

Applicability of International and DOE Target Values to ALD Destructive Measurement Applications (U)

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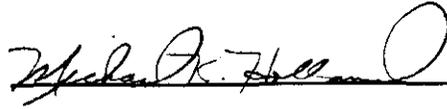
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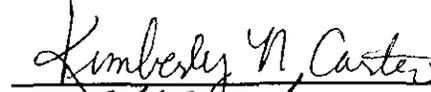
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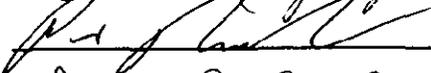
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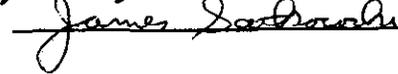
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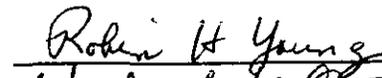
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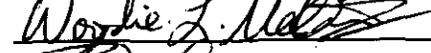
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Key Words

Accountability, Safeguards, International Target Values, Runs Rule, Measurements, Reliability

Abbreviations

ALD	Analytical Laboratories Department
CLAS	Central Laboratory Analytical Services
CTF	Cognizant Technical Function (scientist over a measurement system)
DA	Destructive Analysis
ESARDA	European Safeguards Research and Development Association
ESARDA/WGDA	Working Group on Techniques and Standards for Destructive Analysis
GQ	Goal Quantity – Significant quantity of fissile material safeguarded to prevent diversion and subsequent assembly of a thermal nuclear device.
HEU	High Enriched Uranium
IDMS	Isotope Dilution Mass Spectrometry
IAEA	International Atomic Energy Agency
ISO	International Standards Organization
ITV	International Target Value(s)
LEID	Limit of Error on Inventory Differences
LEU	Low Enriched Uranium [5% ²³⁵ U from SRS HEU Blenddown]
LLNL	NNSA Nuclear Site – Lawrence Livermore National Laboratory
LANL	NNSA Nuclear Site – Los Alamos National Laboratory
NBL	New Brunswick Laboratory [DOE-CH, Argonne, IL]
MBA	Material Balance Area
MC&A	Material Control, and Accountability
MPC&A	Material Protection, Control, and Accountability
NMMD	Nuclear Materials Management Division
NUS	Nuclear Fuel Services, Erwin Tennessee
QC	Quality Control
PUREX	Plutonium and Uranium Extraction Process (previously used in F-Canyon)
Pu ISO	An analysis for Pu Isotopic Distribution (%) by TIMS
TIMS	Thermal Ionization Mass Spectrometer
U ISO	An analysis for U Isotopic Distribution (%) by TIMS
Y-12	NNSA Nuclear Site – Y-12 Plant in Oak Ridge, Tennessee

Purpose

To document Analytical Laboratories Department's (ALD's) technical assessment of compliance requirements and applicability of the International Target Values (ITV) and Central Laboratory Analytical Services' (CLAS's) implementation status. This report also discusses the additional DOE guidance/requirements related to target values.

Abstract

International Target values and target value applicability are a function of the nuclear material processing campaign or application for which the accountability measurement method is being applied. Safeguarding significant quantities of nuclear-grade materials requires that accountability measurements be as accurate, precise, and representative as practically possible. In general, the ITV provides a benchmark for determining generic acceptability of the performance of the various accountability measurement methods, since it represents a performance level that is accepted as highly reliable. There are cases where it is acceptable to select alternative accountability methods not specifically referenced by the ITV, or to use the recognized measurement method, even though the uncertainties are greater than the target values.

These cases include:

- When the material homogeneity or stability is not consistent with the basic assumption associated with application of the ITV;
- When the total quantity of material being protected is small, and thus the total uncertainty associated with the accountability measurement meets the safeguard objective for this material;
- When the measurement uncertainty is not significant relative to other nuclear material accounting uncertainties; and
- When analytical method selection is driven by the need to avoid potential interferences that are (or are sometimes) expected to be present.

It may also be necessary for the laboratory, the customer, and the accountability oversight organizations to accept more liberal method uncertainties than those recommended by ITV because:

- The laboratory is not staffed and funded to achieve the ITV; and/or
- The turnaround time requirements dictate method selection and methodology, not the ITV.

This report discusses the status and applicability of accountability measurement methods performed by Central Laboratory Analytical Services (CLAS), relative to ITV values, and to DOE's endorsement of these ITV as benchmarks.

This report provides additional information related to the CLAS implementation of the "Runs Rule" and the relationship of its technical basis to the International Target Values.

Assumptions

Major steps¹ in accountancy verification measurements that need to be addressed, known, and validated to ensure the entire measurements process is effective are:

1. Bulk measurements – volume or mass of material
2. Sampling – A representative portion of material is taken from the bulk material.
3. Sample conditioning – Precautions taken to ensure the measured characteristics are preserved during packaging and transport.
4. Shipment – Transport of the sample and chain-of-custody
5. Sample Validation
6. Laboratory takes representative subsample / aliquot.
7. Sample Treatment – Bringing the sample into the most appropriate geometrical, physical, and/or chemical form in preparation for measurements.
8. Measurement – Analytical determination of desired sample characteristic.
9. Calculations – Transforming all results of the measurement into the desired estimate.
10. Reporting Results – Prevent clerical errors during report generation and ensuring proper control of the record to allow retrieval consistent with QA plans.

Introduction

The European Safeguards Research and Development Association's Working Group on Techniques and Standards for Destructive Analysis (ESARDA/WGDA) developed the first set of International Target Values. The WGDA's membership included the international commercial nuclear fuel industry and members of International Atomic Energy Agency (IAEA). Their goal in developing the first set of International Target Values was to provide aggressive benchmarks for key accountability and international safeguard measurements performed in commercial nuclear fuel reprocessing.

These ITV were designed to protect goal quantities (GQ) of nuclear-grade materials at various stages in the reprocessing flowsheet, with consideration given to the state-of-the-art, state-of-the-practices, and the technical limitations for the various measurement methods as well as the attractiveness of the type of nuclear material. In general, it is assumed that the nuclear fuel reprocessing organization has invested adequate time, planning, design, funding, and staffing to provide near ideal / state-of-the-art conditions for sampling and measurements (and bulk material measurements). DOE endorses these target values as benchmarks for assessing measurement performance when applied to appropriate nuclear materials and key accountability/safeguard applications.

The "International Target Values" for nuclear material accountability were developed with a clear scope of applicability and basis for their calculation. Large-scale commercial reprocessing activities have the potential for diversion of special nuclear materials into covert weapons programs. The ITV are intended to provide plant operators, laboratories, and safeguards regulators with a benchmark for achievable measurement quality, under well controlled conditions that were considered routine for the European reprocessing facilities and their analytical laboratories.

Isotope Dilution Mass Spectrometry (IDMS) is the method of choice for input accountability measurements for spent fuel dissolver solutions. Measurement of a dissolver solution required optimum accuracy and precision due to the large quantity of nuclear material that was protected by a single measurement. Measurement uncertainty requirements driven by the accountability objectives for dissolver solution presented challenging target values for mass spectrometry when applied to commercial dissolver solutions. Implicit with these target values was the need and capability to obtain and provide for measurement, samples that are representative (with a sampling uncertainty significantly below the measurement target values for precision and accuracy). Sampling uncertainty could be bounded by measurement uncertainty for this type of application because the physical form of the material (solution) and the availability of reliable sample equipment permitted this quality of sampling. In addition, the ability to correlate between measurements, (Pu, U, Density) and validate results of replicate sample measurements and different measurements (Pu, U, Density) aided in ensuring a reliable sampling process.

The requirements for accurate volume measurement of the bulk material supported the assignment of the challenging measurement target values. ITV's that are significantly less than the uncertainty associated with the bulk material measurement are not consistent with the intent of the ITV and are not cost effective.

Evaluation/Discussion

Clearly, stringent/challenging measurement target values are not appropriate or cost effective if large uncertainties exist in the bulk material measurement and/or the sampling process. If the material being sampled is not homogeneous, then the sample process will have larger than ideal random and systematic error components, which are likely to dwarf the International Target Values for measurements. When measurement target values are dwarfed by other sources of accountability error, the ITV's should not be treated as applicable goals for measurement uncertainty in that specific nuclear material processing activity.

Analytical measurement methods that meet or exceed the requirements of the International Target Values for precision and accuracy are accepted as generically appropriate to nuclear material accountability application. DOE should (and does) endorse the International Target Values as a benchmark for assessing measurement quality. When applied to sample types that are within the scope and technical capability of the measurement method, methods that meet the International Target Values automatically have the necessary pedigree for nuclear material accountability.

However, the converse is not true. Measurement methods that have random and systematic error components that exceed the target values do not automatically fail to meet requirements for all accountability applications. The nuclear material processing activities must be evaluated to determine the impact of measurement uncertainty on potential inventory differences. Attention must also be given to all sources of uncertainty including bulk material measurement, representative sampling, material homogeneity, and material stability. The assessment of impact on inventory differences must ensure that these sources of error receive the same challenging level of scrutiny that is more easily and quantitatively applied to destructive measurement methods.

Each of these sources of uncertainty has random and systematic error components. Because of the implied applicability of the International Target Values, appropriate International Target Values for each of these error sources do not exist for all potential applications.

For example, commercial nuclear-grade plutonium and uranium nitrate solutions and oxide materials have product specifications and manufacturing conditions that ensure homogeneity. However, these specifications are not applicable to scrap oxide materials. By their nature, scrap materials have varying degrees of nonhomogeneity and stability. Thus a sampling process may obtain a "representative sample," but samples collected by this process can still have significant random and systematic errors relative to the bulk material. An appropriate target value for sampling these types of materials may be 5-20%, dictated primarily by the homogeneity of the material (not by the limits on the potential inventory differences derived by calculations that are based on goal quantities). For the sampling of 'dirty scrap' materials, the International Target Value 2000 provides a random error target value of 10% for scrap materials, but lists the target value for systematic error as 'not yet defined.' This situation acknowledges the difficulty associated with defining target value requirements for the sampling of scrap and scrap-like nuclear materials, such as the FB-Line and HB-Line processing of mixed scrap materials.

Evaluation/Discussion, continued

A copy of the “Destructive Assay Methods Compendium”² developed by a team composed of representatives from DOE-New Brunswick Laboratory, LLNL, LANL, Y-12, and SRS is attached for information. This document was prepared as an aid to the Joint U.S. – Russia MPC&A Program. Standard Organization–11 is planning to publish this document as an ISO Technical Standard. It expands upon the International Target Values, providing aggressive goals for measurement reliability, while still considering the significant differences between measurements of pure-type materials and scrap materials. Consideration is given to the technical capability of the various measurement methods that can be appropriately used for different types of nuclear material accountability applications. This document also contains some programmatic guidance for calculating appropriate material balance area (MBA) inventory difference limits to estimate uncertainty requirements for destructive assay measurements.

The target value tables within the DA Method Compendium consistently endorse the International Target Value for the material types to which they apply and provide more appropriate measurement target values for materials of lower quality (and lower significance to the safeguards program objectives). Examples where the DA Method Compendium provides more appropriate target values for measuring scrap and waste materials include:

	Random Error (1-sigma)	Systematic Error
Pu Coulometry	1.0%	0.5%
U Titration	0.5%	0.5%
Pu Titration	1.0%	0.5%
U & Pu Fluorescence	3.0%	5.0%
Pu Spectrophotometry	1.0% - 2.0%	1.0%-2.0%
U & Pu IDMS	0.5%	0.5%

Each of these target values presumes that the measurement method being quoted is the method of choice for the application, the bulk material measurement has the customary uncertainty, and the material, although a scrap/waste material, is still reasonably homogeneous and can be representatively sampled with a minimal uncertainty. In the case of U & Pu IDMS, these target values include process and product materials, in addition to waste materials.

The DA Method Compendium provides target values for bulk solution volume measurements using a Ruska Electromanometer of 0.3% random error and 0.3% systematic error, referencing the DOE as the source for these target values. Although target values for the bulk measurement of solid materials are not provided in this document, the solution volume target values should be treated as the bounding case.

In cases where material homogeneity is poor or indeterminate, estimating random and systematic error components for this attribute is difficult to quantify and its impact upon representative sampling (and laboratory sub-sampling) further complicates the error propagation.

When the actual propagated measurement method uncertainty (i.e., random and systematic error combined linearly or as a root-mean square) is less than any of the other sources of accountability error, then the argument for requiring that measurement method target values be satisfied is not valid or cost effective. This is especially true for large errors from material inhomogeneity or nonrepresentative sampling since these error sources are so closely linked to the total uncertainty of the assay or concentration measurement.

Evaluation/Discussion, continued

“Engineering Judgment” should not be the primary mechanism for estimating material homogeneity or sampling uncertainty for solid materials. Replicate samples and multiple measurements need to be taken until these sources of accountability error are quantified and then used in the calculations of the limit of error on inventory differences (LEID). Once these sources of error are quantified, they can be compared to the actual uncertainty of the analytical measurement method to determine if the stringent measurement method target values are really applicable. If improving the measurement methods random or systematic errors to achieve the target values would be complex, expensive, and/or impact mission objectives and would not result in a significant improvement in the LEID, then the measurement target value should not be treated as applicable.

Every step of the process, starting with the bulk material measurement, must be performed under well-controlled conditions. Hence a comprehensive measurement control program that includes quality control measurements at each step in the process is imperative.

Discussion of SRS TIMS

The Pu and U thermal ionization mass spectrometry (TIMS) methods implemented by the ALD/CLAS are designed to support process control, nuclear safety, and accountability measurements. The mass spectrometers are operated by a staff of twenty-four (24) technicians on a 24-hour per day, 365-day per year schedule. This analytical service is designed and funded to provide optimum sample throughput and turnaround time, with a measurement reliability consistent with overall operating requirements of the NMMD Nuclear Facilities providing the funding for these analyses. Accountability measurements by mass spectrometry include both plutonium and uranium isotopic distribution (U ISO; Pu ISO) and concentration/assay by isotope dilution (IDMS). Application of these measurement capabilities include:

- F-Canyon – PUREX Suspended March 2002
- FB-Line Material Characterization (Scrap Pu Oxides; Inhomogeneous/Suspect) [Pu ISO / Pu IDMS, U ISO / U IDMS]
- HB-Line Material Characterization (Scrap Pu Oxides; Inhomogeneous/Suspect) [Pu ISO / Pu IDMS, U ISO / U IDMS]
- H-Area Outside Facilities [U ISO / U DG Titration]
 - HEU/LEU Program [U ISO / U DG Titration] *
- H-Canyon Output Accountability [U ISO / U DG Titration]
- H-Canyon Routine Physical Inventories [U ISO / limited U IDMS]
- H-Canyon Input Accountability [U ISO / U IDMS]

* *U Davies-Gray Titration is used for uranium concentration in support of accountability, process control, and LEU product specification.*

Each of these applications will be reviewed, in the order listed above for applicability of target values and compliance with applicable requirements.

Evaluation/Discussion, continued

F-Canyon PUREX Process

When the SRS was operating the PUREX process to produce weapons-grade plutonium the target values were clearly applicable. When the F-Canyon PUREX process was converted to a material disposition and stabilization process, a graded approach to target value requirements was appropriate. The typical F-Canyon feed for material stabilization contained much higher impurity levels and the isotopic distribution was outside of prior weapon-grade specifications. However, these variations in purity and isotopic distribution did not render the target values non-applicable. These materials were still attractive to theft/diversion and International Target Values were still a good guide for input and output accountability. With the suspension of PUREX processing on March 2002, the target values are no longer applicable to the process control measurements now being provided in support of waste disposal and vessel flushing. Although no longer applicable, it is appropriate to note that TIMS Pu/U ISO measurements have met the stringent International Target Values since these values have been in existence. Pu/U IDMS measurements had met PUREX material stabilization accountability needs, but were greater than the stringent International Target Value.

FB-Line and HB-Line Material Characterization

Plutonium and mixed Pu/U Oxides samples are submitted for characterization to determine/validate the disposition path and/or processing requirements. Measurements include Pu/U ISO and Pu/U IDMS (and may in the future include other measurements that have been applied more traditionally to accountability measurements). These oxide materials are often obviously inhomogeneous (as evidenced by simple visual inspection). NMMD applies an adequate/appropriate sampling process that obtains as representative a sample as possible given the nature of the bulk material. While the isotopic and assay information is used for both material characterization and accountability purposes, the International Target Values and the target values in the attached DA Methods Compendium are not applicable. The uncertainty due to inhomogeneity is significantly greater than any errors being introduced by the Pu/U ISO and Pu/U IDMS. The Pu/U isotopic abundance method by TIMS was selected because it is the best method for the required isotopic abundance analysis. The Pu/U concentration by IDMS was selected because:

- The method, with sample pretreatment and purification, is not seriously affected or challenged by the large and diverse distribution of impurity elements in these scrap/scrap-like materials;
- The assay method is approved for accountability measurement;
- The IDMS exceeded applicable data quality objective for the assay of these low-grade nuclear materials; and
- Pu/U isotopic measurements were already required by TIMS and thus IDMS assay was a small increase in measurement scope that involved adding the ^{244}Pu and ^{233}U spike standards to the samples before the TIMS measurement.

Evaluation/Discussion, continued

H-Area Outside Facilities

The outside facilities are being used to hold the existing HEU inventories in preparation for HEU Blendeddown to LEU for shipment to Nuclear Fuel Services (NFS) in Erwin, Tennessee. The current inventory is relatively static. However, when LEU production and shipping begin, the uncertainties associated with the laboratory measurements for U isotopics by TIMS and U concentration by Davies-Gray become increasingly important. The International Target Values for U ISO and U Titration should be treated as applicable, provided:

- The sample validation protocol is implemented (i.e., solution density agreement between replicates and minimum flush volumes are verified) using limits and controls that ensure optimum sampling reliability (not maximum acceptable sampling error); and
- The volume measurements are performed using Ruska Electromanometers that are maintained and controlled in an environment that consistently achieves the U.S. DOE Target Values for these devices.

Both the optimum sample validation and the Ruska enhancements are planned. However, the condition for applying the Ruska are not ideal and target values may not be achieved.

U isotopic by TIMS meets the International Target Values. U concentration by Davies-Gray will need to improve to meet this benchmark. The impact on the LEID from the actual uncertainty from the random and systematic errors of the Davies-Gray titration versus the target values should be examined. The accountancy benefit should justify the costs associated with improving the analytical measurement. The LEID should also be tested for impact using the possible ranges of uncertainties for bulk volume measurement and sampling uncertainty).

[If the cost is not excessive, it may be appropriate for ALD/CLAS to avoid any criticism even if the impact is small by replacing the existing methodology for Davies-Gray titration with the NBL high-precision Davies-Gray titration methodology to achieve the International Target Values for reliability.]

H-Canyon Output Accountability

H-Canyon Output Accountability for uranium isotopics is performed using TIMS. The CLAS method for U ISO by TIMS meets the International Target Values for uranium isotopic measurements. Refer to the preceding section on the H-Area Outside Facilities for a discussion of: plans for HEU/LEU processing (which will be fed by uranium product stream from the HM-Process); bulk volume and sampling reliability; and application of the Davies-Gray Titration for uranium concentration. H-Canyon accountability assay measurements by U IDMS (and Pu IDMS) have increased uncertainty due to multiple / part-time technicians performing measurement. It is appropriate to note that current sample validation requirements for output accountability are based upon a system of maximum allowable sample errors, not optimum sampling reliability. The differences between these methodologies can affect the applicability of the more stringent International Target Values, as the gain in LEID for achieving compliance can be insignificant relative to the cost.

Evaluation/Discussion, continued

H-Canyon Routine Physical Inventories

Refer to the preceding discussion on H-Canyon and H-Area Outside Facilities. Accountability measurements for uranium isotopics are performed by TIMS and uranium concentration by a variety of accountability methods. The impact of measurement uncertainty varies based upon the quantity of uranium in inventory at a given sample point. Sample validation is applied throughout the physical inventory sampling process, although the acceptance criteria is based on maximum allowable sampling error. The physical inventory is based upon multiple measurements, decreasing the significance of random errors. Target values for measurements should not be aggressively applied to all aspects of the physical inventory sample measurement process because of their decreased significance to the LEID.

H-Canyon Input Accountability

Refer to the preceding sections for applicable discussion. Accountability measurements are performed using U ISO and U IDMS. The International Target Values are applicable, provided sampling error is minimized and bulk volume measurements meet DOE Target Values. Sample validation is currently based upon a maximum allowable sampling error methodology.

For additional information on Sample Validation, refer to ALD/CLAS procedures WSRC L3.06-10059, "Sample Validation:", which is available on Shrine at the ALD Homepage: <http://shrine01.srs.gov/analab/>. [Click on the <<Procedure>> button and then select manual L3.06.] Additional information is available in the technical basis package for this procedure, and from James Satkowski, CTF for Sample Validation (and from Michael K. Holland, author of this report and past CTF for Sample Validation).

Evaluation/Discussion, continued

Runs Rule:

During the course of reviewing the International Target Values for accountability measurements, additional technical basis / justification was available for Central Laboratory Analytical Services' (CLAS) implementation of the "Runs Rule."

CLAS implements the "Runs Rule" using procedure WSRC L2-1-00118, "Accountability Method QC Chart Review," based upon the requirements in site procedure WSRC 14Q Procedure 3.10, "Determining and Responding to Control Limits." WSRC site-MC&A has approved this implementing procedure. The CLAS implementation of the Runs Rule provides a 1-sigma precision range for acceptable systematic error. Eight consecutive measurements must exceed the same side of this 1-sigma central band before a systematic trend is considered to be significant (and thus require action by the method CTF to address the adverse trend).

The Runs Rule is not driven by the DOE Orders that govern nuclear material control and accountability. It is a statistical tool that has limitations when applied to analytical measurements. These limitations are addressed when the 1-sigma band is applied, especially for the high precision and accuracy measurements where the systematic uncertainty of the measurements is comparable to the systematic error of the standard used to assess measurement performance and trending. Reducing the Runs Rule below the 1-sigma level would require significant extra analytical expenses in the area of standards preparation, characterization, and maintenance. The required improvements in standards would be a major, unfunded initiative and is not likely to result in improvement to the control of the accountability measurements that are either significant or valuable relative to purpose for the measurements or the other sources of error associated with material accountability. For these reasons, a revision to procedure L2-1-00118 will not be initiated to change the CLAS implementation of the Runs Rule.

The International Target Values for each measurement technique/methodology (mass spectrometry, titration, coulometry, etc.) provide target uncertainty values (1-sigma) for both random and systematic error. In nearly all cases, the allowed systematic error component is set at the same value as the target for the 1-sigma random error component. The International Target Value system provides clear and direct indication that systematic error is a reality for all measurement methods, calibration methodologies, and standard materials. When short-term and/or long-term systematic errors total less than the 1-sigma random error, the systematic error component is at an acceptable level. When the systematic error of the measurement (or measurement system calibration, including the uncertainty of the standard) is within the 1-sigma precision range, it is not essential to determine the source of the systematic error (or to bias correct the measurement results). When the systematic error is tracked, trended, and controlled to ensure that it is small, then the pedigree of the measurement system is maintained and comparison of measurement performance versus the target values is valid.

Conclusions

The International Target Values are excellent benchmarks for evaluating current performance versus established performance levels that are internationally accepted as state-of-the-practice for a measurement method. The DOE Target Values and the recommended performance criteria provided in the DA Method Compendium provide additional target value information to support this benchmarking process. It is the opinion of the author, based upon reviews of measurement performance within the DOE Complex and at international laboratories, that the state-of-the-practice benchmark for Pu/U IDMS are significantly closer to the state-of-the-art capability for Pu/U IDMS than is observed for the other destructive measurement methods having target values. The ITV for Pu/U IDMS is achievable in a research environment or limited throughput application. The Pu/U IDMS target value benchmark may not be achievable under the current sample throughput, staffing, and funding conditions imposed in the ALD/CLAS. However, if the other sources of accountability errors are not minimized, then efforts to achieve the most restrictive target values for Pu IDMS and U IDMS will not be effective at reducing overall accountancy uncertainty. If the overall accountability uncertainty and LEID are not significantly reduced, then the effort is not cost effective and should not be treated as appropriate or applicable to the processing activity. Achieving the target values for these IDMS methods is not funded beyond those improvement activities that also support achieving required process throughput using a new spectrometer, [The new spectrometer was funded because it was needed to address throughput, down-time, and manufacturer-support issues.]

ITV are not applicable for the accountability-related activities currently supported by Pu isotopics by TIMS and Pu concentration by IDMS and Coulometry. However, Pu ISO by TIMS and Pu Coulometry both meet these stringent benchmarks. Target values for uranium isotopics by TIMS and uranium concentration by IDMS and Davies-Gray Titration are valid benchmarks, but imposing these benchmarks as strict requirements is only cost effective when all aspects of the accountability process are treated equally with regard to their impact on LEID.

