Measurement Control Workshop Instructional Materials

Philip Gibbs/Brookhaven National Laboratory
Charles Harvel/Savannah River National Laboratory
John Clark/Pacific Northwest National Laboratory/Gregg
Protection Services

December 2011

BNL-106049-2011-IR

BROOKHAVEN
NATIONAL LABORATORY

a passion for discovery

U.S. DEPARTMENT OF
ENERGY

Office of
Science

BNL-106049-2011-IR

Measurement Control Workshop Instructional Materials

Philip Gibbs
Brookhaven National Laboratory

Charles Harvel
Savannah River National Laboratory

John Clark
Pacific Northwest National Laboratory / Gregg Protection Services

December 2011

**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

Definitions:

3.1 accountability: The determination of quantities of nuclear materials (NM) and current record maintenance associated with receipts; shipments; measured discards; transfers into, out of, or between material balance areas, item control areas, or both; and total material on current inventory.

3.2 accuracy: A measure of the agreement between the measured value and the true (or assigned) value. See *bias*.

3.3 assigned value: A value assigned to a standard used for calibrating and/or controlling a NM measurement device or system.

3.4 ASTM International: Formerly the acronym for the American Society for Testing and Materials; now used by the Society as its complete name.

3.5 audit: An examination of current activities to assure that they are in compliance with program policies and procedures.

3.6 bias: A systematic error that can be estimated by comparison of the sample mean of a series of measurements with a true or reference value, in which case a correction can be applied to remove the effect of the bias on the measurements.

3.7 calibration: The process of determining the numerical relationship between the observed output of a measurement system and the actual value of the characteristic being measured based upon a certified reference material.

3.8 certified reference material (CRM): A reference material that is certified for the value of one or more of its properties by a technically valid procedure and accompanied by, or traceable to, a certificate or other documentation that is issued by a certifying body.

3.9 chain of custody: A means of assuring that a sample is continually under control to prevent inadvertent or deliberate tampering from the time the sample is taken until its disposal and requiring signed receipts at each point where responsibility for the sample is transferred.
(See also *custody*.)

3.10 confirmatory measurement: A measurement made to test whether some attribute or characteristic of nuclear material is consistent with the expected response for that material when no significant change in the NM content or concentration has occurred.

3.11 control standards: Standards that are representative of the process material being measured. These standards are measured periodically in order to monitor system reliability and to estimate any bias associated with the measurements of the process material.

3.12 custody: A sample is in custody if it is either: in one's actual physical possession, in one's view after being in one's physical possession, in one's physical possession and subsequently secured so that tampering is excluded, or is kept in a secure area that is restricted to authorized personnel.

3.13 distribution:

- The relative spatial location of components of a mixture;
- A well-defined universe of possible measurements arising from a property or relationship under study.

3.14 diversion: The unauthorized removal of nuclear material from its approved use or authorized location.

3.15 documentation: The collection of records that describe the purpose, use, structure, details, and operational requirements of a program, and the performance of activities.

3.16 an estimate: The particular value yielded by a rule or method of estimating a parameter of a parent population.

3.17 homogeneous: A description of a substance that is sufficiently blended to ensure that any sample taken from it is representative of the entire substance.

3.18 Inventory difference (ID): The difference between the quantity of NM on-hand according to accounting records and the quantity of NM on-hand as determined by a physical inventory.

3.19 ISO: The acronym for the International Organization for Standardization.

3.20 limit of error (LE): The boundaries computed as the measured value plus or minus twice its standard deviation (uncertainty). Relative to the uncertainties of the measurement method, the underlying true value of the attribute being determined will lie within such limits for a specified proportion of potential measured values, that is, for approximately 0.95, or 95% of them.

3.21 machine-readable: Material (label, tag, etc.) that is capable of being read by an electronic device.

3.22 matrix: The form or composition of a material that best represents the generic physical makeup of the material with regard to impact on measurement response.

3.23 MC&A: The abbreviation for material control and accountability.

3.24 measured value: A quantitative characteristic, generally with associated uncertainty that has been determined experimentally for a given quantity of material.

3.25 measurement control: The procedures and activities used to ensure that a measurement process generates measurement results of sufficient quality for their intended use, and to determine measurement uncertainty values (or limit-of-error values).

3.26 measurement process: The determination of an attribute, e.g., element concentration, isotopic distribution, and/or bulk quantities.

3.27 NDA: The abbreviation for nondestructive assay.

3.28 net weight: The measured weight (mass) of the contents in a container as determined by subtracting the empty container weight (tare weight) from the gross weight of the container plus contents.

3.29 parameter:

- A quantity entering into the distribution of a statistic or random variable;
- The quantity being estimated.

3.30 physical inventory: A determination by physical means (visual and measurement) of the quantity of nuclear material on-hand at a specified point in time.

3.31 precision: A quantitative measure of the variability of a set of repeated measurements.

3.32 procedure: A document that specifies or describes how an activity is to be performed

3.33 qualification: Demonstration (through specific test requirements) of adequate knowledge and experience for the performance of a task

3.34 random error: The specific variation encountered in a single measurement, characterized by the random occurrence of a positive or negative deviation from the mean value of the measurement.

3.35 reference material (RM): A material or substance one or more properties sufficiently well established to be used for the calibration of an apparatus, the assessment of a measurement method, or the assignment of values to materials. Standard RM (**SRM**) is a reference material distributed and certified by the appropriate national institute for standardization.

3.36 replicate samples: Two or more samples taken independently from the same population.

3.37 shelf life: *The time that elapses before a stored material or device is rendered inoperative or unusable for its intended purpose due to age or deterioration.*

3.38 special nuclear material (SNM): U-233, uranium enriched in U-233 and/or U-235, plutonium, or any combination thereof, and any other material which, pursuant to the provisions of Section 51 of the Atomic Energy Act of 1954, as amended, has been determined to be special nuclear material, but does not include source material; it also includes any material artificially enriched by any of the foregoing, not including source material as defined by the Atomic Energy Act, Title 42, U. S. Code, Section 2002, et. seq.

3.39 standard deviation: The positive square root of the variance.

3.40 standard error (of a parameter estimate): The standard deviation of the parameter estimate.

3.41 statistical sampling: A statistically valid technique used to select elements from a population, including probability sampling, simple random sampling, systematic sampling, stratified sampling, and cluster sampling.

3.42 systematic error: The mean that would result from an infinite number of measurements of the same measurand carried out under the same conditions of measurement minus a true value of the measurand.

3.43 tare: The weight of a container or wrapper that is deducted from the gross weight to obtain the net weight.

3.44 traceability: The ability to relate individual measurement results to national standards (primary standards) or nationally accepted measurement systems through an unbroken chain of comparisons.

3.45 uncertainty: A concept employed to describe the inability of a measurement process to measure the true value exactly.

3.46 variance: A measure of the dispersion of a set of results.

3.47 variance propagation: The determination of the value to be assigned as the uncertainty of a given quantity using mathematical formulas for the combination of uncertainty components. Variance propagation involves many considerations, and the computational formulas for computing the uncertainty depend upon the functional relationships of the measurement parameters involved.

3.48 verification measurement: A quantitative measurement to verify an existing measured value as previously recorded.

3.49 verisimilitude: A concept applied to standards that represent the material to be analyzed, characterized, or tested as closely as necessary.

ABBREVIATIONS AND ACRONYMNS:

ANSI -- American National Standards Institute
BIMP --International Bureau of Weights and Measures
CALEX -- Calorimetry Exchange Program
C -- Celsius
CY -- Calendar year, January to December
DA -- Destructive Analysis
D&G -- Davies and Gray Titration
DOE --(United States) Department of Energy
DU -- Depleted Uranium ($^{235}\text{U} < 0.3 \text{ wt } \%$)
GUM --Guide to the Expression of Uncertainty in Measurement
GSMS --Gas Source Mass Spectrometry
HEU -- High-enriched uranium (^{235}U 20 wt %)
IAEA -- International Atomic Energy Agency
ICPMS -- Inductively Coupled Plasma Mass Spectrometry
ID -- Inventory Difference
IDMS -- Isotope Dilution Mass Spectrometry
INMM -- Institute of Nuclear Materials Management
ISO -- International Organization for Standardization
ITV -- International Target Value
LE -- Limit of Error
LEID -- Limit of Error on Inventory Difference
LEU -- Low-enriched uranium ($1 \text{ wt } \% < ^{235}\text{U} < 20 \text{ wt } \%$)
MBR -- Material Balance Report
MBA -- Material Balance Area
MCP -- Measurement Control Program
ME -- Measurement Evaluation
MUF -- Material Unaccounted For
NBL -- New Brunswick Laboratory
NIST -- National Institute of Standards and Technology
NMCC -- Nuclear Material Control Center
NRC -- Nuclear Regulatory Commission
QC -- Quality Control
PMAP -- Process Measurement Assurance Program
RD -- Relative deviation (expressed in percent); also written as % RD
SC -- Office of Science
SD -- Standard deviation
SME -- Safeguards Measurement Evaluation
SMES -- Safeguards Measurement Evaluation System
SPC -- Statistical Process Control
TUR -- Test Uncertainty Ratio
TIMS -- Thermal Ionization Mass Spectrometry
UF₆ -- Uranium hexafluoride
UNH -- Uranyl nitrate hydrate (solution)
UO₂ -- Uranium dioxide **UO₃** Uranium trioxide **U₃O₈** Uranium (mixed) oxide
u(c) -- Combined Uncertainty
u(r) -- Random component of uncertainty (indicative of precision) of ITV
u(s) -- Systematic component of uncertainty (indicative of bias) of ITV
VP -- Variance Propagation
VIM -- International Vocabulary of basic and general terms in Metrology
XRF -- X-Ray Fluorescence

About the Instructors

John Clark currently works as a consultant, with 50 years of work experience in the nuclear and chemistry fields as chemist, laboratory supervisor, quality assurance engineer, manager and senior fellow technical advisor. His work experience includes special nuclear materials and chemical standards preparation for calibration, training & testing, QC and inter laboratory sample exchange programs; developing and managing measurement control programs; quality assurance program development and auditing; measurement control manager for MC&A in safeguards and security; and physical standards calibration and tolerance testing in the field of metrology. John has over 30 publications and/or papers written for national and international technical organizations and participated in writing standards for these groups. As a metrologist and consultant he has helped educate chemists, scientists and engineers in methods for determining and managing measurement errors/uncertainty.

Phil Gibbs has 28 years of project management and subject matter expert experience in Nuclear Safeguards with emphasis in Material Control and Accountability (MC&A) for the U.S. Department of Energy (DOE) domestic and international programs. Mr. Gibbs currently is working as the Project Lead and MC&A Subject Matter Expert (SME) for the U.S. MPC&A program. Prior to moving to international work, Mr. Gibbs served as the Local Area Network Material Accounting System (LANMAS) Project Manager managing the development and implementation of LANMAS, a standardized inventory and control system for nuclear components and inventories among DOE contractors. At the U.S. DOE Savannah River Site, he worked as an MC&A Manager for Accounting, Technical Support, Procedures, and Training. Prior to that time, Mr. Gibbs worked as a measurement control engineer in the area of mass measurements and process tank calibrations.

Chuck Harvel is a Fellow Scientist at the DOE Savannah River National Laboratory. He has over 20 years experience with MC&A statistical and software development applications. He has been involved with advisory and technical work in the areas of measurement method qualification and uncertainty estimation for tanks, scales, hydride beds and NDA and analytical methods; development of guidance for accepting measurement methods as qualified for accountability measurements; calculation of limits-of-error (LOEs) and combined limits-of-error (CLOES) for material receipts and shipments; development of guidance for resolving shipper/receiver differences; development of limits-of-error for inventory difference (LEID) models for several material processes; development of guidance for resolving ID problems; technical consulting regarding MC&A related statistical applications. Chuck has over 30 years experience with software design and development applications. His work in this area includes the design, development and maintenance of software systems for automating the calculation of LEIDs. Chuck has a BS in Mathematics and Computer Science from Eastern New Mexico University (1973), and an MS in Applied Statistics and Computer Science from the University of New Mexico (1976).

MEASUREMENT CONTROL

TRAINING COURSE

Course Objectives

The objectives of this course are to identify, study, and discuss best measurement practices for the accountability of nuclear material. This will be accomplished 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 will be used to demonstrate the various measurement concepts discussed during the lecture/discussion sessions.

Attendees

Participants attending this workshop should currently, or in the near future, be responsible for metrology, accounting, and statistical analysis of nuclear materials. The ideal size of the class is 10 - 15 participants.

Course Length

This is a five-day workshop consisting of lectures and hands-on exercises.

Dates of Implementation

December 12-16, 2011 at the CIAE in Beijing, China.

Equipment required

General

- Student books (CIAE)
- 2 Flip charts or dry erase board and colored markers (CIAE)
- Laptop computers: one per group of 4-5 students (CIAE)
- Flash drive or CD pre-loaded with data files required for exercises-one per group of 4-5 students (CIAE)
 - measurement qualification exercise.xls,
 - balance linearity exercise.xls,
 - balance repeatability exercise.xls,
 - pipette exercise.xls
- tweezers or tongs (one per each mass standard set) (USPT)
- computer and data files (balance.xls) as listed above
- printer (CIAE)

NDA exercise

- NDA equipment (CIAE)

Pipette exercise

- Laptop computer and data file (pipette.xls) as listed above
- 1 one gram and 1-ten gram calibrated E2 class mass standards (CIAE)
- cotton or insulated gloves – one per student (CIAE)
- Tweezers or tongs (one per each mass standard set) (USPT)
- One barometer with calibration certificates or manufacturer specifications (+ or - 1 %) (CIAE)
- Two thermometers (at least one capable of reading water) with readability to tenth of a degree (0.1C) with calibration certificates (CIAE)
- Humidity meter with calibration certificate or manufacturer specifications (CIAE)
- 5- 1 ml fixed volume air displaced pipettes with calibration certificates and 5 boxes of disposable tips (CIAE)
- Two liters of water (CIAE)
- Five 50 ml volumetric flask – glass (CIAE)
- Five 250 ml bottles- any glass or plastic bottle/beaker with big opening (CIAE)

Height exercise

- Tape measure (CIAE and USPT)
- Ruler (USPT)
- Scotch tape (USPT)
- Plain paper (CIAE)

Measurement method qualification exercise

- Laptops and data files (listed above)
- Microsoft Excel support person; to assist with data plots and ANOVA (analysis of variance) application (CIAE and USPT)

Balance exercise

- 1 per group: analytical balances (four decimal places minimum (0.1 mg), at least 100 gram capacity) (CIAE)
- 4-5 1, 10, 50 and 100 gram weights (USPT)
- cotton or insulated gloves- one per student (CIAE)

