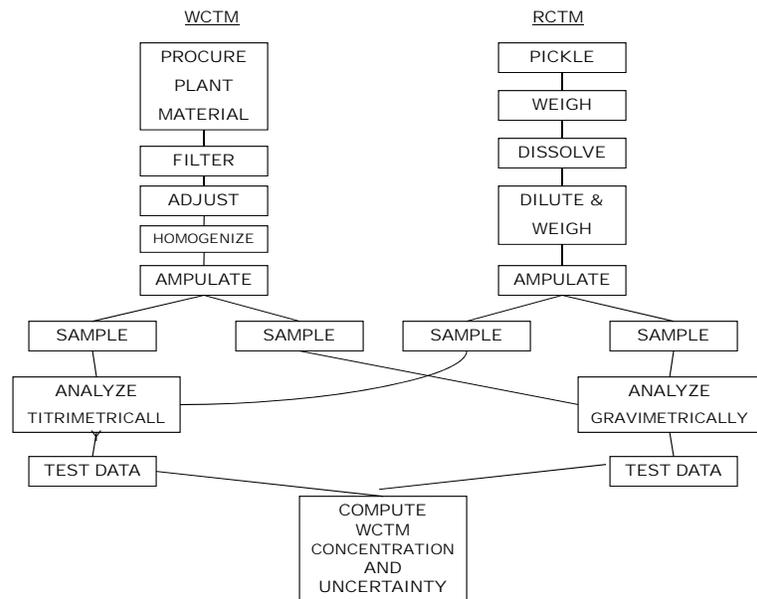


Module 12 - 8

## Methods for Preparation of WCTMs

- 1. Synthesize from well characterized starting material**
  - Obtain Standard Reference Material (SRM)
  - Prepare using standard gravimetric and volumetric methods
  - Integrity of SRM transferred to the WCTM
- 2. Characterize a plant product by two analysis methods**
  - Traceability is established using the Reference Material
  - This is done by analyzing both solutions concurrently
  - Bias correcting the WCTM with biases observed on RCTM

Module 12 - 9



Preparation scheme for calibration and test materials<sup>10</sup>

## Case Study of the Preparation of a Uranyl Nitrate Solution

---

- ~80 Liters of 300 gU/L solution obtained from the plant
- Solution filtered, acidity adjusted & thoroughly mixed.
- Transferred to pre-cleaned glass ampoules & flame sealed
  - ~one hundred & eighty 500 ml, ~ fifty 50 ml and ~ fifty 10 & 20 ml ampoules
- SRM-960 U metal used to synthesize a 300 gU/L solution
  - Metal was cleaned, dried, weighed, dissolved, diluted & weighed
  - The concentration and associated uncertainty were calculated
  - 50, 20 and 10 ml ampoules were filled and sealed for future use
- Characterization work done from the various ampoules

Module 12 - 11

## Characterization

---

- Target uncertainty is 1/3 of method uncertainty
  - Target for method at that time was 0.25%
  - Target for WCTM's uncertainty was ~0.08% (0.25%/3)
- Two accurate and precise methods were selected
  - Gravimetric Uranium evaporate and ignite to form U<sub>3</sub>O<sub>8</sub>
  - NBL modified Davies and Gray titrimetric method
- Two Laboratories were involved in the program
  - The Department of Energy Standards Laboratory (NBL)
  - Private commercial laboratory
- A another RCTM was prepared & the whole characterization repeated in 1978

Module 12 - 12

## Module 1. Course Introduction

### 1976 Synthesized RCTM Uranyl Nitrate Reference Standard I

Symbol	Component	Mean Value g/g	Standard Deviation g/g
A =	assigned makeup value		0.000024
S <sub>A=</sub>	associated standard deviation	0.2268495	
F =	purity of starting material	0.99975	0.000085
b =	air buoyancy	0.99992	0
W <sub>1</sub> =	Weight of the starting material	166.45221	0.00019
W <sub>2</sub> =	tare weight of the flask	176.695	0.034
W <sub>3</sub> =	gross weight of the solution & flask	910.209	0.034
W <sub>4</sub> =	(W <sub>3</sub> - W <sub>2</sub> ) = net weight of solution	733.514	0.048
S =	standard deviation		
S <sub>A=</sub>	(F*b*W <sub>1</sub> )/W <sub>4</sub>	0.2268495	
S =	$(1/W_4) * (b^2 * (F^2 * Sw_1^2 + W_1^2 * S_F^2) + A^2 * (Sw_2^2 + Sw_3^2))^{.5}$		0.000024

Final Concentration in mg U/g=	226.85 (+/- 0.024 mgU/g)
--------------------------------	--------------------------

Module 12 - 13

### 1978 Synthesized RCTM Uranyl Nitrate Reference Standard II

Symbol	Component	Mean Value g/g	Standard Deviation g/g
A =	assigned makeup value	0.216578	
S <sub>A=</sub>	associated standard deviation		0.000019
F =	purity of starting material	0.99975	0.000085
b =	air buoyancy	0.99992	0
W <sub>1</sub> =	Weight of the starting material	155.3783	0.00011
W <sub>2</sub> =	tare weight of the flask	164.858	0.0083
W <sub>3</sub> =	gross weight of the solution & flask	882.044	0.0132
W <sub>4</sub> =	(W <sub>3</sub> - W <sub>2</sub> ) = net weight of solution	717.186	0.0156
S =	standard deviation		
S <sub>A=</sub>	(F*b*W <sub>1</sub> )/W <sub>4</sub>	0.216578444	
S =	$(1/W_4) * (b^2 * (F^2 * Sw_1^2 + W_1^2 * S_F^2) + A^2 * (Sw_2^2 + Sw_3^2))^{.5}$		0.000019

Final Concentration in mg U/g=	216.58 (+/- 0.024 mgU/g)
--------------------------------	--------------------------

Module 12 - 14

## Summary of Uranyl Nitrate WCTM Plant Material Characterization

LABORATORY	METHOD	CORRECTED MEAN
IN-HOUSE - 76	GRAVIMETRIC	219.20
OUTSIDE #1		219.18
IN-HOUSE - 78		219.24
IN-HOUSE - 76a	NBL-MODIFIED D.G.	219.17
IN-HOUSE - 76b		219.20
OUTSIDE #2		219.26
IN-HOUSE - 78		219.18

THE AVERAGE OF THESE 7 MEANS IS 219.20 mgU/g  
SOLUTION.