The ALD/CLAS may wish to evaluate the NBL high-precision uranium titration methodology if current efforts to reduce random and systematic error in the standard Davies-Gray titration are not effective.

References

1. IAEA Department of Safeguards Report STR-327, International Target Values 2000 for Measurement Uncertainties in Safeguarding Nuclear Materials, April 2001. [Also published as ESARDA Bulletin No. 31, April 2001.]
2. Destructive Analysis Method Compendium, DOE-NBL Report – Final Issue Pending. Working copy transmitted by DOE-NBL on May 1, 2002.
3. Memorandum SEO-MCA-2002-00032, “International Target Values as Goals for Facility Measurements Systems,” from Edward T. Sadowski, WSRC-MPC&A to Thomas L. Williams, DOE-SROO, January 31, 2002.
4. Memorandum TSD-CLS-2001-00070, “Application of the Runs Rule to Accountability Measurements in Central Laboratory Analytical Services,” Robin H. Young, ALD/CLAS, and Michael K. Holland, ALD/AP to Scott E. Federman, ALD/CLAS, October 10, 2001.

Attachments

1. International Target Values 2000 for Measurement Uncertainties in Safeguarding Nuclear Materials, IAEA Report STR-327.
2. Destructive Analysis Method Compendium.
3. Memorandum SEO-MCA-2002-00032, “International Target Values as Goals for Facility Measurements Systems.”
4. Memorandum TSD-CLS-2001-00070, “Application of the Runs Rule to Accountability Measurements in Central Laboratory Analytical Services.”

Appendix

None

Attachment 1
International Target Values 2000 for Measurement Uncertainties in Safeguarding Nuclear
Materials
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**International Target Values 2000
for Measurement Uncertainties
in Safeguarding Nuclear Materials**

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Attachment 1
**International Target Values 2000 for Measurement Uncertainties in Safeguarding Nuclear
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Notice

This paper is the Millennium Edition of the International Target Values (ITVs) and contains some minor corrections from the version originally published in the International Atomic Energy Agency report STR-327 dated April 2001. In addition, certain non-essential sections of the original report have been removed to reduce the length of this article for publication. Additional comments on the ITVs by the reader are solicited and should be sent to Charles Pietri at cpietri@aol.com for response.

Abstract

This issue of the International Target Values (ITVs) represents the fifth revision, following the first release of such tables issued in 1979 by the ESARDA/WGDA. The ITVs are uncertainties to be considered in judging the reliability of analytical techniques applied to industrial nuclear and fissile material, which are subject to safeguards verification. The tabulated values represent estimates of the "state of the practice" which ought to be achievable under routine measurement conditions. The most recent standard conventions in representing uncertainty and reliability data have been considered, while maintaining a format that allows comparison with the previous releases of the ITVs. The present report explains why target values are needed, how the concept evolved and how they relate to the operator's and inspector's measurement systems. The ITVs 2000 are intended to be used by plant operators and safeguards organizations, as a reference of the quality of measurements achievable in nuclear material accountancy, and for planning purposes. The report suggests that the ITVs can be used with benefit for statistical inferences regarding the significance of operator-inspector differences whenever valid performance values are not available.

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1. Introduction

Safeguarding nuclear material involves a quantitative verification of the accountancy of fissile materials by independent measurements. The effectiveness of these verifications depends to a great extent upon the quality of the accountancy measurements achieved by both the facility operator and the safeguards inspectorate. For this reason a typical model of Safeguards Agreements^{1,2} stipulates that:

"The Agreement should provide that the system of measurements on which the records used for the preparation of reports are based shall either conform to the latest international standards or be equivalent in quality to such standards".

Although the above requirement was directed to the facility operators, it indeed applies equally well to the safeguards inspectorates.

In the absence of relevant international standards of measurements, the International Atomic Energy Agency (IAEA) had defined in the 1970s a set of international standards of nuclear material accountancy³, which lists the "expected measurement accuracy associated with the closing of a material balance" at five different types of nuclear facilities. However, these values have never been reviewed despite numerous technological changes since their adoption by consensus by a group of experts designated by their Governments. Safeguards officials and evaluators but also plant measurement specialists need more current and informative references regarding the performance capabilities of measurement methods used for the determination of the volume or mass of a material, for its sampling, its elemental and isotopic assays. Such information is needed for the various nuclear materials encountered in the nuclear fuel cycle.

The Working Group on Techniques and Standards for Destructive Analysis (WGDA) of the European Safeguards Research and Development Association (ESARDA) pioneered the way in 1979 by presenting a list of "Target Values" for the uncertainty components in destructive analytical methods⁴ to the safeguards authorities of Euratom and of IAEA. Revised estimates were prepared in collaboration and published as the 1983 Target Values⁵ after four years of extensive discussion and consultation with and within operators' laboratories and safeguards organizations. The international acceptance of the concept grew further with the next review, which involved, besides the ESARDA/WGDA and IAEA, the active participation of the members of two specialized committees of the Institute of Nuclear Materials Management (INMM). The 1987 Target Values, published as a result of this review⁶, defined, like the previous editions, the values of "random" and "systematic" error parameters to be aimed for in elemental and isotopic analyses of the most significant types of materials using common destructive analytical methods. The same groups took a new step when they agreed to define with the 1988 edition⁷ the values of the random error parameter to be met in the elemental assays as a result of sampling. Unfortunately, it was not possible at this time to include values for sampling uncertainties arising from systematic effects.

Following a 1988 recommendation of the IAEA Standing Advisory Group on Safeguards Implementation (SAGSI), the IAEA convened a Consultants Group Meeting in June 1991 to provide expert advice on international standards of measurements applicable to safeguards data. A concept of International Target Values (ITVs) was proposed on the model of the 1988 ESARDA Target Values and included estimates of the "random and systematic error" uncertainties originating from the measurements of volumes or masses of nuclear materials. The scope of ITVs was also extended to include a consideration of the non-destructive assay methods (NDA) which had won acceptance as accountancy verification tools.

Specialists from four continents took part in the discussion of the proposed concept. The ESARDA/WGDA held joint meetings with the ESARDA Working Group on NDA methods (ESARDA/WGNDA). The IAEA organized a series of Consultants Group Meetings with the

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participation of a representative from a large European reprocessing plant, of Brazilian and Japanese nuclear national authorities along with representatives of ESARDA, INMM, the International Organization for Standardization (ISO), the European Commission (EC) and IAEA inspectorates. The result was the publication of an IAEA Safeguards Technical Report in March 1993, titled "1993 International Target Values for Uncertainty Components in Fissile Isotope and Element Accountancy for the Effective Safeguarding of Nuclear Materials"^[8]. Articles in the ESARDA Bulletin^[9] and in the Journal of the INMM^[10] widely publicized the IAEA technical report. The report itself was translated into Japanese^[11].

International experts and panels have now reviewed the experience gained with the use of the 1993 ITVs and the progress made since 1993 in accountancy and safeguards verification measurements. These include ESARDA/WGDA, ESARDA/WGND, the Institute for Nuclear Material Management (INMM), the Japanese Expert Group on ITV 2000, Working Groups of the International Standardization Organization (ISO) dealing with analytical measurements in nuclear fuel industry and the Brazilian/Argentinean Agency of Accountability and Control of Nuclear Materials (ABACC). This report contains the changes made in the presentation of the ITVs and in some of the target values to reflect the latest recommendations of the experts.

An effort was made to bring the nomenclature in line with the latest recommendations of ISO^[12], the National Institute of Standards and Technology (NIST)^[13] and the European Association of Chemical Measurements (EURACHEM)^[14]. A clear distinction for example is made between the meaning of the term "error" and the term "uncertainty". The ITVs 2000 indeed represent target standard uncertainties, expressing the precision achievable under stipulated conditions. These conditions typically fall in one of the two following categories: "repeatability conditions" normally encountered during the measurements done within one inspection period; or "reproducibility conditions" involving additional sources of measurement variability such as "between inspections" or "between laboratories" variations.

As in earlier publications the values listed in the present document have been derived from an evaluation of actual measurement data. Four sources of information were considered. The most relevant and complete set of measurement data still comes from the information gathered by safeguards inspectorates during the statistical evaluation of the results of the measurements reported by the facility operators and the results of independent measurements performed on the same materials by the inspectors^[15,16]. This approach will be referred to as the "top-down" approach. These data were complemented and confirmed by "bottom-up" assessments of measurement uncertainty components published by measurement specialists^[17,26] and derived according to the ISO^[12], NIST^[13] and EURACHEM^[14] guides. In addition and whenever possible, it was verified that the proposed ITVs were consistent with the results of laboratory intercomparisons^[27-33] or measurement quality evaluation programmes^[34-48]. In cases where little or no statistical data was available (particularly for sampling uncertainties), some values were defined on the basis of expert opinion.

The ITVs 2000 bear a date like the ESARDA Target Values and 1993 ITVs issued previously. This reflects the experience that the quality of measurements may improve with the development of newer methods and instruments. ITVs also reflect the current understanding of the structure of the uncertainty components in nuclear material accountancy measurements. Changes can also occur in the future as this understanding improves or varies.

As with the previous lists, the ITVs 2000 should be achievable from today forward under the conditions normally encountered in typical industrial laboratories or during actual safeguards inspections. They do not represent the measurement uncertainties, which would only be achieved under exceptional or ideal laboratory conditions, or with most recently developed methods, which have not yet found wide use for daily and routine measurements.

Significant changes in the application of instruments and techniques have taken place since the previous edition. Measurements with instruments like high level neutron coincidence

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counters (HLNC), K-edge X-ray absorptiometer and fluorescence analyzers (HKED) are used routinely at the plants by inspectors with great success, not only to detect partial defects but also to verify the flow and balance of nuclear materials. This has allowed to decrease strongly the fraction of items, which need to be verified by chemical analysis. The latter methods are used now mainly for verifying the quality of operators' measurement systems and the absence of small but measurable biases in the closing of the material balances. Here, improvements were also observed with the combined use of Large Size Dried Spikes (LSD) and thermal ionization mass spectrometers with multidetectors and total sample evaporation for the verification of the uranium and plutonium content in spent fuel solutions and U/Pu fuel materials by isotope dilution mass spectrometry (IDMS).

It is expected that the ITVs 2000 will continue to be a motivating goal for beginner laboratories and a reasonable reference for experienced laboratories and safeguards evaluators. With the growing acceptance of modern quality assurance concepts it is suggested that the ITVs 2000 can also constitute a good reference against which analytical laboratories would validate their measurement system.

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2. Safeguards Accountancy Verification Measurements

As evident from the title of the report and the introduction, the principal application of the ITVs should be in safeguards activities. The safeguards verification data also form the major source of information on which the ITVs are based. A description of the origin of the safeguards data is therefore relevant.

Figure 1 describes the basic measurement scheme followed in safeguards measurement verifications. For each inspection, j , the inspector selects, in accordance with a random sampling plan, the items or batches of nuclear materials to be verified by an independent measurement. The inspector then compares the result of his verification measurement, Y_j , to the result, X_j , which the operator has obtained on the same batch or item i , and which the operator has declared to the inspectorate. The ability of the inspector to detect whether the difference d_j is significantly different from zero depends upon the overall uncertainties in the results X_j and Y_j . Figure 1 identifies the major steps of the measurement process where uncertainties can arise, although not all steps may be relevant for every method (e.g., several of the steps may be omitted or combined under a single step for NDA methods).

Step 1 corresponds to the measurement of the volume or mass of the item or batch of material. This so-called "*bulk*" measurement, when needed, takes place in the plant area and involves a calibration procedure.

Step 2, the "*sampling*", involves removing, for the purpose of the analytical measurement, a representative portion of the material from the batch or item to be analyzed. This portion may be a complete item in the case of an NDA measurement. This step is also done in the plant area.

Step 3 concerns the precautions which must be taken in the way the sample is "*conditioned*" and packaged at the sampling station so that all characteristics to be measured are preserved during its transport to the location or laboratory where the characteristics will be measured⁽⁴⁹⁾.

Step 4, the "*shipment*", is the transport of the sample to the location where it can be measured. This is rarely a trivial operation even when the movement is very short, as in the case of an NDA measurement, which is often done practically on the spot.

Step 5, the "*treatment*", is intended to bring the sample into the most appropriate geometrical, physical and/or chemical form for the measurement. This step is skipped when a complete item is subject to an NDA measurement. The treatment of a sample taken for destructive analysis may involve a sequence of individual steps, such as subsampling, dissolution, dilution, spike or standard addition, chemical treatment or chemical separation, etc.

Step 6, represents the "*measurement*" itself. In general terms, a measurement is based on a calibration from which the parameters linking the observed signal and the measurand are determined. Typical examples are HLNC calibration curves for Pu mass determination, calibrations of Gamma Spectrometers for ^{235}U abundance determination or the determination of the mass-discrimination correction factor for a mass-spectrometer. The standardization of a titrant solution is another example of a calibration, although it is frequently not recognized as such. Calibration functions may be as simple as a single calibration factor (actually representing a straight line through the origin), or may be complex and represented by an empirically determined calibration curve. Calibrations based on recognized references, such as certified reference materials or well-known physical constants, establish the traceability chain between the measurement result and the International System of Units (SI). Calibrations may be valid and used without modifications for long times, repeated on a daily basis or even performed with each individual measurement. Sometimes, calibration is performed in two steps: elaborate calibration exercises for determining the fundamental characteristics of the calibration function are

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combined with more frequently repeated "normalization" measurements to correct for short-term effects or minor deviations from the overall calibration function at the specific working range.

Step 7, the "calculation", consists in transforming the results of the physical or chemical measurement obtained in the preceding step into an estimate of the amount of fissile element or isotope in item or batch i . Particularly when the operator and inspector use DA, this involves estimating the total element content, by combining the result of the bulk measurement w_{ij} with the elemental concentration c_{ij} . In the case of Uranium materials, this is combined with the isotope abundances f_{ij} of the fissile isotope (^{235}U or ^{233}U) to yield a measure of the amount of fissile isotope in item or batch i , according to equations (1) and (2), respectively.

$$X_{ij} = w(O)_{ij} \cdot c(O)_{ij} \cdot f(O)_{ij} \quad (1)$$

$$Y_{ij} = w(I)_{ij} \cdot c(I)_{ij} \cdot f(I)_{ij} \quad (2)$$

Every stage of the process, starting with bulk measurements must be performed under well-controlled conditions. Hence quality control measures are imperative at every step of the process. Quality control on sampling can be done by taking replicate samples after different mixing times or taking samples from a number of items of the same batch of bulk materials. Quality control materials or samples can be introduced at specific steps to monitor the quality of the whole process or any part of it, including the conditioning and shipment steps. Figure 1 shows an example where control materials are used independently by the operator and the inspector to check the quality of the processes following the sampling. Quality control measures should be performed in the frame of a documented quality system^[46-53].

The uncertainties in the measurements of element concentrations and isotope abundances in the ITVs refer to the combined effects of the uncertainties in Steps 3 to 6 occurring after the taking of the sample in Step 2.

Step 8, the "reporting" of the results, is purely clerical but unfortunately it can be a source of errors. Uncertainties arising from such errors are not considered in the ITVs proposed in this document. Yet it is essential that appropriate quality assurance measures be taken to avoid the occurrence of clerical errors.

When NDA is used the attention focuses most on the measurement (Step 6) as the preceding steps have usually less impact or may even be omitted. For example, bulk measurements and sampling are not needed if the NDA method allows direct measurement of the total amount of fissile element or isotope contained in a whole item or batch of nuclear material, as with various neutron counters or calorimeters.

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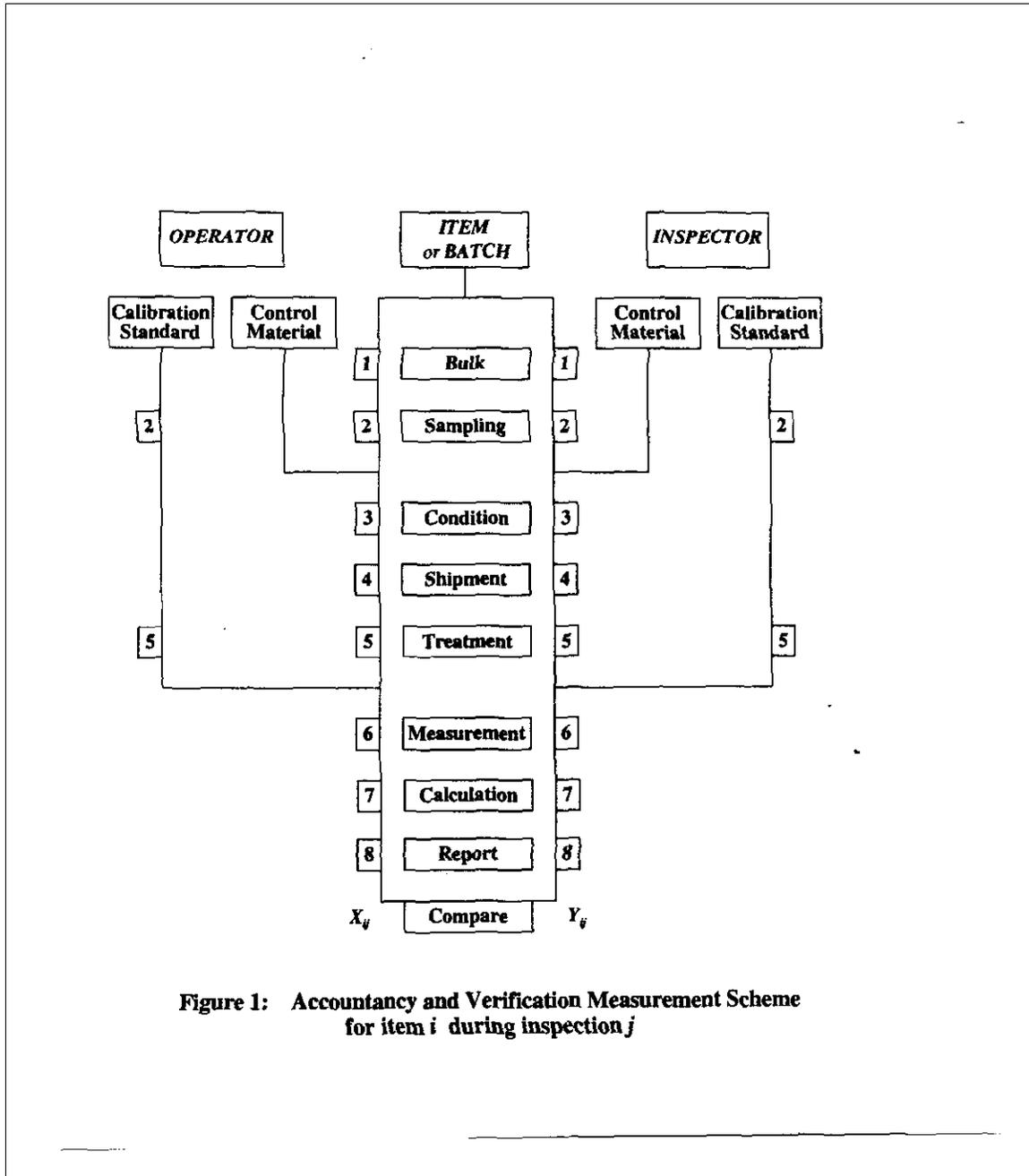


Figure 1: Accountancy and Verification Measurement Scheme for item i during inspection j

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3. Evaluation of Safeguards Accountancy Verification Measurements

The statistical terms used in this document are defined in Annex 1 in an effort to promote the understanding of the statistical concepts used here.

The safeguards inspectors examine the operator-inspector paired differences to determine whether these remain within upper and lower limits, which are commensurate with the characteristic uncertainties of the operators' and inspectors' measurement systems. For this purpose, the inspectors need to quantify the major uncertainties of the actual data collected during their verification activities.

Two categories of uncertainties play an important role in planning for inspections and in drawing inferences from inspection data; uncertainties due to repeatability effects, which are of a purely random nature, and uncertainties resulting from systematic effects within a given set of data, corresponding to an inspection period^[54,55]. These uncertainties will be designated by the symbols $u(r)$ and $u(s)$, respectively:

- **random uncertainty components, $u(r)$,** are due to errors varying in an unpredictable way among individual items or results. Counting statistics or the repeatability of measurements within a short period of time under constant conditions are typical examples for random uncertainty sources. Simply stated, the effects of random uncertainties can be reduced by repeated measurement, sampling and analysis, but it is not possible to correct for random errors.
- **uncertainty components of a systematic character, $u(s)$,** are due to errors affecting an entire group of items in the same way, like all measurement results interpreted with the same calibration curve, normalized with the same normalization experiments, or affected by the same background subtraction. But also uncertainties in the certified values of reference materials, nuclear data uncertainties or constant instrument or laboratory biases will appear to have a systematic character. The effects of uncertainties of a systematic character cannot be reduced by repetition under a fixed set of conditions encountered during a given inspection period. The cause of systematic errors may be known or unknown. If both the cause and the value of a systematic error are known, it can be corrected for, but there will still remain an uncertainty component of systematic character, which is associated with this correction.

A basic assumption is that $u(r)$ and $u(s)$ are characteristics of the type of material, its chemical and physical form and of the method of measurement. A further assumption is that the component of systematic character, $u(s)$, is constant for a given inspection period, but that it varies in a random manner from one inspection to another, for both the operator and the inspector.

Consequently, the inspectors group the data pairs originating from one inspection period, j , by material balance areas (MBA), by strata of materials of similar characteristics and by measurement methods^[56]. For a given MBA and stratum, call:

$$d_{ij} = (X_{ij} - Y_{ij}) / X_{ij} \quad (3)$$

the operator-inspector difference, d_{ij} , for item i in inspection j , with

$$i = 1 \quad ? \quad m$$

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$$j = 1, 2, \dots, K$$

Note: to simplify the presentation, relative differences are treated here. In practice, absolute differences, $(X_{ij} - Y_{ij})$, would be used when the size of the items of a given stratum vary widely.

The assumed error model is

$$d_{ij} = d + \Delta_j + \epsilon_{ij} \quad (4)$$

where

- d is the mean difference over the K inspections,
- Δ_j is the systematic error of the operator-inspector difference during inspection j , and
- ϵ_{ij} is the random error of the operator-inspector difference for item i during inspection j .

The expected values of Δ and ϵ are both zero (i.e., they are both centred random variables in a statistical sense). An analysis of variance components of the operator-inspector differences, d_{ij} , according to this model equation gives estimates of the variance $s^2(\epsilon)$ of the random component and of the variance $s^2(\Delta)$ of the component due to systematic effects within the given inspection period⁵⁶⁻⁵⁹. In performing this analysis of variance components, it is generally assumed that Δ_j and ϵ_{ij} are normally distributed and that the variances of the random error are the same for all inspections. The set of results are therefore screened for outliers prior to performing this evaluation.

Paired comparisons of this type are done separately for bulk measurements, element concentrations and isotope abundances, as well as for the masses of fissile elements and isotopes. One obtains, for each type of measurement, an estimate of the combination of the actual uncertainty components for the operator's and inspector's measurement systems:

$$s^2(\epsilon) = u^2(r,O) + u^2(r,I) - 2r(\epsilon) u(r,O) u(r,I) \quad (5)$$

$$s^2(\Delta) = u^2(s,O) + u^2(s,I) - 2r(\Delta) u(s,O) u(s,I) \quad (6)$$

where

- $u(r,O)$ and $u(r,I)$ are the standard uncertainties due to random error components for the operator and the inspector respectively,
- $r(\epsilon)$ is the Pearson correlation coefficient between the operator's and the inspector's random errors,

and

- $u(s,O)$ and $u(s,I)$ are the standard uncertainties due to effects of systematic character for the operator and the inspector respectively
- $r(\Delta)$ is the Pearson correlation coefficient between the operator's and inspector's systematic errors.

It can be expected that the uncertainties of operator's and inspector's data have similar magnitudes when both are obtained with similar methods. Under the assumption that the errors of the operator and of the inspector are independent from each other, i.e.

$$r(\epsilon) = r(\Delta) = 0, \quad (7)$$

the values

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$$u^2(r,O) = u^2(r,I) \approx s^2(\epsilon) / 2 \tag{8}$$

and

$$u^2(s,O) = u^2(s,I) \approx s^2(\Delta) / 2 \tag{9}$$

provide good estimates of the standard uncertainties.

In other situations operator's DA results may be compared with much less precise and/or much less accurate inspector's results obtained for example by some NDA methods. If, for example

$$u(r,I) \gg u(r,O) \tag{10}$$

and

$$u(s,I) \gg u(s,O) \tag{11}$$

Then,

$$s(\epsilon) \approx u(r,I) \tag{12}$$

and

$$s(\Delta) \approx u(s,I) \tag{13}$$

i.e., the total fluctuation originates practically solely from the uncertainties in the measurements of one party only, the inspector in this example. In such a case, $u(r,O)$ and $u(s,O)$ must be derived from a comparison with inspector's measurements also obtained by DA.