MEASUREMENT CONTROL TRAINING COURSE AGENDA

<i>Time</i>	<i>Topic</i>	<i>Presenter</i>
Monday		
8:00	USPT arrival and equipment check	USPT/CIAE staff
9:00-9:30	Introductions and Workshop Opening	All
9:30-10:30	Module 1 Measurement Control Program Workshop Objectives and Overview	Gibbs
10:30-10:45	<i>Break</i>	
10:45-11:45	Module 1 Exercise: Height Measurements	Clark
11:45-12:30	Module 2 Measurement Method Qualification	Harvel
12:30-13:30	<i>Lunch</i>	
13:00-14:30	Module 2 (continued) Module 2 Exercise	Harvel
14:30-14:45	<i>Break</i>	
14:45- 16:00	Module 3 Sampling Variability: Solids and Oxides	Harvel
Tuesday		
9:00-10:30	Module 4 Proficiency Training & Testing Program and Sample Exchange Programs	Clark
10:30-10:45	<i>Break</i>	
10:45-11:45	Module 5 Accreditation	CIAE
11:45-12:30	Module 6 Control Charts and Measurement Control	Gibbs
12:30-13:30	<i>Lunch</i>	
13:30-15:00	Module 6 Control Charts and Measurement Control (continued)	Harvel
15:00-15:15	<i>Break</i>	
15:15-16:15	Module 7 Calibration	Harvel
Wednesday		
9:00-10:00	Module 8 Balance Measurement Control Program	Clark
10:00-10:15	<i>Break</i>	
10:15-12:00	Module 8 Exercise: Balance Calibration	Clark
12:00-12:30	Module 9 Tank Sampling and Mixing	Harvel
12:30-13:30	<i>Lunch</i>	
13:30-15:00	Module 10 Analytical Chemistry Measurement Control	Clark
15:00-15:15	<i>Break</i>	
15:15-16:15	Module 10 Exercise: Pipette Validation	Clark
Thursday		
9:00-9:30	Module 11 Case Study: Uranium Standards Preparation	Clark
9:30-10:30	Module 12 NDA presentation	CIAE
10:30-10:45	<i>Break</i>	
10:45-12:30	Module 12 Exercise: NDA exercise	CIAE
12:30-13:30	<i>Lunch</i>	
13:30-16:30	Module 13 Inventory Difference Assessment Activity 1 and 2	Harvel/Gibbs
Friday		
9:00-12:00	Module 13 Inventory Difference Assessment (continued)	Harvel/Gibbs
12:00-13:00	<i>Lunch</i>	
13:00-14:00	Module 13 Conclusion	Harvel/Gibbs
14:00-15:00	Course wrap-up: Student Feedback and Presentation of Certificates	All

MEASUREMENT CONTROL COURSE

STUDENT CRITIQUE SHEET

Name: (optional) _____ Date: _____

We are committed to obtaining information on the quality of the learning experience and will actively encourage participant responses. Please help us improve our training and materials by answering the following questions. Your reactions, comments, and suggestions are needed and appreciated.

Part I - Demographics

1. Identify your responsibilities (check all that apply).

- ☐ Material Control and Accounting ☐ Manager
☐ Measurement Professional ☐ Other _____

2. Before you attended this training, what level of knowledge did you have in the subject matter?

- ☐ Expert-level knowledge – *I had a complete understanding.*
☐ Working-level knowledge – *I had a good understanding.*
☐ Familiarity-level knowledge – *I only had an understanding of the general concept(s).*
☐ Little or no knowledge

Part II - Training

Please use the additional comments section of this form to provide comments and suggestions about items that you have strong opinions, either positive or negative. Indicate the number of each item to which you are referring. Your constructive feedback is appreciated.

Please rate the following:

	Not Applicable	Poor	Fair	Good	Very Good	Excellent
3. How well the training met my current/future job needs.	☐	1	2	3	4	5
4. Usefulness of the student materials (e.g., notebook and handouts) during the training.	☐	1	2	3	4	5
5. Training aides (e.g., slides, videos, models).	☐	1	2	3	4	5
6. Materials and equipment	☐	1	2	3	4	5
7. Clarity and organization (well structured and easy to follow) of the training.	☐	1	2	3	4	5
8. Length of training	☐	1	2	3	4	5
9. Pace of the training	☐	1	2	3	4	5
10. Sequence of instruction	☐	1	2	3	4	5

11. Exercises/activities reinforced training
12. Organization and preparation of the Instructor(s)
13. Achievement of program goals
14. Adequacy of training facilities
15. Attention to safety
16. Overall quality of the training

[illegible]

17. The material covered was interesting to me.
18. I have learned new skills and techniques in this field.
19. My understanding of concepts and principles in the subject(s) has improved.
20. The instructors explained the relevance of the material to my job.

Not Applicable	Yes	No
☐	☐	☐
☐	☐	☐
☐	☐	☐
☐	☐	☐

21. Please provide constructive comments on the instructor(s) (subject knowledge, teaching ability, and skill at working with students):

This image shows a full page of white paper with horizontal blue or grey ruling lines. The lines are evenly spaced and run across the width of the page, providing a template for writing. There are no margins, text, or other markings on the page.

22. What lessons/parts of the training were most useful?

23. How could this training be improved?

24. Additional comments: *(use back of this page if more room is needed.)*

References

1. ANSI/INMM N15.51-2007 for Methods of Nuclear Materials Control --Measurement Control Program – Nuclear Materials –Analytical Chemistry Laboratory
2. ANSI/INMM N15.41-1984 American National Standard for nuclear facilities – derivation of measurement control programs – general principles.
3. ISO/IEC 17025,"General requirements for the Competence of Testing and Calibration Laboratories", International Organization for Standardization, 2005
4. NIST Technical Note 1297, 1994 Edition, *Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results*, Taylor & Kuyatt
5. BIPM - JCGM 200:2008 – *International vocabulary of basic and general terms in metrology*, (VIM) Third Ed. 2008.
6. BIPM – JCGM 100:2008 “ Evaluation of measurement data -- Guide to the expression of uncertainty in measurements. (GUM 1995 with minor corrections)
7. BIPM – JCGM 1004:2009 “Evaluation of measurement data – An introduction to the “Guide to the expression uncertainty in measurements” and related documents. July 2009
8. NISTIR 6919, *Recommended Guide for Determining and Reporting Uncertainties from Balances and Scales*. 2002.
9. NISTIR 6969, *Selected Laboratory and Measurement Practices and Procedures to Support basic Mass Calibrations*. 2003.
10. IAEA STR – 368 “International Target Values for Measurement Uncertainties in Safeguarding Nuclear Materials”, Vienna, November 2010 (ITVs)
11. EURACHEM / CITAC Guide CG 4, *Quantifying Uncertainty in Analytical Measurement*, Second edition 2000 ISBN 0 948926 15 5
12. International Laboratory Accreditation Cooperation (ILAC) Website <http://www.ilac.org/home.html>
13. OIML R 76-2 International Recommendation “Non-automatic weighing instruments Part 2: Test report format”, Edition 2007 (E)
14. OIML R111-1-E, International Recommendation, “Weights of classes E 1, E 2, F 1, F 2, M 1, M 1–2, M 2, M 2–3 and M 3 Part 1: Metrological and technical requirements”, 2004, <http://www.oiml.org/publications/R/R111-1-e04.pdf>
15. J. P. Clark & C. H. Jackson, "Establishing the Traceability of a Uranyl Nitrate Solution to a Standard Reference Material", AGNS-10-2, Proceedings of the American Nuclear Society Meeting, Williamsburg, VA, 1978.
16. S. S. Yamamura, J. P. Clark, et al, NUREG-0253, Preparation of Working Calibration Test Materials: Uranyl Nitrate Solution, 1977
17. Troemner's “Proper Pipetting Techniques & Tips”, <http://www.troemner.com/pdf/ProperPipettingTechniques.pdf>
18. Rainin Instrument Inc. “Procedure for Evaluating Accuracy and Precision of Rainin Pipettes”, http://www.pipette.com/Support/OnlineLecture/Rainin_PipetteAccuracyandPrecision.pdf
19. ISO 8655-2 “Piston-operated volumetric apparatus – Part 2: Piston Pipettes
20. ISO/TR 20461:2000(E) “Determination of uncertainty for volume measurements using the gravimetric method.
21. DOE-STD-1194-2011 “Nuclear Material Control and Accountability”, DOE Standard, June 2011
22. DOE Order 474.2, “Nuclear Material Control and Accountability” Approved: 6-27-2011
23. Jaech, J. L., *Statistical Methods in Nuclear Material Control*, Technical Information Center, United States Atomic Energy Commission, 1973
24. Smith, P. L., *A Primer for Sampling Solids, Liquids, and Gases: Based on the Seven Sampling Errors of Pierre Gy*, Society for Industrial and Applied Mathematics (SIAM), 2001
25. Pitard, F. F., *Pierre Gy's Sampling Theory and Sampling Practice, Volume I Heterogeneity and Sampling*, CRC Press, Inc., 1992
26. Pitard, F. F., *Pierre Gy's Sampling Theory and Sampling Practice, Volume II Sampling Correctness and Sampling Practice*, CRC Press, Inc., 1989
27. Taylor, John Keenan, “Quality Assurance of Chemical Measurements”, Lewis Publishers, 1987.
28. Paper on “Assignment of Values to In-House Standard Uf6 Cylinders Using the Fast 4-1 Series” by Cindy Murdock, Portsmouth, Ohio, 1988
29. Ryan, T. P., *Statistical Methods for Quality Improvement*, Wiley, NY.
30. ISBN 0-948926-08-2, “Quantifying Uncertainty in Analytical Measurements, Eurachem English Publication 1995
31. CITAC Guide 1 "International Guide to Quality in Analytical Chemistry--An Aid to Accreditation", ISBN 0948926 09 0 English First Edition 1995.

2/68

21.

The lecturer has strong knowledge in the profession and is a professional teacher and trainer but has yet to adjust to the characteristics of Chinese students.

22.

I think the valuation of inventory differences is most useful of all, but it would be nice to have more real world application.

3/68

23.

The training can focus more on the current processes and regulations in the United States, and it would be best to analyze and explain the reasoning and goals of these processes and regulations.

6/68

21.

(1) The lecturing was already very good. I have just one opinion that I wish the lecturer has had some understanding on the NDA plan and the course would cover analyses of nuclear materials in China.

(2) I hope the lecturer would systematically explain methods, such as the uranium analysis by droppers, as real examples to evaluate the uncertainty.

22.

A lot of the professional knowledge covered was familiar to me prior to the course, but the details provided by the lecturer was the key to my learning such as the reason some samples need to be analyzed twice in the process of collecting samples. These are details easily overlooked normally.

23.

(1) Insist on the training of professional analysts.

(2) Emphasize the details in the practice of analyses.

(3) The materials should tailor more toward China. For example: "uncertainty" best to be translated as "the degree of uncertain" to be easily accepted.

10/68

21.

Use more practical examples.

12/68

21.

I hope there would be some simpler professional knowledge and that the lecturer could have more interactions with students to combine theory and practice.

22.

Sampling and measuring parts are more practical. Valuation in inventory differences is the most useful part.

23.

Continue strengthening training, and then problems encountered in different times can be solved in a timely manner.

16/68

22.

Practice of standard control method and practical exercises.

23.

Should have more exercises and case analyses.

20/68

21.

These kinds of classes have relatively high requirements in the mathematical and science knowledge of the students.

These classes are very professional.

I hope the classes can go from easy to in depth, covers both practicalities and theories, and perhaps provide some more actual participation opportunities.

More basic knowledge introduction

22.

NDA technology introduction

Inventory differences

Measurement errors

23.

More practical applications. The class requires fundamental math skills.

Training on general knowledge

I hope the course covers the basic mathematical skills required.

Also, more real world applications.

28/68

The performance of the lecturer can be improved. There should be more interaction in classes, and not just require ...

22.

Nuclear materials controls and calculations

23.

Class should have more materials, more case studies.

24.

The Chinese materials of the class should be proofread, and the errors need to be corrected prior to the course.

32/68

21.

The professional knowledge, lecturing ability, and interaction skills with students of the lecturer are superior.

22.

The contents covering laboratory certification, sampling, and measuring methods; contents covering Inventory differences calculating and judging

23.

I suggest there be more opportunities for students to express their opinions so the students can combine the professional knowledge with their own work content and share through feedbacks!

Also, there should be lecturing and training on the prerequisites and applications of the subjects this training covered.

24.

If the conditions allow, I hope I can have a copy of the audio and video files of the course. I also hope the course would focus more on exercises and experiments.

I hope this training like this are held more often.

36/68

21.

All the lectures are experts in this field, and they all have a lot of experience in this field. Also, they emphasize on interaction with students and keep a light and lively classroom atmosphere. However, many of the students have relatively weak understanding in professional knowledge and have some difficulty understanding some of the professional issues. Take the graphs as example, I hope the lecturers can explain more in detail the different axis's before proceeding to questions and answers may lead to better results. Also, the case studies can have more detailed analyses to improve understanding and application of the concepts and theories.

22.

(1) The evaluation of uncertainty, and where the errors could occur.

(2) Things to take note of when taking samples, preparation of standards of analyses

23.

The course can improve by increasing the depth of the training to make the contents of the training more in-depth.

40/68

21.

Does not too closely tie with the practical aspects of our work.

22.

"Inventory difference is not 0" could possibly be used on work in the future.

23.

I have no idea, either.

48/68

21.

The lecturers have a lot of experience, comfortable and spontaneous lecturing skills, and interactive styles in teaching. These are worth learning for us, and these are all lacking in Chinese lecturers. The humorous language and facial expression attracts everyone's attention. Although, to loosen up the mood of the classroom and encourage a better grasp of the knowledge, the lecturers should choose some students to help explain the exercise or put students in groups to discuss so that everyone can understand the contents of the training better.

22.

I feel that the variance of the sampling, as in solid body and oxide, the control plan of measurement by balances, the measurement and controls of chemical analysis, control graphs, measurement controls, and the inventory sampling of NDA mentioned in the training are all very useful. These are all necessary skills I need for work. The training we had this time helped me understand more deeply the portions I need for work, and can effectively improve my job performance.

23.

With the premise of not increasing content of the training materials, the depth of the training should be increased, and the length of the training should be as well, so the students and the lecturers can have more effective communications.

24.

There should be more training like this one to improve the quality nuclear materials calculation workers in China. Also, there should be evaluations or examinations included in the course and certificates can be awarded according to the results of such evaluations or examinations.

52/68

21.

Can explain more in depth by using one specific case.

22.

Sampling, exchange of samples, transmission of discrepancies are the most useful areas.

23.

Systematically introduce ID evaluation cases, including error calculation in the past, zoning, and ID evaluation system.

24.

Could there be more site visits to countries with advanced technologies such as the United States, Russia, or European Union countries?

56/68

21.

I would recommend future trainings to provide knowledge on MuF evaluation, introduce the key measurement points in the MuF evaluation system and the choice of analytical methods, training on the relevant transmission formulae and methods regarding errors, and introduce NDA measurement's international standards and technologies. If conditions allowed, could we have site visits to more advanced NDA technologies and site application in foreign countries.

22.

Quality control and ID evaluation.

23.

Lecturing should not be the job of just the lecturer. It is best that different offices can combine their actual situations and focus the training on different offices' common problems on nuclear materials calculation. During the training process, there should be time for students and lecturers to communicate.

60/68

21.

The lecturer has sufficient professional knowledge in nuclear material and is skillful in combining the professional knowledge with real life application. The sequence of which the lecturer arranges the materials is adequate, and it combines theory and practice effectively to ... (not legible). The lecturing style is lively and can encourage students to interact with the lecturers. The translation is also good.

22.

Sampling, measurement plans, and evaluation of inventory differences.

62/68

21.

Include more practical methods in chemical analytical methods and calculation.

22.

Quality control, sampling methods.