The target RLE of 0.08% is >0.014% of the WCTM,  
therefore the WCTM characterization is  
satisfactory

Module 12 - 15

## Statistics Used in Characterizing a Working Standard

**Note:** See spreadsheet (handout and display)

1. **Data collected in confirmation working from 1978 In-house Analysis**
  - The Mean (M) and Standard Deviation (S) of each set of results from each method on both the CRM & WRM.
2. **F-Test of Precision**
  - Calculated F ratios for both methods are compared to tabulated F values at the 95% confidence levels.
  - If different, pooled estimates of precision may be used
3. **Calculation of Method Means Based on CRM**
  - WRMS is bias corrected by the biases determined on CRM

Module 12 - 16

## Statistics Used in Characterizing a Working Standard<sub>(continued)</sub>

---

4. **Calculation of the Equality of the Means**
  - The approximate variances (V) and degrees of freedom (f) for each mean are calculated.
  - These f are used in testing the means using a t-test
5. **Compute the T statistic with f degrees of freedom (df) by dividing the difference D&G and Gravimetric method means by the RMS of the two S estimates and using a special formula to estimate the f.**
6. **Assignment of WRM Concentration Value (A) by weighting the bias corrected means from each method.**

Module 12 - 17

## Statistics Used in Characterizing a Working Standard<sub>(continued)</sub>

---

7. **Calculation of the SD ( $S_A$ ) Associated with A, with  $f_A$  Degrees of Freedom.**
  - $f_A$  is the df used in the calculation of the limit of error for A.
8. **Calculation of the Limit of Error (LE) and Relative Limit of Error (RLE)**
9. **Test to determine if the RLE meets the requirement of <1/3 of the plant RLE of 0.25%**
10. **Calculation of the 95% Confidence Interval (CI) for the assigned value of the WRMS.**
  - $CI = A \pm t(1 - \alpha/2, n_a) (S_A)$
  - $t = (0.975, 16) = 2.120$
  - $CI = 219.22 \pm (2.120 * 0.0318) = 219.15 \text{ to } 219.29 @ .95 \text{ CI}$

Module 12 - 18

## Accomplishment

---

- A large quantity of Uranyl Nitrate stock solution was prepared from plant material, traceable to a CRM
- Enough material was prepared so it could be used to synthesize standard for all Uranium methods used.
- The WCM uncertainty was less than the target uncertainty
- This standard has been used for 30 years at the Savannah River Site

Module 12 - 19

## Uranium Certified Reference Materials

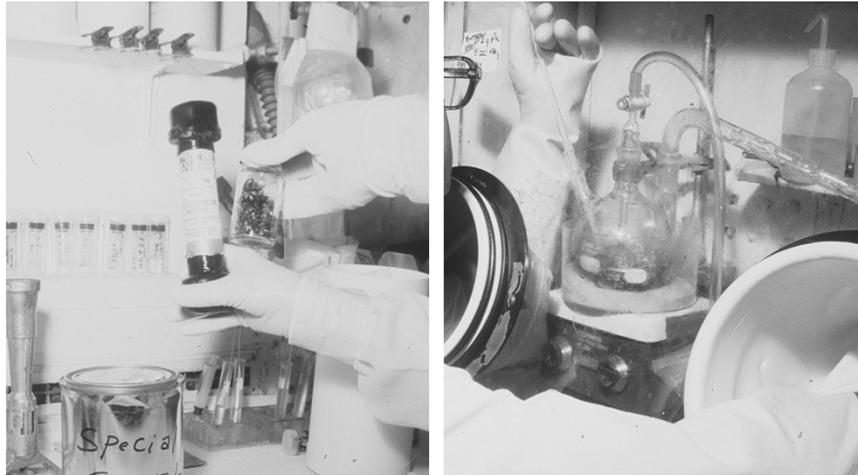
---

- CRM metal used to make calibration solutions.
- Depleted Uranium metal used to make synthetic process streams to be used for calibrations, QC, R&D and training & testing personnel.



Module 12 - 20

## **Plutonium Nitrate Standards can be produced the same way, Using a CRM and Plant material**



Module 12 - 21

## **Summary**

- **Understand how to produce a standard that has an uncertainty of 1/3 or less of the uncertainty of the measurement it is meant to control**
- **Reviewed a case study on the production of a Uranium Nitrate Solution to use as working calibration material (WRM) that is traceable to a Certified Reference Material.**
- **Reviewed the statistical tests used in assigning a concentration value with associated estimate of the uncertainty of the WRM that is traceable to the CRM.**

