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Fundamentals of Materials Accounting for Nuclear Safeguards

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PREFACE

This manual is prepared for the safeguards technology course titled "Materials Accounting for Nuclear Safeguards" offered by the Los Alamos National Laboratory. This course is intended primarily for employees of the U.S. Department of Energy and the U.S. Nuclear Regulatory Commission as well as contractors and licensees involved in the control and accounting of special nuclear material (SNM) as part of an overall safeguards system. Designed for entrants to safeguards, this course introduces the fundamentals and systematics of implementing conventional and near-real-time materials accounting, statistical concepts and decisions, destructive and nondestructive assays for nuclear materials, data security, and facility-specific materials accounting practices. Specially designed workshops on materials control and accounting system design, nondestructive assay of SNM, near-real-time accounting, and variance propagation are interwoven through the course format.

The paucity of textbooks for the topics covered by this course prompted the preparation of this manual. However, limited time and resources preclude a comprehensive first edition to cover all allied topics relevant to materials accounting for nuclear material safeguards. Although the manual does not address each topic covered in the course, the fundamentals offered here are valuable for understanding the topics presented in the classroom. This manual also will serve as a post-course reference for participants. Additional topical briefs and addenda will be distributed during class presentations.

This manual was prepared with the help of many instructors who participated in earlier sessions of this course. We are grateful to all the authors for their assistance in preparing this manual. Also, we wish to thank others who are updating their manuscripts and/or preparing new material for distribution during course presentation. We wish to especially acknowledge the word processing dedication of Sharon Hurdle of the Safeguards Systems Group in preparing the manuscript for publication.

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FUNDAMENTALS OF MATERIALS ACCOUNTING FOR NUCLEAR SAFEGUARDS

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K. K. S. Pillay

ABSTRACT

Materials accounting is essential to providing the necessary assurance for verifying the effectiveness of a safeguards system. The use of measurements, analyses, records, and reports to maintain knowledge of the quantities of nuclear material present in a defined area of a facility and the use of physical inventories and materials balances to verify the presence of special nuclear materials are collectively known as materials accounting for nuclear safeguards. This manual, prepared as part of the resource materials for the Safeguards Technology Training Program of the U.S. Department of Energy, addresses fundamental aspects of materials accounting, enriching and complementing them with the first-hand experiences of authors from varied disciplines. The topics range from highly technical subjects to site-specific system designs and policy discussions. This collection of papers is prepared by more than 25 professionals from the nuclear safeguards field. Representing research institutions, industries, and regulatory agencies, the authors create a unique resource for the annual course titled "Materials Accounting for Nuclear Safeguards," which is offered at the Los Alamos National Laboratory.

CHAPTER I

BASIC CONCEPTS OF MATERIALS ACCOUNTING

by

J. T. Markin

I. INTRODUCTION

Accounting for material at a nuclear facility is essential to efficient and economical operation, to the health and safety of the facility workers and the public, and to prevention of misuse of these materials, particularly for proliferation of nuclear weapons. Materials accounting contributes to safeguarding of nuclear material by deterring unauthorized acquisition through the threat of detection and by detecting diversion of material when it occurs. The principal objectives of an accounting system for safeguarding nuclear materials are (1) to provide assurance that all material quantities are present in the correct amount, (2) to provide timely detection of a materials loss, and (3) to estimate the amount of any loss and its location. These objectives are attained through a system for acquiring materials measurements, for analyzing the measurement data, and for disseminating the data and conclusions in reports describing the status of materials accounting within a facility. This document describes the fundamental concepts that form the basis for an accounting system to perform these essential functions.

II. MATERIALS BALANCE EQUATION

Verification that the material amounts within a facility are correct is based on the concept of a materials balance equation that expresses the fact that material inventories and flows must conserve mass. For a well-defined area of a process and for a specified time, the conservation of mass would require that

$$\text{ending inventory} - \text{beginning inventory} = \text{input transfers} - \text{output transfers}, \tag{1}$$

where the terms on the left side of Eq. (1) are the actual amounts of material present in the area at the end and beginning of the period and the terms on the right side of Eq. (1) are the actual amounts of material that have moved into and out of the area during the period. This situation is illustrated in Fig. 1, which shows the area boundary, the inventory within the area, and the material flows across the area boundary.

Of course, the equality in Eq. (1) assumes that all of the inventories and transfers can be known precisely; however, in practice, these quantities must be estimated and, in some instances, may not be accessible even for estimation. Thus, the equality in Eq. (1) will, in general, never hold as it would if all quantities were precisely known and no material were missing. Instead, for practical applications, a modified equation is appropriate. This equation has the form

$$\text{MB} = \text{"beginning inventory"} - \text{"ending inventory"} + \text{"input transfers"} - \text{"output transfers"} \ , \tag{2}$$

where the quotation marks indicate that the quantities on the right side of Eq. (2) are estimated. The left side of Eq. (2) is the *materials balance* (MB) [also known as *inventory difference* (ID) or *material unaccounted for* (MUF)], which will, in general, assume nonzero values reflecting the fact that estimation errors or materials unavailable for estimation can cause an apparent deviation from conservation of mass. A positive MB indicates an apparent loss of material and a negative MB indicates an apparent excess of material.