64/68

21.

The lecturer has great work ethic, and is skilled in teaching. The course would be even more perfect if the materials are more detailed.

22.

Unit 10. Analyzing Chemical Measurement Controls

23.

Language barrier, lecturing and expression caused problems at some point.

67/68

Unit 13. Evaluation of Inventory Differences

23.

Before sending the notification for the training, students should be given the opportunity to understand or familiarize the relevant mathematical or professional knowledge to make the training more effective.

24.

The interpreters should know the professional materials better so that the communication, understanding, and interaction could be better.

Module 1 - Exercise

Height Measurement Exercise

Objectives

- **To see measurements are comparisons of unknowns to reference standards**
- **To understand measurements have uncertainty**
- **To understand that reference standards also have uncertainty**
- **To understand measurements need uncertainty estimates with specified confidence intervals to have value**

Exercise Module 1 - 2

Measurement Basics

- Measurement is the process of determining the value of some quantity in terms of a standard unit
- It involves the comparison of a known to an unknown
- It has uncertainty and the "true value" is never known exactly
- In general, the result of measurement is only an approximation or estimate of the "true value"
- Its uncertainty is always more than the uncertainty of the calibration standards

Exercise Module 1 - 3

Height Estimation Work Sheet

Your Name:		Your Height:		
Line	Subject Number	1	2	3
	Subject Name			
1	First estimate of height*			
2	Second estimate of height**			
3	Third estimate of height***			
4	Bias (3rd estimate - 2nd estimate)			
	Estimate range containing true height (uncertainty)			
5	State probability level; 67 %, 95% or 99.7%			
6	Your bet that line 5 includes "true values"			
7	Final measurement with tape measure #			
8	Calculate corrected "bias" (Line 8-Line 3)			
9				
10	Win if within range or lose if outside			

* your height is compared against others individually
 ** Your estimates are compared against each other
 *** Your comparisons against a known reference standard
 # A calibrated standard is used to measure the heights

Exercise Module 1 - 4

First Measurement

- **Write your name & height on worksheet**
- **This is a measurement exercise**
- **Measurements are comparisons of a known to an unknown**
- **Estimate each person's height as they stand using your height for the comparison**
- **Write their name & your estimate under first measurement column for each person on line 1**

Exercise Module 1 - 5

Second Measurement

- **All 3 people that we are measuring will stand together in the front of the room**
- **Make your second estimate of each person's height and record it under the second measurement: line 2**
- **If you are satisfied with your first estimate write it down again**

Exercise Module 1 - 6

Third Measurement

- A fourth person will join the first 3 and tell you his height
- Compare the heights of 3 people to the known height of the 4th person
- Record your new estimates of their true heights on line 3 of the worksheet

Exercise Module 1 - 7

Bias Correction

- Measurements usually have random and systematic error. If the systematic error is often called measurement bias
- Subtract the estimates on line 2 from those on line 3 and record the differences on line 4
- Examine the 3 values and if they all have the same sign and small variation between the values, you may be able to estimate the bias making measurements using your height as the standard

Exercise Module 1 - 8

Estimate Your Measurement's Uncertainty

- Measurement Uncertainty is a concept employed to describe the inability of a measurement process to exactly measure the correct value:
- It is an estimate of the range of values about the measured value in that includes the true value.
- Estimate the uncertainty (range or +/- value) of each of your measurements and write them on line 5
- Example: +/- 2 cm

Exercise Module 1 - 9

Probability & Confidence Levels

- "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 to provide statistical predictability"

John Keenan Taylor "QA of Chemical Measurements"

Exercise Module 1 - 10

Probability and Risks

- On line 6 write the confidence level you assign to the probability that the true values of your "measurements" are within your uncertainty ranges
- How much are you willing to "bet" or wager that your measurements are within your uncertainty range?
- Of the two quarters you were given, decide if you will bet 0, 1 or 2 of them that all of your measurements' biases are within the +/- uncertainty estimates
- Record decision on line 7

Exercise Module 1 - 11

Fourth and Final Measurement

- A calibrated tape measure will be used to make the final measurement of our 3 unknowns
- Each subject's height will be compared to the scale on the tape measure and reported to the group
- Record the measured values on line 8

Exercise Module 1 - 12

Evaluation of Biases & Uncertainties

- Evaluate the accuracy of your measurements against the final values by subtracting the results of line 3 from those on line 8 and record these bias estimates on line 9
- How accurate were your measurements?
 - Are the biases smaller than the uncertainty estimates?
 - Determine the out come of your bet or wager
 - Settle up on the bets

Exercise Module 1 - 13

Discussion Questions

- What variables contributed to the uncertainty of your measurement estimates?
- What may have caused the “bias” in your estimates?
- How can the uncertainty of the last measurement be reduced?
- Who had the smallest uncertainty estimates, which contained the true values?
- Who had the smallest bias estimates? Why?
- Were these measurements “fit for purpose?”

Exercise Module 1 - 14

Summary:

- **Measurements:**
 - Involve the comparison of a known to an unknown (measured value is compared to an expected value).
 - Have uncertainty and the "true value" is never known exactly.
 - In general, the result of measurement is only an approximation or estimate of the "true value."
 - Are of little value, unless they have uncertainty estimates & confidence levels.

Exercise Module 1 - 15

Exercise 1

Height Measurement 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:

+ .75 hours completing exercise
+ .25 hours in large group discussion
1.0 hours total

Materials needed:

1. Work sheets for each participant
2. 3 individuals with varying heights to serve as volunteer measurement objects
3. 1 individual to serve as the working standard
4. 1 calibrated length measurement standard (tape measure)
5. 1 ruler
6. 1 marker or pencil
7. 1 roll of tape
8. Several pieces of plain paper

Instructions:

1. Write your height and name on the worksheet.
2. Write the name and your 1st estimated measurement for each person's height on the worksheet in the 1st row marked "First Estimate" as they sequentially stand and give their name.
3. After all 3 individuals stand together in the front of the room; make your second estimated measurement of each person's height and record it in the row 2, marked "second estimate". (If you are confident of your first estimate, then write it down again for your second estimate.)
4. After a fourth person joins the first 3 and states his height with a +/- uncertainty. (It should be in the same units being used by the class, if not, convert it.) Compare the heights of the 3 people to the

known height of the 4th person. Record these estimated measurements on the worksheet on line 3 marked “Third Estimate.”

5. If your 3rd estimate is different from your second estimate, you made a “bias” correction after you had a “working standard” to use for your third “measurement.” Determine the difference between the second and third “measurements” by subtracting the 2nd estimate from the 3rd estimate and record the results on line 4, marked Bias. These are the “bias” corrections you applied.
6. Since you do not know the “true height” of the people you have “measured” there is uncertainty in your measurements. Estimate a +/- interval of maximum and minimum heights for each person that should contain their “true heights.” These ranges will be the Measurement Uncertainty estimates for your final measurements. For example +/- 2 cm. Record these uncertainty estimates on line 5.
7. How much confidence do you have in the “uncertainty” estimates listed in step 8? Select one of the following probabilities: 67%, 95%, 99.7% and write answer on line 6
8. On line 6, enter how much of your money you are willing to bet, that all three of your “uncertainty estimates” contain the true heights? (Your confidence interval should be considered.)
9. Use a calibrated tape measure to measure the heights of the 3 people.
 - a. (Tape enough white papers on the wall to cover the range of the subject’s heights.)
 - b. Have each person stand with their back against the wall.
 - c. Place the ruler or paint stick level on their head and touch the wall.
 - d. Draw a line on the wall and write the person’s name beside it.
 - e. With the end of the tape on the floor, extend it to one of the marks and read the corresponding mark from the scale on the ruler. Repeat for the other two people.
10. Record these measured values on Line 8 for each person.
11. Calculate the bias of each of your estimates in (Line 4 – Line 8) and record them on Line 9.
12. Evaluate the accuracy of your measurements by seeing if the values in Line 9 are < the corresponding uncertainty estimates in line 5. If all are within the +/- range you WIN, if not you loose your bet.
13. Discuss the following:
 - a. What variables contributed to the uncertainty of your measurement estimates?
 - b. What may have caused the “bias” in your estimates?
 - c. How can the uncertainty of the last measurement be reduced?
 - d. Who had the smallest uncertainty estimates, which contained the true values?
 - e. Who had the smallest bias estimates? Why?
 - f. Were these measurements “fit for purpose”?

Your Name:		Your Height:		
Line				
	Subject's number	1	2	3
	Subject's name			
1	First estimate of height*			
2	Second estimate of height**			
3	Third estimate of height***			
4	Bias (3rd estimate - 2nd estimate)			
5	Estimate range containing true height			
6	State probability level; 67 %, 95% or 99.7%			
7	Your bet that line 5 includes "true values"			
8	Final measurement with tape measure #			
9	Calculate corrected "bias"(Line 8-Line 3)			
10	Win if within range or lose if outside			
<p>* Your height is compared against others individually</p> <p>** Your estimates are compared against each other</p> <p>*** Your comparisons against a known reference standard</p> <p># A calibrated standard is used to measure the heights</p>				

Module 2 Exercise: Measurement Method Qualification

Session Objectives:

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

1. Plan the method qualification process
2. Produce a qualification planning document
3. Collect the measurement data
4. Analyze the data (estimate uncertainties)
5. Produce a qualification document

Estimated Time:

1.0 hour in subgroup
+0.5 hours in large group discussion
1.5 hours total

Materials needed:

1. 1 computer with Microsoft Excel for each group of 5 students.
2. Spreadsheet support person

Instructions:

1. Complete discussion topics
2. Enter data into a spreadsheet
3. Produce a plot of the data
4. Perform an ANOVA using the spreadsheet
5. Discuss the results

Listing of HBL AWCC Pu Qualification Data

File #	Standard Id	True Pu mass (g)	Measured Pu mass (g)	Relative Difference (g)
162K0410	SGB-30	29.989	36.2	0.207
162I1040	SGB-30	29.989	33.8	0.127
162M1846	SGB-30	29.989	35.5	0.184
162N2438	SGB-30	29.989	35.3	0.177
162O3955	SGB-30	29.989	34.8	0.160
15UI3558	SGB-100	99.964	99.7	-0.003
15UJ4120	SGB-100	99.964	89.6	-0.104
15UM0935	SGB-100	99.964	81.7	-0.183
15UO2454	SGB-100	99.964	88.2	-0.118
15U2943	SGB-100	99.964	93.7	-0.063
15VO5519	SGB-200	199.927	232.7	0.164
15VQ0230	SGB-200	199.927	176.1	-0.119
161J0906	SGB-200	199.927	184.5	-0.077
161K3809	SGB-200	199.927	207.1	0.036
161O0600	SGB-200	199.927	213	0.065

Plot of Relative Differences from HBL AWCC Pu Qualification Data

ANOVA Results for HBL AWCC Calibration and Random Uncertainty Analysis

The GLM Procedure

Class Level Information

Class	Levels	Values
std_id	3	SGB-100 SGB-200 SGB-30

Number of observations 15

The GLM Procedure

Dependent Variable: reldiff

Source Pr > F	DF	Sum of Squares	Mean Square	F Value
Model 0.0006	2	0.17757951	0.08878975	14.59
Error	12	0.07304037	0.00608670	
Corrected Total	14	0.25061987		

R-Square	Coeff Var	Root MSE	reldiff Mean
0.708561	257.2216	0.078017	0.030331

Source Pr > F	DF	Type I SS	Mean Square	F Value
std_id 0.0006	2	0.17757951	0.08878975	14.59

Source Pr > F	DF	Type III SS	Mean Square	F Value
std_id 0.0006	2	0.17757951	0.08878975	14.59

The GLM Procedure

Source	Type III Expected Mean Square
std_id	Var(Error) + 5 Var(std_id)

HBL AWCC Pu Uncertainty Components

Bias	Bias Uncertainty	Calibration Uncertainty	Random Uncertainty
3.03%	$\pm 7.69\%$	$\pm 12.86\%$	$\pm 7.80\%$

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. Accreditation by Recognized Accrediting Body
10. Proficiency Testing Programs

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

Vocabulary – Primary Source

- International vocabulary of metrology –Basic and general concepts and associated terms (VIM)
- Published by the International Bureau of Weights and Measures (BIPM)
- The BIPM's Joint Committee for Guides in Metrology (JCGM) has two working groups (WG)
- JCGM/WG1 worked on the "Guide to the Expression of Uncertainty in measurement" GUM
- JCGM/WG2 worked on the VIM
 - It is written in English and French
 - JCGM 200:2008 is the 3rd edition that will be quoted.
 - Definitions are numbered. Those in parentheses are 2nd edition

Module 1 - 20

Metrology VIM 2.2 (2.2)

- **Science of measurement and its application**
 - NOTE: Metrology includes all theoretical and practical aspects of measurement, whatever the measurement uncertainty and field of application
- **Measurand** VIM 2.3 (2.6)
 - quantity intended to be measured
 - NOTE 1 The specification of a measurand requires knowledge of the kind of quantity, description of the state of the phenomenon, body, or substance carrying the quantity, including any relevant component, and the chemical entities involved

Module 1 - 21

Measurement VIM 2.1 (2.1)

- **Process of experimentally obtaining one or more quantity values that can reasonably be attributed to a quantity**
 - NOTE 1 Measurement does not apply to nominal properties.
 - NOTE 2 Measurement implies comparison of quantities and includes counting of entities.
 - NOTE 3 Measurement presupposes:
 - a description of the quantity commensurate with the intended use of a measurement result,
 - a measurement procedure, and a
 - calibrated measuring system operating according to the specified measurement procedure,
 - including the measurement conditions.

Module 1 - 22

Measurement Uncertainty VIM 2.26 (3.9)

- **Non-negative parameter characterizing the dispersion of the quantity values being attributed to a measurand, based on the information used**

NOTE 1: Measurement uncertainty includes components arising from systematic effects, such as components associated with corrections and the assigned quantity values of measurement standards, as well as the definitional uncertainty. Sometimes estimated systematic effects are not corrected for but, instead, associated measurement uncertainty components are incorporated.

Module 1 - 23

Measurement Uncertainty Components

- Type A evaluation of measurement uncertainty from the statistical distribution of the quantity values from series of measurements and can be characterized by standard deviations.
- Type B evaluation of measurement uncertainty, can also be characterized by standard deviations, evaluated from probability density functions based on experience or other information.
- NOTE 4 In general, for a given set of information, it is understood that the measurement uncertainty is associated with a stated quantity value attributed to the measurand. A modification of this value results in a modification of the associated uncertainty.

Module 1 - 24

Evolution of Measurement Uncertainty

- **Dates & Documents dealing with Measurements**
 - 1960's beginning of uncertainty budgets 4:1 TUR.
 - Mid 1980's ISO/IEC 9000 Series Quality Management focus was documentation of elements & traceability of standards.
 - 1993 ISO "Guide to the Expression of Uncertainty in Measurements" (GUM) focused on complete measurement Process that include standards and other elements.
 - In USA MIL-STD -45662A was superseded by the adoption of ISO/IEC Guide 25 "General Requirement for the Competence of Calibration and Testing Laboratories, which complied with the ISO 9000 series. ANSI/NC SL Z-540-1-1994, became the accepted U.S. industry standard.
 - In 1999, ISO/IEC 17025 replaced ISO/IEC Guide 25 as the requirements document for calibration and testing laboratories.