Module 12 - 22

**1976 Synthesized RCTM Uranyl Nitrate Reference Standard I**

Symbol	Component	Mean Value g/g	Standard Deviation g/g
A =	assigned makeup value		0.000024
S <sub>A</sub> =	associated standard deviation	0.2268495	
F =	purity of starting material	0.99975	0.000085
b =	air buoyancy	0.99992	0
W <sub>1</sub> =	Weight of the starting material	166.45221	0.00019
W <sub>2</sub> =	tare weight of the flask	176.695	0.034
W <sub>3</sub> =	gross weight of the solution & flask	910.209	0.034
W <sub>4</sub> =	(W <sub>3</sub> - W <sub>2</sub> ) = net weight of solution	733.514	0.048
S =	standard deviation		
S <sub>A</sub> =	$(F \cdot b \cdot W_1) / W_4$	0.2268495	
S =	$(1/W_4) \cdot (b^2 \cdot (F^2 \cdot Sw_1^2 + W_1^2 \cdot S_F^2) + A^2 \cdot (Sw_2^2 + Sw_3^2))^{1/2}$		0.000024

<b>Final Concentration in mg U/g=</b>	<b>226.85 (+/- 0.024 mgU/g)</b>
---------------------------------------	---------------------------------

**1978 Synthesized RCTM Uranyl Nitrate Reference Standard II**

Symbol	Component	Mean Value g/g	Standard Deviation g/g
A =	assigned makeup value	0.216578	
S <sub>A</sub> =	associated standard deviation		0.000019
F =	purity of starting material	0.99975	0.000085
b =	air buoyancy	0.99992	0
W <sub>1</sub> =	Weight of the starting material	155.3783	0.00011
W <sub>2</sub> =	tare weight of the flask	164.858	0.0083
W <sub>3</sub> =	gross weight of the solution & flask	882.044	0.0132
W <sub>4</sub> =	(W <sub>3</sub> - W <sub>2</sub> ) = net weight of solution	717.186	0.0156
S =	standard deviation		
S <sub>A</sub> =	$(F \cdot b \cdot W_1) / W_4$	0.216578444	
S =	$(1/W_4) \cdot (b^2 \cdot (F^2 \cdot Sw_1^2 + W_1^2 \cdot S_F^2) + A^2 \cdot (Sw_2^2 + Sw_3^2))^{1/2}$		0.000019

<b>Final Concentration in mg U/g=</b>	<b>216.58 (+/- 0.024 mgU/g)</b>
---------------------------------------	---------------------------------



## **Module 14**

---

# **Inventory Difference (ID) Assessment**

# Objectives

---

- 1. Identify how control limits can be used as a method of evaluating ID**
- 2. Identify how various types of errors contributing to the ID affect the ID mean and the ID standard deviation**
- 3. Calculate the loss detection probabilities**
- 4. Identify the characteristics of historic and variance propagation (VP) ID control limits**
- 5. Calculate the uncertainty of the ID**

# **DOE-STD-1194-2011 Chapter 6.5.5**

## **Evaluating Inventory Programs**

---

**6.5.5.1 - A program for evaluating all special nuclear material (SNM) IDs, including those involving missing items must be developed, documented and implemented...**

**6.5.5.2 - Procedures for establishing control limits for IDs of SNM must be based on Variance Propagation (VP) using current data.**

**6.5.5.3 - Assessments of IDs must include statistical tests (for example, tests of trends and biases...**

# **DOE-STD-1194-2011 Chapter 6.5.5 Evaluating Inventory Programs**

---

## **Chapter 6.5.5.2**

**Other methodologies may be used but they must be approved by the DOE cognizant security authority and must be justified based on factors such as limited data, low transfer rates, and/or material category**

# **DOE-STD-1194-2011 Performance Requirements MC&A System Elements**

---

## **6.1.7.4 (7)**

**For Category I and II material balance areas (MBAs), limits-of-error (LE) must not exceed two percent of the active inventory during the inventory period and must not exceed a Category II quantity of material**

# Objective 1

---

**Identify how control limits can be used as a method of evaluating ID**

# ID Definition

---

- **ID = Book - EI**
  - **Book inventory - Ending physical inventory (EI)**
  - **Book = Beginning Inventory (BI) + R – S** where R represents receipts (or additions) and S represents shipments (or removals)
- **The ID is the fundamental indicator of loss of material from the accounting system**

# Assessment

---

- **Construct a control chart for a specific material type for a specific MBA**
- **X-axis will be an inventory period**
- **Y-axis will be the value of the ID**
- **Plot the cumulative ID on the X-axis**

# Assessment

---

- **Calculate the overall mean and standard deviation and the 2s and 2.6s limits**
  - **The probability exists that an observation from a normal distribution will fall within 2.6 standard deviations from the mean is 0.99 (99%)**
  - **Many control charts use 3s limits, but the DOE requirement for alarm limits to be set at the 99% confidence level suggests 2.6s be used**

# Concerns of the ID Control Chart Methodology

---

- **All periods are not necessarily independent**
  - **Measurements are correlated**
  - **BI for the  $n$ th period is identical to the EI of the  $n-1$  period**

# Concerns of the ID Control Chart Methodology

---

- **Since the magnitude of the ID is correlated with the throughput, inventory periods with large or small throughputs will produce erroneous results**
- **Nevertheless, ID control charts provide a reasonable picture of an MBA's performance**

# Objective 2

---

**Identify how various types of errors contributing to the ID affect the ID mean, and the ID standard deviation.**

# IDs Are Not Zero Because

---

- **Measurement uncertainty: measurement system effects**
  - **Location of material**
    - In calorimeter, on scale, etc.
    - For example, heat distribution, weight distribution, etc.
  - **Calibration of scales**
  - **Fluctuations in air pressure, temperature, etc.**

# IDs Are Not Zero Because

---

- **Measurement uncertainty: non-measurement-system effects**
  - **Power fluctuations**
  - **Electronic functioning of equipment**
  - **Non-homogeneity of material being measured**
  - **Statistical nature of radioactive decay**
  - **Improper or incomplete background measurements**