In the IAEA data analysis, various statistical techniques⁽⁶⁰⁾ are used to derive separate estimates of the operator's and inspector's uncertainty parameters based on the collection of historical operator-inspector differences. The results of these evaluations are "Performance Values" obtained for each MBA/stratum/measurement method combination. These Performance Values are generally updated once a year as more historical data becomes available for DA and NDA. A similar approach is also applied by other Safeguards organizations⁽⁶⁰⁻⁶³⁾.

Annex 2 describes how the Performance Values are used in planning inspections⁽⁶¹⁻⁶⁴⁾ and in drawing inferences based on the declared values of the operator and on the measured values of the inspector. There are, however, situations where insufficient historical data is available to derive Performance Values. In these instances ITVs are used until sufficient measurement history is accumulated.

Conversely the most recent and best Performance Values may be used to justify a revision of the ITVs. The relationship between the ITVs and the Performance Values is explained in Section 6 and Figure 2.

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4. Results of Laboratory Intercomparisons

Laboratory intercomparisons also offer a documented set of relevant experimental data for defining Target Values. The most useful information stems from experiments, where the participants analyze very well characterized materials or measure well known volumes or masses of nuclear materials in industrial tanks or containers, and where their results are directly compared to the certified composition of the materials or to the certified value of the respective quantities. Permanent or periodic measurement evaluation programmes have a greater value for our present purpose than one-shot intercomparison experiments, because the participants tend to follow more closely their routine measurement procedure when the intercomparison samples are submitted sufficiently frequently.

The Institute for Reference Materials and Measurements (IRMM, Geel), the Commission d'Établissement des Méthodes d'Analyse (CETAMA) of the Commissariat à l'Énergie Atomique (CEA, France) and the New Brunswick Laboratory at Argonne (NBL, USA) administer such programmes in the area of nuclear material measurements. The discussion of the present edition of the ITVs made extensive reference to the reports published on the results obtained in the Regular European Interlaboratory Measurement Evaluation Programme (REIMET)⁽³⁷⁻⁴¹⁾, the programme of Evaluation de la Qualité des Résultats d'Analyses dans l'Industrie Nucléaire (EQRAIN)⁽⁴²⁻⁴⁴⁾, and the Safeguards Measurement Evaluation Programme (SME)^(45,46,65) run respectively by these three organizations. The calorimetry Exchange Programme of the Mound Laboratory^(47,48) and the Waste Drum Measurement Evaluation Programme of NBL are examples of too rare NDA measurement evaluation programmes. Unfortunately also, there exists still no permanent measurement evaluation programme regarding bulk measurements and the quality of sampling procedures.

Mass measurements are rather straightforward, so that actual inspection data probably provide sufficiently reliable estimates of their uncertainties. The measurement of volumes of solutions in industrial tanks using pneumatic level indicators is a more complex procedure and has been the object of several scientific experiments with international participation. The results of these experiments have been reported⁽⁴⁹⁻⁵⁵⁾ and were used in the discussion of the relevant Target Values. The uncertainties to be expected in the use of tracer techniques for volume measurements have been evaluated in the same or similar experiments^(67,70-73).

There are numerous references of interest regarding one-shot intercomparisons of the quality of elemental and isotopic assays by DA^(29-33,74-76), as well as extensive intercomparisons of non destructive measurements by gamma spectrometry^(37,28,31,39).

The evaluations of such one-shot experiments are usually much more elaborate than those of actual inspection data or those of permanent measurement evaluation programmes. They provide, therefore, a better insight into the structure of the sources of measurement uncertainties.

A frequent drawback of interlaboratory comparisons is that they too rarely involve the measurements of actual industrial materials under industrial conditions. The report of the cooperative certification of working reference materials of plutonium and uranium oxides for NDA constitute exceptions⁽⁷⁷⁻⁷⁹⁾.

The ITVs 2000 were defined to be consistent with the standard uncertainties observed in the most recent interlaboratory comparisons and measurement evaluation programmes involving the use of current technologies, with due consideration to the comments made above.

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5. Results of Method Validations and Quality Control Measurements

The experimental validation of measurement methods has become a standard practice for metrological and analytical laboratories required by most quality systems. Consolidated guidelines for the standardized performance of such studies are just emerging, however^{132, 301}. This sometimes makes it difficult to compare the respective results obtained by different laboratories. The most trustworthy studies of this type are certainly those which identify the basic metrological parameters of the measurement process, estimate the contributions of the uncertainties occurring in these elementary steps, and compare the expected performance with the results of actual measurements of well-known amounts of materials^{17-26,81-91}. When the uncertainty propagation model yields larger values than the experimental determinations of the total uncertainty, it is probable that the design of the experiments failed to include one or several sources of potential uncertainties. These cases must receive specific attention. The ESARDA/WGND has undertaken a comprehensive examination regarding the propagation of the uncertainties in NDA measurements for safeguards, and in general to the Quality Control and Quality Assurance aspects of NDA measurements. Workshops^{102,131} discussed QC and QA in the whole process of NDA assay, starting with the instrument design, down to the use in laboratory conditions, in verification measurement, preparation and use of RMs, traceability, qualification and certification of the measurement results.

The reports on the developments of isotope dilution mass spectrometric assay of spent fuel solutions using Large Size Dried (LSD) Spikes¹⁹², metal spike¹⁹³, internal standard¹⁹⁴ and total evaporation techniques (TET)¹⁹⁵ were considered with a particular interest because the analyses of spent fuel dissolver solutions at large reprocessing plants should be of the highest possible accuracy.

The EURACHEM document¹⁴⁴ contains model cases for the uncertainty propagation for various types of analytical techniques. The IAEA is preparing a technical report on the propagation of uncertainties in radiochemical measurements and nuclear material analyses¹⁶⁶. The latter report includes examples dealing with uranium and plutonium assays of spent fuel solutions by isotope dilution mass spectrometry (IDMS), α -spectrometry and X-ray fluorescence analysis (XRFA). These documents describe how the elementary sources of uncertainties in each step of the assay are identified. This leads to the expression of the final result, y , as a function of the elementary parameters of the assay, x_i :

$$y = f(x_i) \tag{14}$$

The combined uncertainty¹¹²⁻¹⁴⁴ can be derived according to equation (15) when the (x_i) are actually independent variables:

$$u_c^2 = \sum_i c_i^2 \cdot u_i^2 \tag{15}$$

where u_c is the combined standard uncertainty for the assay result y
 u_i the standard uncertainty for parameter x_i
 c_i a coefficient of sensitivity defined in equation (16) below.

$$c_i = (\partial y / \partial x_i) \tag{16}$$

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Quality control measurements carried out in parallel with the assay of actual samples are a particularly relevant and convenient source of information. These measurements follow as far as possible the same process than the one applied to the samples. The control materials used in these measurements are preferably characterized or certified materials with well documented traceability to the International System (IS) of Measurements. "Type A" ⁽¹²⁾ estimates of several standard uncertainties u_i can usually be derived from a variance component analysis of the results of the quality control measurements collected over a sufficiently long period of time. Physical data, certificates of reference materials, weights, physical standards and instruments, such as balances, provide "Type B" ⁽¹²⁾ estimates of the other standard uncertainties. This approach is meanwhile applied at several laboratories and has yielded comparative assessments of the respective uncertainties of major nuclear analytical techniques, such as mass-spectrometry, IDMS^(2,97), radiometry (HRGS, GS, α -spectrometry), and the potentiometric titration of uranium and plutonium.

The standard uncertainties obtained from the above studies are grouped in two categories:

- The standard uncertainties of purely random character, $u(r)_i$,
- The standard uncertainties of systematic character, $u(s)_i$.

Equation (15), applied to the random uncertainties, $u(r)_i$, provides an estimate the combined standard uncertainty of the random effects, $u_c(r)$. The combined standard uncertainty of systematic character, $u_c(s)$, is calculated similarly by applying equation (15) to combine the contributions of the standard uncertainties $u(s)_i$.

Such studies establish the necessary quantification of the traceability of nuclear material analyses, and constitute an essential source of information for the selection of the ITVs 2000.

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6. Meaning of International Target Values 2000 for Uncertainty Components

The International Target Values 2000 for Measurement Uncertainties (ITVs 2000) are values for uncertainties associated with a single determination result; e.g., this may be the result reported by one laboratory on one sample (independent of the analytical scheme applied internally in the laboratory), or the result of an NDA measurement performed on a single item. The ITVs 2000 take into account actual practical experiences and should be achievable today under the conditions normally encountered in typical industrial laboratories or during safeguards inspections.

The ITVs 2000 were selected on the basis of a critical discussion of the inspectorates' performance evaluations of actual historical data and their comparison with the 1993 ITVs. They are also chosen to be consistent with uncertainty assessments provided by:

- experimental validation of measurement methods and instrumentation,
- interlaboratory measurement evaluation programmes, or
- individual laboratories.

The ITVs 2000 are applicable to the accountability data collected by the inspectorates. They do not represent the ultimately achievable performance of a measurement system, which would be obtained under exceptional or ideal laboratory conditions. However, they reflect reasonably well the progress observed during the past several years in the routine performance of measurements done for the purpose of material accountability and verification.

Figure 2 visualizes the conceptual relationship between Performance Values and ITVs. Performance Values are described by a range of values of the parameters measuring the uncertainties observed during actual industrial operations and safeguards inspections. This range is sometimes said to represent the State-of-the-Practice. The uncertainties achieved under "ideal" conditions by research laboratories or laboratories producing and certifying primary reference materials can be represented by another range of values which may be taken to illustrate the State-of-the-Art in analytical measurements. At a given time, the two ranges of values can overlap to various degrees depending upon the nature of the measurement and the spread of analytical technology advances at that time. The ITV for a given type of measurement is a single value, which has been selected to be a goal of acceptable level, achievable in practice.

The ITVs 2000 intend to take also into account all sources of measurement uncertainties, including sources which may not be apparent in Performance Values resulting from paired comparisons of operator's and inspector's measurements.

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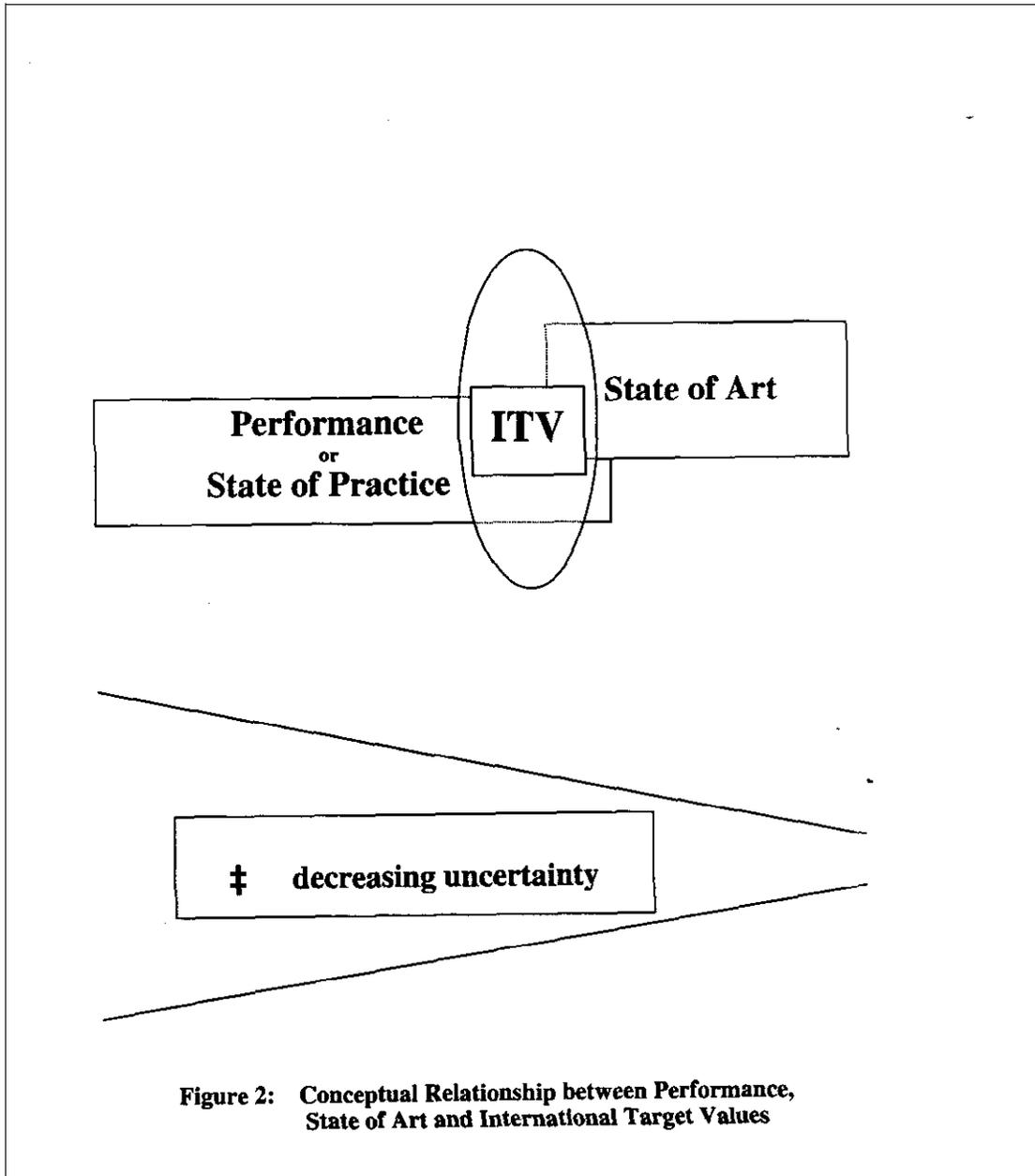


Figure 2: Conceptual Relationship between Performance, State of Art and International Target Values

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7. Structure and Content of the ITVs 2000

The presentation of the 1993 ITVs involved 16 different tables. A different format was chosen for the presentation of the ITVs 2000, which include only 7 tables.

- Table 1 provides a list of the codes used to identify the measurement methods in Tables 2 to 7. The methods used by the IAEA are described briefly in Reference [98].
- Tables 2 to 6 list the ITVs 2000 for bulk and density measurements, sampling, the determination of element concentration, of ²³⁵U isotope abundance, and of plutonium isotope ratios, respectively.
- ITVs for total amount of fissile element or isotope are given in Table 7 for NDA techniques providing a direct measurement.
- Each table identifies separate ITVs according to the type of material and measurement method, as appropriate.
- Two parameters, $u(r)$ and $u(s)$, characterize the quality, which should be aimed for in a specific measurement of a given material using a specified method at a single laboratory; $u(r)$ and $u(s)$ are specific subsets of the combined standard uncertainty comprising all uncertainties arising from random effects and systematic effects, respectively, according to the description in chapter 3.

These parameters should include all uncertainty components, which determine the potential difference between the measured and the true value. For example, the values specified for the element and isotope concentration measurements include all uncertainties generated in steps 3 to 6 of Figure 1 as well as the uncertainties of the calibration measurements, and the uncertainties of the reference data and materials used for the calibration.

- It has not yet been possible to propose ITVs for the term $u(s)$ applicable to sampling, except in a few cases, where this parameter was found to be actually measurable. It should also be noted that random sampling errors were frequently not assessed on the basis of experimental data (due to lack of such) and are based on expert opinion and facility experience.
- The combination of the $u(r)$ and $u(s)$ parameters

$$u_c(t) = [u(r)^2 + u(s)^2]^{1/2} \quad (17)$$

is equivalent to the relative combined standard uncertainty of the measurement, as it is defined in the ISO^[12], NIST^[13] and EURACHEM^[14] Guides, when it is applied to the measurement of a single laboratory.

- The ITVs in Tables 2 to 7 apply to situations where the measured quantity is large enough so that the relative uncertainty of the measurement remains essentially constant for the given range of measurements.
- The $u(r)$ and $u(s)$ parameters of bulk measurements, sampling, element concentration and isotope abundance measurements from Tables 2 to 6 must be combined according to equations (18) and (19), in order to obtain the ITVs, $u_c(r)$ and $u_c(s)$, applicable to analytical data resulting from a given combination of several measurement steps.

$$u_c(r)^2 = \sum_n u(r)^2 \quad (18)$$

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$$u_c(s)^2 = \sum_l u_l(s)^2 \quad (19)$$

where l refers to an individual step of the analytical process,

and $l = 1, 2, \dots, n$

Examples of such calculations are given in Chapter 8.

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Table 1: Measurement Method Codes

Method /Instrument Code	Technique
ANCC	Advanced Neutron Coincidence Counter
AWCC	Active Well Coincidence Counter
CALR	Calorimeter
COMP	Combined Product Uranium Concentration and Enrichment Assay (COMPUCEA)
DIPT	Dip Tube
EBAL	Electronic Balance
FRSC	Fuel Rod Scanner
GRAV	Gravimetry
GSMS	Gas Source Mass Spectrometry
HKED	Hybrid K-Edge/K-XRF Densitometer
HLNC	High Level Neutron Coincidence Counter
HRGS	Infield High Resolution Gamma Spectrometer
IDMS	Isotope Dilution Mass Spectrometry
INVS	Inventory Sample Coincidence Counter
KED	K-Edge Densitometer
LCBS	Load-Cell Based Weighing System
LMCA	Laboratory Multichannel Analyzer/Hi-resolution GS
LMCN	Laboratory Multichannel Analyzer, NaI-detector
PCAS	Plutonium Canister Assay System
PHON	Photon Neutron Interrogation Device
PMCG	Portable Multichannel Analyzer, GeLi-detector
PMCN	Portable Multichannel Analyzer, NaI-detector
PSMC	Plutonium Scrap Multiplicity Counter
TIMS	Thermal Ionization Mass Spectrometry
TITR	Titration
UNCL	Uranium Neutron Coincidence Collar
VTDM	Vibrating Tube Density Meter
WDAS	Waste Drum Assay System

Note: Measurement codes for NDA instruments correspond to the codes adopted in the IAEA Safeguards Manual⁽⁹⁹⁾

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Table 2: Bulk & Density Measurements

Measurement	Instrument	Uncertainty Component (% rel. Std. Uncertainty)	
		u(r)	u(s)
Mass	LCBS	0.05	0.05
	EBAL	0.05	0.05
Volume ^{1/}	DIPT	0.30	0.20
Density	DIPT	0.30	0.20
	VTDM	<0.05	<0.05

1.) Volume determinations are made on the basis of level pressure, density and temperature measurements. The volume measurement uncertainties are highly dependent on the homogeneity of the liquid, the quality of the density measurements and of the calibration equation determined in the calibration process. The volume measurements may also involve an absolute error component which has to be taken into consideration when determining the overall uncertainty of volume measurements. For accountability tanks in large-throughput facilities, uncertainties of 0.05% for u(r) and 0.1% for u(s) at full volume are achievable if: i.) A carefully designed calibration procedure has been implemented under well-controlled environmental and stable temperature conditions; and ii.) Measurements are performed on a well-characterized and homogenized liquid.

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**Table 3: Sampling Uncertainties for
Elemental Concentration and ²³⁵U Abundance**

Material	Uncertainty Component (% rel. Std. Uncertainty)				Recommended Minimum Sample Size ⁵⁾
	Concentration		²³⁵ U Abundance		
	u(r)	u(s) ¹⁾	u(r)	u(s) ¹⁾	
DUF ₆	0.10	nd	1	nd	5-10 g
HEUF ₆ & LEUF ₆ & NUF ₆	0.05	nd	0.10	nd	5-10 g
U-oxide Powder	0.20	nd	nd	nd	10-20 g
U-oxide Pellets	< 0.05 ²⁾	< 0.05	< 0.05	< 0.05	1 pellet
U Scrap (clean) ³⁾	1	nd	1	nd	30 g
U Scrap (dirty) ⁴⁾	10	nd	10	nd	2 x 30 g
Reprocessing Input Sol.	0.30	0.20	< 0.05	nd	2 x 1 ml
U Nitrate Sol.	0.10	nd	< 0.05	nd	10 ml
Pu, U/Pu Nitrate Sol.	0.20	nd	< 0.05	nd	10 ml
Pu-oxide	0.10	nd			2 x 1 g
FBR & LWR MOX	0.70(Pu) 0.20(U)	nd	0.10	nd	2 x 1 pellet or 2 x 2 g (FBR MOX) or 2 x 5 g (LWR MOX)
MOX Scrap(clean) ³⁾	1	nd	1	nd	2 x 5 g
MOX Scrap(dirty) ⁴⁾	10	nd	10	nd	2 x 10 g
U Metal	0.05	nd	< 0.05	nd	1-5 g
HEU Alloys	0.20	nd	< 0.05	nd	5-10 g

- 1.) Missing values (nd) have not yet been defined.
- 2.) 0.20 for Gadolinium-containing pellets.
- 3.) Scrap with low impurity content and suitable for direct recycling.
- 4.) Sampling errors can vary widely depending on material heterogeneity and sample size.
- 5.) According to STR-69^[100]

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Table 4: Element Concentration

Method	Material	Uncertainty Component (% rel. Std. Uncertainty)				Notes ¹
		U-Conc.		Pu-Conc.		
		u(r)	u(s)	u(r)	u(s)	
GRAV	U Oxides(pure), U ₃ O ₈	0.05	0.05			2/
	Pu Oxide			0.05	0.05	2/
TITR	U Oxides, UNH, U ₃ O ₈	0.1	0.1			
	U Alloys	0.2	0.2			
	Pu Oxide, Pu Nit.			0.15	0.15	3/
	MOX, U/Pu Nit.	0.1	0.1	0.2	0.2	3/
IDMS	U & Pu Compounds					4/5/
	Hot Cell Conditions	0.2	0.2	0.2	0.2	
	Glove Box Conditions	0.15	0.1	0.15	0.1	
KED	U in solution	0.2	0.15			6/
	Pu in solution			0.2	0.15	6/7/
	FBR MOX			0.3	0.2	6/
HKED	Spent Fuel Solution	0.2	0.15	0.6	0.3	8/
	LWR MOX					
COMP	U Compounds	0.2	0.15			2/6/9/
ANCC	Pu Oxide, MOX			0.2	0.2	10/
INVS	Pu Oxide, MOX			2	1.5	11/12/
	MOX Scrap			10	2.5	11/

- 1.) Concentration measurements on powders and solutions require weight change correction because of sample instability.
- 2.) Material containing non-volatile impurities < 1000 ppm
- 3.) Equivalent performance may be expected when applying coc.
- 4.) Materials typically encountered in the nuclear fuel cycle
- 5.) Under conditions of sufficiently different isotopic compositions of spike and sample and near-optimum sample:spike ratio[83]
- 6.) Measurement time 1000 sec., adjusted for age of source when necessary
- 7.) For samples in solution with >50 g/l Pu
- 8.) 150 g/l U, 1.5 g/l Pu
- 9.) 200 g/l U
- 10.) For: 2g sample; 4 hour counting time; isotopic determination by mass spectrometry; detector efficiency > 40%
- 11.) Measurement time 300 sec.
- 12.) Isotopic determination by mass spectrometry.

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Table 5: ²³⁵U Abundance

Method	Material	Uncertainty Component (% rel. Std. Uncertainty)		Notes
		u(r)	u(s)	
GSMS	DUF ₆ & NUF ₆	0.1	0.1	
	LEU ₆	0.05	0.05	
	HEU ₆	0.02	0.02	
TIMS	DU (< 0.3 wt. % ²³⁵ U)	0.5	0.5	
	U (0.3% < ²³⁵ U < 1%)	0.2	0.2	
	LEU (1% < ²³⁵ U < 20%)	0.1	0.1	
	HEU (> 20 wt. % ²³⁵ U)	0.05	0.05	
COMP	LEU Compounds	0.4	0.2	1/
LMCN ^{2/}	LEU Oxides	0.3	0.3	
	HEU Oxides	0.2	0.2	
PMCN ^{2,3/}	DUF ₆	20	15	4/
	NUF ₆	10	8	4/
	LEU ₆	5	3	4/
	NU Oxides	5	5	
	LEU Oxides	3	2	
	NU & LEU Scrap (clean) ^{5/}	5	5	6/
	NU & LEU Scrap (dirty)	15	10	6/
	LEU Fuel Rods	2.5	1	
	LEU Fuel Assemblies	2.5	1	
	HEU Metal	0.5	0.5	7/
	HEU Alloys	1	1	7/
PMCG ^{3/}	DUF ₆	15	10	4/
	NUF ₆	8	5	4/
	LEU ₆	4	2	4/
	LEU Oxides	3	2	
	HEU Metal	0.5	0.5	7/
	HEU Alloys	1	1	7/

- 1.) Measurement time 1000 sec., adjusted for age of source when necessary; see Ref. [21]
- 2.) For materials not containing reprocessed uranium.
- 3.) Measurement time 300 sec.
- 4.) Includes uncertainty component associated with ultrasonic thickness gauge measurement of the UF₆ cylinder.
- 5.) Scrap with low impurity content and suitable for direct recycling.
- 6.) Uncertainties for scrap represent average performance observed on historical data. Material matrix heterogene contributor to the observed uncertainties and can vary widely.
- 7.) Calibration against reference material certified to 0.3 % or better & uncertainties in the correction of container absorption of 0.5 % or less.