The materials balance Eq. (2) includes all of the material movements across the area boundary during the period between two successive inventory determinations. This interval is called the *materials balance period*. In practice, the ending inventory value for one period becomes the initial inventory value for the next period. This fact allows the MB for an arbitrary balance period n to be written as

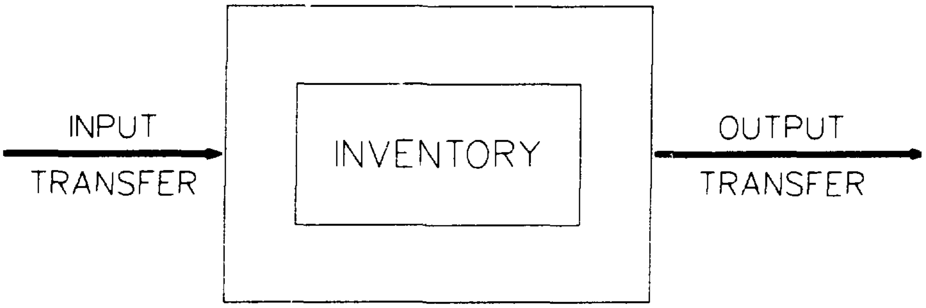

Fig. 1.
Materials accounting area.

$$MB_n = I_n - I_{n+1} + T_n \quad ,$$

where I_n is the measured inventory at the beginning of period n and T_n is the net transfer measurement (measured input transfers minus measured output transfers) for period n.

Each of the terms on the right side of Eq. (2) may be composed of many individual measurements. For example, the inventory terms could be the sum of materials in several tanks, and the transfer terms could be the sum of several material movements in the form of feed or product transfers across the area boundary. In general, inventory quantities exist as material in process, stored material, and material distributed throughout process equipment as inaccessible holdup. Transfers of material are feed and product streams, scrap and waste streams, and normal operating losses.

The inventory and transfer terms in the MB equation are either estimated directly through measurements of material to which these terms refer or indirectly through a model that gives the inventory or transfer term as a function of measured values. Direct measurements of material are made with bulk methods (such as balances or dip tube manometers), analytical methods applied to samples (such as gravimetric analysis of a UO_2 sample), and nondestructive assay methods (such as a K-edge densitometer measurement).[1] These measurement methods are discussed in detail in Chaps. III and XI.

Indirect estimates of material amounts are employed where the quantity of interest is inaccessible for direct measurement. Examples of indirect methods are (1) the estimation of in-process inventory from the difference between input and output transfers across the materials balance area boundary ("by-difference method"), (2) estimation of material inventory in a solvent-extraction contactor using a model that relates the contactor inventory to flows and concentrations in input and output streams, and (3) estimation of material holdup in glove boxes or ducts using models based on the history of cleanouts in these areas.[2]

Where possible, all inventories and transfers of material should be represented in Eq. (2). However, in practice, some terms, such as waste streams, may be difficult to measure. Also, the process operation may be such that a particular inventory measurement cannot be made at the time of balance closure. Incompleteness of the terms in Eq. (2) can contribute to a nonzero MB.

The process area around which the materials balance is closed is a materials balance area (MBA). A facility may have one or more MBAs, whose boundaries are defined so that all material inventories are contained in an MBA. In selecting the MBA structure, the designer of the accounting system should consider the physical layout of the process, the places and times of materials transfers, the locations of material inventories, the locations of measurements for process control, and locations for additional measurements for materials accounting. The selected MBA boundaries should permit measurement of all transfers across the boundaries. Coordinating the frequency of balance closure with process operations helps to avoid difficult inventory measurements by closing a balance when the inventories are absent. The issues involved in structuring MBAs for a nuclear facility are discussed in Chap. VI, Appendix.

III. ITEM CONTROL AREAS

In MBAs where material quantities are in the form of discrete items (such as a storage vault for cans of uranium oxide), materials accounting may take the form of item control, whereby the identity and integrity of individual items are periodically confirmed. In such item control areas (ICAs) the material integrity is confirmed (1) by verifying that a sealed container or other form of containment has remained intact since the last inventory or (2) by a measurement that verifies the item has physical characteristics (such as weight or radiation emissions) consistent with the accounting records. Thus, in an ICA, accounting is based on a count of uniquely identifiable items combined with some confirmation that the item amount is correct.

A closed container is sealed so that it cannot subsequently be opened without detectable alteration. When the seal is found undisturbed during an inspection, this may be taken as sufficient evidence of no tampering. However, a tampered seal requires that the item be classified as defective until further investigation can establish whether material is missing.