Module 1 - 25

A Robust Measurement Control Program has:

- Documented measurement control procedures implemented for all measurement methods for accountability and process control
- Methods that are validated before use by:
 - the analyst using a specific instrument
 - in the current environmental conditions
 - with available support equipment and/or reagents
 - by measuring a standard (blind or known)
 - whose result must be within control limits before
 - measuring process or accountability samples
- QC data that are periodically evaluated to provide new estimates of bias, precision, uncertainty and limits of error

Module 1 - 26

Summary

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

Module 1 - 27

Module 2

Measurement Method Qualification

Objectives

- **To understand measurement models**
- **To understand working standards**
- **To understand method selection/qualification process**

Measurement Models

- **Two main types:**
 - **Absolute**
 - Also called additive
 - Used for scales
 - **Relative**
 - Also called multiplicative
 - Used for NDA measurements or analytical methods that require dilutions
 - **Mixed Models also possible**
- **Measurement type determines appropriate model**
- **Data plots can assist with model determination**

Additive Model: Example

$$Y_{ijk} = \mu + \theta_i + \xi_j + \varphi_{ijk}$$

Where,

Y_{ijk} = measurement value associated with ijk

μ = true value associated with measurement

θ_i = systematic measurement effect associated with i

ξ_j = systematic measurement effect associated with j

φ_{ijk} = random measurement effect associated with ijk

The θ_i are iid $N(0, \sigma_\theta^2)$, the ξ_j are iid $N(0, \sigma_\xi^2)$, and the φ_{ijk} are iid $N(0, \sigma_\varphi^2)$. In addition, the θ_i , ξ_j , and φ_{ijk} are independent.

Relative Model: Example

$$Y_{ijk} = \mu \times (1 + \eta_i + \tau_j + \varepsilon_{ijk})$$

Where,

- Y_{ijk} = measurement value associated with ijk
- μ = true value associated with measurement
- η_i = systematic measurement effect associated with i
- τ_j = systematic measurement effect associated with j
- ε_{ijk} = random measurement effect associated with ijk

The η_i are iid $N(0, \sigma_\eta^2)$, the τ_j are iid $N(0, \sigma_\tau^2)$, and the ε_{ijk} are iid $N(0, \sigma_\varepsilon^2)$. In addition, the η_i , τ_j , and ε_{ijk} are independent.

Measurement Models

Discussion Topics:

1. How are the model terms different between the additive and multiplicative models?
2. What is the measurement variance of Y_{ijk} for the relative 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?

Measurement Models

Discussion Topics:

Background: Consider an analytical method for concentration involving dilutions. Process measurements are as follows: two samples, two analysts, and two measurements per sample.

- A. Specify a reasonable model for this measurement scenario.**
- B. What kind of effects are the samples and analysts?**
- C. Are sample and analyst effects different from random measurement effects?**
- D. What would a significant analyst variance or effect represent?**
- E. How could an analyst effect be used?**

Working Standards

- Typically fabricated from standard or certified reference materials (SRM or CRM)
- Characterized by assignment of a reference value and an uncertainty to the standard
 - The assigned value and uncertainty depend on the preparation or processing steps applied to the CRM in the derivation
 - Variance propagation techniques are typically used to derive uncertainties
- Used daily for laboratory quality control (QC) purposes

Working Standards

Discussion Topics:

- 1. Can a process sampling variance be estimated using QC data?**
- 2. What data would be needed to estimate a sampling variance component?**
- 3. What personnel should make the working standards?**
- 4. Discuss the ways in which a reference value can be established.**

Method Qualification Process

- **Measurement methods are selected and qualified based on the material type and the method uncertainty.**
- **The qualification process characterizes or estimates the uncertainty components for a measurement method.**
- **The selection/qualification process proceeds as follows:**
 - 1. The appropriate method for the required measurement is selected (precision and accuracy)**
 - 2. Facility personnel produce a qualification plan for the method**
 - 3. A measurement plan for method evaluation is developed**
 - 4. Evaluation data are collected**
 - 5. Data are analyzed by MC&A statistician**
 - 6. Statistician produces a method qualification report**
 - 7. Qualification report is submitted to DOE MC&A for approval**

Method Qualification Process

- **Laboratory QC data are typically used for method qualification**
- **In some cases, experimental designs that utilize laboratory QC data may be needed for uncertainty estimation**
- **Analysis of Variance (ANOVA) techniques are typically used to estimate method variance components**
 - **For a multiplicative model, relative differences are calculated**
 - **For an additive model, absolute differences are calculated**

Method Qualification Process

Discussion Topics:

- 1. What protocol should be followed when collecting the measurements for the qualification process?**
- 2. What should be documented in the qualification report?**
- 3. What personnel should receive a copy of the qualification report?**

Method Qualification Process

Scale Qualification for the Savannah River Site HB-Line Facility

HB-Line Scale HBL-08: Qualification Plan

10/11/04 10:52 FAX

10/11/04 10:53 FAX

003

WESTINGHOUSE SAVANNAH RIVER COMPANY
INTEROFFICE MEMORANDUM

To: L. A. Geary, Site MC&A

From: J. L. Shaffer, HBL Operations *JLS*

Cc: C. D. Harvel, Site MC&A
M. B. Gaines, HBL MC&A
C. W. Gardner, HBL Engineering

Date: October 6, 2004

QUALIFICATION PLAN FOR HB-LINE BALANCE HBL-08 (U)

1. Instrument to be Qualified

HB-Line (HBL) requests the qualification of a Mettler-Toledo balance (Model: PG8) balance to be qualified is identified as HBL-08 (Serial #: 1125170974). This balance MonoBloc™ weighing cell technology and has a range of 0 – 8100 grams. The balance display with a readability of 0.1 grams.

2. Reason for Qualification

The balance will be used to perform weighing of Special Nuclear Material (SNM) in This SNM may be plutonium, uranium and/or neptunium. The measurements involve & Security inventory of material being processed or repackaged in HBL Phase I. If it also be able to replace the HBL Phase II Mechanical Line or Operating Area 5 Balance.

Additionally, this balance may be used during performance of HBL vessel calibration of spanning solution during these calibrations. The calibration/spanning will ultimately vessel level instrumentation as MC&A qualified level instrumentation.

3. Process and Product Specifications

SNM to be handled in the HBL Phase I facility will be weighed prior to processing or repackaging. The SNM to be handled is normally between 100 and 4000 grams. The balance will be set up to perform measurements in the Phase I gloveboxes and/or supporting areas.

When used for vessel calibration/spanning, the balance will be used to measure the weight of a poly bottle containing water. This may be performed in various locations within the HBL facility.

Bounding environmental conditions for all these locations are 5 to 40 degrees C and 10% to 85% relative humidity.

4. Composition of Materials Used for Qualification Process

NIST traceable weight standards will be used for balance calibrations and baseline measurements. The weight set designated for qualification and use of this balance is HW-986. The weight standards included in this weight set are two (2) 500-gram, two (2) 1000-gram, two (2) 2000-gram and one (1) 5000 gram weight standards. These standards are intended to bracket the expected weight of the items to be weighed by the balance, while also covering the overall range of the balance.

5. Amount and Description of Test Data to be Generated

Baseline data will be generated over various shift time periods in HBL with approved procedures that implement the random weighing plan, which will be supplied by MC&A.

6. Qualification Acceptance Criteria

Initial calibration of the balance and weight standards has been performed by the Savannah River Standards Lab (SRS), and this calibration data will be supplied to Site MC&A. After baseline data is collected in accordance with the random weighing plan, it will be supplied to Site MC&A for evaluation. This data will be used to determine the accuracy and stability of the balance. The balance must demonstrate stable measurement characteristics during the qualification process as determined by Site MC&A. Site MC&A will determine the target values and control limits (warning and alarm limits) and provide that information to HBL in a Qualification Report.

7. Approval of Qualification Plan

JLS 10/8/04
HBL Operations Manager Date

CW 10/8/04
HBL Engineering Date

Shaffer 10/8/04
Site MC&A Date

ORIG

HB-Line Scale HBL-08: Qualification Data

Result in grams	Reference Value in grams	Absolute Difference	Relative Difference
1000	1000	0	0
3999.9	4000	-0.1	-0.000025
5999.8	6000	-0.2	-0.000033
500.1	500	0.1	0.0002
2000	2000	0	0
7999.7	8000	-0.3	-0.000038
500	500	0	0
2000	2000	0	0
7999.7	8000	-0.3	-0.000038
6999.7	4000	2999.7	0.749925
1000.1	1000	0.1	0.0001
500.1	500	0.1	0.0002
2000	2000	0	0
7999.8	8000	-0.2	-0.000025
5999.9	6000	-0.1	-0.000017
4000	4000	0	0
3999.9	4000	-0.1	-0.000025
500.1	500	0.1	0.0002
...	...	...	...

HB-Line Scale HBL-08: Plot of Qualification Data

HB-Line Scale HBL-08: Estimation of Calibration Equation

----- Measurement Range=0 to 8,100 grams -----

The REG Procedure
Model: MODEL1
Dependent Variable: result

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	1	353468245	353468245	7.3E10	<.0001
Error	45	0.21782	0.00484		
Corrected Total	46	353468245			

Root MSE	0.06957	R-Square	1.0000
Dependent Mean	3574.42766	Adj R-Sq	1.0000
Coeff Var	0.00195		

Parameter Estimates

Variable	DF	Parameter Estimate	Standard Error	t Value	Pr > t
Intercept	1	0.06634	0.01667	3.98	0.0002
refval	1	0.99997	0.00000370	270232	<.0001

Covariance of Estimates

Variable	Intercept	refval
Intercept	0.0002779391	-4.894524E-8
refval	-4.894524E-8	1.369301E-11

Discussion Topics

- **Can this scale be used for weight measurements?**
- **If so, how would these measurements be adjusted?**
- **Discuss methods or actions for improving the measurements for this scale**

Exercise : Active Well Coincidence Counter (AWCC) Qualification Process

- **Purpose: Qualify an Active Well Coincidence Counter for Pu Accountability Measurements**
- **Discussion topics**
 - **Selection process (target precision and accuracy values)**
 - **Qualification plan**
 - **Training and qualification of measurement personnel**
 - **Data collection and standards**
 - **Data analysis**
 - **Final documentation**
 - **Approvals**

Active Well Coincidence Counter (AWCC)– Neutron Measurement Basics

Most nuclear materials emit neutrons. An AWCC is a non-destructive assay (NDA) device used to measure neutrons. The amount of neutrons measured can be correlated to the amount of nuclear material.

An AWCC has two modes of operation:

- **Passive Mode - Plutonium**

- Plutonium fissions spontaneously

- **Active Mode - Uranium**

- Uranium measurements are done by using an external source (active) of neutrons to excite the U235

Active Well Coincidence Counter –cont'd

Active well coincidence counter

Exercise : AWCC Qualification Process

Listing of HBL AWCC Pu Qualification Data

File #	Standard Id	True Pu mass (g)	Measured Pu mass (g)	Relative Difference (g)
162K0410	SGB-30	29.989	36.2	0.207
162I1040	SGB-30	29.989	33.8	0.127
162M1846	SGB-30	29.989	35.5	0.184
162N2438	SGB-30	29.989	35.3	0.177
162O3955	SGB-30	29.989	34.8	0.160
15UI3558	SGB-100	99.964	99.7	-0.003
15UJ4120	SGB-100	99.964	89.6	-0.104
15UM0935	SGB-100	99.964	81.7	-0.183
15UO2454	SGB-100	99.964	88.2	-0.118
15U2943	SGB-100	99.964	93.7	-0.063
15VO5519	SGB-200	199.927	232.7	0.164
15VQ0230	SGB-200	199.927	176.1	-0.119
161J0906	SGB-200	199.927	184.5	-0.077
161K3809	SGB-200	199.927	207.1	0.036
161O0600	SGB-200	199.927	213	0.065

Exercise : AWCC Qualification Process

Plot of Relative Differences from HBL AWCC Pu Qualification Data

Exercise : AWCC Qualification Process

ANOVA Results for HBL AWCC Calibration and Random Uncertainty Analysis

```

The GLM Procedure
Class Level Information
Class      Levels      Values
std_id      3      SGB-100 SGB-200 SGB-30

Number of observations      15

The GLM Procedure
Dependent Variable: reldiff

Source      DF      Sum of Squares      Mean Square      F Value      Pr > F
Model      2      0.17757951      0.08878975      14.59      0.0006
Error     12      0.07304037      0.00608670
Corrected Total      14      0.25061987

R-Square      Coeff Var      Root MSE      reldiff Mean
0.708561      257.2216      0.078017      0.030331

Source      DF      Type I SS      Mean Square      F Value      Pr > F
std_id      2      0.17757951      0.08878975      14.59      0.0006

Source      DF      Type III SS      Mean Square      F Value      Pr > F
std_id      2      0.17757951      0.08878975      14.59      0.0006

The GLM Procedure
Source      Type III Expected Mean Square
std_id      Var(Error) + 5 Var(std_id)

```

Exercise : AWCC Qualification Process

HBL AWCC Pu Uncertainty Components

Bias	Bias Uncertainty	Calibration Uncertainty	Random Uncertainty
3.03%	$\pm 7.69\%$	$\pm 12.86\%$	$\pm 7.80\%$

Summary

- **To understand measurement models**
- **To understand working standards**
- **To understand method selection/qualification process**

Module 3

Sampling Variability Solids and Oxides

Objectives

- **Understand the issues with sampling a batch of material**
- **Specify the activities that can be done to minimize the problems of heterogeneity within the batch**
- **Be able to apply correct sampling principles, analyses, tools, and techniques**

Sampling Variability

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

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:

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

- 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, 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 3rd 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.

Closure of a Liquid Waste Tank

What are the considerations to characterize the residual dried material on the floor of a liquid waste tank?

Waste tanks with Individual capacity of 4.9 million liters at time of construction.

Tank interior prior to closure.

Liquid Waste Tank Sampling Locations

Waste Tank Sampling Locations

Samples are numbered based on retrieval priority order

Considerations for Tank Sampling:

- Distribution and depth of material on the floor of the tank
- Individual or composite sampling
- Sample location
- Prior data
- Sampling device and transfer containers
- Analytes for lab analyses and final use of the data
- Number of samples and amount of material sampled
- Radiation exposure
- Number and location of archived samples for contingency
- Ability of the Crawler to locate, reach, and retrieve each sample

Discussion Exercise

Discuss the details for designing a sampling plan for characterizing the material left in the tank

Sampling Details

Purpose: Characterization of the residual material in the Tank prior to closure

- Residual material is not uniformly distributed. Approx. 3,407 liters are in the North hemisphere and 4,164 liters in the South. Approx. 50% of the material is in the outer ring. We want to test for differences between hemispheres and also for differences between the inner and outer regions for combining data.
- Crawler needs to find the sample location within the tank: The tank risers were used for a landmarks.
- Accessibility of sampling locations: Some tanks have numerous cooling coils and obstructions. Crawler can and did get stuck in other tanks.

Sampling Details (continued)

- The recommended sample size was determined when the reduction in uncertainty from an additional sample no longer has a practical impact on the results.
- Two in-process (cleaning) samples, one in each hemisphere, were used as a starting point.
- The number of samples needed was determined by the decrease in uncertainty as more and more additional samples and analyses are obtained.
- The decrease becomes smaller and smaller as more samples are added. Six additional samples were selected as a point of diminishing returns.