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**Table 6: Plutonium Isotope Assay
of Pu Oxide and MOX**
(% Relative Standard Uncertainties)

Material Type	Isotope Ratio	Typical Value for Ratio (*100)	Method					
			TIMS ^{1/}		HRGS ^{2/}		LMCA ^{3/}	
			u(r)	u(s)	u(r)	u(s)	u(r)	u(s)
High-Burnup Pu	²³⁸ Pu/ ²³⁹ Pu	1.7	1.5	1	2	2	1	1
	²⁴⁰ Pu/ ²³⁹ Pu	43	0.1	0.05	1	1	0.7	0.7
	²⁴¹ Pu/ ²³⁹ Pu	13	0.2	0.2	1	1	0.7	0.7
	²⁴² Pu/ ²³⁹ Pu	8	0.2	0.3				
Low-Burnup Pu	²³⁸ Pu/ ²³⁹ Pu	0.02	10	10	10	10	5	5
	²⁴⁰ Pu/ ²³⁹ Pu	6	0.15	0.1	2	2	1.5	1.5
	²⁴¹ Pu/ ²³⁹ Pu	0.2	1	1	2	2	1	1
	²⁴² Pu/ ²³⁹ Pu	0.05	2	2				

- 1.) ²³⁸Pu/²³⁹Pu by alpha spec./TIMS combination
- 2.) Measurement time 3 x 100 sec.
- 3.) Measurement time 3 x 1000 sec.; 0.5 g Pu

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Table 7: Total Mass - ²³⁵U & Pu
by Direct NDA Measurement Techniques

Instrument	Material	Uncertainty Component (% rel. Std.Dev.)				Notes
		²³⁵ U Mass		Pu Mass		
		u(r)	u(s)	u(r)	u(s)	
AWCC	HEU Metal, HEU Alloys	5	3			1/
	HEU Fuel Elements	3	2			1/
FRSC	U Fuel Rods	1	1			
PHON	LEU Oxides	2	1			
	LEU Scrap	4	1			
UNCL	U Fuel Assemblies	4	2			
HLNC	Pu Oxide Powder			1	0.5	2/3/
	FBR MOX (> 10% Pu)			2	0.5	2/3/
	LWR MOX (< 10% Pu)			4	1.5	2/3/
	MOX Scrap			10	3	2/4/
	Pu Fuel Rods			1.5	1	2/3/
	MOX Fuel Rods			2	1	2/3/
	MOX Fuel Assemblies			1.5	1	2/3/
PCAS	FBR MOX			1.5	1	3/
	MOX Scrap			8	2	4/
PSMC	MOX Scrap (clean)			2.5	1	3/5/
	MOX Scrap (dirty)			8	2	4/
WDAS	MOX Waste			8	2	4/
CALR	Pu Oxide and MOX			0.4	0.4	3/6/7/

- 1.) Measurement time 600 sec.
- 2.) Measurement time 300 sec.
- 3.) Isotopic determination by mass spectrometry and alpha spectrometry.
- 4.) Uncertainties for scrap represent average performance observed on historical data. Material matrix heterogeneity is the main contributor to the observed uncertainties and can vary widely.
- 5.) Scrap with low impurity content and suitable for direct recycling
- 6.) ²⁴¹Am content determined by gamma spectrometry or alpha spectrometry
- 7.) Lower uncertainties are achievable for materials containing low burn up Pu

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8. Use of ITVs

ITVs are considered to be achievable in routine measurements involved in the determination of the amount of nuclear materials for materials accountancy and safeguards verification purposes. They are intended to be used as a reference by plant operators, state systems and international safeguards organizations. They should, however, not be normally used in place of values based on actual measurements in estimating the statistical significance of operator-inspector differences or MUF. Analytical laboratories can find it useful to determine experimentally the actual uncertainties of their measurements, and to compare them with the corresponding values, which can be derived from the ITVs 2000.

Safeguards authorities regularly compare the performance values with the current ITVs. They will examine with the relevant authorities and laboratories means of improving the performance, in cases where the performance values are significantly higher than the ITVs, and too high to allow the IAEA to meet its detection goals^[101]. When reliable performance values are not available, ITVs may be used instead to calculate sampling plans, to set reject limits and to calculate estimates of the combined uncertainties of inventories, throughputs, MUF and D's, as described in Annex 2.

Such applications of the ITVs require having a good insight of the measurement and verification systems. It is in particular important to recognize that, because of practical constraints, some measurement steps may be common to the operator and the inspector. It should also not be forgotten that the operator-inspector differences can carry errors which are not related to measurement uncertainties.

The following three examples illustrate how the tabulated ITVs can be used to calculate ITVs for combined uncertainties applicable to practical situations. Further examples are presented in Reference [102].

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Example 1:

Target Values for the Determination of the Total Mass of Fissile Element on Independent Samples

Consider a situation where the operator and the inspector determine fully independently the total amount of plutonium in a batch of LWR pellets. The operator measures the plutonium concentration by titration on ten randomly selected pellets, the inspector by IDMS on an independently selected but single pellet.

The Target Values for the combined relative standard uncertainties applicable to the determination of the total mass of plutonium by the operator are derived from the following equations, respectively for the random errors, the errors of systematic character and their combination:

$$u_c(r, O) = \sqrt{\sum_i u_i^2(r, O)/n_i(O)} \quad (20)$$

$$u_c(s, O) = \sqrt{\sum_i u_i^2(s, O)} \quad (21)$$

$$u_c(O) = \sqrt{u_c^2(r, O) + u_c^2(s, O)} = \sqrt{(0.0555 + 0.0425)} = 0.31\% \quad (22)$$

The above values would be used in the calculation of Target Values for the relative standard uncertainties to be expected in the inventory, throughput and MUF declared by the operator.

Similar equations are used to calculate the corresponding values applicable to inspector's measurements, $u_c(r, I)$, $u_c(s, I)$ and $u_c(I)$. The Target Value for the combined uncertainties on the total Pu mass measured by the inspector is equal to:

$$u_c(I) = \sqrt{u_c^2(r, I) + u_c^2(s, I)} = \sqrt{(0.5150 + 0.0125)} = 0.73\% \quad (23)$$

Its magnitude is determined essentially by the random sampling uncertainty component. This is also true for the Target Value applicable to the Operator-Inspector difference:

$$u_d = \sqrt{u_d^2(r) + u_d^2(s)} = \sqrt{(0.5705 + 0.0550)} = 0.79\% \quad (24)$$

Assuming that the values of Target Values, u_c 's, given in Table 8 and equations (22), (23) and (24), are effectively achieved, the 95% confidence intervals of the final results of the operator, of the inspector and of their difference, would be respectively equal to:

$$CL(O) = k u_c(O) = 2 \times 0.31 = 0.62\% \quad (25)$$

$$CL(I) = k u_c(I) = 2 \times 0.73 = 1.46\% \quad (26)$$

$$CL(d) = k u_c(d) = 2 \times 0.79 = 1.58\% \quad (27),$$

where the coverage factor k is 2.

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**Table 8: Target Values for Total Pu Mass
with Independent Samples and DA (Example 1)**

	Step	Method Instr.	n _i	ITV (% rel. Std. Dev.)			Variance Component		
				u _i (r)	u _i (s)	Table	u ² _i (r)/n _i	u ² _i (s)	
O P E R A T O R	1- Bulk	EBAL	1	0.05	0.05	2	0.0025	0.0025	
	2- Sampling Pu-Conc.		10	0.70	nd	3	0.0490		
	6- Pu-Conc.	TITR	10	0.20	0.20	4	0.0040	0.0400	
	Sum of variance components							0.0555	0.0425
	Combined Std. Uncertainties, μ(r,O) and u(s,O), (in % rel.)							0.24	0.21
I N S P E C T O R	1- Bulk	EBAL	1	0.05	0.05	2	0.0025	0.0025	
	2- Sampling Pu-Conc.		1	0.70	nd	3	0.4900		
	6- Pu-Conc.	IDMS	1	0.15	0.10	4	0.0225	0.0100	
	Sum of variance components							0.5150	0.0125
	Combined Std. Uncertainties, μ(r,I) and u(s,I), (in % rel.)							0.72	0.11
D I F F	Variance of Rel. Operator-Inspector Difference							0.5705	0.0550
	Standard Uncertainties of Rel. Diff., μ(r) and u _i (s), (in %)							0.76	0.23

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Example 2:

Target Values for the Determination of the Total Mass of Fissile Element on a Common Sample.

In situations where the inspector analyzes a subsample of a homogeneous operator's sample, the sampling errors no longer contribute to the uncertainty of the Operator-Inspector difference. An example of this situation could be a co-operative effort to identify the existence of biases in the chemical analysis.

Apply these conditions to the first example. In this case, as shown in Table 9, the Target Value for the Operator-Inspector difference and its 95% confidence interval will be:

$$u_d = \sqrt{(0.0675 + 0.0550)} = 0.35\% \quad (28)$$

$$CL(d) = k u_d = 2 \times 0.35 = 0.70\% \quad (29)$$

Table 9: Target Values for Operator-Inspector Difference on Total Pu Mass, with Common Sample and DA (Example 2)

	Step	Method Instr.	n _i	ITV (% rel. Std. Dev.)			Variance Componen	
				u _i (r)	u _i (s)	Table	u _i ² (r)/n _i	u _i ² (s)
O P E R A T O R	1- Bulk	EBAL	1	0.05	0.05	2	0.0025	0.0025
	2- Sampling Pu-Conc.		1	0.70	nd	3		
	6- Pu-Conc.	TITR	1	0.20	0.20	4	0.0400	0.0400
	Sum of variance components contributing to Op-In Differ.							0.0425
I N S P E C T O R	1- Bulk	EBAL	1	0.05	0.05	2	0.0025	0.0025
	2- Sampling Pu-Conc.		1	0.70	nd	3		
	6- Pu-Conc.	IDMS	1	0.15	0.10	4	0.0225	0.0100
	Sum of variance components contributing to Op-In Differ.							0.0250
D I F F	Variance components of relative difference						0.0675	0.0550
	Standard Uncertainties of Rel. Diff., u_i(r) and u_i(s), (in %)						0.26	0.23

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Example 3:

**Estimation of the Uncertainty of Operator-Inspector
Differences for NDA Sampling Plan Calculations**

Consider a situation where an inspector must calculate a sample size for verifying the content of LEUF₆ containers using a PMCN. The operator declarations for the material are based on DA measurements of ²³⁵U abundance and the stoichiometric value for U-concentration in UF₆. No historical inspector measurement data is available. Therefore ITVs need to be used to provide an estimate of the uncertainty which may be associated with the operator-inspector difference.

The variance components calculated from the ITVs 2000 are given in Table 10. The standard combined uncertainty associated with the operator-inspector difference in this example is equal to:

$$u_d = \sqrt{u_d^2(x) + u_d^2(s)} = \sqrt{(25.0175 + 9.0075)} = 5.83\% \quad (30)$$

In the absence of an uncertainty estimate based on historical measurement data, the inspector would thus use the above value calculated from the ITVs for performing sample size calculations and establishing rejection limits. In this example, the relatively large uncertainty associated with the NDA measurement almost entirely determines the overall uncertainty of the operator-inspector difference.

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**Table 10: Target Values for Operator-Inspector difference
(Example 3)**

	Step	Method/Instr.	ITV (% rel. Std. Dev.)			Variance Component	
			$u_1(r)$	$u_1(s)$	Table	$u_1^2(r)$	$u_1^2(s)$
O P E R A T O R	1- Bulk	EBAL	0.05	0.05	2	0.0025	0.0025
	2- Sampling ²³⁵ U wt. %		0.1		3	0.0100	
	6- U-Conc.	Stoichiom. Val.					
	6- ²³⁵ U wt. %	GSMS	0.05	0.05	5	0.0025	0.0025
	Sum of variance components					0.0150	0.0050
I N S P E C T O R	1- Bulk	EBAL	0.05	0.05	2	0.0025	0.0025
	6- U-Conc.	Stoichiom. Val.					
	6- ²³⁵ U wt. %	PMCN	5	3	5	25.0000	9.0000
	Sum of variance components					25.0025	9.0025
D I F F	Variance components of relative difference					25.0175	9.0075
	Standard Uncertainties of Rel. Diff., $u_1(r)$ and $u_1(s)$, (in %)					5.00	3.00

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9. Future Developments

It is intended to keep updating the ITV tables regularly in order to incorporate the latest relevant information. The following activities will be especially important for this purpose:

- Growing emphasis is being placed on reassessing the uncertainties of chemical measurements according to the ISO⁽¹²⁾, NIST⁽¹³⁾ and EURACHEM⁽¹⁴⁾ guides. This should be done systematically for the methods in current use. It should become a part of the process of qualification of new measurement methods and instrumentation.
- The inspectorates will continue to update actual performance evaluations.
- It is important that interlaboratory measurement evaluation programmes continue to be conducted, particularly in the area of Pu measurements. Operator and inspector laboratories should participate in such programmes. Their results should be published as it was done in the past.
- Models more specific to the NDA measurement processes are being reviewed by the ESARDA/NDA Working Group to monitor and assess the sources of major uncertainties in actual inspectors' measurements. This will hopefully involve uncertainty assessments in line with the above guides as well as periodical estimates of actual Performance Values and the development of interlaboratory measurement evaluation programmes for NDA.
- Results of experimental qualifications of recommended sampling procedures⁽¹⁰⁾⁻⁽¹²⁾ should be made available to the inspectorates to substantiate and expand ITVs for the uncertainty components in sampling procedures.
- The IAEA will also follow with the greatest interest developments in bulk measurements and elemental assays of spent fuel solutions and their impact on the accuracy of the accountability of large throughputs and inventories of nuclear materials at large plants now coming under safeguards.

The IAEA will continue its cooperation on the above topics with Euratom, with State authorities and with the expert groups, which were involved in the review of the ITVs 2000. The next revision of the ITVs will also be another opportunity to seek further contributions from more countries and organizations.

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Annex 1

Statistical Terminology

The statistical terminology used in this document is given here in an effort to promote better understanding of the statistical concepts discussed herein. The terminology is divided into four groups as follows:

- Group 1: Basic terms**
(true value, conventional true value, measurand, measurement, measurement result, measurement error, uncertainty, uncertainty component, expectation, expected value, mean, variance, standard deviation, sample standard deviation, experimental standard deviation, error parameter, sample, estimation, statistic, estimator, estimate).
- Group 2: Selected sources and classes of error**
(bulk measurement error, sampling error, random error of result, random error of measurement, systematic error of result, systematic error of measurement, calibration error, bias, relative error).
- Group 3: Descriptors**
(precision, accuracy, repeatability, repeatability conditions, reproducibility, reproducibility conditions).
- Group 4: Safeguards specific use of terms**
(random sampling, inspection by attribute, alarm level, significant difference, defect, discrepancy, detection probability, false alarm, risk).

The definitions of these terms, as used in this document, are given to the extent feasible, in a way which is consistent with the latest internationally recognized standards or manuals. The relevant source^[14,54-56,114] of the definition is specified in the following tables.

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GROUP 1: BASIC TERMS		
Term	Definition	Ref.
true value	Value consistent with the definition of a given particular quantity. NOTES: 1. This is a value that would be obtained by a perfect measurement. 2. True values are by nature indeterminate.	[55] 1.19
conventional true value	Value attributed to a particular quantity and accepted, sometimes by convention, as having an uncertainty appropriate for a given purpose. NOTE: "Conventional true value" is sometimes called <i>assigned value, best estimate of the value, conventional value, or reference value.</i>	[55] 1.20
measurand	Particular quantity subject to measurement.	[55] 2.6
measurement	Set of operations having the object of determining a value of a quantity.	[55] 2.1
measurement result	Value attributed to a measurand, obtained by measurement NOTES: 1. When the term "result of a measurement" is used, it should be made clear whether it refers to: - the value indicated by the measurement instrument - the uncorrected result - the corrected result and whether several values are averaged. 2. A complete statement of the result of a measurement includes information about the uncertainty of measurement.	[55] 3.1
measurement error	Result of a measurement minus a true value of the measurand. NOTES: 1. Since a true value cannot be determined, in practice a conventional true value is used. 2. The quantity is sometimes called <i>absolute error</i> of measurement when it is necessary to distinguish it from <i>relative error</i> .	[55] 3.10
uncertainty (of measurement)	Parameter associated with the result of a measurement, characterizing the dispersion of the values that could reasonably be attributed to the measurand. NOTE: The parameter may be, for example, a standard deviation (in which case the uncertainty is also called the <i>standard uncertainty</i>), or the width of a confidence interval.	[55] 3.9
uncertainty component	Uncertainty arising from a distinct source contributing to the overall uncertainty. NOTES: 1. If there is correlation between any components then this has to be taken into account by determining the covariance. 2. It is often possible to evaluate the combined effect of several components. 3. Where components whose contribution is evaluated together are correlated, there may be no additional need to take account of the correlation	[14] 2.3.1
expectation, expected value, mean	If X is a continuous random variable having the probability density function $f(x)$ then the expectation (or expected value or mean), if it exists, is $\mu_x = E(X) = \int x \cdot f(x) dx$ (the integral being extended over the intervals of variation of X).	[54] 1.18
variance	$\sigma^2 = V(X) = E [X - E(X)]^2$ The variance is the expectation of the square of the <i>centred random variable</i> (i.e. a random variable the expectation of which equals zero).	[54] 1.22

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GROUP 1: BASIC TERMS		
Term	Definition	Ref.
standard deviation	$\sigma = \sqrt{V(X)}$	[54] 1.23
sample standard deviation, experimental standard deviation	<p>For a series of n measurements of the same measurand, the quantity s characterizing the dispersion of the results and given by the formula:</p> $s = \sqrt{\frac{\sum_{i=1}^n (x_i - \bar{x})^2}{n-1}}$ <p>x_i being the result of the i^{th} measurement and \bar{x} being the arithmetic mean of the n results considered.</p> <p>NOTES:</p> <ol style="list-style-type: none"> 1. Considering the series of n measurements as a sample of a population, \bar{x} is an unbiased estimate of the mean μ, and s^2 is an unbiased estimate of the variance σ^2 of that distribution. 2. The expression s/\sqrt{n} provides an estimate of the standard deviation of the distribution of \bar{x} and is called the experimental standard deviation of the mean (it is sometimes, but incorrectly, called <i>standard error</i> or <i>standard error of the mean</i>). 	[55] 3.8
error parameter	<p>Synonymous for error variance.</p> <p>In general, the result of a particular measurement, x_i, may be modelled by</p> $x_i = \mu + \epsilon_1 + \epsilon_2 + \epsilon_3 + \dots$ <p>where μ is the true value of the measured quantity and the ϵ_i are individual errors made during the particular measurement i according to the various potential sources of errors 1, 2, 3, ...</p> <p>If, for example, the error ϵ_1 is a representation of a centred random variable ϵ_1 (mean zero): $E(\epsilon_1) = 0$, then the variance $E(\epsilon_1^2) = V(\epsilon_1) = \sigma_{\epsilon_1}^2$ is called an error parameter.</p> <p>If the individual sources of error (or fluctuation) are independent from each other, then the overall variance of the measurement results can be calculated by</p> $V(X) = \sigma_X^2 = \sigma_{\epsilon_1}^2 + \sigma_{\epsilon_2}^2 + \sigma_{\epsilon_3}^2 + \dots = \sum (\sigma_{\epsilon_i}^2)$	
sample	<ol style="list-style-type: none"> 1. One or more of the individual items into which a population is divided, taken with the intention to provide information on that population. 2. A portion of material taken from a larger batch of material with the intention to be representative for that larger batch with respect to the characteristics under consideration. 	various
estimation	The operation of assigning, from the observations in a sample, numerical values to the parameters of a distribution chosen as the statistical model of the population from which this sample is taken.	[54] 2.49
statistic	<p>A function of the sample random variables.</p> <p>NOTE:</p> <p>A statistic, as a function of random variables, is also a random variable and as such it assumes different values from sample to sample. The value of the statistic obtained by using the observed values in this function may be used in a statistical test or as an estimate of a population parameter, such as a mean or a standard deviation.</p>	[54] 2.45
estimator	A statistic used to estimate a population parameter.	[54] 2.50
estimate	The value of the estimator obtained as a result of an estimation.	[54] 2.51

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GROUP 2: SELECTED SOURCES and CLASSES of ERRORS		
Term	Definition	Ref.
bulk measurement error	The measured mass (volume) of an item minus its true mass (volume).	[55] 3.10
sampling error	The true value for the portion of material constituting the sample minus the true value for the larger batch of material for which the sample is intended to be representative.	
random error (of result)	A component of the error, which, among a number of test results for the same characteristic, varies in an unpredictable way. NOTE: The random error of an analytical result cannot be compensated for, but it can be usually reduced by increasing the number of observations.	[54] 3.9
random error (of measurement)	Result of a measurement minus the mean that would result from an infinite number of measurements of the same measurand carried out under repeatability conditions. NOTE: 1. Random measurement error is equal to measurement error minus systematic measurement error. 2. Because only a finite number of measurements can be made, it is possible to determine only an estimate of random error.	[55] 3.13
systematic error (of result)	A component of the error, which, among a number of test results for the same characteristic, remains constant or varies in a predictable way. NOTES: 1. Systematic errors and their causes may be known or unknown. 2. Under constant measurement conditions, the systematic error is independent of the number of measurements made and therefore cannot be reduced by increasing the number of analyses.	[54] 3.10
systematic error (of measurement)	Mean that would result from an infinite number of measurements of the same measurand carried out under repeatability conditions minus a true value of the measurand. NOTES: 1. It is important to observe the restriction "under repeatability conditions". The value of the systematic measurement error may remain constant as long as the measurement conditions remain unaltered. However it may vary, in an unpredictable manner, with the changing of the measurement conditions or the settings of the measurement system. The systematic measurement error is therefore systematic (or constant) only with respect to a given set of measurement results, while it is at the same time a random component of the error on a long term perspective. Hence the systematic measurement error possesses a probability distribution (with expectation zero) and can be represented by a random statistical variable over a sufficiently long period of time. 2. The systematic error components under consideration in the present document are all of this dual nature.	[55] 3.14
calibration error	An error associated with a given calibration. Hence, a systematic measurement error component with respect to all measurements performed with the same calibration.	[114] 7.9
bias	The difference between the expectation of the test result and an accepted reference value (conventional true value). NOTE: 1. Bias can also be described as the total of all long term systematic error components; i.e., those components of the error that do not vary even under reproducibility conditions. 2. Like the <i>true value</i> , bias is by nature indeterminate. 3. If the bias is estimated and corrected for, the uncertainty of the correction must still be taken into account.	[54] 3.13
relative error	The absolute error of the measurement divided by the true value of the measurand. Frequently expressed as a percentage value (i.e. multiplied by hundred).	