# IDs Are Not Zero Because

---

- **Sampling effects**
  - **Improper or incomplete blending in a destructive analysis sample**
- **Nondestructive Analysis (NDA) limitations**
  - **Material composition of the NDA standards does not match the material composition of the measured items**
  - **Failure to account for background effects**

# IDs Are Not Zero Because

---

- **Accounting system effects**
  - **Better measurement to correct estimates**
  - **Decay, rounding errors, etc.**
- **Human error**
  - **Clerical mistakes (transcription errors, etc.)**
  - **Failure to follow procedures**

# IDs Are Not Zero Because

---

- **Unmeasured streams or inventories**
  - **Solids entrained in liquid systems settle in tanks**
  - **Holdup can take the form of material associated with specific equipment**
- **Factors or estimates**

# Objective 3

---

**Calculate the loss detection probabilities**

# Evaluating ID

---

- **In general, recall the following:**
  - **Errors can be total or composed of systematic or random, calculated from standards and/or process materials**
  - **The ID equation contains terms for BI, receipts (or additions/inputs), shipments (removals/outputs), and EI**

# Evaluating ID

---

- **In general, recall:**
  - **$ID = BI + R - S - EI$** 
    - **In this equation, we have “signed” sums (for example, S and EI have the minus sign in front of them)**
    - **The impact of the sign is not only on the ID, but also on the systematic error (for example, a bias on an addition and a similar bias on a removal will cancel a systematic error but will not cancel a random error)**

# Uncertainty of ID

---

- **If all terms are random then the following result:**
  - $ID = BI + R - S - EI$
  - $Var (ID) = Var (BI) + Var (R) + Var (S) + Var (EI)$
  - $Limit\ of\ Error\ about\ the\ ID\ (LEID) = 2\ sqrt (Var(ID))$
- **We know that many terms are systematic, however, hence a more complicated formula must be used**

**(Note that variances are additive even though there are minus signs in the ID equation)**

# Combining Uncertainties

---

The general formula used is the following:

$$\text{Var}(M) = [\sum_i (s_r m_i)^2] + (s_s M)^2$$

Note the difference between sum the squares and square the sums

**Where:**

$m_i$  is the content of each of the individual items that are in the same strata

$s_r$  = Random uncertainty (1s)

$s_s$  = Systematic uncertainty (1s)

$M = \sum_i m_i$  = Total for the items within a stratum

# Combining Uncertainties

---

- **This must be done for all strata:**
  - **For example, you can have an inventory with oxide, nitrate, and scrap**
    - **Each would have random and systematic errors for weighing, sampling, and analytical**
    - **Each of the strata could contain BI, R, S, EI terms**

# Variance of ID

---

$$\text{Var}(\text{ID}) = [\sum_i (\sigma_r m_i)^2] + (\sigma_s M)^2$$

Summed over all items in the ID equation

Signed sum over all items in the material balance equation.

BI and R items are + and EI and S are -.

Example: A site with 10 material types (oxide, metal, etc.) and errors for weight//volume, sampling, analytical, NDA, isotopic could require routine calculation and maintenance of 25-100 uncertainties

# ID Uncertainty Considerations

---

- **Only active inventory items are used in the calculation**
  - **Active inventory is nuclear material contained within the MBA that enters into the calculation of the limit of error and control limit for the MBA**
  - **Noncontributing terms are eliminated from the equation**
  - **Systematic errors**

# Example

## Material Balance Report (MBR) format

ID Component	Measurement Type/Method		kg
Beg. Inventory	Feed	14 Measurements of 2 kg batches	28
	In-process	12 kg in 1 batch	12
	Finished Fuel	75 Measurements of .4 kg batches	30
Receipt	Feed	28 Measurements of 2 kg batches	56
Shipment	Finished Fuel	215 Measurements of .4 kg batches	-86
End Inventory	Feed	18 Measurements of 2 kg batches	-36
	Scrap	4 kg in 1 batch	-4
			ID is 0

# Example

## Measurement type

ID Component	Measurement Type/Method		kg
Beg. Inventory	In-process	12 kg 1 batch	12
End Inventory	Scrap	4 kg in 1 batch	-4
Beg. Inventory	Finished Fuel	75 Measurements of .4 kg batches	30
Shipment	Finished Fuel	215 Measurements of .4 kg batches	-86
Beg. Inventory	Feed	14 Measurements of 2 kg batches	28
Receipt	Feed	28 Measurements of 2 kg batches	56
End Inventory	Feed	18 Measurements of 2 kg batches	-36
			ID is 0

# Calculate the LEID Assuming the Following Uncertainties

Measurement Uncertainty (Relative Standard Deviation in %)		
Material Type	Random	Systematic
In-process	0.3	-
Scrap	0.7	0.2
Finished Fuel	0.25	0.05
Feed Material	0.5	0.1

# Solution

---

- **Apply the variance of ID equation to each material type**
- **Construct a table that summarizes the variances**
  - **Calculate the LEID**
- **Construct a table where the variances are expressed as a percentage of the total variance to determine where the largest contributors are.**

# Finding the In-Process Variance Contribution

---

$$\begin{aligned}M_{In-Process} &= BI_{In-Process} + R_{In-Process} - S_{In-Process} - EI_{In-Process} \\ &= 12kg + 0 - 0 - 0 = 12kg\end{aligned}$$

$$\begin{aligned}\Sigma(\sigma_r m_i)^2 &= (0.003 \times 12kg)^2 + (0.003 \times 0)^2 + (0.003 \times 0)^2 + (0.003 \times 0)^2 \\ &= 0.001296kg^2 + 0 + 0 + 0 \\ &= 0.001296kg^2\end{aligned}$$