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

Sampling Details (continued)

- Upper 95% confidence limits for the mean were calculated for the concentrations.
- Number and location of archived samples: In addition to the six samples, two more samples will be obtained and archived, bringing the final number of additional samples to eight.
- Approximately 30 grams of solids are required for the entire suite of analytical results for each sample.

Summary

- **Understand the issues with sampling a batch of material**
- **Specify the activities that can be done to minimize the problems of heterogeneity within the batch**
- **Be able to apply correct sampling principles, analyses, tools, and techniques**

Module 4

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)**

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

Elements of Training Program

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

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
 - 60 and 9 degrees of freedom for F-test value of 1.74 used

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**

T&T Evaluation Form:

Record trainee's measurands of unknown QC standards

Name:	George				
Method:	U-Titration				
	Reported	Known	R - K	Std. Dev.	(R-K)/SD
Sample	R Value	K Value	Difference	of Known	Normalized
1	1.952				
2	10.006				
3	10.008				
4	25.010				
5	25.001				
6	24.985				
7	2.005				
8	10.000				
9	10.006				
			Total =	$\Sigma(R-K)/SD=$	
	Sum of Squares=			$\Sigma((R-K)/SD)^2=$	
SUM=	Absolute value of Total FF =			SS/N=	
SUM=			TT=	SUM/N ⁵ =	
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					

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%

T&T Data Evaluation Form:

+ known values & their standard uncertainties

Name:	George				
Method:	U-Titration				
	Reported	Known	R - K	Std. Dev.	(R-K)/SD
Sample	R Value	K Value	Difference	of Known	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	
			Total =	$\Sigma(R-K)/SD=$	
	Sum of Squares=			$\Sigma((R-K)/SD)^2=$	
SUM=	Absolute value of Total FF =			SS/N=	
SUM=			TT=	SUM/N ^{0.5} =	
<p>If TT is greater than $T(N)^*$, then the bias is significantly greater than zero</p> <p>If FF is greater than $F(N)^{**}$, then the Std. Dev. Is significantly greater than one.</p> <p>N is the number of analyses in the current quality control program.</p>					
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					

T&T Data Evaluation Form:

Reported – known values = bias (difference)

Name:	George				
Method:	U-Titration				
	Reported	Known	Bias		
Sample	R Value	K Value	R - K Difference	Std. Dev. of Known	(R-K)/SD Normalized
1	1.992	2.000	-0.008	0.0040	
2	10.006	10.000	0.006	0.0120	
3	10.008	10.010	-0.002	0.0120	
4	25.010	25.000	0.010	0.0250	
5	25.001	25.000	0.001	0.0250	
6	24.985	25.000	-0.015	0.0250	
7	2.005	2.000	0.005	0.0040	
8	10.000	10.010	-0.010	0.0120	
9	10.006	10.000	0.006	0.0120	
			Total =	$\Sigma(R-K)/SD=$	
	Sum of Squares=			$\Sigma((R-K)/SD)^2=$	
SUM=	Absolute value of Total FF =			SS/N=	
SUM=			TT=	SUM/N ^{1/2} =	
<p>If TT is greater than T(N)*, then the bias is significantly greater than zero</p> <p>If FF is greater than F (N)**, then the Std. Dev. Is significantly greater than one.</p> <p>N is the number of analyses in the current quality control program.</p>					
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					

T&T Data Evaluation Form:

Bias values normalized by dividing by standard U.

Name:	George				Bias in
Method:	U-Titration				Std. Deviations
	Reported	Known	R - K	Std. Dev.	(R-K)/SD
Sample	R Value	K Value	Difference	of Known	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
			Total =	$\Sigma(R-K)/SD=$	
	Sum of Squares=			$\Sigma((R-K)/SD)^2=$	
SUM=	Absolute value of Total FF =			SS/N=	
SUM=			TT=	SUM/N ^{1/2} =	
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					

T&T Data Evaluation Form:

Bias t-tested & variance ratio F tested (Pass)

Name:	George				
Method:	U-Titration				
	Reported	Known	R - K	Std. Dev.	(R-K)/SD
Sample	R Value	K Value	Difference	of Known	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
			Total =	$\Sigma(R-K)/SD=$	-0.91
	Sum of Squares=			$\Sigma((R-K)/SD)^2=$	7.30
SUM=	Absolute value of Total FF =			SS/N=	0.81
SUM=		TT=		SUM/N ⁵ =	-0.30
	Technican 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	X
STD DEV. IS:		Significant		Not Significant	X
* t-Table value for ($\alpha= 0.1$)/2 and 60 df = 1.67				(-0.91 < 1.67)	
** F Table Value at the 90% CI for df 60 & 9 =1.74				(0.3 < 1.74)	

T&T Data Evaluation Form:

Trainee has significant bias, therefore, fails

Name:	George				
Method:	U-Titration				
	Reported	Known	R - K	Std. Dev.	(R-K)/SD
Sample	R Value	K Value	Difference	of Known	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	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
			Total =	$\Sigma(R-K)/SD=$	-5.66
	Sum of Squares=			$\Sigma((R-K)/SD)^2=$	14.65
SUM=	Absolute value of Total FF =			SS/N=	1.63
SUM=			TT=	SUM/N ⁵ =	-1.89
Tecnician 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					(-1.89 > 1.67)
** F Table Value at the 90% CI for df 60 & 9 =1.74					(1.63 < 1.74)

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

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

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)

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

Graphical Procedure for Sequential Testing

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**

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**

Sample Exchange Programs

- **ITVs utilized data from 3 international programs:**
 - **Safeguards Measurement Evaluation Program (SMEP)**
 - **Regular European Interlaboratory Measurement Evaluation Program (REIMEP)**
 - **Évaluation de la Qualité des Resultats d'Analyses dans l'Industrie Nucléaire, (EQRAIN)**
- **ANSI N15.51-2007 - Measurement Control Program – Analytical Chemistry Laboratory *4.4.6 Measurement of Interlaboratory Comparison Program Samples.**
 - **Data from participation in appropriate interlaboratory comparison programs should be used to provide independent verification of internal analytical quality control**

US Department of Energy's (DOE) New Brunswick Laboratory (NBL)

- NBL manages interlaboratory measurement evaluation programs to provide independent validation of facility nuclear material measurement quality/capabilities.
- The program includes:
 - preparation, characterization, packaging and distribution of samples to participating laboratories
 - The receipt, recording, statistical evaluation and reporting of the measurement data from the participating laboratories are the products of the program
 - Most laboratories perform analyses on a quarterly or semi-annual frequency. No charges to DOE labs. Non-DOE labs participate on a cost-recovery basis

NBL Sample Exchange Programs

- NBL has conducted interlaboratory measurement comparison programs involving more than 50 laboratories from more than 15 countries
- Providing independent oversight of the effectiveness of measurement systems used for safeguards materials accountability and of the quality of measured values
- Specific evaluation programs have also involved the preparation of materials and evaluation of analyses by commercial analytical laboratories in establishing control programs for U-235 in fuel loadings

Two Proficiency Testing Programs

- The destructive analyses results are evaluated in the Safeguards Measurement Evaluation (SME) Program
- The non-destructive analyses results in the Calorimetric Exchange (CALEX) Program
- Test samples of uranium and plutonium bearing materials, sent by NBL, are analyzed in safeguards laboratories by procedures routinely used in material accountability measurements
- The results are evaluated by NBL for accuracy, precision, day-to-day variation, and compliance to method/material specific International Target Values (ITVs). Reports & recommendations are sent to labs

Elemental Uranium in UNH Test Samples by Davies & Gray Titration

< Results from 6 participants to be shown on next 3 slides >

Plot of Participant's Random Error & ITV Target Values for U in UNH by D&G Method

Elemental Uranium in UNH by D&G

Lab Code	Mean% RD	SD	N	ITV Compliance	
				U(s) = 0.1	U(r) = 0.1
BA	-0.130	0.085	10	No	Yes
BC	-0.360	0.114	16	No	No
U	-0.117	0.158	8	No	No
BF	0.064	0.044	8	Yes	Yes
F	-0.75	0.159	16	Yes	No
B	-0.018	0.224	8	Yes	NO

Mean % RD in elemental uranium Determination in UNH test samples by D&G titration compared to IAEA ITVs

Certified Reference Materials at NBL

The following materials are typically available for the indicated analyses:

- Uranyl nitrate solutions for U concentration
- Uranyl nitrate solutions for ^{235}U enrichment
- UO_2 pellets for U concentration and enrichment
- UO_3 powder for U concentration
- UF_6 (normal or low-enriched) solid for U concentration
- UF_6 (low-enriched) solid for ^{235}U enrichment
- Plutonium sulfate for isotopic abundances and IDMS

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**
- **Reviewed US DOE proficiency testing program (sample exchange)**

Module 6

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 ± 2 -sigma or ± 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

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 can be calculated with or without bias corrections**

Control Limits and Control Charts

- **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**

Example Chart for U Chem Chek Method

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?**

Measurement Control Process Example 1 – Davies-Gray Method

Note: See Control Chart next slide

Background: The Davies-Gray method is used for Uranium concentration measurements associated with material inventory determinations. Process measurements are performed as follows: several analysts, 2 samples per tank, one measurement on each sample.

- A. What does the data plot tell you?
- B. What is a possible process sample measurement model for this method?
- C. Is there a bias for this method?
- D. What is the approximate magnitude of the bias?
- E. What is the approximate overall uncertainty for this method?
- F. Discuss overall impressions regarding this method.

Measurement Control Process Example 1 – Davies-Gray

Measurement Control Process Example 2 – Chem Chek Low Method

Note: See Control Chart next slide

Background: The Chem Chek Low method is used for low concentration Uranium measurements associated with material inventory determinations. Process measurements are performed as follows: several analysts, 2 samples per tank, one measurement on each sample.

- A. What does the data plot tell you?
- B. What is a possible process sample measurement model for this method?
- C. Is there a bias for this method?
- D. What is the approximate magnitude of the bias?
- E. What is the approximate overall uncertainty for this method?
- F. Discuss overall impressions regarding this method.

Measurement Control Process Example 2 – Chem Chek

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?**

Runs Rule Criteria Example 1 – Diode Array System

Note: See Control Chart Next Slide

Background: The Diode Array System low method is used for low concentration Uranium measurements associated with material inventory determinations. Process measurements are performed as follows: several analysts, 2 samples per tank, one measurement on each sample.

- A. Have any runs rule violations occurred?**
- B. How likely is this method to have a runs rule violation?**
- C. What could cause a runs rule violation for this method?**

Runs Rule Criteria Example 1 – Diode Array System

Runs Rule Criteria Example 2 – Chem Chek

Note: See Control Chart next slide

Background: The Chem Chek low method is used for low concentration Uranium measurements associated with material inventory determinations. Process measurements are performed as follows: several analysts, 2 samples per tank, one measurement on each sample.

- A. Have any runs rule violations occurred?**
- B. How likely is this method to have a runs rule violation?**
- C. What could cause a runs rule violation for this method?**

Runs Rule Criteria Example 2 – Chem Chek

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 7

Calibration

Objectives

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

Objective 1

**Identify the function of a
calibration model**

Calibration

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

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

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

Thermometer Example

Assume you have a standard ruler and a thermometer with no markings

Your goal is to mark the thermometer so that it accurately reflects the temperature

Standard Temperatures

Ice Water

Boiling Water

25 Degrees C.

75 Degrees C.

Temperature/Liquid Height Comparison

Temperature	Liquid Height
0° C	7.00 cm.
25° C	10.00 cm.
75° C	16.00 cm.
100° C	19.00 cm.

Calibration Model

An expression describing the calibration relationship

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

Temperature vs. Liquid Height

Temperature vs. Liquid Height

Objective 2

**Identify the concept of calibration
equation**

Equation for the Calibration Equation

Using the slope-intercept form of a line from algebra, we get the following regression equation for the line:

$$\text{Liquid Height (cm)} = 0.12 \times \text{Temperature (}^{\circ}\text{C)} + 7.0$$

Thermometer Table

Height (cm)	Temp. (C)	Height (cm)	Temp. (C)	Height (cm)	Temp. (C)
7.00	0	8.56	13	10.12	26
7.12	1	8.68	14	10.24	27
7.24	2	8.80	15	10.36	28
7.36	3	8.92	16	10.48	29
7.48	4	9.04	17	10.60	30
7.60	5	9.16	18	10.72	31
7.72	6	9.28	19	10.84	32
7.84	7	9.40	20		
7.96	8	9.52	21		
8.08	9	9.64	22		
8.20	10	9.76	23	18.76	98
8.32	11	9.88	24	18.88	99
8.44	12	10.00	25	19.00	100

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)**

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:

$$\text{Liquid height} = .12 \times \text{Temperature} + 7.0$$

So far, the temperature has been the known variable and the liquid height was a function of that variable

Deriving the Equation for the Measurement Relationship

Solve the equation for the temperature variable and let the temperature be a function of the liquid height. By doing so, we arrive at the following formula:

$$\text{Temperature} = 8.33 \times \text{Liquid height} - 58.33$$

This will be the prediction equation

Tank Calibration

Tank Calibration

$$\text{Volume} = 588.2 \times \text{Liquid Height} + 170.6$$

Objective 4

Identify the use of regression analysis for calibration uncertainty

Thermometer Example

Introducing Error

Measured Liquid Height (Centimeters)

Day	Ice Water	25° C	75° C	Boiling Water
1	7.5	10.0	16.0	19.0
2	9.0	10.5	16.5	19.5
3	7.5	10.0	15.5	18.0
4	8.5	9.5	16.0	18.5
5	7.0	10.5	15.5	20.0

Repeated Calibration with Error

Repeated Calibration with Error

Objective 5

Identify the concept of measurement uncertainty in calibration equations

Tank Calibration: Repeated Measurements

Tank Calibration: Repeated Measurements

Regression Line With 95% Confidence Limits

Calibration Error: Error in Liquid Height Measurement

Measurement Error: Calibration Error

Tank Calibration: Calibration Error

Tank Calibration:

Calibration Error and Measurement Error

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**
- **Temperature and density corrections may be required**

Lesson Summary

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

Module 8

Balance Measurement Control Program

Objectives

- **Review the elements of a MCP for scales or balances**
- **Discuss the classes of balances & mass standards**
- **Discuss sources and types of error in weighing**
- **Review the GUM's 8 steps for estimating uncertainty**

Good Weight Measurements Require:

- **Choosing the appropriate weighing equipment**
- **Choosing appropriate mass standards**
- **Proper handling and use of standards**
- **Administrative procedures for measurement control**
- **Routine balance testing using appropriate check standards**
- **Reliable uncertainty estimates for weighing systems**

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**

Four classes of scales and balances

Parameters for Accuracy Classes

<i>Class</i>	<i>Value of the Verification Scale Division</i>	<i>Number of Scale Divisions (n)</i>	
		<i>Minimum</i>	<i>Maximum</i>
<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>IIII</i>	<i>equal to or greater than 5 g</i>	<i>100</i>	<i>1 200</i>

OIML Weight Classes

- **Class E1**
 - Used as primary reference standards for calibrating other reference standards and weights
- **Class E2**
 - Can be used as a reference standard in calibrating other weights and
 - is appropriate for calibrating high precision analytical balances with a readability as low as 0.1 mg to 0.01 mg
- **Class F1**
 - Appropriate for calibrating high-precision top loading balances with a readability as low as 0.01 g to 0.001 g

OIML Weight Classes *cont'd*

- **Class F2**
 - For calibration of semi-analytical balances and
 - for student use
- **Class M1, M2, M3**
 - Economical weights for general laboratory, industrial, commercial, technical and educational use
 - Typically fabricated from cast iron or brass
 - Class M2 brass weights are most commonly used for educational purposes

Tolerances for 100 g Metric Standard

Class	E1	E2	F1	F2	M1	M2	M3
mg	0.05	0.15	0.5	1.5	5	15	50
%	0.005%	0.0155	0.05%	0.15%	0.5%	1.5%	5%

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

Factors Influencing Weight Readings

- **Design**
- **Installation**
- **Staff & procedures**
- **Standards**
- **Facility (environment/location)**
- **Method of use**

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

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**

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

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)**

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

Repeatability Condition of Measurement

VIM 2.20

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.