An alternative method for confirming item integrity is a measurement of physical properties of the item to establish agreement with accounting records. A measurement method used to quantify some physical property that determines the amount of material in the item is called a variables measurement, and a measurement used to characterize the item as defective or nondefective is an attributes measurement. Generally, the variables methods are more precise than attributes methods. Variables methods are appropriate for detecting diversions requiring small removals from many items to attain some goal quantity of material, whereas attributes methods are appropriate for detecting diversions requiring large removals from a few items.

In those ICAs containing larger numbers of items, the cost in time, personnel, and radiation exposure to verify the inventory are reduced by use of sampling plans. Usually the stored materials are divided into strata containing material items with similar characteristics. Because it is not practical to inspect every item, a random sample is selected from each stratum or lot for verification of item identity and integrity.[3,4] This provides assurance that item locations and amounts are consistent with inventory records. Procedures for verifying item amounts usually consist of a confirmatory measurement of the material amount and a comparison with facility records. When the confirmatory measurement does not agree sufficiently with the facility records, a defect is said to occur.

Separate samples may be selected for variables and attributes measurements so that diversion strategies employing either many small removals or a few large removals are addressed. When both attributes and variables samples are selected, the variables measurement can be used in two modes: (1) to determine whether the item has a large defect (variables-in-attributes mode) or (2) as part of the procedure to detect many small removals from the total item population. Under the latter procedure, all variables measurements are combined to detect a bias in the total measured value when compared with the accounting records. The sample size for each type of measurement and each stratum depends on the desired probability of detecting some amount of materials loss and the acceptable probability of an incorrect decision that loss has occurred.

IV. MATERIALS BALANCE UNCERTAINTY

The terms in the materials balance equation depend either directly or indirectly on materials measurements that involve errors (such as instrument calibration errors, sampling errors, and errors in the measurement method), so that the true value of the quantity measured can never be known exactly. Instead, these estimates are random variables in the sense that repeated measurements of the same quantity will not yield the same value. The relationship between the true value of the quantity measured and the measured value can be represented by an error model[5] such as the additive model

$$\text{measured value} = \text{true value} + \text{error} \quad ,$$

where the error term may be the sum of many individual errors. The development of error models for measurements of nuclear material is discussed in Chap. IV.

The materials balance calculated from these imprecise measurements is also a random variable that will, in general, be nonzero even in those instances where no material is missing. Because the materials balance is a random quantity that includes errors, a decision about materials loss must attempt to differentiate between a positive materials balance caused by materials loss and a positive materials balance caused by a chance combination of measurement errors. A common procedure is to decide that material is missing only when the materials balance is sufficiently large that it is unlikely to have been produced by a fluctuation in the measurement process. This procedure requires knowledge of the uncertainty in each measured value and the uncertainty of the materials balance when these measured values are combined. Procedures for determining the uncertainty of a materials balance and for deciding when materials loss is indicated are given in Chaps. IV and V.

An important activity for understanding MB variability is a measurement control program, which is a system of procedures for monitoring and controlling sources of measurement uncertainty in a materials accounting system.[6] Because decisions about materials loss are based on knowledge of the variability in the measurement process, the measurement control program provides essential information to the accounting system. A measurement control program monitors errors through a controlled series of experiments that lead to estimates of the magnitudes of the errors. For example, instrument calibration can be monitored through periodic measurements on standard reference materials and the results plotted in the form of a control chart that aids detection of changes in the instrument performance. Current estimates of inventory and transfer measurement uncertainties provided by the measurement control program are useful in calculating the materials balance uncertainty for use in the materials accounting decision process. Measurement control is discussed in detail in Chaps. IV and VII.

In addition to measurement errors, other sources of variability for MBs include changes in the process operation, such as the amount of material processed, and changes in the amount of unmeasured material holdup within the process. Because many measurement errors are proportional to the material amount measured, increases in the size of material inventories or transfers can increase the MB variability. One method for estimating MB uncertainty when a process is not operated in steady state and has inventory or transfer values that vary significantly for each balance period is to simulate the process using a computer model that incorporates variable material amounts. Methods for modeling and simulating process operations are discussed in Chap. X.

Changes in the inventory of unmeasured material within an MBA can also increase MB variability. For example, material accumulations in piping, ducts, or other process equipment inaccessible for measurement combined with infrequent and inconsistent cleanout procedures create apparently unexplained changes in the MB data. This source of MB variability could be estimated through a program of periodic and consistent cleanouts of process equipment followed by measurements of residual holdup, development of holdup models, and estimation and inclusion of the uncertainty in the model in calculating the total MB variability.

V. DECISION PROCEDURES FOR MATERIALS ACCOUNTING

The ultimate purpose of measuring material inventories and transfers, closing materials balances, and monitoring measurement uncertainties is to gather sufficient data to account for all material at a nuclear facility. This decision process is usually formulated as the statistical procedure of testing hypotheses in which one must decide which of two alternative models for the process generating the data are supported by the observed data.[7] For materials accounting, the hypotheses are H_0, no materials loss (the MB mean is 0), and H_1, an anomalous condition that could indicate materials loss (the MB mean is nonzero); the decision is based on observations of the materials balances and their uncertainties due to measurement errors and other known sources of variability.