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GROUP 3: DESCRIPTORS		
Term	Definition	Ref.
precision	The closeness of agreement between independent test results obtained under stipulated conditions. NOTE: 1. Quantitative measures of precision depend critically on the "stipulated conditions". Repeatability conditions and reproducibility conditions are particular sets of extreme stipulated conditions. 2. The standard deviation of the test results is one usual quantitative measure of precision. A larger standard deviation represents less precision. 3. Precision depends only on the distribution of random errors and therefore does not relate to deviations from the true value.	[54] 3.14
accuracy (of measurement)	The closeness of agreement between the result of a measurement and a true value of the measurand. NOTE: 1. "Accuracy" is a qualitative concept. 2. When applied to a set of test results, accuracy involves a combination of random error components and a systematic error component.	[54] 3.11 [55] 3.5
repeatability	Precision under repeatability conditions.	[54] 3.15
repeatability conditions	Conditions where independent test results are obtained with the same method on identical test items in the same laboratory by the same operator using the same equipment within short intervals of time. NOTE: 1. Repeatability conditions constitute one specific and extreme set of conditions. 2. Repeatability relates practically to smallest fluctuation that is reasonably achievable among independent test results.	[54] 3.16
reproducibility	Precision under reproducibility conditions	[54] 3.20
reproducibility conditions	Conditions where test results are obtained with the same method on identical test items in different laboratories with different operators using different equipment. NOTE: 1. Reproducibility conditions constitute another specific and extreme set of conditions. 2. Reproducibility relates practically to the largest fluctuation that is reasonably encountered among independent test results. 3. Operator - inspector differences are typically generated under reproducibility conditions.	[54] 3.21

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GROUP 4: SAFEGUARDS SPECIFIC USE OF TERMS		
Term	Definition	Ref.
random sampling	Random sampling is a method for taking a sample from a group of distinct items. A random sample is selected by a procedure that gives each item a fixed and determinate (usually equal) probability of selection. NOTE: When applied to non-distinct things, such as samples of bulk material, the method of selection does not usually indicate probabilities of selection of the samples. In principle, when drawing samples from a larger bulk of material, its content could conceivably be divided into a large number of possible samples of a certain size; some procedure would be used to give each potential sample an equal chance of being selected. The actual sampling method is designed to achieve the same result in a practical way, so that the statistical theory based on the concept of random sampling can be applied.	[56] 2.8
inspection by attributes	In attributes inspection, the item inspected is classified as being either acceptable or not (i.e. a defect) on the basis of the measurement. NOTE: Attributes inspection has nothing to do with the quality of measurement.	[56] 6.2
alarm level	A synonym for a critical value in the terminology of testing an hypothesis. NOTE: In the subject context, the alarm level is the value of an operator-inspector difference which, if exceeded in absolute value, is cause for labelling the item in question a defect during inspection by attributes.	
significant difference, defect, or discrepancy	Three synonyms for an operator-inspector difference that exceeds the alarm level in absolute value.	[114] 8.21
detection probability	The probability that an item with a true operator-inspector difference of a given amount will be declared to be a discrepancy. More generally, when referring to a safeguards index such as MUF or D, it is the probability that the index will be found to differ significantly from its hypothesised value for a given true value of the index.	[114] 5.17
false alarm	In attribute testing, declaring an item to be a defect when the true operator-inspector difference is zero is a false alarm. A similar definition applies to tests on MUF and \hat{D} 0.	[114] 5.18
risk	A synonym for the probability of reaching the incorrect conclusion in hypothesis testing. Two types of risks are usually considered: 1. the risk of false alarm, defined above, 2. the risk of non-detection, associated with the failure to detect a "true" defect.	

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Annex 2

**Use of Performance Values for Inspection Purposes
and Their Limitations**

The Performance Values (see chapter 3) are used in planning inspections and in drawing inferences based on the declared values of the operator and on the measured values of the inspector¹⁵⁶.

From an inspection planning viewpoint, they allow calculation of sample sizes for NDA and for DA verification methods that are optimal with respect to achieving the desired level of defect detection probability with the minimum number of samples.

When evaluating the verification data, they serve first to define item-level alarms, or reject limits, such that if a given item paired difference, d_{ij} , exceeds the limit L in absolute value, it is identified as a discrepancy, where L is defined by the equation:

$$L = z_{\alpha} \left[u^2(r) + u^2(s) \right]^{1/2} \quad (A2.1)$$

where z_{α} is the normal probability distribution factor associated with the probability α of declaring a false alarm. Current practice is to take $z_{\alpha} = 3$, which results in a false alarm probability of less than 0.3 %.

The item paired differences are calculated on either an absolute or relative basis, as was mentioned in chapter 3. Of course, for a homogeneous stratum, it makes no difference whether absolute or relative differences are calculated.

In addition to defining attribute test reject limits as just described, performance values are also used in calculating the variances used in material balance evaluations for material unaccounted for (MUF), operator-inspector difference (D), and the inspector's estimate of MUF, (MUF-D).

In a large facility the probability of detection will be driven by the amount of material. Regardless of how accurately and precisely material is measured, σ will be large because the amount of material is large. In such cases, the probability of detecting diversion by means of a material balance evaluation will be small and additional safeguards measures such as near real-time accountancy (NRTA) are called for.

The users of the Performance Values must remain aware of a number of limitations in their meaning or content.

Plant operational or economic constraints may inflate the variance components of the operator-inspector differences significantly compared to the capability of current measurement technology. The safeguards inspector must indeed verify that the uncertainties in the plant measurement system are not deliberately inflated in order to reduce the detection capability of the verification measurements. The latter concern increases with the throughput or material inventory of the plant. There will therefore always be a need for Target Values providing an accepted measure of the capability of current measurement technology under reasonably economic and operational conditions encountered in the industry.

Conversely, paired comparisons do not detect the measurement errors or uncertainties, which are common to the operator and inspector. For example, if both use the same reference material for calibration, the uncertainty of the certified value of the reference material will

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appear as a common systematic component in both results. The common component can also be of a random nature; random sampling errors are common, for instance, when the operator and the inspector measure the same sample or separate aliquots of the same sample.

These common components do not affect the uncertainties of the differences between operator's and inspector's measurements on a single stratum. They can, however, mask a potential bias with respect to the true amount of material. Consequently the use of Performance Values can lead to underestimation of the total uncertainties in the operator's declarations or in the material balance differences over the plant. Independent measurement evidence, free from such common mode uncertainties, is hence needed.

The user of the Performance Values must also know that the estimate of the between inspection effects, $s(\Delta)$, becomes less precise as the random uncertainty component, $s(\epsilon)$, increases. When the inspector's uncertainties are large compared to the operator's values, it becomes difficult to obtain a precise estimate of the operator's uncertainties, and vice-versa. This is frequently the case when the operator's data come from DA measurements while the inspector measures by NDA. The paired comparisons can lead to an overestimation of the random uncertainties of the operator's DA measurements, and, at the same time, to a poor estimate of the between-inspection effects in the inspector's NDA results. As a further complication, estimates of these parameters will be affected when the operator's values are based in part on nominal or average values. A separate evaluation of the performance of individual measurement methods is necessary to guard against such potential problems.

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05/07/02 02:20 PM

Subject: FW: Special Note (Red) on DA Compendium Document

Attached is a draft copy of the "Destructive Assay Method Compendium". New Brunswick Laboratory has updated this document with the latest International Target Values. As you may know, SO-11 is interested in publishing this as a Technical Standard. I have been tasked to coordinate the final document (along with Kelly Coady) through the DOE Technical Standard process.

Please review the "DA Compendium" in its entirety (however, most of the changes were made to pages 21-29) and provide comments /suggestions back to me. I am requesting that all comments/suggestions to be sent to me at <mailto:Kimberly.Johnson-Miller@ch.doe.gov> no later than June 3, 2002.

If you have any questions, please feel free to contact me at (630)252-4334. I thank you in advance for your cooperation.

Kimberly Johnson-Miller
Manager, Nuclear Safeguards and Nonproliferation Support Program

<<DA Methods Compendium.doc0.zip>>

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Destructive Assay Methods Compendium¹

I. Introduction.

Analytical chemistry plays a key role in nuclear material control and accounting (MC&A). A large part of Special Nuclear Material (SNM) inventories and virtually all of the highly attractive SNM inventories are based on sampling bulk materials followed by destructive assay (DA) of these materials. These measurements support MC&A in process control, physical inventory verification, evaluation of the effects of process changes, detecting and resolving shipper-receiver differences, and the resolution of IAEA inspector-facility differences. The evaluation and the specification of DA, MC&A techniques have proven difficult, in part, because of the highly specialized and technical nature of DA and because of the wide variety of methods and applications.

II. Purpose.

The purpose of this guidance document is to:

- Recommend criteria to use in evaluation of DA MC&A capabilities.
- Provide a basis for selection of appropriate upgrades where capabilities are inadequate to support MC&A goals.
- Provide a list of DA methods suitable for MC&A with the following information:
 - performance and applications information,
 - strengths and limitations,
 - **references and information on cost.**

III. Scope.

DA involves measurements on samples taken from a larger quantity or batch; typically samples are altered by their preparation such that the sample is not returned to the batch. This document is limited to analytical methods used to quantify and characterize plutonium (Pu) and enriched uranium (EU). The US DOE and NRC identify these materials as Special Nuclear Materials (SNM).

- Limited guidance is provided on bulk measurements and sampling of bulk materials.
- All the included methods, alone or in conjunction with other methods, provide analysis of SNM element or isotope quantities and are appropriate for use in support of MC&A. Most of these methods may also provide information useful for process control.
- Some methods listed herein address the determination of impurities present in SNM. These methods are limited to those typically used to measure impurities to provide interference corrections for certain DA methods.
- Appendix A provides summary information on DA methods. General references are listed which provide in-depth information on each method. For reviews of SNM assay (elemental concentration) methods References 1-4 are recommended.

IV. DA Method Evaluation and Selection Criteria.

The primary criterion for evaluating a DA method used in support of MC&A is determining whether or not the method provides the accuracy required to support statements on inventory assurance. Material Control and Accounting goal quantities are defined to determine the appropriate combination of MC&A elements, including DA and non-destructive assay (NDA) measurements, which support statements of allowable inventory difference. The US approach to inventory assurance encourages and supports using highly precise and accurate analytical measurement values in inventory difference calculations. As processing of SNM has been shut down, more limited US funds have been made available for DA MC&A measurements and a more practical approach may be needed to determine the best use of the available resources. Within established Material Balance Areas (MBAs), MC&A goal-quantities for those MBA's

¹ Price Russ, LLNL; Robert Marshall, LANL; Doyle Hembree, Y-12; Michael Holland, SRS; Wanda Mitchell, NBL.

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can then be used to evaluate existing analytical capabilities and to determine the upgrades required. Nuclear Regulatory Commission (NRC) and International Atomic Energy Agency (IAEA) target values and goal quantities are provided for guidance in Appendix B.

With goal quantities defined, the SNM flow in a specified time period can be estimated, the fraction of that flow which would be determined by analytical chemistry can be estimated, and the acceptable percent uncertainty on the flow for the analytical measurements can be estimated. These estimates allow the precision and accuracy of the analytical measurements required to attain the declared level of assurance to be determined. Note that the performance requirements for DA depend upon the attractiveness of the material. It is absolutely essential that the overall error, which includes the combined errors from every stage of the measurement process, be considered in determining the required precision and accuracy of the analytical method. In general, the precision of the DA method must be higher than that required to simply meet a given level of assurance because errors from other sources, particularly sampling, must be taken into account. A good rule of thumb is that the DA method should contribute no more than 20% to the overall allowable error. Appendix C presents an example of the type of calculation needed to evaluate the limits on DA errors consistent with detecting a goal-quantity loss of SNM from a hypothetical MBA.

A second criterion is technological suitability. All DA methods require some level of technological support, but the requirements vary widely. Readily available electronic and computer support may be needed for some methods together with high purity chemicals and certified reference materials (CRMs). Without these support resources, certain DA methods may be unusable. Each site must include an estimate of the availability of these resources to evaluate the feasibility of sustaining selected methods at a particular facility.

A third criterion is cost effectiveness. DA methods vary widely in their costs to set up and operate. Sustainability bears consideration as additional US facilities are removed from operation.

A fourth criterion is the capacity or throughput of each method. Some methods are relatively labor intensive and can only provide a few analyses per day; others are highly automated and can provide many analyses per day. Automation may be desirable not only to increase the sample throughput, but also to reduce variability in the data.

A fifth criterion is training. In general where chemists are employed, they are knowledgeable and skilled in the methods they employ. However, implementing new or enhanced DA methods at facilities may require training of chemists, technicians and support personnel which adds to the cost of implementing the methods.

V. Sampling and bulk measurements.

The DA of samples alone does not provide a statement of the uncertainty on the SNM inventory for MC&A. The DA of a sample provides the elemental or isotopic information which is multiplied by the mass or volume of the bulk material from which the sample is taken. The calculated SNM mass in the bulk material has an uncertainty which includes uncertainties in the bulk material measurement (mass or volume), the degree to which the sample represents the bulk material, and the quality of the DA measurement.

The capability of the facility to take samples representative of the bulk material must be understood by the DOE oversight and the facility so that sampling error can be included in the calculation of the overall SNM inventory uncertainty. Failure to collect representative samples from bulk SNM can mask theft or cause false alarms, which undermines the credibility of MC&A systems. Therefore, tasking the facility to evaluate its sampling error contribution to inventory difference is advised to identify inadequacies in sampling practices and to establish the accuracy and precision associated with sampling.

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Overall analytical uncertainty depends on both sampling and DA errors. When assessing DA measurement requirements versus assurance goals, the chemist must have a reasonable knowledge of the type and magnitude of the errors from the sample collection process. Since the error from sampling and the DA result on the sample are multiplied by the bulk mass or volume, which is typically a large number, to yield the bulk SNM quantity, the accuracy and precision needed in the measurement of the bulk mass or volume must be carefully considered. The chemist must also know the ability of the laboratory to detect larger than expected sampling errors (by other than the replicate DA measurements). If the laboratory can readily validate a set of replicate samples by a bulk measurement such as sample density measurements (and process tank density measurements, if available), then sample error can be controlled and DA method selection can be based more strictly on measurement uncertainty requirements. To save time and resources, this validation should take place before the DA measurements. If sample validation methodology is not implemented, the reliability requirements for DA measurements must be increased to ensure detection of sample errors from limited data sets on replicate DA measurements. Enhancement of a facility's capabilities for sampling bulk SNM, understanding sampling errors, and measuring bulk volumes or masses to the sufficient level of precision and accuracy may need to be made in parallel with enhancement of DA methods.

VI. REFERENCES

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Appendix A. Destructive Assay Methods

In this appendix, a list of the more common SNM assay and isotopic ratio methods and some supporting impurity measurement methods are provided. For each method a very concise description of the method, sample size and preparation, support equipment and supplies, calibration and standards, performance, and advantages and disadvantages are given. References are given for comprehensive information on the more complicated methods. Where references are not given use References 3 and 4 on the preceding page..

Cost estimates are based upon implementation of a capability, and include the costs for equipment, instrumentation, training and supplies. Exact costs will be facility specific. To provide rough guidance, the Team has broken the cost into the following categories: LOW = <100K dollars; MEDIUM = 100 to 500K; HIGH = >500K

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Appendix A Contents:

Appendix A.1: Plutonium Analysis

- A.1.1 Ignition/Gravimetry
- A.1.2 Controlled-Potential Coulometry
- A.1.3 Plutonium Alpha Spectrometry
- A.1.4 Alpha Counting
- A.1.5 Ceric Titration of Pu with Potentiometric or Spectrophotometric Endpoint
- A.1.6 Amperometric Titration of Pu
- A.1.7 Spectrophotometry of Pu (and U)

Appendix A.2: Uranium Analysis

- A.2.1 Ignition/Gravimetry
- A.2.2 Davies and Gray, Reduction-Oxidation Titrimetry
- A.2.3 Laser-Induced Kinetic Phosphorescence
- A.2.4 Spectrophotometry of U (See A.1.7 Spectrophotometry of Pu)
- A.2.5 Densitometry

Appendix A3: Mass Spectrometry

- A.3.1 Mass Spectrometry: Isotopic Abundance of U and Pu
- A.3.2 Isotope Dilution Mass Spectrometry (IDMS)

Appendix A4: Impurity Analysis

- A.4.1 Spectrophotometry for iron
- A.4.2 DC Arc Emission Spectroscopy for metallic impurities
- A.4.3 Atomic absorption, inductively coupled plasma emission spectroscopy and mass spectrometry

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METHOD A.1.1: Ignition/Gravimetry of Pu	
ELEMENT DETERMINED	Pu
BASIC PRINCIPLE	Convert a weighed portion of plutonium sample to PuO ₂ , a compound of known, specific composition, by heating (ignition) in a furnace to 1200 °C or higher, and calculate the quantity of plutonium from the known composition and the total final mass of the PuO ₂ formed. Correct the final weight of PuO ₂ for any nonvolatile impurities as determined by separate analysis
TYPICAL RESULTS	Random and Systematic errors of 0.05% to 0.2%.
SAMPLE SIZE	5 - 10 grams
SAMPLE TYPES	High purity plutonium materials
ADVANTAGES	Laboratory equipment required is simple. High precision for high purity materials is readily attained. Operator time per determination is small. Solid samples require minimal handling.
LIMITATIONS	Requires known, reproducible composition of the final weighing form, PuO ₂ . Application is limited to high purity materials such as plutonium oxalate, plutonium oxide, plutonium metal, and plutonium nitrate solutions. Nonvolatile impurities must be separately determined and a correction applied. Weighing errors.
REFERENCES	K. A. Swinburn and I. R. McGowan, "An Approach to the Use of Plutonium Dioxide as a Chemical Reference Standard for Plutonium," BNFL-205(W), British Nuclear Fuels Limited, 1975. G. R. Waterbury, R. M. Douglas, and C. F. Metz, "Thermogravimetric Behavior of Plutonium Metal, Nitrate, Sulfate and Oxalate," <i>Anal. Chem.</i> , 33,1018-1023 (1961).
COST ESTIMATE	LOW

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METHOD A.1.2: Controlled Potential Coulometry of Pu	
ELEMENT DETERMINED	Pu
BASIC PRINCIPLE	Quantitative electrolytic oxidation of Pu(III) to Pu(IV) at an electrode maintained at a controlled potential with determination of the quantity of Pu from the quantity of electricity required for the complete oxidation. (Special case of redox titrimetry in which electrons are used as the titrant.)
TYPICAL RESULTS	Random and systematic errors of 0.1% readily attained. For better sample types errors of 0.05% are attained.
SAMPLE SIZE	1 - 10 mg Pu
SAMPLE TYPES	Pu metal, oxides Mixed U, Pu oxides Pu nitrate solutions Dissolver solutions Applicable to most Pu materials when ion-exchange separation is used.
ADVANTAGES	High precision and accuracy on relatively small quantities of Pu. Relatively free of interferences. Readily automated. Adaptable to remote operations and analysis of irradiated materials.
LIMITATIONS	Moderately complex/moderately expensive instrumentation. Electrolysis cell and electrode malfunctions. Several interferences cause problems. Weighing errors. Operator errors.
REFERENCES	W. D. Shults, "Applications of Controlled-Potential Coulometry to the Determination of Plutonium-A Review," <i>Talanta</i> , Vol. 10, 1963, p. 833-849. T. L. Frazzini, M. K. Holland, J. R. Weiss, and C. E. Pietri, "A Digital Integrator for Controlled-Potential Coulometry," <i>Analytica Chimica Acta</i> , Vol. 129, 1981, p. 125. ASTM Standard Test Methods for Controlled-Potential Coulometric Measurement of Pu, C 1108 and C 1165, both in Volume 12.01 International Standard, "Controlled-Potential Coulometric Assay of Plutonium," ISO 12183.
COST ESTIMATE	MEDIUM

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METHOD A.1.3: Alpha Spectrometry of Pu	
ELEMENT DETERMINED	Pu (^{238}Pu in support of mass spectrometry)
TYPICAL RESULTS	Random error of 2% for 0.01% ^{238}Pu .
BASIC PRINCIPLE	From an alpha spectrum of a dissolved and separated Pu sample, determine a ratio from measurements of the total counts from the ^{238}Pu peak regions and $^{239}\text{Pu} + ^{240}\text{Pu}$ peak regions. Calculate the ^{238}Pu abundance from the ratio obtained and abundance measurements of ^{239}Pu and ^{240}Pu obtained from mass spectrometry of a separate portion of the sample.
SAMPLE SIZE	Samples containing 0.01 - 0.7 weight percent ^{238}Pu
SAMPLE TYPES	Used where the ^{238}Pu abundance is too low for mass spectrometric measurement or there is interference from ^{238}U . Pu must be dissolved and separated.
ADVANTAGES	Allows determination of ^{238}Pu where problems occur with mass spectrometry. Method is relatively simple and fast.
LIMITATIONS	Separation from ^{241}Am is required. Mass spectrometric determination of ^{239}Pu and ^{240}Pu is required. Preparation of counting disk to obtain uniform sample distribution requires care. Uncertainties in Pu isotope half-lives.
REFERENCES	
COST ESTIMATE	LOW

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METHOD A.1.4: Alpha Counting of Pu	
ELEMENT DETERMINED	Pu
TYPICAL RESULTS	Random and systematic errors of 2 - 5%
BASIC PRINCIPLE	A sample or a separated Pu fraction is mounted on a counting disk and the gross alpha activity is determined.
SAMPLE SIZE	Adequate to give 1 - 5 X 10 ⁵ counts in 5 - 10 minutes
SAMPLE TYPES	Dissolver solutions, irradiated process solutions and waste solutions.
ADVANTAGES	Method is relatively simple and fast. Applicable to radioactive solutions requiring remote handling.
LIMITATIONS	Specific activity of the Pu in the sample must be known. Generally requires a separation. Thick or nonuniform deposits on counting disks cause errors. None quantitative Pu recovery from separations cause errors.
REFERENCES	
COST ESTIMATE	LOW

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METHOD A.1.5: Ceric Titration of Pu	
ELEMENT DETERMINED	Pu
TYPICAL RESULTS	Random and Systematic errors are 0.05% on good materials.
BASIC PRINCIPLE	Oxidimetric titration of Pu(III) to Pu(IV) using the oxidant Ce(IV) as titrant with spectrophotometric detection of the end point which is observed as a color change of the added ferroin indicator or potentiometric endpoint; the Pu in the initial sample is reduced prior to the titration using a lead reductor column.
SAMPLE SIZE	200 to 250 mg Pu
SAMPLE TYPES	Pu metal, Pu oxides, Pu nitrides Used primarily for relatively pure metal due to interferences. (Use anion exchange separation when several interferences are present)
ADVANTAGES	Simple laboratory equipment. High precision and accuracy on applicable samples.
LIMITATIONS	Subject to numerous common interferences - Fe, Cr, Ti, Mo, W, U, V Relatively large sample size required. Titrant – tedious and lengthy preparation; requires standardization and careful storage; uncertainty of standards used yield errors. Operator errors - weighing errors, titration errors.
REFERENCES	J. Corpel and F. Regnaud, <i>Analytica Chimica Acta.</i> , Vol. 27, pp. 36-39, 1962.
COST ESTIMATE	LOW

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METHOD A.1.6: Amperometric Titration of Pu	
ELEMENT DETERMINED	Pu
TYPICAL RESULTS	Random errors of 0.1 -0.2% are generally attained. Systematic errors are usually better than 0.1%. Random errors under the best conditions are better than 0.05%.
BASIC PRINCIPLE	Reductimetric titration of Pu(VI) to Pu(IV) using the reductant Fe(II) as titrant with amperometric detection of the end point after preliminary oxidation of the Pu to Pu(VI) using excess Ag(II) oxide as an oxidant. Amperometric titration is based on observation of the change in current at a working electrode as titrant is added. In this titration the electrode responds to the Fe(II) titrant; when the end point is exceeded a current flow proportional to the excess Fe(II) is observed allowing detection and determination of the end point.
SAMPLE SIZE	10 - 60 mg Pu
SAMPLE TYPES	Pu as metal, oxide, fluoride, chloride, nitrate, sulfate. Pu in alloys containing uranium, iron, cobalt and aluminum.
ADVANTAGES	Simple laboratory equipment. High precision and accuracy on relatively small samples. Clear, simple end point detection. Initial oxidation state of Pu does not matter; all Pu is oxidized to Pu(VI).
LIMITATIONS	Subject to several interferences - cerium, chromium, vanadium and manganese. Titrant – requires daily standardization; subject to change. Initial titration reaction is slow and difficult to follow. Indicator and reference electrodes subject to problems.
REFERENCES	C. A. Seils, Jr., R. J. Meyer, and R. P. Larsen, "Amperometric Titration of Plutonium (VI) with Iron (II)," <i>Anal. Chem.</i> 35, pp. 1673-1675, 1963.
COST ESTIMATE	LOW

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METHOD A.1.7: Spectrophotometry of Pu (and U)	
ELEMENT DETERMINED	Pu (and U)
TYPICAL RESULTS	Routine samples, Random errors of 1 - 3%; systematic errors of 0.5% High purity plutonium materials, Random error of 0.3%; systematic error of 0.2%
BASIC PRINCIPLE	Rapid determination of the concentration of specific oxidation states of U and Pu by simultaneous measurement of the absorption of light by those oxidation states over a range of wavelengths and fast computer processing of the data based on calibration models.
SAMPLE SIZE	0.2 - 200 g/L U or Pu
SAMPLE TYPES	U and Pu solutions with U(VI) and Pu(III) or Pu(VI)
ADVANTAGES	Rapid measurements. Reasonable precision. Easily interfaced to processes; reliable online measurements. Rugged instrument - no moving parts.
LIMITATIONS	Spectral and chemical interferences. Absorption is temperature and matrix dependent. Calibration model errors (weighing and absorption measurement errors). Operator errors - sample preparation.
REFERENCES	D. R. Van Hare, "Analysis of Special Recovery Samples by Pu (III) Spectrophotometry," Savannah River Plant Report DP-1713, 1985. "Interference Study of the Pu(III) Spectrophotometric Assay," <i>Journal of Radioanalytical and Nuclear Chemistry</i> , Vol 152, No. 1, 1991, pp. 207-218.
COST ESTIMATE	LOW