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

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

Instrumental Bias VIM 4.20 (5.25)

Average of replicate indications minus a reference quantity value

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

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**

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**

Summary

- **Reviewed elements of a MCP for scales or balances**
- **Discussed the classes of balances & mass standards**
- **Discussed sources and types of error in weighing**
- **Reviewed the GUM's 8 steps for estimating uncertainty**

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 9

Tank Sampling & Mixing Study for Liquids

Objective

- **Discuss planning considerations for tank sampling and mixing**
- **Discuss tank sampling and mixing case study**

Tank Sampling & Mixing

- **Sampling and mixing studies have been conducted for many of the input/output accountability tanks at Savannah River Site**
- **The purpose of these studies is to establish a mixing time and to estimate a sampling uncertainty**
- **Sampling uncertainties are typically associated with solution concentration measurements**
- **If a sampling study has not been conducted, sampling uncertainties can be estimated using process sample analytical results**

Study Planning

- **Some planning considerations are as follows:**
 - **What material will be used for the study?**
 - **How long will the tank be mixed?**
 - **At what time intervals will samples be pulled?**
 - **How many samples will be pulled at each time interval?**
 - **How many analyses per sample?**

Tank Sampling & Mixing Study

Background: A particular process was experiencing ID problems. The investigation suggested a sampling/mixing study on the main input accountability tank. This was to ensure the solution was adequately mixed when accountability samples were taken. The tank was at process heel prior to the beginning of the study. Acid was added to the tank to reduce the concentration by approximately 50%. Eventually, process solution from another location was transferred into the tank. The sampling study was then continued. This tank uses air sparging for mixing, but has a recirculation pump as a backup system.

Tank Sampling & Mixing Study

HB-Line Tank JT-71
Sampling and Mixing Study
The Analysis of Np Concentration Data

Sample Desc	Mixing Time Hours	Group No.	Aliquot	Np Concentration mg/g	Density g/ml	Np Concentration g/l
JT71-007-ACCT-1-HEEL	0.0	1	1	6.8839	1.2094	8.3254
JT71-007-ACCT-1-HEEL	0.0	1	2	6.8729	1.2094	8.3121
JT71-007-ACCT-1-HEEL	0.0	1	1	6.8719	1.2094	8.3109
JT71-007-ACCT-1-HEEL	0.0	1	2	6.8669	1.2094	8.3048
JT71-007-ACCT-HEEL	0.0	2	1	6.8631	1.2095	8.3009
JT71-007-ACCT-HEEL	0.0	2	1	6.8744	1.2095	8.3146
JT71-007-ACCT-HEEL	0.0	2	2	6.8726	1.2095	8.3124
JT71-007-00	0.0	3	1	11.4207	1.2377	14.1354
JT71-007-00	0.0	3	2	11.4472	1.2377	14.1682
JT71-007-02	2.0	4	1	11.9467	1.2386	14.7972
JT71-007-02	2.0	4	2	11.9335	1.2386	14.7808
JT71-007-04	4.0	5	1	11.9092	1.2385	14.7495
JT71-007-04	4.0	5	2	11.9082	1.2385	14.7483
JT71-007-06	6.0	6	1	11.9574	1.2388	14.8128
JT71-007-06	6.0	6	2	11.9164	1.2388	14.7620
JT71-007-08	8.0	7	1	11.9049	1.2385	14.7442
JT71-007-08	8.0	7	2	11.8943	1.2385	14.7311
JT71-007-10	10.0	8	1	11.8886	1.2386	14.7252
JT71-007-10	10.0	8	2	11.8845	1.2386	14.7201
JT71-007-12	12.0	9	1	11.9006	1.2390	14.7448
JT71-007-12	12.0	9	2	11.9240	1.2390	14.7738
JT71-007-14	14.0	10	1	11.8904	1.2389	14.7310
JT71-007-14	14.0	10	2	11.9042	1.2389	14.7481
JT71-007-ACCT	16.0	11	1	11.9846	1.2388	14.8465
JT71-007-ACCT	16.0	11	2	11.9478	1.2388	14.8009
JT71-007-ACCT	16.0	11	1	11.8961	1.2388	14.7369
JT71-007-ACCT	16.0	11	2	11.9355	1.2388	14.7857
JT71-007-ACCT-1	16.0	12	1	11.9292	1.2388	14.7779
JT71-007-ACCT-1	16.0	12	2	11.9790	1.2388	14.8396
JT71-007-ACCT-1	16.0	12	3	11.9186	1.2388	14.7648
JT71-007-ACCT-1	16.0	12	1	11.9165	1.2388	14.7622
JT71-007-ACCT-1	16.0	12	2	11.8965	1.2388	14.7374
JT71-007-P001	17.0	13	1	11.8834	1.2387	14.7200
JT71-007-P001	17.0	13	2	11.9100	1.2387	14.7529
JT71-007-P002	18.0	14	1	11.9157	1.2388	14.7612
JT71-007-P002	18.0	14	2	11.9229	1.2388	14.7701
JT71-007-P003	18.5	15	1	11.9518	1.2386	14.8035
JT71-007-P003	18.5	15	2	11.8895	1.2386	14.7263
JT71-007-P003	18.5	15	3	11.8639	1.2386	14.6946

Tank Sampling & Mixing Study

Tank Sampling & Mixing Study

Tank Sampling & Mixing Study

HB-Line Tank JT-71
Sampling and Mixing Study
The Analysis of Np Concentration Data
The Estimation of Sampling and Analytical Method Uncertainty Components

The GLM Procedure

Dependent Variable: npgl Np Concentration g/l

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	11	0.01573826	0.00143075	1.23	0.3360
Error	18	0.02092694	0.00116261		
Corrected Total	29	0.03666520			

R-Square	Coeff Var	Root MSE	npgl Mean
0.429242	0.230984	0.034097	14.76165

Source	DF	Type I SS	Mean Square	F Value	Pr > F
sampleid	11	0.01573826	0.00143075	1.23	0.3360

Source	DF	Type III SS	Mean Square	F Value	Pr > F
sampleid	11	0.01573826	0.00143075	1.23	0.3360

The estimation of the sampling uncertainty is as follows:

Source	Type III Expected Mean Square
sampleid	Var(Error) + 2.4667 Var(sampleid)

Tank Sampling & Mixing Study

HB-Line Tank JT-71
Sampling and Mixing Study
The Analysis of Np Concentration Data
The Estimation of Sampling and Analytical Method Uncertainty Components

Uncertainty Components for Tank JT-71:
Sampling Uncertainty = 0.0104 g/l
Analytical Method Uncertainty = 0.0341 g/l
Average Np Concentration = 14.7617 g/l

Sampling %RSD = 0.0707%
Analytical Method %RSD = 0.2310%

Summary

- **Discussed planning considerations for tank sampling and mixing**
- **Discussed tank sampling and mixing case study**

Module 10

Analytical Chemistry Laboratory Measurement Control Programs

Objectives

- **Understand laboratory measurements must have uncertainty estimates for accountability of NM**
- **Review MCP technical & administrative components**
- **Discuss laboratory techniques for estimating error**
- **Examine 4 levels of measurement controls used to assure measurements are fit for purpose**
- **Understand all uncertainty estimates are based on assumptions**

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 N15.51-2007 “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, and**
- **CITAC Guide 1 "International Guide to Quality in Analytical Chemistry--An Aid to Accreditation," ISBN 0948926 09 0 English First Edition 1995**

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 discussed earlier

MCP Essentials – Documentation

1. Document the measurement control program, including descriptions of the statistical tests performed and the minimum acceptable limits
2. Measurement and measurement control methods are formally qualified and validated as adequate for their intended use
3. 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 Essentials – 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 Essentials – 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 Essentials – Administration

- **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**

Measurement Quality Parameters

- **Accuracy***
- **Precision***
- **Cost**
- **Turn around time, and**
- **Back-up capability limitations**

* Most often required by regulators and 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 Commission require MCPs that comply with international standards

Precision Estimates for a Lab Method

Which is the correct estimate of the method's PRECISION?

SOURCE OF PRECISION ESTIMATE	RELATIVE STANDARD DEVIATION
Chemist's Value for Method	2%
Monthly QC Report	4%
Yearly QC Report	6%

Accuracy Definition

- **Accuracy of measurement is closeness of the agreement between the result of a measurement and a *true 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

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)

Control Programs Levels

- **Level 1: “Go-No-Go”**
 - Tests a standard’s assays
- **Level 2: Statistical Process Control (SPC) Control Charting**
 - Monitors random variation of assays of a control material
- **Level 3: SPC Control Charting**
 - Monitors random & systematic variation of a control standard(s)
- **Level 4: Measurement Assurance Program**
 - Uses SPC control charting to plot assays of a verisimilitude standard(s) (with a certified value) to estimate random & systematic variation and determine an estimate of total measurement uncertainty that includes the standard’s uncertainty

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

Measurement Assurance Program (MAP)

- **The Guide to the Expression of Uncertainty in Measurement (GUM) 8 step method incorporates multiple sources of uncertainty into a combined uncertainty using the root sum square (RSS) method**
- **NIST Office of Weights and Measures uses a Process Measurement Assurance Program (PMAP) that generates similar combined uncertainty estimates**
- **PMAP is the fourth level of MCP. It is a process control that quantifies measurement quality. By merging these techniques with statistical process control results of the product, you can produce a product with an established uncertainty.**

Real Time Estimate of Measurement Uncertainty for an Analytical Method

- **Analysis of the MAP data provides a 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)**
- **Other major sources (drift?)**
- **Combine by RSS for standard estimate of uncertainty**
- **Multiply by appropriate K value (2 for 95% Confidence Interval)**

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!

SOURCE OF PRECISION ESTIMATE	RELATIVE STANDARD DEVIATION
Chemist's Value for Method	2%
Monthly QC Report	4%
Yearly QC Report	6%

Summary

- **Understand laboratory measurements must have uncertainty estimates for accountability of NM**
- **Review MCP technical & administrative components**
- **Discuss laboratory techniques for estimating error**
- **Examine 4 levels of measurement controls used to assure measurements are fit for purpose**
- **Understand all uncertainty estimates are based on assumptions**

Exercise:

Pipette Calibration Exercise

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 μ L tolerances = Accuracy $\pm 0.8\%$ or $\pm 8.0 \mu\text{L}$
Precision $\pm 0.15\%$ or $\pm 1.5 \mu\text{L}$

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”**

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

+0.50 hours in large group discussion

1.50 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
4. One barometer with calibration certificate or manufacturer specifications
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
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.
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, 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	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	Average =						
21	Standard Deviation (Usd)=						
22	Certificate Conventional Wt=						
23	Bias = Ave Wt – Certificate Wt						
24	Bias Uncertainty (Ub) = B/2=						
25	U of standard=(Ustd)						
26	Square Root of 3 =						
27	(Ustd) Certificate U/(3)^.5						
28	Combined Unc** =						
29	Expanded U = Uc x 2						
30	Bias in mg						
31	Repeatability in mg						
32	U in mg (U*1000)						
33	U in %						
** Uc= $(Usd^2 + Ustd^2 + (B/2)^2)^{.5}$							

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	Average =					
21	Standard Deviation (Usd)=					
22	Certificate Conventional Wt=					
23	Bias = Ave Wt - Convent. Wt					
24	Bias Uncertainty (Ub) = B/2=					
25	Uncertainty of standard(s)*=(Us)					
26	Square Root of 3 =					
27	(Ustd) Certificate U/(3)^.5					
28	Combined Unc** =					
29	Expanded U = Uc x 2					
30	** Uc= (Usd^2+Ustd^2+(B/2)^2)^.5					
31	Bias in mg					
32	Repeatability in mg					
33	U in mg (U*1000)					
34	U in %					

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

Balance Exercise 2 Linearity Tests (uncertainty estimates)

姓名 : Name					
日期/时间 : Date/Time					
气压 : Barometric Pressure		湿度 = Humidity		温度 = Temp	
天平 ID = Balance ID		型号 = Model			
砝码质量 Weight Mass	1 g	10 g	50 g	100 g	150 g
砝码 ID Weight ID					50g + 100g
砝码证书常规质量 Wt Cert. Conventional Mass					#VALUE!
砝码证书不确定性 Wt. Cert. Uncertainty					#VALUE!
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!
标准偏移 (Usd) = Std. Deviation	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!
证书常规重量 = Cert. Conventional Wt.					#VALUE!
偏差 = 平均重量 - 证书重量 Bias = Avg Wt. - Conventional Wt.	#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!
标样不确定性 =(Ustd) Uncertainty of standard(s)					#VALUE!
3 的均方根 = Square Root of 3	1.73	1.73	1.73	1.73	1.73
(标样不确定性) 证书 $U/(3)^{.5}$ (Ustd) Certificate $U/(3)^{.5}$	#VALUE!	#VALUE!	#VALUE!	#VALUE!	#VALUE!
合并 Unc** = Combined Unc**	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!
扩展不确定性 = $U_c \times 2$ Expanded U	#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!
可重复性 (mg) Repeatability in (mg)	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!
不确定性 mg ($U \times 1000$) U in mg ($U \times 1000$)	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!
不确定性 % U in %	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!
** $U_c = (Usd^2 + Ustd^2 + (B/2)^2)^{.5}$					

Balance Exercise 2 Linearity Tests (uncertainty estimates)

姓名 : Name					
日期/时间 : Date/Time					
气压 : Barometric Pressure		湿度 = Humidity		温度 = Temp	
天平 ID = Balance ID		型号 = Model			
砝码质量 Weight Mass	1 g	10 g	50 g	100 g	150 g
砝码 ID Weight ID					
砝码证书常规质量 Wt Cert. Conventional Mass					
砝码证书不确定性 Wt. Cert. 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!
标准偏移 (Usd)= Std. Deviation	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!
证书常规重量 = Cert. Conventional Wt.	0.000000	0.000000	0.000000	0.000000	0.000000
偏差 = 平均重量 - 证书重量 Bias = Avg Wt. - Conventional Wt.	#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!
标样不确定性 =(Ustd) Uncertainty of standard(s)	0.000000	0.000000	0.000000	0.000000	0.000000
3 的均方根 = Square Root of 3	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	0.000000	0.000000	0.000000	0.000000
合并 Unc** = Combined Unc**	#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!