$(\sigma_s \Sigma m_i)^2 = 0$ , since there is no systematic error for in-process

$$\begin{aligned}\text{var}(M_{In-Process}) &= \Sigma(\sigma_r m_i)^2 + (\sigma_s \Sigma m_i)^2 \\ &= 0.001296kg^2\end{aligned}$$

# Finding the Scrap Variance Contribution

---

$$\begin{aligned}M_{Scrap} &= BI_{Scrap} + R_{Scrap} - S_{Scrap} - EI_{Scrap} \\ &= 0 + 0 - 0 - 4kg = -4kg\end{aligned}$$

$$\begin{aligned}\Sigma(\sigma_r m_i)^2 &= (0.007 \times 0)^2 + (0.007 \times 0)^2 + (0.007 \times 0)^2 + (0.007 \times 4kg)^2 \\ &= 0.000784kg^2\end{aligned}$$

$$\begin{aligned}(\sigma_s \Sigma m_i)^2 &= (0.002 \times -4kg)^2 = 0.000064kg^2 \\ \text{var}(M_{Scrap}) &= \Sigma(\sigma_r m_i)^2 + (\sigma_s \Sigma m_i)^2 \\ &= 0.000784kg^2 + 0.000064kg^2 \\ &= 0.000848kg^2\end{aligned}$$

# Finding the Finished Fuel Variance Contribution

---

$$\begin{aligned}M_{Final} &= BI_{Final} + R_{Final} - S_{Final} - EI_{Final} \\ &= 75 \times 0.4kg + 0 - 215 \times 0.4kg - 0 = -56kg\end{aligned}$$

$$\begin{aligned}\Sigma(\sigma_r m_i)^2 &= 75(0.0025 \times 0.4kg)^2 + 0 + 215(0.0025 \times -0.4kg)^2 + 0 \\ &= 0.000075kg^2 + 0.000215kg^2 = 0.00029kg^2\end{aligned}$$

$$\begin{aligned}(\sigma_s \Sigma m_i)^2 &= (0.0005 \times -56kg)^2 = 0.000784kg^2 \\ \text{var}(M_{Final}) &= \Sigma(\sigma_r m_i)^2 + (\sigma_s \Sigma m_i)^2 \\ &= 0.00029kg^2 + 0.000784kg^2 \\ &= 0.001074kg^2\end{aligned}$$

# Finding the Feed Material Variance Contribution

---

$$\begin{aligned}M_{Feed} &= BI_{Feed} + R_{Feed} - S_{Feed} - EI_{Feed} \\ &= 14 \times 2kg + 28 \times 2kg - 0 - 18 \times 2kg = 48kg\end{aligned}$$

$$\begin{aligned}\Sigma(\sigma_r m_i)^2 &= 14(0.005 \times 2kg)^2 + 28(0.005 \times 2kg)^2 + 0 + 18(0.005 \times -2kg)^2 \\ &= 0.0014kg^2 + 0.0028kg^2 + 0.0018 = 0.006kg^2\end{aligned}$$

$$\begin{aligned}(\sigma_s \Sigma m_i)^2 &= (0.001 \times 48kg)^2 = 0.002304kg^2 \\ \text{var}(M_{Feed}) &= \Sigma(\sigma_r m_i)^2 + (\sigma_s \Sigma m_i)^2 \\ &= 0.006kg^2 + 0.002304kg^2 \\ &= 0.008304kg^2\end{aligned}$$

# Finding the Total Variance and LEID

---

The total variance for the ID is the sum of the variances for all strata.

$$\begin{aligned}\mathit{var}(ID) &= \mathit{var}(M_{In-Process}) + \mathit{var}(M_{Scrap}) + \mathit{var}(M_{Final}) + \\ &\mathit{var}(M_{Feed}) \\ &= 0.001296\mathit{kg}^2 + 0.000848\mathit{kg}^2 + 0.001074\mathit{kg}^2 + \\ &0.008304\mathit{kg}^2 \\ &= 0.011522\mathit{kg}^2\end{aligned}$$

The 2-sigma limit of error about the ID (LEID) is

$$\begin{aligned}LEID &= 2 \times \sqrt{\mathit{var}(ID)} = 2 \times \sqrt{0.011522\mathit{kg}^2} = \\ &0.214681\mathit{kg}\end{aligned}$$

# Table Solution

Variances	Random	Systematic		
Feed	$14*(0.005*2)^2 + 28*(0.005*2)^2 + 0 + 18*(0.005*-2)^2$	$[(24)(2)(.001)]^2 =$		
	0.006000	0.002304	→	0.008304
In Process	$[(12)(.003)]^2 =$	0		
	0.001296	0.000000	→	0.001296
Finished Fuel	$75*(0.0025*0.4)^2 + 0 + 215*(0.0025*(-0.4))^2 + 0$	$[(140)(.4)(.0005)]^2 =$		
	0.000290	0.000784	→	0.001074
Scrap	$[(4)(.007)]^2 =$	$[(4)(.002)]^2 =$		
	0.000784	0.000064	→	0.000848
	↓	↓		
	0.008370	0.003152	→	0.011522

Units are typically grams<sup>2</sup> or kilogram<sup>2</sup>

sID = 0.107341  
LEID(2s) 0.214681

# Summarize the Variance Terms (kg<sup>2</sup>)

---

Component	Random	Systematic	Total
Feed	0.00600	0.002304	0.008304
In-process	0.001296	0	0.001296
Finished Fuel	0.000290	0.000784	0.001074
Scrap	0.000784	0.000064	0.000848
Total	0.00837	0.003152	0.011522
		$S_{ID}$	0.107341
		LEID ( $2s_{ID}$ )	0.214681