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METHOD A.2.1: Ignition/Gravimetry of U	
ELEMENT DETERMINED	U
BASIC PRINCIPLE	Convert a weighed portion of uranium sample to U ₃ O ₈ , a compound of known, specific composition, by heating (ignition) in a furnace open to the air and calculate the quantity of uranium from the known composition and the total final mass of the U ₃ O ₈ formed. Nonvolatile impurities must be determined by a separate determination.
TYPICAL RESULTS	Random errors of 0.01 to 0.08% and Systematic errors of 0.01 to 0.02%.
SAMPLE SIZE	5 - 10 grams
SAMPLE TYPES	High purity uranium materials - metal, UO ₂ , UO ₃ , U ₃ O ₈ , UF ₄ , UF ₆ , Uranyl nitrate solution
ADVANTAGES	Laboratory equipment required is simple. High precision is readily attained. Operator time per determination is small. Solid samples require minimal handling.
LIMITATIONS	Requires known, reproducible composition of the final weighing form, U ₃ O ₈ . Application is limited to high purity materials; impurity content and corrections can be problems. Weighing errors.
REFERENCES	O. A. Vita, C. R. Walker, and E. Litteral, "The gravimetric Determination of Uranium in Uranyl Nitrate," <i>Anal. Chimica Acta.</i> , Vol 64, pp. 249-257, 1973. F. B. Stephens, R. G. Gutmacher, K. Ernst, J. E. Harrar, and S. P. Turel, "Methods for the Accountability of Uranium Dioxide," NUREG-75/010, pp. 4-44 to 4051, U.S. Regulatory Commission , June 1975.
COST ESTIMATE	LOW

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METHOD A.2.2: Davies/Gray Titration of U	
ELEMENT DETERMINED	U
BASIC PRINCIPLE	Redox titration of U(IV) to U(VI) with potentiometric end point detection after chemical pretreatment of the sample solution to adjust the oxidation states of species present so that uranium is essentially the only substance titratable by the oxidant.
TYPICAL RESULTS	Random and systematic errors of 0.1% readily attained. For better sample types errors of 0.05% are attained.
SAMPLE SIZE	10 - 50 mg U
SAMPLE TYPES	Applicable to uranium materials from essentially all stages of the nuclear fuel cycle - uranium ores, metal, oxides, salts and alloys.
ADVANTAGES	Good precision and accuracy are readily attained. Laboratory equipment is relatively simple. Few interferences; most can be removed or controlled. Groups of 12 - 15 samples handled together. Relatively easily automated.
LIMITATIONS	Operator errors; requires strict adherence to details. Requires full time and attention of analyst. Requires care in selection and testing reagents. Indicator and reference electrode problems occur. Errors/changes in titrant value. Weighing errors.
REFERENCES	W. Davis and W. Gray, "Rapid and Specific Volumetric Method for the Precise Determination of Uranium Using Ferrous Sulfate as Reductant," <i>Talanta</i> , 1964, p. 1203. A.W. Eberle and M. W. Lerner, "Effect of Added Vanadyl Ion on the Accuracy of the New Brunswick Laboratory Method (Ferrous Ion Reduction) of Determining Uranium," NBL-258, 1971, p. 22.
COST ESTIMATES	LOW for Manual MEDIUM if Automated

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METHOD A.2.3: Laser-Induced Kinetic Phosphorescence	
ELEMENT DETERMINED	U
BASIC PRINCIPLE	The method utilizes the measurement of the intensity of the green phosphorescence of U which results from excitation with ultraviolet light from a pulsed nitrogen/dye laser. The phosphorescence of the UO_2^{+2} is filtered, amplified, and measured by a computer which also calculates the result. To prevent quenching of the phosphorescence, a phosphate-based complexing reagent is added. The kinetic analysis of the uranyl phosphorescence provides a highly precise and accurate measurement, thus, eliminating the need for an internal standard.
TYPICAL RESULTS	Precision of 3% for solutions with 0.001 - 5.0 μ g U/g solution. Accuracy of 2% for 0.001 – 5.0 μ U/g solution
SAMPLE SIZE	0.001 – 5.0 μ g U/g solution Detection limit is 2×10^{-5} μ g
SAMPLE TYPES	Low and trace level U solutions.
ADVANTAGES	Method is rapid and relatively simple. Sensitive to low levels of U. Generally directly applicable to solutions without separations. Pu does not interfere.
LIMITATIONS	Uranium must be present as U(VI). Contamination with U from reagents or sample treatments must be carefully avoided. Alcohols, halides, and oxidizable metals are strong quenching agents which interfere with phosphorescence of uranium. Other materials such as chromate may absorb at the same excitation wavelength as uranium (425 nm). Suspended particles interfere with the normal decay curve of uranium phosphorescence.
REFERENCES	W. Campen and K. Bachmann, "Laser-Induced Fluorescence for the Direct Determination of Small Concentrations of Uranium in Water," <u>Mikrochim. Acta</u> [Wien], 1979 II, pp. 159-170. A. C. Zook, L. H. Collins, and C. E. Pietri, "Determination of Nanogram Quantities of Uranium by Pulsed-Laser Fluorimetry," <u>Mikrochim. Acta</u> [Wien], 1981 II, pp. 457-468.
COST ESTIMATE	LOW

Method A.2.4 Spectrophotometry of U (See Method A.1.7)

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Method A.2.5: Densitometry	
Physical Property Measured	Density in mass per volume. Very precise specific gravity values may be calculated at specified temperatures from the measured density at specified temperatures.
BASIC PRINCIPLE	A vibrating hollow U-shaped tube is caused to oscillate at a high frequency. The frequency squared of the tube oscillation is proportional to the mass of the tube. Filling the hollow tube with a liquid changes the mass of the tube and the tube oscillation. The density meter is calibrated by injection of two standards of different density into the hollow tube and measuring the tube oscillation for each standard. The density of an unknown sample is determined by relating the tube oscillation of the sample to the tube oscillation of the standards. Temperature is controlled either with a constant temperature bath or Peltier cooler.
TYPICAL RESULTS	Instrumentation is available that provides density values to four, five, or six decimal places.
SAMPLE SIZE	Approximately 1 ml.
SAMPLE TYPES	Any liquid that can be injected with a syringe and not vigorously attack glass. Instruments are available that have stainless steel U tubes instead of glass.
ADVANTAGES	Very fast analyses, easy to automate, data obtained in electronic format and easy to transmit electronically. Very precise temperature control (instrumentation easy to calibrate at various temperatures). Instruments operate for years with minimal maintenance.
LIMITATIONS	Suspended solids and air/gas bubbles can interfere.
REFERENCES	Calculating Density Meter with a built-in thermostat, DMA 46 Instruction Manual, Anton Paar™, Graz/AUSTRIA.
COST ESTIMATE	LOW

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METHOD A.3.1: Mass Spectrometry: Isotopic Abundance of U and Pu	
ELEMENT DETERMINED	U & Pu
TYPICAL RESULTS	Random and systematic errors of 0.01 - 0.1% depending on sample size.
BASIC PRINCIPLE	Conversion of a sample to a gaseous, ionic form; separation of the ions according to their mass to charge ratios in a magnetic field; and measurement of the relative intensities of the separated ion beams.
SAMPLE SIZE	U - 10^{-8} to 10^{-5} g Pu - 10^{-9} to 10^{-6} g
SAMPLE TYPES	All U & Pu materials - after separation
ADVANTAGES	Method gives essentially complete isotopic information over a wide range of isotopes with good precision and accuracy. Requires very little sample. Instrumentation is readily automated.
LIMITATIONS	Complex, expensive instrument requires care in operation; mass discrimination and nonlinearities require corrections. Usually require separations due to problems from interferences and impurities.
REFERENCES	"Thermal Ionization Mass Spectrometry of Uranium with Electrodeposition as a Loading Technique", D.J. Rokop, et al., <u>Anal. Chem.</u> , <u>54</u> 957 (1982). "High-precision Isotopic Analyses of Uranium and Plutonium by Total Sample Volatilization and Signal Integration", E.L. Callis and R.M. Abernathy, <u>Int. J. Mass Spect. Ion Processes</u> , <u>103</u> 93-105 (1991).
COST ESTIMATE	HIGH

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METHOD A.3.2: Isotope Dilution Mass Spectrometry of U and Pu	
ELEMENT DETERMINED	U & Pu
BASIC PRINCIPLE	Variation of mass spectrometry involving addition of a known quantity of enriched isotope (Spike) to the sample which allows calculation of the elemental concentration from the measured isotopic ratios of the mixture, the measured ratios of an unspiked sample, and the known isotopic composition of the spike.
TYPICAL RESULTS	Random and systematic errors of 0.25%
SAMPLE SIZE	U - 10^{-8} to 10^{-5} g Pu - 10^{-9} to 10^{-6} g
SAMPLE TYPES	All U & Pu materials - subject to availability of Spike materials
ADVANTAGES	Method determines both isotopic composition and elemental concentration. Good precision and accuracy can be achieved. Requires only small amounts of sample.
LIMITATIONS	Complex, expensive instrumentation. Problems with attaining chemical and isotopic equilibration. Inadequate separation of U and Pu. Uncertainties in assay of spike solutions. Weighing errors for the sample or spike. Mass spectrometer operational errors.
REFERENCES	"The Determination of Plutonium by Mass Spectrometry Using a 242-Plutonium Tracer," R. K. Webster, A. A. Smales, D. F. Dance, and L. J. Slee, <i>Anal. Chim. Acta</i> <u>24</u> 371-380 (1961). "The Application of Isotope Dilution Mass Spectrometry to the Determination of Uranium and Plutonium in Nuclear Fuels," J. E. Rein and C. F. Metz, in <i>Analytical chemistry of Nuclear Fuels</i> , Proc. Panel, Vienna, July 13-17, 1970, (International Atomic Energy Agency, Vienna, Austria, 1972), pp. 97-109. The Use of a Combined Internal Standard and Assay Spike for the Isotope Dilution Mass Spectrometric Assay of Plutonium, D. W. Crawford, M. A. Legel, M. I. Spaletto, and N. M. Trahey, NBL-318(a), pp. 17-19, March 1988. "Isotope Dilution Mass Spectrometry," K.G. Heumann, in <i>Inorganic Mass Spectrometry</i> , edited by F. Adams, R. Gijbels, and R. Van Grieken. John Wiley and Sons, New York, 1988, pp. 301-376.
COST ESTIMATE	LOW (assumes suitable mass spectrometer already available, a HIGH cost item)

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METHOD A.4.1: Spectrophotometry for iron	
ELEMENT DETERMINED	Fe
BASIC PRINCIPLE	Iron is measured spectrophotometrically as the Fe(II) o-phenanthrolate complex at a wavelength of 508 nm after removal of plutonium by oxalate precipitation. The quantity of iron is calculated from the measured absorbance and the absorbance per microgram of iron obtained for prepared solutions having known iron contents. [Fe Standard prepared from electrolytic iron or ferrous ammonium sulfate hexahydrate.]
TYPICAL RESULTS	The relative standard deviation is approximately 1%.
SAMPLE SIZE	10-40 micrograms Fe [capability to 1 microgram with wider precision].
SAMPLE TYPES	Iron in the range 100 – 1000 µg Fe per gram of uranium-plutonium oxide
ADVANTAGES	Rapid and simple measurement to allow for iron correction of plutonium results. Typical elapsed time for analysis of 3 hours.
LIMITATIONS	If nickel is present in quantities greater than that of iron, it will produce a bias in the iron measurement that is greater than 1.5%.
REFERENCES	Los Alamos National Laboratory Report, LA-4622, "Methods of Chemical Analysis for FBR Uranium-Plutonium Oxide Fuel and Source Materials," J. E. Rein, G. M. Matlack, G. R. Waterbury, R. T. Phelps, and C. F. Metz, pp 55-58, (1971).
COST ESTIMATE	LOW

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METHOD A.4.2: DC Arc Emission Spectroscopy for metallic impurities	
ELEMENT DETERMINED	Metal impurities
BASIC PRINCIPLE	Powdered samples are loaded into graphite electrodes. A dc arc is induced across the electrodes producing arc temperatures from 4000 to 8000°K. Emission lines from primarily neutral atoms are detected using either photographic plates or photomultiplier tubes. Intensities of emission lines are related to those of standards to obtain quantitative information.
TYPICAL RESULTS	The technique is used to measure metal impurities in the range of 0.1 – 2000 μ g/g (lower and upper limits are element specific).
SAMPLE SIZE	Electrodes are loaded with approximately 50-mg of sample. Samples are usually homogenized before loading electrodes.
SAMPLE TYPES	All types of samples (must be solid to load into electrode)
ADVANTAGES	<ul style="list-style-type: none"> - Relatively low cost - Large number of metal impurities detected simultaneously - Almost any sample matrix can be analyzed
LIMITATIONS	<ul style="list-style-type: none"> - Relatively large error (better than spark source mass spectrometry but worse than inductively coupled plasma optical emission) - Susceptible to contamination (like any impurity analysis). - Requires highly trained technician.
REFERENCES	H. H. Willard, L.L. Merritt, Jr., and J.A. Dean, <i>Instrumental Methods of Analysis</i> , 5 th Ed., D. Van Nostrand, New York, 1974, p. 390.
COST ESTIMATE	Medium

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METHOD A.4.3: Atomic absorption (AA), inductively coupled plasma optical emission spectroscopy (ICP-OES) and inductively coupled plasma emission mass spectrometry (ICP-MS)	
ELEMENT DETERMINED	Metallic sample components and isotopic composition when using ICP-MS
BASIC PRINCIPLE	<p><u>Detection mechanisms:</u></p> <ul style="list-style-type: none"> - AA: absorption of element-specific wavelengths - ICP-OES: emission of element-specific wavelengths generated by the inductively coupled plasma - ICP-MS: ions generated in an inductively coupled plasma are mass analyzed by one of several methods (e.g., quadrapole or magnetic sector mass spectrometer).
TYPICAL RESULTS	Typically, impurities can be determined from 1 – 5000 ppm.
SAMPLE SIZE	Depends on dilution factor (0.1-g or larger).
SAMPLE TYPES	Liquids and solids (solids require dissolution).
ADVANTAGES	High precision Wide dynamic range Multiple element, simultaneous analyses (with the exception of AA)
LIMITATIONS	Samples must be in solution Requires highly skilled technicians Subject to contamination
REFERENCES	
COST ESTIMATE	MEDIUM (except for AA which is LOW)

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Appendix B. International Regulations and Guidelines.

Appendix B.1. Code of Federal Regulations (CFR)

10 CFR Part 70.51

The limits of error on the material unaccounted for (MUF) on any total plant in-process MBA are:

- | | |
|---|-------|
| 1) Pu or ²³³ U in chemical reprocessing plant: | 1.0% |
| 2) U elemental and fissile isotope in reprocessing plant: | 0.7% |
| 3) Pu, ²³³ U, high-enriched U elemental and
fissile isotope in all other: | 0.5% |
| 4) Low-enriched uranium element and
fissile isotope in all other: | 0.5%. |

10 CFR Part 74.13

A report to the Nuclear Regulatory Commission (NRC) is required if inventory difference exceeds both:

- 1) Twice the standard error of the estimated measurement uncertainty associated with the inventory difference; and
- 2) Two hundred grams of plutonium or ²³³U, 300 grams of high enriched ²³⁵U contained in high-enriched uranium, or 9000 grams of ²³⁵U contained in low enriched uranium.

Appendix B.2. International Atomic Energy Agency (IAEA) Guidance

IAEA/SG/INF/4; "IAEA Safeguards Aims, Limitations, Achievements" IAEA, Vienna, 1983, p. 26

For direct-use material, the significant quantities (SQs) have been set to coincide in weight (though not exactly in composition) with threshold amounts:

- 1) 8 kg of plutonium element (containing less than 80% ²³⁸Pu)
- 2) 25 kg of ²³⁵U contained in uranium enriched to 20% or more
- 3) 8 kg of ²³³U

Appendix B.3. Target Values (US Department of Energy Guidance)

Target Values for Tank Volume Measurements of Solutions using a Ruska Electromanometer

<u>Material/Type</u>	<u>Element</u>	Precision	Bias
		<u>% Rel. Ran. Error</u>	<u>% Rel. Sys. Error</u>
U Solutions/Pure Pu		0.3	0.3

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Appendix B.4. Target Values (Working Group on Techniques and Standards for Destructive Analysis (WGDA) of the European Safeguards Research and Development Association (ESARDA).²⁾

B.4.1 Target Values for Titrimetry Measurements for Process, Product, Scrap, and Waste Materials

<u>Material/Type</u>	<u>Element</u>	Precision		Bias	
		<u>% Rel. Ran. Error</u>	<u>% Rel. Sys. Error</u>	<u>% Rel. Ran. Error</u>	<u>% Rel. Sys. Error</u>
UF ₆	U ^a	0.1 ³	0.1 ³	0.1 ³	0.1 ³
U Solutions/pure	U	0.15	0.15	0.15	0.15
U Solutions/scrap	U ^b	0.3	0.3	0.5	0.5
U Oxide/powder, NG	U ^c	0.1 ³	0.1 ³	0.1 ³	0.1 ³
U Oxide/powder, scrap	U	0.3	0.3	0.5	0.5
U Oxide/sintered materials	U	0.15	0.15	0.1	0.1
<hr/>					
UF ₄ Powder/NG	U ^c	0.15	0.15	0.3	0.3
U-metal/NG	U	0.2 ³	0.2 ³	0.2 ³	0.2 ³
U-Al based materials/NG	U	0.2	0.2	0.3	0.3
U-Al based/scrap	U	0.3	0.3	0.5	0.5
U-Si based materials/NG	U	0.2	0.2	0.3	0.3
Zr-U materials	U	0.5	0.5	0.3	0.3
<hr/>					
U/Carbides	U	0.3	0.3	0.5	0.5
(Th,U)O ₂ /Kernals & BISO ^d	U	0.15	0.15	0.2	0.2
	Th	0.2	0.2	0.2	0.2
(Th,U)O ₂ or UO ₂ /TRISO ^d	U	0.2	0.2	0.2	0.2
	Th	0.2	0.2	0.3	0.3
U-scrap/dirty & diluted	U	0.5	0.5	2.0	2.0

^a Control of decomposition required if subjected to chemical decomposition.

^b Shall be free of turbidity.

^c Control of oxidation and/or moisture pickup required.

^d BISO, TRISO: binary, trinary sealed oxide coated particles.

² P. De Bièvre, J. Dalton, S. Baumann, R. E. Perrin, T. Görgenyi, C. Pietri, E. Kuhn, and S. Deron, "1987 Target Values for the Uncertainty Components in Fissile Isotope and Element Assay," *Journal of Nuclear Materials Management*, pp. 99-106, July 1987.

³ H. Aigner et al., "International Target Values 2000 for Measurement Uncertainties in Safeguarding Nuclear Material", *International Atomic Energy Agency Report*, STR-327, Millennium Edition, April 2001.

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B.4.1 (continued) Target Values for Titrimetry Measurements for Process, Product, Scrap, and Waste Materials

<u>Material/Type</u>	<u>Element</u>	<u>Precision % Rel. Ran. Error</u>	<u>Bias % Rel. Sys. Error</u>
Spent Fuel inputs/	U	0.3	0.3
HWR & LWR	Pu	—	—
Spent Fuel Inputs/FBR	U	0.3	0.2
	Pu	0.3	0.2
Pu Nitrate/Pure	Pu	0.15 ³	0.15 ³
U,Pu Nitrate Solutions/Pure	U ^a	0.1 ³	0.1 ³
	Pu	0.15 ³	0.15 ³
PuO ₂ /Powders	Pu ^b	0.15 ³	0.15 ³
(U,Pu)O ₂ MOX/LWR	U	0.3	0.2
	Pu ^{b,c}	0.5	0.5
(U,Pu)O ₂ MOX/FBR	U	0.3	0.2
	Pu ^{a,b}	0.2	0.2
(U,Pu)O ₂ MOX/Scrap	U	0.5	0.5
	Pu	1.0	0.5

^a U/Pu = 3.

^b Control of oxidation and/or moisture pickup required.

^c 1-4% Pu.

³ H. Aigner et al., "International Target Values 2000 for Measurement Uncertainties in Safeguarding Nuclear Material", *International Atomic Energy Agency Report*, STR-327, Millennium Edition, April 2001.

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B.4.2 Target Values for Coulometry Measurements for Process, Product, and Scrap Materials

<u>Material/Type</u>	<u>Element</u>	<u>Precision % Rel. Ran. Error</u>	<u>Bias % Rel. Sys. Error</u>
UF ₆	U ^a	0.2	0.2
U Solutions/pure	U	0.15	0.15
U Oxide/powder, NG	U ^b	0.15	0.15
U Oxide/powder, scrap	U	0.3	0.5
U Oxide/sintered materials	U	0.15	0.15
UF ₄ Powder/NG	U ^b	0.15	0.3
U-metal/NG	U	0.15	0.1
U-Al based materials/NG	U	0.2	0.3
U-Al based/scrap	U	0.3	0.5
U/Carbides	U	0.3	0.5
Pu Nitrate/Pure	Pu	0.2	0.2
U,Pu Nitrate Solutions/Pure	U ^c	0.2	0.2
PuO ₂ /Powders	Pu	0.2	0.2
	Pu ^b	0.2	0.2
(U,Pu)O ₂ MOX/LWR	U	0.3	0.2
	Pu ^{b,d}	0.5	0.5
(U,Pu)O ₂ MOX/FBR	U	0.3	0.2
	Pu ^{b,c}	0.2	0.2
(U,Pu)O ₂ MOX/Scrap	U	0.5	0.5
	Pu	1.0	0.5

^a Control of decomposition required if subjected to chemical decomposition.

^b Control of oxidation and/or moisture pickup required.

^c U/Pu = 3.

^d 1-4% Pu.

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B.4.3 Target Values for Gravimetry Measurements for Process and Product Materials

<u>Material/Type</u>	<u>Element</u>	Precision		Bias	
		<u>% Rel. Error</u>	<u>Ran. Error</u>	<u>% Rel. Error</u>	<u>Sys. Error</u>
UF ₆	U ^a	0.05 ³		0.05 ³	
U Solutions/pure	U	0.1		0.15	
U Oxide/powder, NG	U ^b	0.05 ³		0.05 ³	
U Oxide/sintered materials	U	0.05		0.1	
UF ₄ Powder/NG	U ^b	0.15		0.15	
U/Carbides	U	0.2		0.5	
Pu Nitrate/Pure	Pu	0.1		0.15	
PuO ₂ /Powders	Pu ^b	0.05 ³		0.05 ³	
(U,Pu)O ₂ MOX/LWR	U ^c	0.1		0.15	
	Pu	---		---	

^a Control of decomposition required if subjected to chemical decomposition.

^b Control of oxidation and/or moisture pickup required.

^c After Pu and Am correction.

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B.4.4 Target Values for K-edge Densitometry Measurements for Process, Scrap, and Waste Materials

<u>Material/Type</u>	<u>Element</u>	<u>Precision % Rel. Ran. Error</u>	<u>Bias % Rel. Sys. Error</u>
U Solutions/pure	U	0.2	0.15 ³
U Solutions/scrap	U ^a	0.2	0.2
Pu Nitrate/Pure	Pu	0.2	0.15 ³
U,Pu Nitrate Solutions/Pure	U ^b	0.2	0.2
	Pu	0.3	0.3
U,Pu Solutions/Waste	U	0.3	0.3
	Pu	---	---

^a Shall be free of turbidity.

^b U/Pu = 3.

³ H. Aigner et al., "International Target Values 2000 for Measurement Uncertainties in Safeguarding Nuclear Material", *International Atomic Energy Agency Report*, STR-327, Millennium Edition, April 2001.