Balance Exercise 2 Linearity Tests (uncertainty estimates)

偏差(mg) Bias in (mg)	#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!
不确定性mg (U*1000) U in mg (U*1000)	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!
不确定性 % U in %	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!
** Uc= (U _{sd} ² +U _{std} ² +(B/2) ²) ^{.5}					

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 μ L tolerances = Accuracy $\pm 0.8\%$ or $\pm 8.0 \mu$ L

Precision $\pm 0.15\%$ or $\pm 1.5 \mu$ 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. One must be able to be used to read the temperature of water.
5. Humidity meter with calibration certificate or manufacturer specifications
6. Four 1 ml fixed volume air displaced pipettes with current calibration certificates.
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 H₂O
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- μL tolerances for 1 ml?
5. Is the standard deviation within the +/- 1.5 μL 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					
$U_c = (U_{sd}^2 + (B/2)^2)^{.5}$					
Expanded U = $U_c \times 2$					
Relative % Uncertainty					
	TEAM AVERAGE EVALUATION OF BIAS & PRECISION				
Average =					
Standard Deviation=					
Z-Factor =					
Volume (Z x Ave Wt.) =					
Volume in micro liters (μL)=					
SD x Z*1000 = μL					
Bias					
$U_c = (U_{sd}^2 + (B/2)^2)^{.5}$					
Expanded U = $U_c \times 2$					
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 H₂O
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					
	TEAM AVERAGE EVALUATION OF BIAS &PRECISION				
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					

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	分析员-5 Analyst 5
重量 1 Weight 1	0.9977	0.9977	0.9977	0.9977	0.9977
重量 2 Weight 2	0.9966	0.9966	0.9966	0.9966	0.9966
重量 3 Weight 3	0.9945	0.9945	0.9945	0.9945	0.9945
重量 4 Weight 4	0.9937	0.9937	0.9937	0.9937	0.9937
重量 5 Weight 5	0.9945	0.9945	0.9945	0.9945	0.9945
重量 6 Weight 6	0.9993	0.9993	0.9993	0.9993	0.9993
重量 7 Weight 7	0.9915	0.9915	0.9915	0.9915	0.9915
重量 8 Weight 8	0.9967	0.99	0.9999	0.9966	1.001
重量 9 Weight 9	0.9955	1	1.0010	0.9966	1.0015
重量 10 Weight 10	0.9956	1.01	0.9940	0.9988	1.0019
平均 = Average	0.99556	0.99678	0.99627	0.99598	0.99722
标准偏差 = Std. Deviation	0.0022	0.0056	0.0031	0.0024	0.0036
Z系数 = Z-Factor	1.0032	1.0032	1.0032	1.0032	1.003
体积 (Z x 平均重量) = Volume (Z x Avg. Wt.)	0.99875	0.99997	0.99946	0.99917	1.00021
体积, 微升 (µL)= Volume in micro liters (µL)	998.7	1000.0	999.5	999.2	1000.2
标准偏差 x Z = +/- ml	0.0022	0.0057	0.0031	0.0024	0.0037
标准偏差 ml x 1000= SD in µL	2.20	5.66	3.13	2.43	3.65
标称体积 = Nominal Volume	1000	1000	1000	1000	1000
计算体积, µL= Calculated Volume in µL	998.7	1000.0	999.5	999.2	1000.2
偏差 (不准确) Bias (inaccuracy)	-1.3	0.0	-0.5	-0.8	0.2
(+/-8.0µL) 体积容差 = Volume Tolerance	8	8	8	8	8
(+/- 1.5 µL 标准偏差容差) SD Tolerance	1.5	1.5	1.5	1.5	1.5
通过, 如果标准偏差和偏差小于容差 Pass if SD & Bias < Tolerances					
$Uc = (Usd^2 + (B/2)^2)^{.5}$	2.3	5.7	3.1	2.5	3.7
扩展 U = Uc*2 Expanded	4.6	11.3	6.3	4.9	7.3
相对 % 不确定性 Relative % Uncertainty	0.46%	1.13%	0.63%	0.49%	0.73%
偏差和精度小组平均评价 TEAM AVERAGE EVALUATION OF BIAS & PRECISION					
平均 = Average	0.996362	0.9933	0.985	0.9945	1.0075
标准偏差 = Standard Deviation	0.00352	0.0045	0.0025	0.005	0.006
Z系数 = Z Factor	1.0032	1.0031	1.0033	1.0032	1.0032
体积 (Z x 平均重量) = Volume (Z x Avg. Wt.)	0.99955	0.99638	0.98825	0.99768	1.01072
体积, 微升 (µL)= Volume in micro liters (µL)	999.6	996.4	988.3	997.7	1010.7
标准偏差 x Z*1000 = µL SD x Z*1000 = µL	3.528	4.514	2.508	5.016	6.019
偏差 Bias	-0.4	-3.6	-11.7	-2.3	10.7
$Uc = (Usd^2 + (B/2)^2)^{.5}$	3.5	4.9	6.4	5.1	8.1
扩展不确定性 = Uc*2 Expanded U = Uc*2	7.07	9.73	12.78	10.30	16.12
相对 % 不确定性 Relative % Uncertainty	0.71%	0.97%	1.28%	1.03%	1.61%

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

End user

Troemner Inc
201 Wolf Drive
Thorofare NJ 08086

Page 1 of 1

Weight

Certificate Number : JOEWTS-1
Date of Calibration : 09-SEP-2011
Next Due Date : 09-SEP-2012

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/NCCL Z540-1-1994.

Weights listed in the calibration report have been compared to reference standards that are directly traceable to 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 measurement. 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 $8.0\text{g}\cdot\text{cm}^{-3}$ and balanced in air density of $0.00120\text{g}\cdot\text{cm}^{-3}$.

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.

Inventory Difference Assessment Exam

(Instructor Key)

Name: _____

Date: _____

1. (Objective 7.2) What is one reason why inventory differences (ID) are nonzero.
- TIDs are not in their proper locations.
 - Sometimes static inventory items are not remeasured.
 - Transfer checks are not performed.
 - Measured values include measurement error.**

Given the hypothetical MBA structure, circle the correct answer for the following questions.

2. (Objective 7.5) Suppose the measurement of the discard stream of liquid waste (4) from the recovery MBA overestimates the actual amount of material discarded: the actual amount is 10 grams, and the measured value is 30 grams. What will this do to the ID in the recovery MBA?
- The ID will decrease by 20 grams.**
 - The ID will increase by 20 grams.
 - The ID will increase by 40 grams.
 - The ID will not be affected by the situation.

3. (Objective 7.5) Suppose the measurement of recovered oxide (9) from the recovery MBA to the reduction MBA overestimates that actual amount of material: the actual amount is 2.1 kgs and the measured value is 2.2 kgs. What will this do to the ID in the two MBAs.
- The ID in the recovery MBA will increase by 0.1 kgs and the ID in the reduction MBA will decrease by the same amount.
 - The ID in the recovery MBA will decrease by 0.1 kgs and the ID in the reduction MBA will increase by the same amount.**
 - Both IDs will decrease by 0.1 kgs.
 - Both IDs will increase by 0.1 kgs.
4. (Objective 7.5) Suppose there is a tank of material in the reduction MBA whose content is overestimated at the June 30th 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 (the ID computed for the period July 1–31)?
- Both IDs will decrease.
 - Both IDs will increase.
 - The June ID will decrease and the July ID will increase.**
 - The June ID will increase and the July ID will decrease.
5. (Objective 7.1) Suppose that every month for many months the oxide measurements are overstated. This would affect the ID
- Mean.**
 - Standard deviation.
 - Mean and standard deviation.
6. (Objective 7.3) Suppose that the random error of a significant measurement method increased during the month of May. This would affect the ID
- Mean.
 - Standard deviation.**
 - Mean and standard deviation.

(Objective 7.4) Identify the following as characteristics of historical ID limits (H), variance-propagated ID limits (V), or both (B).

7. Relatively easy to calculate H
8. Requires assessing measurement errors V
9. Requires the use of past ID data H
10. Generates an estimate of the standard deviation of the ID B
11. Yields standard deviations based on error propagation V

Inventory Difference Assessment – Activity 2

Effects of Various Types of Errors on the Inventory Difference (ID) (Instructor Key)

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?

It will reduce it by 20 grams.

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?

It will reduce the ID in the recovery MBA but increase (loss) in the reduction MBA by the same amount. When one MBA ID runs consistently in the opposite direction from the ID of an MBA for which there is a flow between, it indicates errors in the flow measurement.

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?

It will reduce (gain) the ID in the June ID, but increase (loss) it in the July ID. A month to month up and down behavior of the ID indicates uncertainties in the inventory measurement are dominant.

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)

In June it will be a loss to ID
In July it will be a gain to ID

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?

Since the material is not remeasured (is static in the storage MBA) there will be no effect on the ID: generally, the ID in such MBAs will be zero. The recovery ID in June will be driven down, in August it will be driven up.

Module 11

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**
- **Understand how to produce a working calibration material that is traceable to the international standards**

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**
- **Data evaluation**
- **Assigned concentrations & uncertainties**

Standards & Data Quality Objectives

- **Standard Reference Material (SRM)**
- **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**

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**

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

Preparation scheme for calibration and test materials

Uranyl Nitrate Solutions Prepared

- ~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

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 U₃O₈
 - NBL modified Davies and Gray titrametric method
- **Two laboratories were involved in the program**
 - The Department of Energy Standards Laboratory (now New Brunswick Laboratory (NBL))
 - Private commercial laboratory
- **Another RCTM was prepared & the whole characterization repeated in 1978**

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 _A =	associated standard deviation	0.2268495	
F =	purity of starting material	0.99975	0.000085
b =	air buoyancy	0.99992	0
W ₁ =	weight of the starting material	166.45221	0.00019
W ₂ =	tare weight of the flask	176.695	0.034
W ₃ =	gross weight of the solution & flask	910.209	0.034
W ₄ =	(W ₃ - W ₂) = net weight of solution	733.514	0.048
S =	standard deviation		
S _A =	(F*b*W ₁)/W ₄	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)
--------------------------------	--------------------------

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 _A =	associated standard deviation		0.000019
F =	purity of starting material	0.99975	0.000085
b =	air buoyancy	0.99992	0
W ₁ =	weight of the starting material	155.3783	0.00011
W ₂ =	tare weight of the flask	164.858	0.0083
W ₃ =	gross weight of the solution & flask	882.044	0.0132
W ₄ =	(W ₃ - W ₂) = net weight of solution	717.186	0.0156
S =	standard deviation		
S _A =	$(F \cdot b \cdot W_1) / W_4$	0.216578444	
S =	$(1/W_4) \cdot (b^2 \cdot (F^2 \cdot W_1^2 + W_1^2 \cdot S_F^2) + A^2 \cdot (W_2^2 + W_3^2))^{.5}$		0.000019

Final Concentration in mg U/g=	216.58 (+/- 0.024 mgU/g)
--------------------------------	--------------------------

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

Data Collected in Confirmation Work from Outside Laboratories using 1976 RCTM

The Mean (M) and Standard Deviation (S) of each set of results were calculated using the following equations:

$M = (\sum X_i) / n$									
$S = ((\sum (X_i - M)^2) / (n-1))^{1/2}$									
n= number of samples in each set									
Outside Laboratory-Gravimetric				Outside Laboratory NBL Modified D&G					
	RCTM		WCTM		RCTM		WCTM		
	226.99		219.25		226.95		219.39		
	226.98		219.24		226.99		219.40		
	227.02		219.38		227.01		219.38		
	227.00		219.24		226.96		219.37		
	226.96		219.38		226.98		219.40		
	227.04		219.32		227.03		219.38		
					226.98		219.39		
					226.98		219.39		
					227.01		219.40		
M₁=	226.998	M₂=	219.30	M₃=	226.988	M₄=	219.389		
S₁=	0.03	S₂=	0.068	S₃=	0.025	S₄=	0.011		
RSD₁=	0.013%	RSD₂=	0.031%	RSD₃=	0.011%	RSD₄=	0.005%		
n₁=	6.00	n₂=	6	n₃=	9	n₄=	9		
				pooled S3	0.087	pooled S4	0.087		
F-Test of Precision:									
Calculated F ratios for both methods are compared to tabulated F values at the 95% Confidence Level.									
Outside Laboratory - Gravimetric.									
Calculated F=	$S_1^2/S_2^2 =$	0.178		1/F=	5.604				

7	<u>Calculation of the Standard Deviation (S_A) associated with A,</u>						
	with f_A degrees of Freedom						
	$S_A \approx$	$(1/W*((1+4*W_2*W_4)*(1/f_2+1/f_4)))^{.5}$					
	$W \approx$	$(1/V_2+1/V_4)$	=	1741			
	$S_A \approx$	0.015					
	Na is the number of degrees of freedom used in calculating the limit of error for A.						
	$Na \approx$	$1/((W_2^2/f_2)+(W_4^2/f_4)) \approx$		14	*		
	* = Rounded to the nearest whole integer.						

2	F-Test of Precision:						
	Calculated F ratios for both methods are compared to tabulated F values at the 95% Confidence Level.						
	Outside Laboratory - Gravimetric.						
	Calculated F=	$S_1^2/S_2^2 =$	0.178		1/F=	5.604	
	F - Table =	F (1- α /2, n ₁ -1, n ₂ -1)	F(.975, 5,5	7.15	1/F =	0.14	
	The precisions are not different because 0.178 and 5.60 are <7.15 and > 0.14						
	Outside Laboratory - NBL Modified D&G						
	Calculated F=	$S_3^2/S_4^2 =$	5.800		1/F=	0.172	
	F - Table =	F (1- α /2, n ₁ -1, n ₂ -1)	F(.975, 8,8	4.43	1/F =	0.22	
	The precisions are different because 5.80 is >4.43.						
	A pooled standard deviation of 0.087 was calculated from these and past data from this laboratory's						
	NBL Modified D&G method. This value will be used in all subsequent calculations, because their						
	precision on the titrations of the WCTM was better than their past performance.						

3	Calculation of the Methods Means Based on the RCTM						
	The two WCTM means (X) are bias corrected for the differences observed on the RCTM analyses.						
	The 1967 RCTM reference value R = 226.8495 mgU/g						
	$X_2 = M_2 * (R / M_1)$		219.158				
	$X_4 = M_4 * (R / M_3)$		219.255				
	$(X_2 + X_4) / 2$		219.207				

4	<u>Calculation of the Equality of the Means</u>						
	The appropriate variances (V) and degrees of freedom (f) for each mean are calculated.						
	$V_2 \approx$	$X_2^2 * ((S_1^2 / (n_1) * M_1^2) + (S_2^2 / (n_2) * M_2^2))$					
	$V_2 \approx$	0.00089					
	$V_4 \approx$	$X_4^2 * ((Sp_3^2 / (n_3) * M_3^2) + (Sp_4^2 / (n_4) * M_4^2))$					
	$V_4 \approx$	0.00162					
	$f_2 \approx$	$V_2^2 / (((X_2^2 * S_1^2) / (n_1 * M_1^2)) / (n_1 - 1)) + ((X_2^2 * S_2^2) / (n_2 * M_2^2)) / (n_2 - 1))$					
	$f_2 \approx$	7					
	$f_4 \approx$	$V_4^2 / (((X_4^2 * S_3^2) / (n_3 * M_3^2)) / (n_3 - 1)) + ((X_4^2 * S_4^2) / (n_4 * M_4^2)) / (n_4 - 1))$					
	$f_4 \approx$	16					
	* = Rounded to the nearest whole integer.						