# Solution Percent Contributors

---

<b>Component</b>	<b>Random</b>	<b>Systematic</b>	<b>Total</b>
<b>Feed</b>	<b>52.1</b>	<b>20.0</b>	<b>72.1</b>
<b>In-process</b>	<b>11.2</b>	<b>0.0</b>	<b>11.2</b>
<b>Finished Fuel</b>	<b>2.5</b>	<b>6.8</b>	<b>9.3</b>
<b>Scrap</b>	<b>6.8</b>	<b>0.6</b>	<b>7.4</b>
<b>Total</b>	<b>72.6</b>	<b>27.4</b>	<b>100.0</b>

# Analysis of LEID

---

- **What are the largest uncertainty contributors?**
- **How would you reduce the overall uncertainty?**
- **If a variance component is very large, is it because the uncertainty was very large or because the amount of material subject to that uncertainty was very large?**

# **Activity 1**

---

## **Material balance**

# Activity 1

---

- **Compute the overall uncertainty of the ID and LEID**
- **Determine where to allocate efforts to reduce the overall uncertainty**
  - **Discuss the implications of how the nitrate BI, receipts, and EI affect the LEID**
  - **Develop at least three recommendations and be prepared to defend them**

# Activity 1

---

## Analyses Using Variance Contributions

	Random (percent)	Systematic (percent)
Nitrate	28.5%	28.5%
Oxide	0.1%	0.9%
NDA	15.6%	1.0%
Buttons	0.3%	13.7%
Waste Oxide	0.6%	10.8%
Totals	45.0%	55.0%

# Objective 4

---

**Identify the characteristics of historic and Variance Propagation ID control limits**

# Factors Affecting ID Mean and Standard Deviation

---

- **What will the following do to the mean and standard deviation of the ID sequence?**
  - **A loss each inventory period of  $X$  grams of material**
  - **A large constant systematic error or bias in a flow (S or R) measurement**

# Factors Affecting ID Mean and Standard Deviation

---

- **What will the following do to the mean and standard deviation of the ID sequence?**
  - **A large constant systematic error or bias in an inventory measurement**
  - **A large random error in an inventory or flow measurement**

# Characteristics of Historical Limits

---

- **Easy to compute, reflect real process**
- **Process stable**
- **Large uncertainty in standard deviation unless a large quantity of ID data is used**

# Characteristics of Historical Limits

---

- **Abnormal conditions can unduly affect control limits**
- **Do not encourage improvement of practices**

# Validating Variance Propagation Calculations

---

**DOE-STD-1194-2011 6.5.5.2 states:**

**“Significant differences between historical limits and limits based on variance propagation must be investigated for the purpose of validating, revising, and refining the variance propagation model.”**

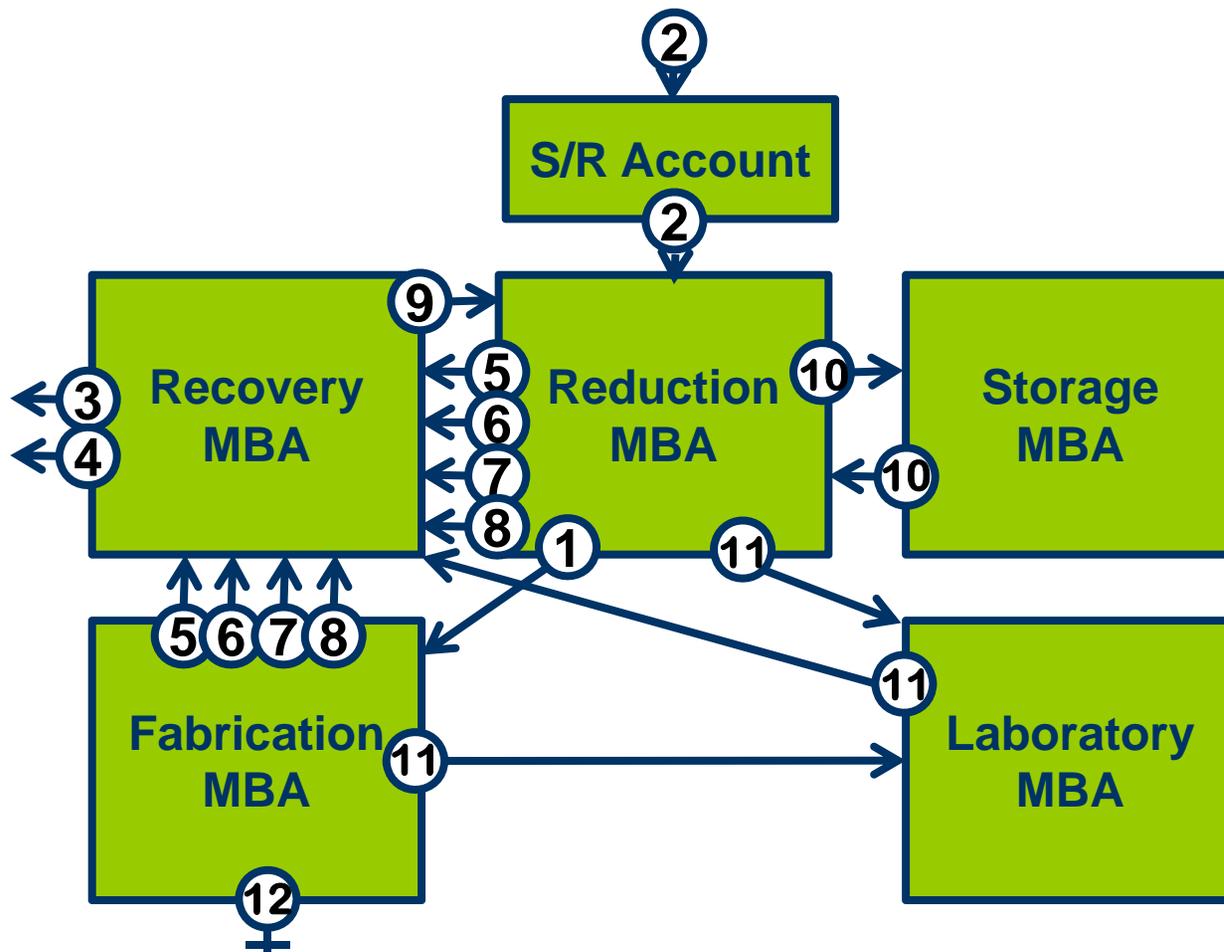
- **What do you do when they disagree?**
- **What limits do you use?**