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B.4.5 Target Values for X-ray Fluorescence Measurements for Process, Product, Scrap, and Waste Materials

<u>Material/Type</u>	<u>Element</u>	<u>Precision</u>		<u>Bias</u>	
		<u>% Rel. Error</u>	<u>Ran. Error</u>	<u>% Rel. Error</u>	<u>Sys. Error</u>
U Solutions/pure	U	0.5		0.5	
U Solutions/scrap	U ^a	2.0		2.0	
U Oxide/powder, scrap	U	1.0		1.0	
Zr-U materials	U	1.0		1.0	
(Th,U)O ₂ /kernals & BISO ^b	U	1.0		0.5	
	Th	1.0		0.5	
(Th,U)O ₂ or UO ₂ /TRISO ^b	U	1.0		1.0	
	Th	1.0		1.0	
U-scrap/dirty & diluted	U	3.0		5.0	
Spent Fuel inputs/ HWR & LWR	U	0.5		0.5	
	Pu	1.0		1.0	
Spent Fuel Inputs/FBR	U	0.5		0.5	
	Pu	1.0		1.0	
Liquid Waste/HAW	Pu	5.0		10.0	
Pu Nitrate/Pure	Pu	0.5		0.5	
U,Pu Nitrate Solutions/Pure	U ^c	0.5		0.5	
	Pu	0.5		0.5	
U,Pu Solutions/Waste	U	3.0		5.0	
	Pu	3.0		5.0	
(U,Pu)O ₂ MOX/FBR	U	0.5		0.5	
	Pu ^{c,d}	0.5		0.5	
(U,Pu)O ₂ MOX/Scrap	U	3.0		5.0	
	Pu	3.0		5.0	

^a Shall be free of turbidity.
^b BISO, TRISO: binary, trinary sealed oxide coated particles.
^c U/Pu = 3.
^d Control of oxidation and/or moisture pickup required.

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B.4.6 Target Values for Spectrophotometric Measurements for Process, Product, Scrap, and Waste Materials

<u>Material/Type</u>	<u>Element</u>	<u>Precision % Rel. Ran. Error</u>	<u>Bias % Rel. Sys. Error</u>
U Solutions/scrap	U ^a	3.0	5.0
U-scrap/dirty & diluted	U	5.0	10
Spent Fuel inputs/ HWR & LWR	U Pu	--- 1.0	--- 1.0
Spent Fuel Inputs/FBR	U Pu	--- 1.0	--- 1.0
Pu Nitrate/Pure	Pu	0.5	0.5
U,Pu Nitrate Solutions/Pure	U Pu	--- 0.5	--- 0.5
U,Pu Solutions/Waste	U Pu	5.0 2.0	5.0 2.0
PuO ₂ /Powders	Pu ^b	0.5	0.5
(U,Pu)O ₂ MOX/LWR	U Pu ^{b,c}	--- 0.5	--- 0.5
(U,Pu)O ₂ MOX/FBR	U Pu ^{b,d}	--- 0.5	--- 0.5
(U,Pu)O ₂ MOX/Scrap	U Pu	--- 1.0	--- 1.0

^a Shall be free of turbidity.

^b Control of oxidation and/or moisture pickup required.

^c 1-4% Pu.

^d U/Pu = 3.

B.4.7 Target Values for Fluorimetry Measurements for Scrap Materials

<u>Material/Type</u>	<u>Element</u>	<u>Precision % Rel. Ran. Error</u>	<u>Bias % Rel. Sys. Error</u>
U Solutions/scrap	U ^a	10	10
U Scrap/dirty & diluted	U	10	10

^a Shall be free of turbidity.

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B.4.8 Target Values for Alpha Counting Measurements for Waste Materials

<u>Material/Type</u>	<u>Element</u>	Precision		Bias	
		<u>% Rel. Error</u>	<u>Ran. Error</u>	<u>% Rel. Error</u>	<u>Sys. Error</u>
Liquid Waste/HAW	Pu	10		10	
/MAW	Pu	5		5	
/LAW	Pu	5		5	
U,Pu Solutions/Waste	U	5		5	

B.4.9 Target Values for IDMS Measurements for Process, Product, and Waste Materials

<u>Material/Type</u>	<u>Element</u>	Precision		Bias	
		<u>% Rel. Error</u>	<u>Ran. Error</u>	<u>% Rel. Error</u>	<u>Sys. Error</u>
Spent Fuel inputs/	U	0.5		0.5	
HWR & LWR	Pu	0.5		0.5	
Spent Fuel Inputs/FBR	U	0.5		0.5	
	Pu	0.5		0.5	
U,Pu Solutions/Waste	U	0.5		0.5	
	Pu	0.5		0.5	

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B.4.10 TARGET VALUES FOR UNCERTAINTY COMPONENTS IN ISOTOPIC ASSAY

Isotope	(%) Abund.	GMS ^a		TIMS ^b		Gamma Spec. ^c		Alpha Spec.		IDMS ^d	
		Prec. ^h	Bias ⁱ	Prec.	Bias	Prec	Bias	Prec	Bias	Prec	Bias
²³⁵ U	0.2 ^e	0.1	0.1	0.7	0.5	5	3	--	--	0.5	0.5
	0.7 ^e	0.05	0.1	0.5	0.5	2	1	--	--	0.5	0.5
	3 ^e	0.03	0.1	0.3	0.3	0.5	0.5	--	--	0.5	0.5
	20 ^f	0.02	0.1	0.1	0.1	0.5	0.5	--	--	0.5	0.5
	90 ^f	0.01	0.03	0.05	0.05	0.2	0.5	--	--	0.5	0.5
²³⁸ Pu	0.3 ^g	---	---	2	2	--	--	2	2	--	--
	1.5 ^g	---	---	0.7	0.7	--	--	3	2	--	--
²³⁹ Pu	50-80 ^g	---	---	0.1	0.1	--	--	--	--	0.3	0.3
²⁴⁰ Pu	10-30 ^g	---	---	0.2	0.2	--	--	--	--	--	--
²⁴¹ Pu	3 ^g	---	---	0.3	0.3	--	--	--	--	0.3	0.3
	15 ^g	---	---	0.3	0.3	--	--	--	--	0.3	0.3
²⁴² Pu	1-5 ^g	---	---	0.3	0.3	--	--	--	--	--	--

a Gas isotope mass spectrometry (UF₆).

b Thermal ionization mass spectrometry.

c Only for materials free of ²³²U (²³²U/²³⁵U < 10⁻⁹).

d Isotope dilution mass spectrometry. Direct assay of isotope against spike, e.g. ²³³U.

e All materials.

f Pure uranium compounds.

g Pure Pu materials.

h % Relative Random Error

i % Relative Systematic Error

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Appendix B.5 TYPICAL AMOUNTS OF ELEMENT NEEDED TO PERFORM ONE MEASUREMENT

<u>Method</u>	<u>U</u>	<u>Pu</u>	<u>Unit</u>
Titrimetry	20-100	5-50	milligram
Coulometry	2-20	2-10	milligram
Gravimetry	2-20	0.2-3	gram
X-ray Fluorescence	0.1-30	0.1-30	milligram
IDMS ^a	10-1000	1-1000	microgram
Spectrophotometry	20-500	1-100 ^b 0.1-10 ^c	microgram milligram
Fluorimetry	2-500	---	nanogram
Alpha Counting	2-500	0.1-1	microgram
K-edge Densitometry	0.2-1	0.3-1	gram
Gas MS ^a	20	---	milligram
Thermal Ion. MS ^a	1-1000	1-1000	microgram
Gamma Spectrometry	0.1-1	---	microgram
Alpha Spectrometry	---	0.1-1	microgram

a Amount of sample required. In these cases an analysis can be performed on smaller amounts of element.

b Colorimetry

c Direct measurement at 830 nm of Pu(VI).

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APPENDIX C: An Example of Using an MBA Inventory Difference Limit to Estimate Uncertainty Criteria for Destructive Assay Measurements

Introduction. The question of how “good” do analytical chemistry measurement need to be to meet safeguards goals can be estimated by evaluating all measurements performed for a material balance area (MBA). To begin this process, one must first establish a goal-quantity for detection of theft. One criteria for making this goal-quantity is the IAEA “Significant Quantity” of 8 kg Pu and 25Kg ²³⁵U. These significant quantities are probably for inventory differences (ID) of entire sites and too large for a single MBA in a facility. A more realistic goal-quantity is the US DOE criterion of 2% of the MBA throughput. The most restrictive criteria is that of the US NRC allowable IDs. They are typically <1% of throughput for U and <0.5% for Pu.

Estimation Procedure. The steps one may follow to estimate the material measurement uncertainties required for theft detection are:

1. Determine the MBAs for the facility.
2. Establish the safeguards goal-quantity for the MBA and the statistical tests and degree of confidence to be associated with the detection of an inventory difference.
3. Determine the inventory period (monthly, bimonthly, etc.) for each MBA.
4. Determine the quantity and type of special nuclear material (SNM) stored in or processed in each MBA.
5. Establish key measurement points (KMP) for each MBA.
6. Identify the destructive analysis (DA) and non-destructive analysis (NDA) measurements to be used for SNM control (or process control or QA) for each MBA.
7. Make a chart or table showing the quantities of SNM, which will be measured at each KMP for each inventory period and the uncertainties, systematic and random, for each measurement method. These uncertainties may be estimated or, in the case of this example, the DA uncertainties left as unknowns to be determined. In addition to measurement errors, uncertainties should include all known sources of variation such as sampling errors, moisture uptake, and temperature and pressure effects.
8. Calculate the measurement uncertainties for each inventory period’s SNM flow and beginning and ending inventories.
9. Combine these uncertainties and subtract the combined uncertainties from the total allowable uncertainty for theft detection. The difference will be the uncertainty “budgeted” for DA.
10. *From this DA uncertainty ‘budget’, calculate the target uncertainty values for the DA methods.*

This process is involved and material flows may not be well known at the beginning or NDA measurement uncertainties may not be well known. However, the factors that do not contribute much to the overall uncertainty can be roughly estimated. If ‘conservative or somewhat overstated’ estimates are made for the critical parameters, the final result will be a ‘worst case’ estimate. Often such an estimate is adequate for making DA upgrades decisions.

The outcome of such analyses will differ widely with the nature of the MBA and the confidence level desired for the detection of a diversion. For instance the acceptable random error for a measurement will be quite different depending on whether it is a single measurement of a large quantity of material or measurements on a large number of objects. For this appendix, a specific example has been selected and the parameters varied to show their relative effect. The reader is reminded that the following discussion is only an example and should not be considered as typical or representative of a real situation. It is particularly important to note that the statistical treatment used has been simplified.

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Estimation Example. Consider the case of a MOX reactor fuel production facility that uses low burnup Pu and natural uranium oxides to make fuel pellets. A flow diagram for this facility is shown in Figure 1.

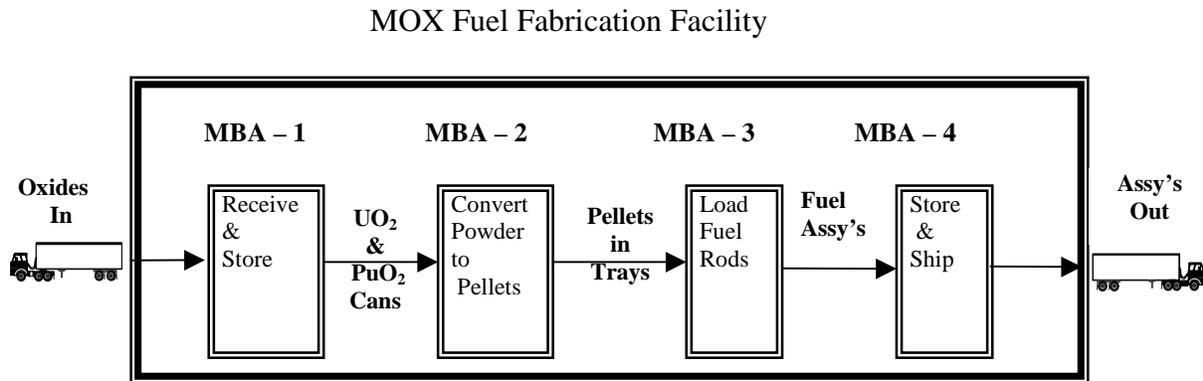


Figure 1

Step 1: Defining MBA's is outside the goal of this exercise. Take them as given in Figure 1.

Step 2: For this example only MBA-2, where oxide powder is converted to pellets, will be considered. The DOE 2%-of-throughput criterion will be used. Having identified the goal-quantity, one must decide on the statistical tests to be used to identify whether observed IDs are "real". In addition IDs that are less than the goal-quantity, would be used to identify significant problems with the system. Confidence levels for both "false positives" and "false negatives" should also be established. These issues are beyond the scope of this appendix. The reader should consult statistical texts such as references ³⁻⁶ for more details on this subject. For this exercise, the statistical significance of the uncertainties associated with measurements at the various parts of the process will not be specified. For a real situation, one must make a determination of the desired level of confidence required before identifying an inventory difference as such. To increase confidence that differences are "real", "wider" errors would be used. Unfortunately while decreasing the number of "false positives", this increases the chances of "false negatives"; *i.e.*, not detecting diversions. In order to detect a goal-quantity ID, the total error "budget" for measurements, including DA, must be less than the goal-quantity. For this example, the error budget will be taken as one half to the goal-quantity. The relationships among bias, precision, and number of samples will be illustrated.

Step 3: Accountancy will be monthly.

³ M. G. Natrella, Experimental Statistics: Handbook 91, U.S. Government Printing Office, Washington, 1963.

⁵ Guide to the Expression of Uncertainty in Measurement, ISO/TAG4/WG3, June 1992.

⁶ Evaluation and Control of Inventory Differences in the DOE Complex, TSO-87-9/BNL-40221, J. Sanborn, August 1987.

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Step 4: Because the facility uses natural uranium (not an SNM), uranium can be ignored. Only Pu needs to be considered. Assume the “beginning inventory” is the same as the ending inventory for the prior month and consists of one input can containing 2 kg of Pu as PuO₂ plus one tray of MOX pellets containing 1.9 kg Pu. All scrap is removed from the MBA before the ending inventory, i.e. the MBA is cleaned out between inventories. Assume holdup is measured annually, and does not contribute significantly to a single month ID. Finally assume the end of month inventory is the same as the beginning inventory. During the month the material flowed as follows: “N” new cans of Pu oxide each containing 2 kg Pu entered the process and the oxide was converted into MOX pellets; N trays of MOX pellets, each containing 1.9 kg Pu, exited the process. The balance of the material (5% or 0.1 kg (Pu)/can) was in the form of scrap powder. Defining throughput as the sum of inputs and outputs from the MBA, the throughput was 2N kg of Pu. Based on the 2% of throughput criteria for a theft-detection goal-quantity, the MBA 2 goal-quantity is 2% of 2N kg Pu. The value of N will be allowed to vary to illustrate the effect of the number of items on permissible uncertainties.

Step 5: Within MBA-2 samples will be taken for assay of both incoming and outgoing material. Figure 2 illustrates this MBA’s SNM flows and locations of KMPs with their associated measurement methods.

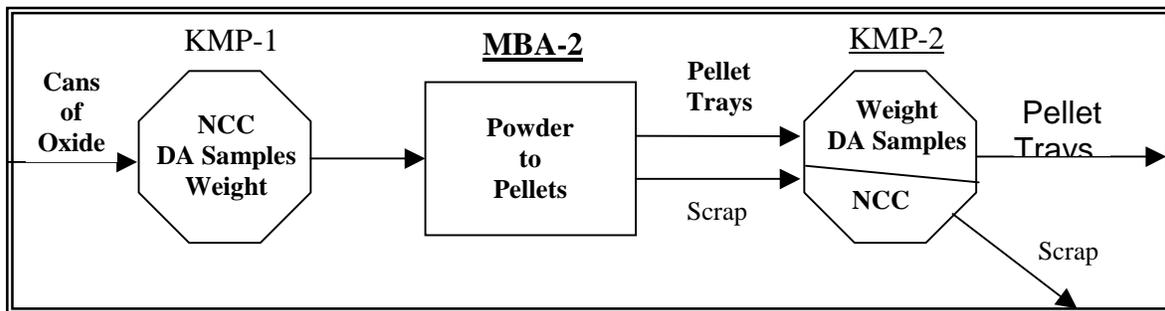


Figure 2, Key Measurement Points in MBA-2

Step 6: The measurements applied to the inventories and material flows are as follows:

The PuO₂ can “passport” (shipper) values are used until the cans arrive at KMP-1.

Upon receipt at KMP-1, incoming cans are measured by neutron coincidence counting (NCC) and gamma spectroscopy to confirm the passport values. The cans are then weighed and sampled. The samples are submitted for Pu assay by DA techniques.

Before leaving the MBA through KMP-2, MOX pellets in trays are weighed and samples taken for DA. Confirmatory measurements by NCC and gamma spectroscopy may also be made.

Scrap; i.e., oxide powder spilled or otherwise not successfully converted to pellets, is collected, weighed, and measured by NCC. This is also done at KMP-2.

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Step 7: Table 1 summarizes the quantities of SNM, the measurement methods and systematic (bias) and measurement (random) uncertainties. . Because this exercise is to evaluate the permissible DA uncertainties, approximate weighing and NDA measurement uncertainties have been assigned without further justification. “TBD” means “To Be Determined.” In this example, errors associated with sampling the powder and the pellets may be thought of as included in the errors of the measurement method. In a more realistic case, the sampling errors and statistical methods of sampling should be treated explicitly.

Table 1. Summary of Material Quantity, Measurements and Measurement Uncertainty Data

KMP #	Material Form and Pu mass, kg	Measurement Method	Bias (Systematic uncertainty, %)	Precision (Random uncertainty, %)
1	PuO ₂ powder cans 2 kg/can	Weight	0.1%	0.2%
1	PuO ₂ powder samples	DA	TBD	TBD
1	PuO ₂ powder cans, 2 kg/can	NCC + gamma Spectroscopy	confirmatory	confirmatory
2	ScrapU/Pu oxide can 5% of total Pu	NCC	5%	2%
2	MOX Pellets in trays	NCC + gamma Spectroscopy	confirmatory	confirmatory
2	MOX Pellet Samples	DA	TBD	TBD
2	MOX Pellets in trays	Weight	0.5%	0.2%

Step 8: Calculate the uncertainties for the mass of Pu flowing through MBA-2 over the 1 month period and for the mass of Pu present in the beginning and ending inventory.

Tables 2 and 3 show the uncertainties, expressed as Pu mass, for the beginning and ending inventories and monthly throughput, respectively. The exact method for combining uncertainties can be complex. For a first approximation, one can add the systematic errors linearly and the random errors quadratically; *ie*, use the square root of the sum of the squares of the individual random uncertainties.

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Table 2, Beginning and Ending Inventory Measurement Uncertainties

Pu Form and Mass	Measurement	Bias (Systematic uncertainty, kg)	Precision (Random uncertainty, kg)
1 Can of PuO ₂ powder 2 kg Pu	Weighing	0.002	0.004
Samples from above can of powder	DA	TBD	TBD
1 tray of MOX pellets 1.9 kg Pu	Weighing	0.010	0.004
Samples from above MOX pellet tray	DA	TBD	TBD

Table 3. Monthly Throughput Measurement Uncertainties

Pu Form and Mass	Measurement	Bias (Systematic uncertainty, kg)	Precision (Random uncertainty, kg)
N cans PuO ₂ powder 2 kg Pu each	Weighing	$N \times 2 \times 0.001$	$\text{Sqrt}(N \times (2 \times 0.002)^2)$
Samples from above cans of powder	DA	TBD	TBD
15 trays MOX pellets 1.9 kg each	Weighing	$N \times 1.9 \times 0.005$	$\text{Sqrt}(N \times (1.9 \times 0.002)^2)$
Samples from above trays of pellets	DA	TBD	TBD
Scrap U/Pu powder 5% of total Pu (1 can)	NCC	$N \times 2 \times 0.05 \times 0.05$	$N \times 2 \times 0.05 \times 0.02$

Step 9: Combine the uncertainties for the monthly throughput, and the beginning and ending inventories adding the systematic uncertainties directly and the random uncertainties quadratically. To satisfy the aim of being able to detect the theft of a “goal-quantity” of material, the overall uncertainty must be less than the goal-quantity. A conservative method for combining the systematic and random errors to obtain the overall uncertainty on the inventory is to add them together linearly. In this example, the resulting equation for the overall uncertainty has 5 unknowns – number of cans, bias and precision of both the DA of the powder and the DA of the pellets. To simplify we will combine the DA uncertainties of the powder and pellets and consider only the total DA precision and accuracy budget.

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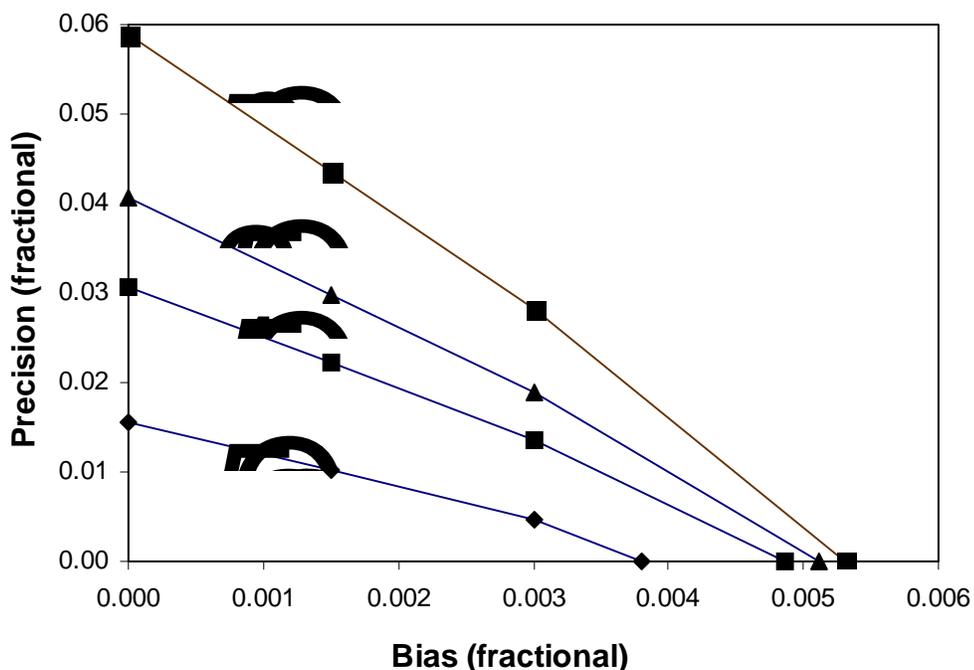
Step 10: One must now determine the target uncertainties for the DA method(s). Given that the equation for the overall uncertainty has three unknowns, it has a family of solutions. An easy way to study the effects of the various variables is to use a spreadsheet to model the behavior. If one fixes the number of cans and assumes the DA uncertainty is dominated by bias, one can set the precision uncertainty to zero and iteratively enter bias values until the calculated uncertainty equals the target value. One can then assume the DA uncertainty is dominated by precision and repeat the exercise. This sets the limits for the set of solutions. Intermediate cases can then be calculated. Finally, the number of cans can be changed and the calculations repeated. Results for several cases are presented in Figure 3. For a given number of cans, all points lying to the left of the line are combinations of bias and precision that will allow the DA goal to be met.

From Figure 3 one sees that both the precision and bias requirements for the DA analysis become less severe as the number of items (cans in this example) increases. The effect is greater for precision because the chance of the mean being offset by poor precision decreases as the number of measurements increases. (Another advantage of sampling and measuring more frequently is that it reduces the chance of theft from any single item going undetected.) The allowable bias is substantially less than the allowable precision uncertainty. Even for 50 cans the maximum allowable bias is only 0.5%. If the bias is greater than this, it will be impossible to detect the diversion of a goal-quantity. This emphasizes the importance of recognized standards in determining bias.

If facilities employ gravimetric methods to assay their Pu and U oxides and metals. These methods, without impurity corrections, will be biased. If impurity corrections are made, the bias may be small. However, without standards bias estimates are subjective.

If facilities employ gravimetric methods to assay their Pu and U oxides and metals. These methods, without impurity corrections, will be biased. If impurity corrections are made, the bias may be small.

However, without standards bias estimates are subjective.



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Figure 3

The fact that the allowed precisions shown in Figure 3 are as high as 6% results from the particular example used. It was not selected to represent a challenging situation and should not be interpreted as implying that precision is generally of little concern. It does illustrate the importance of evaluating the specific situation before committing to upgrades. Evaluations of the need for measurement upgrades, DA or otherwise, should include similar calculations for the MBAs evaluated.

Conclusion: Systematic evaluation of the bias and precision at each measurement point, allows the determination of how “good” a particular measurement needs to be and whether theft-detection at the goal-quantity level can be achieved. Even using estimates of some of the uncertainties, a systematic approach is useful in determining which errors are dominant, how to “budget” the allowable errors, and how to invest wisely to improve accountancy. The 10 step process described and the suggested simplifications and approximations facilitate a simple calculation to make assessments of the adequacy of existing methods or to determine what upgrades would be required to allow the DA method to meet theft detection goal quantities. While the example given is hypothetical, it illustrates how one must carefully identify and estimate systematic uncertainties, which may sum to become the dominant source of the overall uncertainty.