A decision about the status of accounting is made with a decision rule that chooses either H_0 or H_1 depending on the observed data. For example, one procedure that is frequently used in materials accounting consists of defining an interval about zero that should contain 95% of the observed MBs when known sources of uncertainty are acting as a source of MB variability and there is no materials loss. When the observed MB lies within this interval, H_0 is chosen; when the MB lies outside the interval, H_1 is chosen. This is illustrated in Fig. 2 where the first three MBs are within the limits accepted as reasonable bounds for MB variations

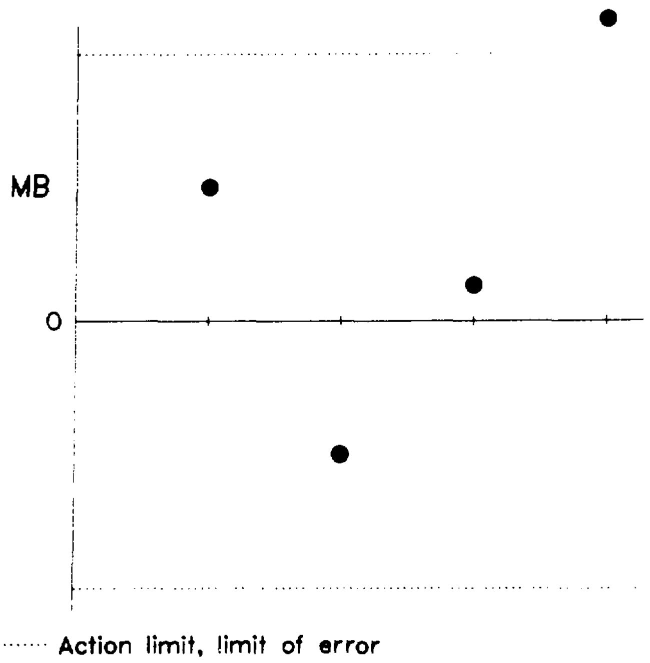

Fig. 2.
Decision thresholds.

caused by measurement errors and the fourth MB is not, resulting in acceptance of the hypothesis H_1 at the fourth balance. This procedure uses only information available in the current balance period and is suited to detection of a single large loss in that period. However, sequences of small losses over multiple balance periods require sequential testing procedures that incorporate data from multiple periods. These decision procedures are discussed in Chap. V.

Several decision procedures for materials accounting are in the computer program DECANAL, developed in the Safeguards Systems Group at Los Alamos.[8] This program analyzes sequences of materials balance data to detect evidence of materials loss then estimates the loss. Data requirements for the program are just those necessary for calculating a materials balance and its uncertainty due to measurement errors.

Because of the inherent uncertainty in materials balances, any decision procedure based on these data is subject to two types of error: a false alarm, in which H_1 is accepted when H_0 is true, and a miss, in which H_0 is accepted when H_1 is true. For a decision procedure to be useful, these probabilities of error should be known. For example, in the simple decision procedure just described, the false-alarm probability for a single decision is 0.05. This probability can be controlled by adjusting the size of the interval. However, the false-alarm and miss error probabilities are inversely related so that a decrease in one error type implies an increase in the other.

A decision procedure is characterized by four parameters whose values determine the adequacy of the procedure for the purpose of materials accounting: (1) the amount of materials loss to be detected, (2) the time over which the loss occurs, (3) the probability of detecting the loss (or one minus the miss probability), and (4) the false-alarm probability. When three of these parameters have been fixed, the fourth is also determined. Usually one selects a decision procedure that compromises a low false-alarm rate that avoids process disruption with the timely detection of low-level material losses. Methods for implementing decision procedures to detect materials loss are described in Chap. V.

VI. CONVENTIONAL AND NEAR-REAL-TIME ACCOUNTING

Two basic approaches to designing a materials accounting system are conventional materials accounting and near-real-time materials accounting. Conventional materials accounting relies on a materials balance closure following a periodic physical inventory in which all material quantities within the MBA are measured. This form of materials accounting has balance periods determined by the allowable frequency of physical inventories, which is typically limited to 6-month or 1-year intervals to minimize process shutdown. Figure 3 illustrates a MBA for conventional materials accounting.