# Objective 5

---

**Calculate the uncertainty of the ID**

# Hypothetical MBA Structure



- 1: Buttons
- 2: Scrap Oxide
- 3: LL Solid Waste
- 4: LL Liquid Waste
- 5: Solid Waste
- 6: Liquid Waste
- 7: Metal Scrap
- 8: Scrap Powder
- 9: Recovered Oxide
- 10: Sweepings
- 11: Samples
- 12: Metal Parts

# ID Questions

---

1. Suppose that the solid waste stream (5) is measured by an NDA instrument that has a positive bias (overstates the amount)
  - What will this do to the ID in the reduction MBA and the recovery MBA?
  - What will it do to the plant ID?

	BI+	R+	EI-	S-	ID
Reduction MBA	5			5+2	-2
Recovery MBA		5+2		5+2	0

# ID Questions

---

2. Suppose that an item of metal scrap (7) is removed from the reduction MBA and fed to the recovery MBA, but is not logged in the accounting records through human error

- What is the effect on the IDs?

	BI+	R+	EI-	S-	ID
Reduction MBA	4		0		4
Recovery MBA	0		4		-4

# ID Questions

3. Suppose that the value of an intermediate-product inventory item (for example, a can of off-spec oxide) in the recovery MBA is overestimated on the June 30 physical inventory.
- What does this do to the June ID?
  - If it is processed in July, what does it do to the July ID? If it is not processed?

	BI+	R+	EI-	S-	ID
June ID	6		6+3		-3
July ID	6+3		6		3

# Activity 2

---

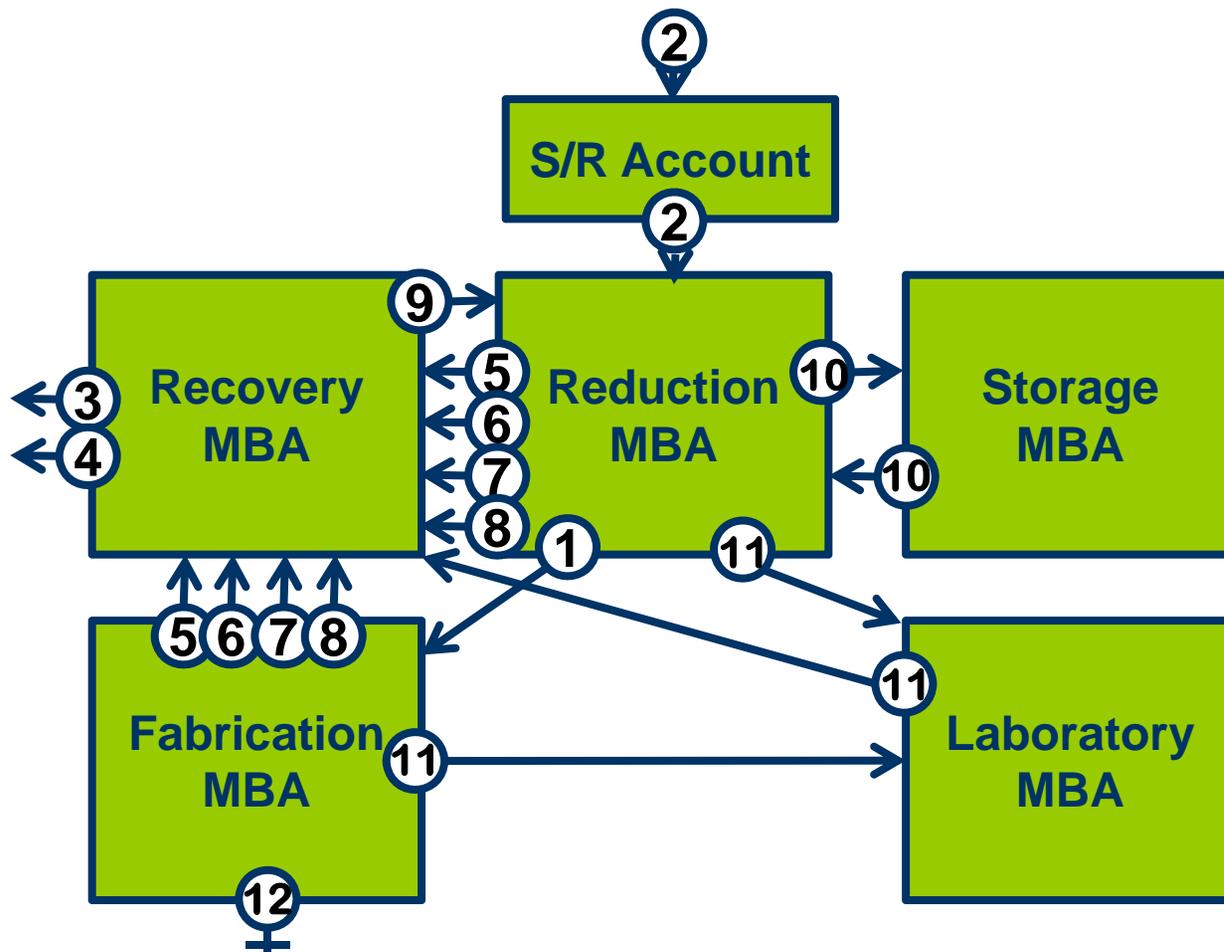
**Effects of various types of errors on the ID**