5	<u>Compute the T static with F Degrees of Freedom Using the Following Equation:</u>							
	T =	X ₂ - X in which	219.158 - 219.255 - X	/ (0.00089 + 0.00162) √.5	=	1.94		
	f ≈	(V ₂ + V ₄) ² / ((V ₂ ² / f ₂) + (V ₄ ² /	22	*				
	T from T-Table @ (1-α/2, f) = T (0.975, 22) =				2.074			
	Because 1.94 is < 2.074, the means are not different							
	* = Rounded to the nearest whole integer.							

6	<u>Assignment of WCTM Concentrations Value (A)</u>				
	<u>by weighting the Bias Corrected Means from Each Method.</u>				
	A =	$W_2 X_2 + W_4 X_2$			
	$W_2 =$	$1/v_2/(1/v_2+1/v_4)$		=	0.646
	$W_4 =$	$1 - W_2$		=	0.354
	A =	219.192			

7	<u>Calculation of the Standard Deviation (S_A) associated with A,</u>					
	with f _A degrees of Freedom					
	S _A ≈	(1/W*((1+4*W ² *W ⁴)*(1/f ² +1/f ⁴))) ^{.5}				
	W≈	(1/V ₂ +1/V ₄)	=	1741		
	S _A ≈	0.015				
Na is the number of degrees of freedom used in calculating the limit of error for A.						
	Na≈	1/((W ²² /f ²)+(W ⁴² /f ⁴)) ≈		14	*	
* = Rounded to the nearest whole integer.						

8. Calculation of the Limit of Error (LE) and Relative Limit of Error (RLE) of $<1/3$ of the Plant RLE of 0.25% (0.08%)

$$LE = 2SA = 0.031 \quad RLE = 100\% \times L \ 0.014\%$$

9. Test to Determine if the RLE Meets the Requirement

The target RLE of 0.08% is $> 0.014\%$ of the WCTM, therefore the WCTM characterization is satisfactory>

10. Calculation of the 95% Confidence Interval for the Assigned Value

- $CI - A \pm t(1-\alpha/2, Na)(SA) \quad t(0.975, 14) = 2.145$
- $CI = 219.192 \pm 2.145 \times 0.015 = 0.032$

291.160 to 219.224 mgU/g solution WCTM

Summary

- **A large quantity of Uranyl Nitrate stock solution was prepared from plant material**
- **Enough material was prepared so it could be used to make dilutions to cover all methods used**
- **The WCTM uncertainty was less than the target uncertainty**
- **This standard has been used for 30 years at the Savannah River Site**

Module 13

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

$$\text{Var(ID)} = [\sum_i (\sigma_r m_i)^2] + (\sigma_s M)^2$$

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

$$\begin{aligned} M_{In-Process} &= BI_{In-Process} + R_{In-Process} - S_{In-Process} - EI_{In-Process} \\ &= 12kg + 0 - 0 - 0 = 12kg \end{aligned}$$

$$\begin{aligned} \Sigma(\sigma_r m_i)^2 &= (0.003 \times 12kg)^2 + (0.003 \times 0)^2 + (0.003 \times 0)^2 + (0.003 \times 0)^2 \\ &= 0.001296kg^2 + 0 + 0 + 0 \\ &= 0.001296kg^2 \end{aligned}$$

$$\begin{aligned} (\sigma_s \Sigma m_i)^2 &= 0, \text{ since there is no systematic error for in-process} \\ \text{var}(M_{In-Process}) &= \Sigma (\sigma_r m_i)^2 + (\sigma_s \Sigma m_i)^2 \\ &= 0.001296kg^2 \end{aligned}$$

Finding the Scrap Variance Contribution

$$\begin{aligned} M_{Scrap} &= BI_{Scrap} + R_{Scrap} - S_{Scrap} - EI_{Scrap} \\ &= 0 + 0 - 0 - 4kg = -4kg \end{aligned}$$

$$\begin{aligned} \Sigma(\sigma_r m_i)^2 &= (0.007 \times 0)^2 + (0.007 \times 0)^2 + (0.007 \times 0)^2 + (0.007 \times 4kg)^2 \\ &= 0.000784kg^2 \end{aligned}$$

$$\begin{aligned} (\sigma_s \Sigma m_i)^2 &= (0.002 \times -4kg)^2 = 0.000064kg^2 \\ var(M_{Scrap}) &= \Sigma(\sigma_r m_i)^2 + (\sigma_s \Sigma m_i)^2 \\ &= 0.000784kg^2 + 0.000064kg^2 \\ &= 0.000848kg^2 \end{aligned}$$

Finding the Finished Fuel Variance Contribution

$$\begin{aligned} M_{Final} &= BI_{Final} + R_{Final} - S_{Final} - EI_{Final} \\ &= 75 \times 0.4kg + 0 - 215 \times 0.4kg - 0 = -56kg \end{aligned}$$

$$\begin{aligned} \Sigma(\sigma_r m_i)^2 &= 75(0.0025 \times 0.4kg)^2 + 0 + 215(0.0025 \times -0.4kg)^2 + 0 \\ &= 0.000075kg^2 + 0.000215kg^2 = 0.00029kg^2 \end{aligned}$$

$$\begin{aligned} (\sigma_s \Sigma m_i)^2 &= (0.0005 \times -56kg)^2 = 0.000784kg^2 \\ var(M_{Final}) &= \Sigma(\sigma_r m_i)^2 + (\sigma_s \Sigma m_i)^2 \\ &= 0.00029kg^2 + 0.000784kg^2 \\ &= 0.001074kg^2 \end{aligned}$$

Finding the Feed Material Variance Contribution

$$\begin{aligned} M_{Feed} &= B I_{Feed} + R_{Feed} - S_{Feed} - E I_{Feed} \\ &= 14 \times 2kg + 28 \times 2kg - 0 - 18 \times 2kg = 48kg \end{aligned}$$

$$\begin{aligned} \Sigma(\sigma_r m_i)^2 &= 14(0.005 \times 2kg)^2 + 28(0.005 \times 2kg)^2 + 0 + 18(0.005 \times -2kg)^2 \\ &= 0.0014kg^2 + 0.0028kg^2 + 0.0018 = 0.006kg^2 \end{aligned}$$

$$\begin{aligned} (\sigma_s \Sigma m_i)^2 &= (0.001 \times 48kg)^2 = 0.002304kg^2 \\ var(M_{Feed}) &= \Sigma(\sigma_r m_i)^2 + (\sigma_s \Sigma m_i)^2 \\ &= 0.006kg^2 + 0.002304kg^2 \\ &= 0.008304kg^2 \end{aligned}$$

Finding the Total Variance and LEID

The total variance for the ID is the sum of the variances for all strata.

$$\begin{aligned} \text{var}(ID) &= \text{var}(M_{In-Process}) + \text{var}(M_{Scrap}) + \text{var}(M_{Final}) + \\ &\quad \text{var}(M_{Feed}) \\ &= 0.001296\text{kg}^2 + 0.000848\text{kg}^2 + 0.001074\text{kg}^2 + \\ &\quad 0.008304\text{kg}^2 \\ &= 0.011522\text{kg}^2 \end{aligned}$$

The 2-sigma limit of error about the ID (LEID) is

$$\begin{aligned} LEID &= 2 \times \sqrt{\text{var}(ID)} = 2 \times \sqrt{0.011522\text{kg}^2} = \\ &0.214681\text{kg} \end{aligned}$$

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 grams² or kilogram²

sID = 0.107341
LEID(2s) 0.214681

Summarize the Variance Terms (kg²)

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

Component	Random	Systematic	Total
Feed	52.1	20.0	72.1
In-process	11.2	0.0	11.2
Finished Fuel	2.5	6.8	9.3
Scrap	6.8	0.6	7.4
Total	72.6	27.4	100.0

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

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

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 ²)	Systematic (grams ²)
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: $2,833,662 + 3,457,689 = 6,291,351$ gram²
SEID = $\text{sqrt}(6,291,351) = 2,508$ grams
LEID = LEMUF = $2 * 2,508 = 5,016$ grams

Inventory Difference Assessment

Activity 1, Sample Detailed Material Balance

Using the material balance, uncertainty information, and variance contributions tables from a facility that produces metal plutonium buttons and has nitrate input, and oxide conversion, complete the following tasks:

1. Compute the overall uncertainty of the inventory difference (ID) and limit of error of the ID (LEID).
 - Ignore sample, liquid waste, and air discards.
2. Determine where to allocate efforts to reduce the overall uncertainty.
 - Discuss the implications of how the nitrate BI, receipts, and EI impact the LEID.
 - Develop at least three recommendations and be prepared to defend them.

Material Balance Table

Component	Detail	Quantity [Pu-grams (g)]	Totals
Beginning Inventory			
Nitrate	200 liters (L) @ 325 g/L; one batch	65,000	
Oxide	8 cans @ 1500 g/can	12,000	
Equipment Holdup (NDA)	1850 g; one batch	1,850	
		Total BI	78,850
Receipts (Additions)			
Nitrate	10 batches @ 50 L/batch & 350 g/L	175,000	
		Total Add	175,000
Shipments (Removals)			
Metal Buttons	100 buttons @ 2,000 g	200,000	
Solid Waste	Off-specification oxide 3 cans @ 1,100 g/can	3,300	
		Total Removals	203,300
Ending Inventory			
Nitrate	150 L @ 300 g/L; one batch	45,000	
Equipment Holdup (NDA)		3,500	
		Total EI	48,500
		BI + A – R – EI = ID	2,050

Uncertainty Information Table

Method		Random (percent)	Systematic (percent)
Nitrate	Calibration	1.000	0.400
	Sampling	0.750	0.500
	Analytical	0.600	0.250
Oxide	Weight	0.150	0.100
	Sampling	1.500	1.750
	Analytical	1.250	0.900
Equipment	NDA	25.000	15.000
Metal	Weight	0.150	0.100
	Sampling	0.050	0.060
	Analytical	0.700	0.450
Solid Waste	NDA	10.000	25.000

Variance Contributions Table

	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%

Inventory Difference Assessment – Activity 2

Effects of Various Types of Errors on the Inventory Difference (ID) (Instructor Key)

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?

It will reduce it by 20 grams.

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?

It will reduce the ID in the recovery MBA but increase (loss) in the reduction MBA by the same amount. When one MBA ID runs consistently in the opposite direction from the ID of an MBA for which there is a flow between, it indicates errors in the flow measurement.

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?

It will reduce (gain) the ID in the June ID, but increase (loss) it in the July ID. A month to month up and down behavior of the ID indicates uncertainties in the inventory measurement are dominant.

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)

In June it will be a loss to ID
In July it will be a gain to ID

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?

Since the material is not remeasured (is static in the storage MBA) there will be no effect on the ID: generally, the ID in such MBAs will be zero. The recovery ID in June will be driven down, in August it will be driven up.

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?

Limit of Error on Inventory Difference (LEID)

Note: Handout for Module 13. See slides 13-26 through 13-38

Measurement Uncertainty (Relative Standard Deviation in Percent)

Material Type	Random	Systematic
Feed Material	0.5	0.1
Finished Fuel	0.25	0.05
Scrap	0.7	0.2
In Process	0.3	-

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

75 of these same as Beg. Inventory

18 of these same as Additions

Measurement Type/Method	ID Component		kg
Feed	Beg. Inventory	14 Measurements of 2 kg batches	28
	Receipt	10 Measurements of 2 kg batches	20
	Receipt	18 Measurements of 2 kg batches	36
	End. Inventory	18 Measurements of 2 kg batches	-36
In Process	Beg. Inventory	12 kg in 1 batch	12
Finished Fuel	Beg. Inventory	75 Measurements of .4 kg batches	30
	Shipment	75 Measurements of .4 kg batches	-30
	Shipment	140 Measurements of .4 kg batches	-56
Scrap	End. Inventory	4 kg in 1 batch	-4
		ID is	0

} Combine for shared systematic error

} Ignore since not active inventory

} Ignore since not active inventory

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

sID =

0.107341

LEID

0.214681

$\sigma_{ID}^2 = 0.007772$
 $\sigma_{ID} = 0.088159$
 $LEID = 2\sigma_{ID} = 0.176318$

Variance Summary				Percentages			
Component	Random	Systematic	Total	Component	Random	Systematic	Total
Feed	0.006	0.002304	0.0083	Feed	52.1	20	72.1
In Process	0.001296	0	0.0013	In Process	11.2	0	11.2
Finished Fuel	0.00029	0.000784	0.0011	Finished Fuel	2.5	6.8	9.3
Scrap	0.000784	0.000064	0.0008	Scrap	6.8	0.6	7.4
Total	0.00837	0.003152	0.0115	Total	72.6	27.4	100
		SID	0.1073				
		LEID	0.2147				

Inventory Difference Assessment Exam

Name: _____

Date: _____

1. What is one reason why inventory differences (ID) are nonzero.
 - a. TIDs are not in their proper locations.
 - b. Sometimes static inventory items are not remeasured.
 - c. Transfer checks are not performed.
 - d. Measured values include measurement error.

Given the hypothetical MBA structure, circle the correct answer for the following questions.

2. Suppose the measurement of the discard stream of liquid waste (4) from the recovery MBA overestimates the actual amount of material discarded: the actual amount is 10 grams, and the measured value is 30 grams. What will this do to the ID in the recovery MBA?
 - a. The ID will decrease by 20 grams.
 - b. The ID will increase by 20 grams.
 - c. The ID will increase by 40 grams.
 - d. The ID will not be affected by the situation.

3. Suppose the measurement of recovered oxide (9) from the recovery MBA to the reduction MBA overestimates that actual amount of material: the actual amount is 2.1 kgs and the measured value is 2.2 kgs. What will this do to the ID in the two MBAs.
 - a. The ID in the recovery MBA will increase by 0.1 kgs and the ID in the reduction MBA will decrease by the same amount.
 - b. The ID in the recovery MBA will decrease by 0.1 kgs and the ID in the reduction MBA will increase by the same amount.
 - c. Both IDs will decrease by 0.1 kgs.
 - d. Both IDs will increase by 0.1 kgs.
4. Suppose there is a tank of material in the reduction MBA whose content is overestimated at the June 30th 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 (the ID computed for the period July 1-31)?
 - e. Both IDs will decrease.
 - f. Both IDs will increase.
 - g. The June ID will decrease and the July ID will increase.
 - h. The June ID will increase and the July ID will decrease.
5. Suppose that every month for many months the oxide measurements are overstated. This would affect the ID
 - i. Mean.
 - j. Standard deviation.
 - k. Mean and standard deviation.
6. Suppose that the random error of a significant measurement method increased during the month of May. This would affect the ID
 - a. Mean.
 - b. Standard deviation.
 - c. Mean and standard deviation.

Identify the following as characteristics of historical ID limits (H), variance-propagated ID limits (V), or both (B).

7. Relatively easy to calculate _____
8. Requires assessing measurement errors _____
9. Requires the use of past ID data _____
10. Generates an estimate of the standard deviation of the ID _____
11. Yields standard deviations based on error propagation _____