Several methods can be applied to determine the physical inventory. These include

(1) a cleanout physical inventory in which the process line is drained and flushed into holding tanks for measurement and residual holdup in the process is measured directly or is estimated from historical data (this method of taking the physical inventory is the most accurate but requires the most lengthy shutdown period) or

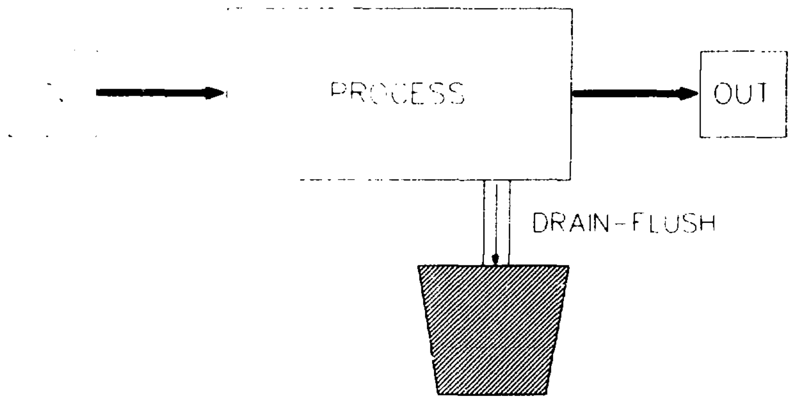

Fig. 3.
Conventional materials accounting.

(2) a drain-down physical inventory that is similar to the cleanout inventory except there is minimal flushout of the process line (this method is not as accurate as a cleanout inventory but is more economical because the process shutdown time is less).

Conventional accounting lacks both timeliness and sensitivity in detecting a materials loss. Physical inventories are infrequent so that losses may not be detected for extended periods. Often MBAs include the entire plant; consequently, the large amount of material in the MBA inventory can reduce detection sensitivity, masking loss. When a loss is detected within a large MBA, it is not localized to a particular area.

An alternative accounting procedure is near-real-time accounting (NRTA), which uses in-process inventory estimation to supplement conventional shutdown and cleanout physical inventories so that materials balances are closed during the interval between physical inventories.[9] Implementing NRTA requires a frequent determination of the in-process inventories through direct methods (such as volume, flow, or concentration measurements) or indirect methods (such as estimating inaccessible material in process equipment based on historical cleanout data). In-process inventory estimates of this kind allow more frequent balance closures, which improve the timeliness of detection of materials loss. The NRTA should be viewed as supplementing conventional accounting with materials balance closures between physical inventories. Both conventional and NRTA require the measurement of all materials transfers across the MBA boundary and differ only in the frequency of inventory taking, which for NRTA requires frequent estimates of in-process inventory.

Because NRTA provides frequent inventory estimates, a MBA may be partitioned into smaller balance areas called unit process accounting areas (UPAAs). Each UPAA is chosen on the basis of process logic and the ability to draw a materials balance. Dividing MBAs into UPAAs allows one to account for smaller quantities of material on a timely basis and localizes discrepancies to an individual UPAA. Of course, subdivision of MBAs into UPAAs may require additional transfer measurements. The relationship between a MBA and UPAA for a NRTA system is shown in Fig. 4.

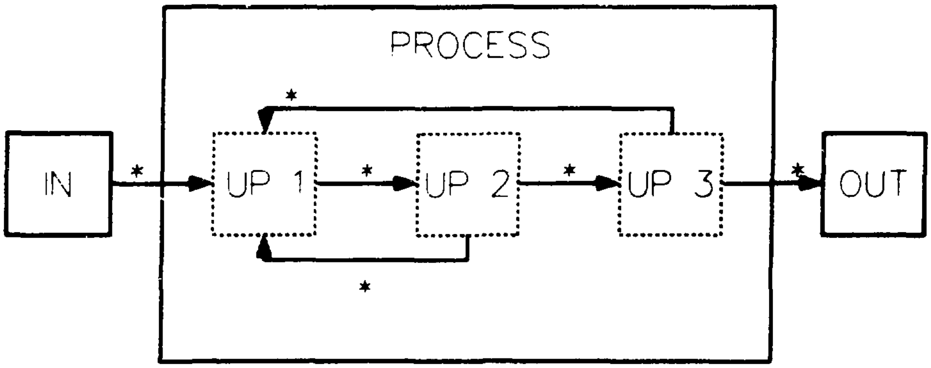

Fig. 4.
Near-real-time materials accounting. (The asterisks indicate points of frequent or continuous measurement.)

VII. REGULATORY REQUIREMENTS

A. Department of Energy Regulations

The DOE regulations relating to materials accounting are described in DOE Order 5633.3, which specifies procedures for accounting in DOE license-exempt facilities. These regulations apply to nuclear materials that include special nuclear materials (SNMs), such as uranium enriched in ^{233}U or ^{235}U and plutonium; source material, such as depleted and natural uranium and thorium; and many other materials, such as americium, deuterium, and tritium.

Special nuclear material has four categories based on material amounts, and these categories are used in defining graded safeguards requirements in which the larger Category I amounts have more stringent accounting procedures.

The following is a summary of those aspects of DOE Order 5633.3 that are particularly relevant to the design of a materials accounting system.