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Memorandum SEO-MCA-2002-00032, "International Target Values as Goals for Facility
Measurements Systems"
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Westinghouse
Savannah River Company
Aiken, SC 29808



JAN 31 2002

SEO-MCA-2002-00032

Mr. T. L. Williams, Director
Nuclear Safeguards Division
Savannah River Operations Office
U. S. Department of Energy
P. O. Box A
Aiken, SC 29802

Dear Mr. Williams:

INTERNATIONAL TARGET VALUES AS GOALS FOR FACILITY MEASUREMENT SYSTEMS (U)

Reference: NFC-01-030, T. L. Williams to E. T. Sadowski, *Guidelines for Measurement Performance as Identified by International Target Values*, December 21, 2000.

DOE M 474.1-1A, Chapter II 4 b, Selection and Qualification of Measurement Methods, states "Each facility must select, qualify, and validate measurement methods capable of providing the required levels of precision and accuracy. ... Target values for precision and accuracy of nuclear material measurements endorsed by recognized national and international nuclear organizations must be used as goals for performance of facility measurement systems." The operations office approves facility precision and accuracy requirements associated with Category I and II material balance areas (MBAs). WSRC MC&A has authority for approval of facility precision and accuracy requirements associated with Category III and IV MBAs. Precision and accuracy requirements have often been based on achievable, historic measurement system performance and do not necessarily reflect recognized international target values as goals.

In response to the reference, a comparison of international target values to WSRC precision and accuracy limits approved by DOE-SR/SED has been completed. The results of this analysis show that

- SRS error estimates are mainly in-line with international target values,
- Many of the international target values address methods not used and/or materials not measured at SRS,
- Several SRS primary measurement methods and materials do not have promulgated international target values, and
- Some limited measurements at SRS do not meet international target values.

Current WSRC measurement methods for which recognized international target value goals exist are listed in Attachments 1-3. These include

- Davies Gray,
- Coulometry,
- Active Well Coincidence Counting (AWCC),
- Balances,
- Tank volumes,
- Solution sampling,
- Lab density measurements, and
- Tank solution density measurements.

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Disconnects between SRS measurement methods and materials and international target values include

- A primary NDA measurement method used at SRS for plutonium materials is calorimetry. There are no international target values for calorimeter performance,
- Plutonium metal material is a major item measured at SRS. Plutonium metal is not a material addressed in international target values,
- The method used to measure input solutions for MBA FCA (F-Canyon) and MBA HBL (HB-Line Phase II) is diode array spectrophotometry (DAS) or Pu-TEVA (an alpha counting method). Neither of these methods is addressed by international target measurement values.

SRS methods are the same as those stated in the international target measurement document in the case of MBA HCA (H-Canyon) input measurements. The target document also provides a method for calculating or combining measurement errors. Comparisons between international target values and SRS values for HCA input measurements are given in Attachment 4 and show SRS is aligned with these target values.

One example where SRS does not meet international target values is the IDMS method used for measuring Pu and U concentration for materials packaged out of the material characterization cabinet in FB-Line. The target values for both Pu and U measurements of oxides using the IDMS methods show that SRS measurements are 4 to 10 times less accurate than the target values. (It should be noted that these methods have only been used for the last 1 to 2 years.) SS&ES Commitment Tracking System Action 2002-0029 (due date 4/30/02) commits MPC&A to (along with Analytical Laboratories Special Laboratories Section) identify improvements in/alternatives to the current IDMS methodology that will result in performance more closely matching the international target values for IDMS when measuring FB-Line Material Characterization oxides. The IDMS method as it is used for H-Canyon input measurements is in line with the equivalent international target values.

Questions concerning this topic may be addressed to D. Malizia, 703-42A, 725-6824, Bpr. 15619.

Sincerely,



Dr. E. T. Sadowski, Manager
Materials Protection Control and Accountability

cc: J. T. Terrell, 703-42A
M. K. Holland, 704-3F
D. Malizia, 703-42A
F. G. Armstrong, 703-42A
D. J. Campbell, 703-42A
T. M. Barnett, 703-73A
G. T. Meyers, 703-42A
D. M. Smith, 703-42A
MC&A Files, 703-42A

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ATTACHMENT 1

International Target Values at SRS
Bulk & Density Measurements

Measured Material	Measured Property	Measurement Method	International Target Values		SRS Performance	
			Random %, (1s)	Systematic %, (1s)	Random %, (1s)	Systematic %, (1s)
Solutions	Volume	DIPT	0.30	0.20	0.50	0.10
Solutions	Density	DIPT	0.30	0.20	0.60	0.40
Solutions	Density	VTDM	0.05	0.05	0.04	0.03
Any	Mass	EBAL	0.05	0.05	0.02	0.02
Any	Mass	LCBS	0.05	0.05	0.21	0.06

DIPT Dip Tube
EBAL Electronic Balance
LCBS Load-Cell Based Weighing System
VTDM Vibrating Tube Density Meter

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ATTACHMENT 2

INTERNATIONAL TARGET VALUES AT SRS
ANALYTICAL TECHNIQUES

Measured Material	Measured Property	Measurement Method	International Target Values		SRS Performance		
			Random %, (1s)	Systematic %, (1s)	Random %, (1s)	Systematic %, (1s)	Bias %, (1s)
UO ₂ (NO ₃) ₂	U	D/G	0.1	(nd)	0.2	0.1	
Pu(NO ₃) ₄	Pu	COUL	0.15	0.15	0.11	0	0.13
Reprocessing solution	U	Sampling	0.3	0.2	0.2	(nd)	(nd)
Other solutions	U	Sampling	0.2	(nd)	0.2	(nd)	(nd)
Reprocessing solution	Pu	DAS	N/A	N/A	1.18	1.08	0.27
Other solutions	Pu	Sampling	0.2	(nd)	0.2	(nd)	
U & Pu compounds	Pu	IDMS	0.15	0.1	0.565	0.987	0.65
	U	IDMS	0.15	0.1	0.745	0.745	0.537
Solutions	Density	VTDM	0.05	0.05	0.05	0.03	
HEU	U-235	TIMS	0.05	0.05	0.04	0.06	0.05

(nd) International Target Values have yet to be defined
 COUL Coulometry
 D/G Davies Gray
 DAS Diode Array Spectrometry
 IDMS Isotope Dilution Mass Spectrometry
 N/A Not Applicable
 TIMS Thermal Ionization Mass Spectrometry
 VTDM Vibrating Tube Density Meter

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ATTACHMENT 3
International Target Values at SRS
NDA Measurement Techniques

Measured Material	Measured Property	Measurement Method	International Target Values		SRS Performance		SRS Instrument
			Random %, (1s)	Systematic %, (1s)	Random %, (1s)	Systematic %, (1s)	
HEU Alloys	U-235	AWCC	5	3	1	6	KAO AWCC (Verification measurements only. Not used for Accountability.)
Pu Oxide Samples	Pu	INVS	2	1.5	N/A	N/A	FBL Neutron Coincidence Counter FBL Neutron Coincidence Counter
MOX Samples	Pu	INVS	10	2.5	N/A	N/A	
Pu Oxide Powder	Pu	HLNC	1	0.5	N/A	N/A	FBL Neutron Multiplicity Counter FBL Neutron Multiplicity Counter
	MOX Scrap	Pu	HLNC	10	3	N/A	
MOX Scrap - Metal	Pu	PSMC	8	2	0.54	3.7	FBL Neutron Multiplicity Counter FBL Neutron Multiplicity Counter
	MOX Scrap - Oxide	Pu	PSMC	8	2	7.9	
MOX Waste	Pu	WDAS	8	2	Currently being qualified.		FBL 3rd Level PHA
Pu - Various Forms	Pu	Calorimeter	(nd)	(nd)	0.13	0.21	HBL Calorimeters

(nd) International Target Values have yet to be defined
 AWCC Active Well Coincidence Counter
 HLNC High Level Neutron Coincidence Counter
 INVS Inventory Sample Coincidence Counter
 N/A Not Applicable
 PSMC Plutonium Scrap Multiplicity Counter
 WDAS Waste Drum Assay System

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F. Sadowski

January 31, 2002
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International Target Values at SRS
Use of ITVs

A typical example of the use of ITVs at SRS is based on measurement of solutions entering the HCA In-Process subMBA.

Measurement	Method/Instrument	ITV				H-Canyon			
		Random		Systematic		Random		Systematic	
		% rel. Std. Dev.	Variance						
Volume	DIPT	0.3	0.09	0.2	0.04	0.1	0.01	0.1	0.01
Sampling	Sampling	0.3	0.09	0.2	0.04	0.2	0.04	na	
Element Concentration	IDMS	0.15	0.0225	0.1	0.01	0.53	0.2809	0.05	0.0025
Isotope Concentration	TIMS	0.05	0.0025	0.05	0.0025	0.1	0.01		
Total			0.205		0.0925		0.3409		0.0125
Total Variance			0.2975			0.3534			
1s			0.55			0.59			
2s			1.09%			1.19%			

DIPT Dip Tube
IDMS Isotope Dilution Mass Spectrometry
TIMS Thermal Ionization Mass Spectrometry

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Westinghouse
Savannah River Company
Aiken, SC 29808



TSD-CLS-2001-00070

October 10, 2001

TO: Scott E. Federman, 772-F, CLAS Manager

FROM: *Robin H. Young*
Robin H. Young, 772-F
Michael K. Holland, 772-3F
RHY to: MKH

Application of the Runs Rule to Accountability Measurements in Central Laboratory Analytical Services (U)

This analysis concludes that Westinghouse Savannah River Company (WSRC) is not employing a valid statistical basis in its application of the Runs Rule to special nuclear material control and accountability. Department of Energy (DOE) orders do not require any use of a Runs Rule, but Central Laboratory Analytical Services (CLAS) believes that a statistically valid interpretation of the Runs Rule can be used for more effective measurement control, even with its high-precision instruments. CLAS plans to continue its present measurement control practices until critical changes in its Laboratory Information Management System (LIMS) can be implemented. In the interim, CLAS has issued procedural guidance to Cognizant Technical Functions (CTFs) directing them to periodically review accountability method control charts for adverse trends, including appropriate Runs Rule scenarios.

Background

In a recent audit finding (01May17-SR-3804-SSPS-NMCA.2-008-C-O), DOE noted that CLAS was not complying with the Runs Rule requirement for accountability samples as described in WSRC Manual 14Q, Procedure 3.10. Specifically, DOE observed that CLAS CTFs did not investigate instrument performance when 8 consecutive measurements of the working standard fell on the same side of the centerline (known value).

CLAS has a rigorous measurement control program in place which tracks the performance of all measurement systems through the use of quality control synthetics (QCS). The performance for each method is tracked automatically by a Laboratory Information Management System (LIMS), which can be queried to determine if the measurement of a QCS exceeds the warning or alarm limits. The LIMS is not programmed to flag the occurrence of a Runs Rule violation.

All calibration and QCS solutions used for accountability measurements are prepared by mass from concentrated stock solutions. These stock solutions are characterized using the highest accuracy and precision analytical methods as well as primary reference standards. The calibration standards are utilized to calibrate the instruments while the QCS are employed to verify the method is in control.

Once a QCS solution is prepared, it is submitted by the QC organization for verification by the Operations lab staff. If the measurement of the QCS by the Operations lab is within two sigma of the known value (Case 1 LIMS classification), the standard is put into service.

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Key Principles

The application of the Runs Rule to accountability measurements at Savannah River Site should be based on sound quality control principles which consider the following points:

- the requirements in DOE Order M 474.1-1A
- the technical limitations associated with preparing, maintaining, and distributing standards in solution form
- the cost to implement and maintain a program for production of high-accuracy standards
- the accuracy and precision requirements (data quality objectives) of the Material Control and Accountability customers

Requirements from DOE Order M 474.1-1A

DOE Order M 474.1-1A defines the required components for the control and accountability of nuclear materials. In Chapter II, Section 4.e, Paragraph 8, DOE states "Control limits must be established at the two-sigma level (warning limits) and three-sigma level (alarm limits). Control data exceeding the two-sigma levels must be investigated, and, when warranted, timely corrective action must be taken. If a single data point exceeds the three-sigma level, the measurement system in question must not be used for an accountability measurement until the measurement system is demonstrated to be within statistical control".

In view of the lack of a DOE requirement to use the Runs Rule, CLAS believes that WSRC is not using a graded approach in this area, particularly for analytical instruments with high precision. While the Runs Rule is a reasonable tool to observe instrument performance trends, it should not be applied when the technical basis for this control tool cannot be satisfied. The rule should be modified to address the technical basis issues.

Technical Limitations in Production of High-Accuracy Standards

To satisfy the technical basis for applying the Runs Rule, the total uncertainty associated with the individual vials of QC synthetics must be significantly better than the systematic and random uncertainties of the measurement method being controlled. At a minimum, the total uncertainty of the standard should be one-quarter (4-to-1) that of the method's short-term uncertainty if the current Runs Rule in 14Q is to be satisfied.

To comply with the Runs Rule as a control for high-precision methods (coulometry, uranium Davies-Gray, mass spectrometry, density), a substantial improvement in the uncertainty of standards currently used in Central Laboratory Analytical Services would be necessary. At present, the uncertainty of the standards used for coulometry, uranium by Davies-Gray, mass spectrometry, and density are approximately equal to the uncertainty of the respective methods (1-to-1 rather than 4-to-1).

To illustrate, CLAS personnel reviewed the control charts for the methods used for accountability measurements. In the case of high-precision measurement systems (see attached charts for density and coulometry), the deviations of the 8 points comprising potential Runs Rule violations were within 0.2% of the known value. This magnitude of error is within the overall uncertainty of the standard and is not a clear indicator of measurement error as intended by the Runs Rule. In order to avoid a Runs Rule violation in these circumstances, the

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uncertainty on the standard value would have to be so small that the preparation of the standard is not possible or is cost prohibitive. CLAS proposes that no action is necessary in this case.

The basis for the Runs Rule also has limitations when the short-term and long-term measurement precisions are significantly different. Uncertainty in the calibration standard can contribute to this effect and limit the ability of the Runs Rule to detect real measurement control problems. A hypothetical example illustrates the need for a graded approach to the Runs Rule. Suppose that a standard with a uncertainty of 0.3% is used in a method with a long-term precision one-sigma of 1%. The warning limit for the method is then +/- 2 % of the known value and the alarm limit is +/- 3%. Further suppose that 8 consecutive points differ from the known value by +0.1 to +0.5%, which matches short-term instrument precision. The instrument would be treated as out of control using the current 14Q Runs Rule interpretation, and the working standard must be remeasured three times. For the CTF to place the unit back in service, all three remeasurements must fall within the two-sigma method uncertainty and one of the three must fall on the opposite side of the centerline. Again, CLAS proposes that no action is necessary in this case.

Now suppose the same hypothetical conditions apply but the deviation of the 8 consecutive points vary between +1.3 and +1.7% of the known value. The bias exceeds the uncertainty of the standard and the precision one-sigma, which is clearly an undesirable trend. In this case, CLAS recommends that the CTF investigate the adverse trend, determine the root cause, and take corrective action, as warranted. Additional details on this follow-up are included below in the "CLAS Proposal for Runs Rule Violations" section.

Cost Limitations in Production of High-Accuracy Standards

The customer data quality objectives of CLAS accountability methods are at or near 4-to-1 versus the uncertainty of CLAS standards. However, CLAS does not have standards with uncertainties that are four times better than the optimum performance of its coulometry, Davies-Gray titration, mass spectrometry, or density methods. In most cases, standards that would meet this criterion cannot be prepared. While the accuracy of each of these standards could be improved somewhat by changes in their preparation, storage, and characterization (which is dependent upon the uncertainty of the measurement method used for characterization), the cost of the accountability measurement program would grow considerably. Additional manpower and instrumentation would be necessary to handle standard preparation, which would likely become a full-time endeavor.

Customer Data Quality Objectives

In addition to historical reliability of the measurement method and the total uncertainty of the QCS, the data quality objectives (accuracy and precision) of the customer must enter into the proper application of the Runs Rule.

If a method with a supposed Runs Rule violation provides data that exceeds the accuracy/precision needs of the customer, the actual uncertainty may not be significant. As an example, CLAS normally provides accountability results for plutonium by one of three methods: Pu TEVA 3 Column - Alpha Spectrometry, Pu - Diode Array Spectrometry, and Pu - Coulometry. The method uncertainties for these three methods are approximately 8.5%, 3.5%, and 0.5%, respectively. If a customer has traditionally received accountability measurements from a higher-uncertainty method, such as Pu TEVA, then results from a more

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precise method, such as Pu - Coulometry, should be more than sufficient, even if the coulometry QCS show a Runs Rule violation that does not exceed the uncertainty on the QCS. The magnitude of the error on the coulometry is insignificant compared to the Pu TEVA uncertainty.

CLAS Proposal for Runs Rule Violations

Trends falling outside both of the following Runs Rule criteria will be investigated.

1. Eight consecutive points on one side of the known value that exceed established uncertainties of the specific QCS and, if used, the calibration standards.
2. Eight consecutive points on one side of the known value that exceed 1-sigma of the method (see "Technical Basis for Limiting the Runs Rule to Eight Measurements Outside Method 1-sigma" below).

For any adverse Runs Rule trend, CLAS will document its investigation on a Control Chart Trending Problem Form, which will be copied to site Material Control and Accountability and the affected Material Balance Area custodians. Corrective actions required to return the measurement system to statistical control will be noted on the form. These corrective actions may entail re-calibration of the instrument, preparation of new standards and/or reagents, decontamination of the instrument, correction of calculation errors, or other actions deemed appropriate by the CTF. Before the system is returned to service, the working standard should be remeasured (recommended two or three times) to demonstrate that the adverse trend has been resolved.

Technical Basis for Limiting the Runs Rule to Eight Measurements Outside Method 1-sigma

The basis for limiting the Runs Rule to eight measurements outside of 1-sigma includes the following points:

- Short-term method precision and accuracy are often different than long-term method precision and accuracy. Significant degradation in short-term precision will be detected by alarm limits and warning limits. Less significant degradation will be detected as a significant trend indicator by CLAS's implementation of the Runs Rule. However, short-term precision improvements and minor shifts in measurement bias will generate insignificant trend indicators within the long-term 1-sigma precision band.
- The measurement parameters and environmental sources that cause short-term improvements in random error and minor shifts in systematic errors are normally very difficult to detect and corrective actions are not always possible or appropriate. (For example, stable weather conditions have caused more stable laboratory temperatures, which may be the source of a significantly improved short-term precision during approximately the same period. This cause and effect may be correct, but corrective action is not appropriate).
- Interrupting analytical services for small errors (~1-sigma or less) is not practical or cost effective for either the customer or the laboratory when the likelihood of quickly identifying the source of the error is small and being able to implement effective corrections actions is even smaller.

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- Measurement errors in the range of 1-sigma or less are typically of the same order of magnitude as sampling error, sample validation requirements, and the uncertainty in process tank volume measurements (these errors are root-mean-squared to produce total uncertainty).
- Under conditions where the random error is consistent with the long-term precision of the method and the data appear to be normally distributed, eight measurements will allow the method CTF to detect a significant systematic error provided it is greater than 0.84-standard deviations (Student's-t at 7 degrees of freedom/Sqrt(8); 2.37/2.83). Allowing conditions where the total uncertainty is on the order of 1-sigma, or less, is not a significant degradation in measurement control.
- It is appropriate to accept inherent systematic and random error in the range of 1-sigma, or less, from instrument calibration when it uses standard solutions that have to be processed through the entire measurement method to make them applicable/traceable. The number of calibration standards, the corresponding uncertainty, and the data quality objectives must be considered from both a technical basis and a practical/logistic (cost effectiveness) basis when calibrating measurement systems.

Conclusion

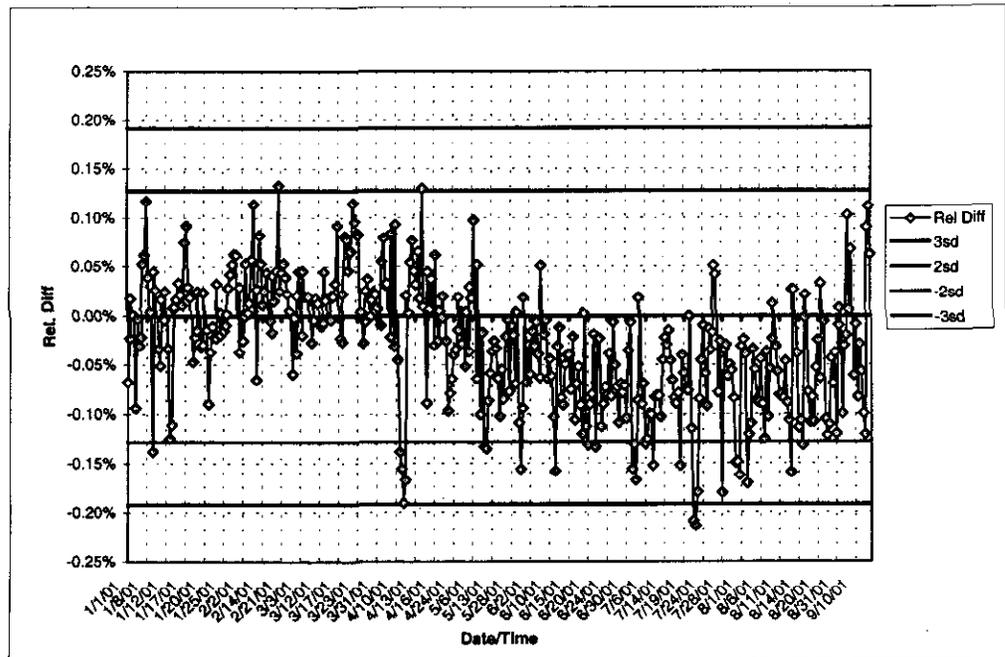
Without modification, the Runs Rule as defined in WSRC 14Q is not an effective tool to apply as a control for CLAS accountability methods. CLAS has implemented a procedure (WSRC L2-1-00118, "Accountability Method QC Chart Review", 10/09/01) that requires CTFs to periodically review accountability method control charts for adverse trends, including Runs Rule trends (where eight consecutive points exceed both the uncertainty of the standard and the 1-sigma uncertainty of the method).

CLAS plans to continue its present measurement control practices (system declared out-of-control when one point falls outside the alarm limits or two consecutive points fall outside the warning limits) until critical changes in its LIMS can be implemented. CLAS will develop a schedule for implementation of an automated review and control system once it determines if the current LIMS can be reprogrammed or if a new LIMS system must be procured and configured.

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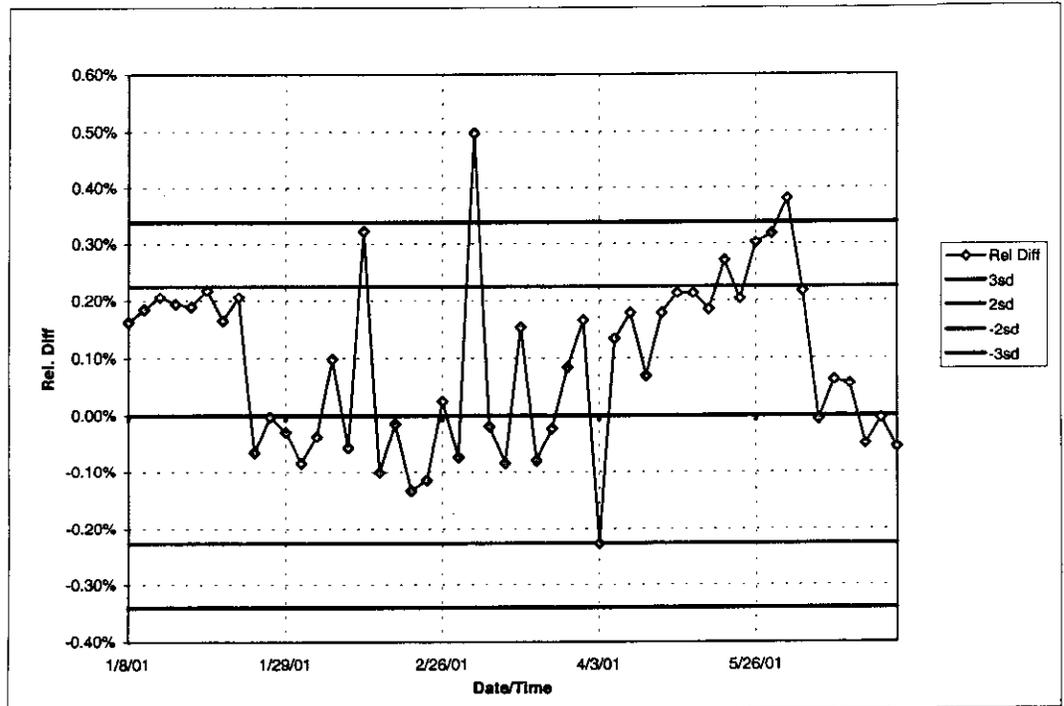
DENSITY_CELL



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PU_COULOMETRY



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