# Activity 2

---

**On the Activity 2 worksheet, answer the questions about the effect of various types of errors on the ID**

# Hypothetical MBA Structure



- 1: Buttons
- 2: Scrap Oxide
- 3: LL Solid Waste
- 4: LL Liquid Waste
- 5: Solid Waste
- 6: Liquid Waste
- 7: Metal Scrap
- 8: Scrap Powder
- 9: Recovered Oxide
- 10: Sweepings
- 11: Samples
- 12: Metal Parts

# Lesson Summary

---

- 1. Identify how control limits can be used as a method of evaluating ID**
- 2. Identify how various types of errors contributing to the ID, effect the ID mean and the ID standard deviation**
- 3. Calculate the loss detection probabilities**
- 4. Identify the characteristics of historic and Variance Propagation ID control limits.**
- 5. Calculate the uncertainty of the ID**

---

# Activity 1

---

Answers

# Activity 1

---

## Random error of nitrate

$$\Sigma_i (\sigma_r M_i)^2:$$

$$(0.01^2 + 0.0075^2 + 0.006^2) * (65,000^2 + 175,000^2/10 + 45,000^2) = 1,790,328 \text{ grams}^2$$

# Activity 1

---

- Systematic error of nitrate that has BI, A, and EI components and three systematic uncertainties
- The term  $\sigma_{sj}^2 ( \sum_i m_{ij} )^2$  is evaluated as  
 $(0.004^2 + 0.005^2 + 0.0025^2) * (65,000 + 175,000 - 45,000)^2$   
 $= 4.725 \times 10^{-5} * 3.8 \times 10^{10}$   
 $= 1,795,500 \text{ grams}^2$

# Activity 1

---

## Random and systematic errors of oxide

- **Random**

$$(0.0015^2 + 0.015^2 + 0.0125^2) * [12,000^2/8] = 6,903$$

- **Systematic**

$$(0.001^2 + 0.0175^2 + 0.009^2) * [12,000]^2 = 55,908$$

# Activity 1

---

## Errors for equipment via NDA

- Random

$$(1,850^2 + 3,500^2) * 0.25^2 = 979,531$$

- Systematic

$$(1,850 - 3,500)^2 * 0.15^2 = 61,256$$

# Activity 1

---

**Random error of the 100 buttons, each button with 2,000 grams of Pu**

- $(0.0015^2 + 0.0005^2 + 0.007^2) * (2000^2 + 2000^2 + \dots) = 20,600 \text{ grams}^2$

Or

- $(0.0015^2 + 0.0005^2 + 0.007^2) * 200,000^2/100 = 20,600$

**Systematic error of metal buttons**

- $(0.0010^2 + 0.0006^2 + 0.0045^2) * 200,000^2 = 864,400 \text{ grams}^2$

# Activity 1

---

## Random error of solid waste

- $0.1^2 * (1,100^2 + 1,100^2 + 1,100^2) = 36,300 \text{ grams}^2$

Or

- $0.1^2 * (3,300^2/3) = 36,300 \text{ grams}^2$

## Systematic error of solid waste

- $0.25^2 * 3,300^2 = 680,625$

# Activity 1

---

Component	Random (grams <sup>2</sup> )	Systematic (grams <sup>2</sup> )
Nitrate	1,790,328	1,795,500
Oxide	6,903	55,908
NDA	979,531	61,256
Buttons	20,600	864,400
Waste Oxide	36,300	680,625
Total	2,833,662	3,457,689

Total Variance:  $2,833,662 + 3,457,689 = 6,291,351$  gram<sup>2</sup>  
SEID =  $\text{sqrt}(6,291,351) = 2,508$  grams  
LEID = LEMUF =  $2 * 2,508 = 5,016$  grams

---

## Inventory Difference Assessment – Activity 2

---

### Effects of Various Types of Errors on the Inventory Difference (ID)

1. Suppose the measurement of the discard stream (4) of liquid waste from the recovery material balance area (MBA) overestimates the actual amount of material discarded (for example, the actual amount is 10 grams and the measured value is 30 grams). What will this do to the ID in the recovery MBA?

---

---

---

---

2. Suppose the measurement of recovered oxide (9) from the recovery MBA to the reduction MBA overestimates the actual amount of material. What will this do to the ID in the two MBAs?

---

---

---

---

3. Suppose there is a tank of material in the reduction MBA whose content is overestimated at the June 30 inventory. What effect does this have on the reduction MBA June ID (the ID computed for the period June 1–30) and the July ID?

---

---

---

---

4. A solid deposit forms on the walls of a tank in the reduction MBA in June; such a deposit will not be measured by the inventory on June 30 and is not known to have occurred. In July, the deposit dissolves and the material reenters the process stream. What will be the effect on the June and July IDs? (Similar examples occur with filter holdup)

---

---

---

---

5. Cans of the powder that is an intermediate product in the reduction MBA are measured and removed temporarily to the storage MBA during June. In August, the cans are brought back and processed in the reduction MBA. Suppose the measurement overestimates the amount of material in the cans. What will be the effect on the IDs of the storage and reduction MBAs?

---

---

---

---