1. General
   - a. All nuclear materials shall be controlled and accounted for under a graded material control and accountability plan.
   - b. Each facility shall designate a management official who will be directly responsible for nuclear materials accounting. This individual should be organizationally independent of the facility operations.
   - c. For facilities possessing SNM, a material control and accountability plan shall be developed that includes measurements, statistics, records, and inventory certifications in terms of how precisely the inventory is known at a stated confidence level. The plan should also include a measurement control program for balances.
2. Accounting
   - a. Accountability data should be maintained for MBAs for receipts, shipments, and inventories with a single individual responsible for accountability in the MBA.
   - b. Each facility shall implement procedures for evaluating SNM inventory differences. The procedures shall establish control limits and include statistical tests for trends and biases.
3. Measurement Control

   Each facility shall implement a program to analyze measurement data for the purpose of determining and maintaining the accuracy and precision of measurements.
4. Material Inventory

   Each facility shall implement a physical inventory plan with a frequency ranging from bimonthly to annual depending on the material category. For inventories containing a large number of items, approved statistical sampling plans may be utilized.

B. Nuclear Regulatory Commission Regulations

The Nuclear Regulatory Commission (NRC) requirements concerning materials accounting are stated in the Code of Federal Regulations, Title 10, Part 70, entitled "Domestic Licensing of Special Nuclear Material." The special nuclear material (SNM) to be accounted for under these regulations is plutonium and uranium enriched in the isotopes ^{233}U or ^{235}U. The following is a summary of NRC regulations relevant to materials accounting.

1. General

a. Each licensee should maintain records showing the receipt, inventory, disposal, and transfer of all SNM in its possession.

b. Each licensee authorized to possess more than one effective kilogram of SNM shall establish, maintain, and follow written material control and accounting procedures.

c. The overall planning, coordination, and administration of the accounting functions should be vested in a single individual independent of production functions.

2. Accounting

a. A system of materials balance areas (MBAs) and inventory control areas (ICAs) should be established for physical and administrative control of nuclear material. Each MBA is a physical area such that all materials moving in and out are measured. An ICA is established on the same basis as a MBA except control is by item identity and count of previously measured materials whose validity is assured by tamper-safed or sealed containers.

b. Each licensee possessing more than 350 g of ^{233}U, ^{235}U, or plutonium shall conduct a physical inventory of all SNM at intervals not exceeding 12 months. For uranium enriched in ^{235}U to not more than 20%, the inventory period should not exceed 6 months; for plutonium or for uranium enriched in ^{233}U or ^{235}U to more than 20%, the inventory period should not exceed 2 months.

c. Coincident with each physical inventory, the facility should close a materials balance and calculate the associated limit of error (a measure of MB uncertainty due to measurement error defined as a 95% confidence interval).

3. Measurement Control

a. The licensee should establish and maintain a measurement control program for SNM. Responsibility for the program should reside with an individual involved with neither the analytical laboratory nor material processing, but with someone having the authority to obtain information about measurement quality. The program should include estimates of biases and of random and systematic error variances and other parameters needed to establish measurement uncertainty.

VIII. SUMMARY

Developing a materials accounting system to implement the basic concepts described in this chapter includes three procedures, or stages: defining the problem, stating the system objectives, and designing the system.

A. Problem Definition

Design of an accounting system for nuclear material begins by specifying the attributes of the material to be safeguarded and the diversion scenarios to be detected. System design is strongly influenced by the material type, physical form, amount, and location. For example, the material type dictates the measurement methods. Bulk material can require statistical methods to detect losses, whereas accounting for item quantities could demand the identification and count of discrete units.

Threats to the safeguarded material are specified in the form of diversion scenarios that describe the means of diverting material. The parameters of these scenarios include the type and amount of material to be diverted and the number of balance periods that the scenario spans.

Usually at least two general scenarios are considered: an abrupt diversion that confines the total loss to a single period and a protracted diversion that involves relatively smaller losses over multiple periods.

B. System Objectives

Accounting system objectives should be stated in terms of the required system performance for detecting loss. These requirements are given in terms of the probability of detecting particular loss scenarios (such as abrupt, protracted, or random loss patterns), the total amount of the loss to be detected, the duration of the loss, and the probability of an incorrect decision that loss has occurred. Some requirements of this kind are stated in the DOE and NRC regulations so that consideration of performance requirements for a materials accounting design is essential to ensuring regulatory compliance of the system. Also, an explicit statement of these performance objectives in the early stages of system design provides the analyst with useful criteria for judging the worth of system design options.

C. System Design

Designing a system for materials accounting consists of specifying the physical layout of the system, stating the methods for acquiring information, and selecting the methods of analyzing the information to reach safeguards conclusions. The physical layout or geometry of the system consists of the measurement points and MBAs or UPAAs chosen for their compatibility with these points. In selecting key measurement points and accounting areas, the analyst considers the uncertainty of a materials balance dependent on individual measurement uncertainties and the material inventory and material throughput of the area.

Information acquisition for materials accounting is based on a system of measurement instruments for acquiring inventory and transfer measurements, planned experiments for determining models that estimate material amounts not directly accessible for measurement, and activities (such as measurements on standards to calibrate instruments) that monitor and control measurement uncertainties.

Data analysis for materials accounting consists of (1) combining individual measurements to close a materials balance, (2) determining the uncertainty of the materials balance caused by measurement uncertainty and other sources of variability (such as modeling errors for holdup estimation), and (3) applying statistical testing procedures to decide whether the accounting information supports the hypothesis of no loss or the hypothesis of materials loss.

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Jack Markin received his Ph.D. in mathematics from the University of Southern California. He joined the Los Alamos National Laboratory in 1976, working in the weapons program. In 1978, he joined the Safeguards Systems Group and is currently Group Leader. His technical interests include systems analysis and mathematical methods applied to both domestic and international safeguards and arms control verification issues.

CHAPTER II

THE STRUCTURE OF NUCLEAR SAFEGUARDS SYSTEMS*

by

C. A. Coulter

SUMMARY

Safeguards systems for facilities that handle special nuclear material combine procedural, protective, and materials accounting elements to prevent and/or detect sabotage and diversion or theft of material. Because most of the discussion in this course is devoted to materials accounting topics only, this chapter provides a brief introduction to some of the procedural and protective elements of safeguards systems, placing the materials accounting system in its proper context. We begin by reviewing certain pertinent DOE definitions and then survey some protection requirements and technology--protective personnel, personnel identification systems, barriers, detectors, and communication systems. We next consider the procedures of personnel selection and monitoring, definition and division of job functions, and operation. We then describe the way the procedural, protective, and materials accounting elements can be combined, becoming a total safeguards system. We conclude by noting that although such a system necessarily requires elements of procedure, protection, and materials accounting, only the materials accounting gives positive assurance that nuclear material is not diverted or stolen.

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*Because recent revisions to DOE orders affect Safeguards, this chapter is being revised. The revision will be available in April 1989.

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Alton Coulter holds a Ph.D. from Harvard University in physics. After graduation, he served on the faculties of the University of Alabama and Clark University and took sabbatical leaves at the Massachusetts Institute of Technology and Los Alamos National Laboratory. Since 1982, he has been a staff member in the Safeguards Systems Group at Los Alamos, where his current work involves systems analysis, computer modeling, and simulation.

CHAPTER III

ELEMENTS OF NONDESTRUCTIVE ASSAY (NDA) TECHNOLOGY

by

C. R. Hatcher and H. A. Smith

I. INTRODUCTION

A. History of NDA

When we speak of NDA in the context of nuclear safeguards, we generally refer to the use of nuclear radiation to measure the quantity of fissionable material present in a given sample or container. Since the initiation of the Manhattan project, NDA techniques have been applied to special nuclear materials in the U.S., at least to some extent. But it was not until 1967, when the Office of Safeguards and Material Management was established by the Atomic Energy Commission, that effort focused on the development of NDA techniques specifically designed for nuclear safeguards. The Los Alamos National Laboratory has been involved in this development work since its inception and is currently the DOE lead laboratory for nuclear materials measurement and accounting. Other laboratories in the U.S., including Brookhaven, Hanford, Argonne, Livermore, Idaho, Oak Ridge, Savannah River, New Brunswick, Mound, and National Bureau of Standards, have also contributed, as have instrument companies such as Eberline, Canberra, National Nuclear, Jomar, and IRT Corporation. Significant advances in NDA technology also continue to be made by organizations in Europe, as well as in other countries, such as the USSR, Canada, and Japan.

B. Uses of NDA

The NDA methods are widely used throughout the nuclear fuel cycle primarily because they can measure the material in its existing form; in addition, they provide rapid assay results. Applications include

- ore location and assay,
- process control,
- quality control,

- health and safety,
- criticality,
- materials accounting,
- containment and surveillance, and
- waste disposal.

Nondestructive assay technology is also being considered for use in several possible aspects of arms control verification.

C. Strengths and Limitations of NDA

During the past few years, NDA techniques have become established as a fundamental element of nuclear safeguards programs throughout the world. Nondestructive assay is particularly well suited for safeguards applications when

- obtaining a representative sample for chemical analysis is difficult--for example, with nonuniform solids, material in sealed containers, spatially distributed material (for example, in-plant holdup), or valuable finished products;
- many repetitive measurements are needed--such as might be the case for receiving stations, process lines, or waste streams; and
- timely material accountability is required--that is, the need to close material balances in a matter of hours rather than days or weeks.

The arguments in favor of NDA are compelling, but certain limitations and consequences must also be noted.

- Adequate NDA standards are frequently not available in the particular geometry, material form, and isotopic composition that would be ideal for instrument calibration. Consequently, variations in these factors may complicate instrument calibration and data interpretation and, in many cases, may limit the accuracy of the assay result.
- Absolute calibration of NDA instruments usually depends, in the final analysis, on chemical methods, such as gravimetric analysis, fixed stoichiometry, titration, and mass spectrometry.
- The large quantity of data made practical through NDA can be fully utilized only if adequate computer methods are used for assisting with data analysis and interpretation.

D. Classifications of NDA Methods

The block diagram of Fig. 1 classifies NDA techniques into passive and active methods. According to Fig. 1, passive NDA methods include all techniques that derive their primary information from the natural radioactive decay of the sample, whereas active NDA methods include techniques that derive their primary information from the interaction of an external radiation source with the sample. Similar classifications[1] have been made by Dragnev[2] and by Smith and Canada.[3] Extensive treatises on both active and passive NDA techniques have been prepared for the U.S. Nuclear Regulatory Commission by Gozani,[4] by Reilly _et al._,[5] and by Rogers _et al._[6]

In Fig. 1, applications are listed for each of the NDA techniques shown, along with at least one instrument (in parenthesis) that uses the principle. The information presented in Fig. 1 covers most of the widely used NDA methods, but for the sake of brevity, is not totally inclusive.

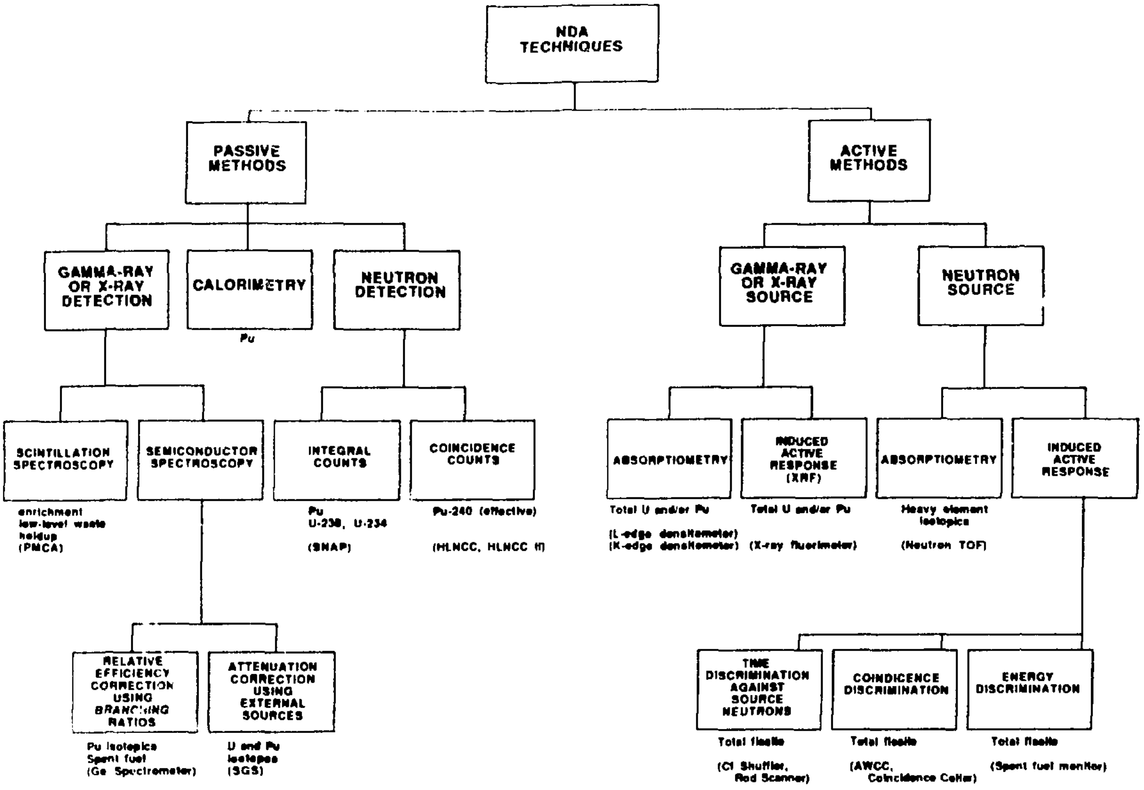


Fig. 1.
Classification of nondestructive assay (NDA) techniques used for the measurement of fissionable materials.

In following sections, each of the techniques shown in Fig. 1 is discussed; the advantages and disadvantages of various NDA methods are compared for different types of nuclear materials.

II. PASSIVE GAMMA-RAY METHODS

A. General Information

All isotopes of uranium and plutonium are radioactive and decay by alpha emission, beta emission, or spontaneous fission. Following either alpha or beta emission, the nucleus is sometimes left in an excited energy state, which then decays by the emission of gamma rays to the ground state. Each isotope has a unique decay scheme, and when gamma rays are detected, a determination of gamma-ray energies provides a way of identifying the specific isotopes present.

Table I lists some of the gamma-ray energies and emission rates for uranium, plutonium, and americium isotopes that are commonly used for the NDA of these materials. A more complete list of gamma-ray energies and other properties of heavy element nuclides can be found in Ref. 1.

TABLE I

URANIUM, PLUTONIUM, AND AMERICIUM GAMMA-RAY EMISSION RATES

Isotope	Half-Life (yr)	Activity Level (Ci/g)	Principal Gamma Rays (keV)	Emission Rate (gamma ray/s/g)
^{235}U	7.04×10^8		185.7	4.5×10^4
^{238}U	4.47×10^9		766.4	39
			1000.1	103
^{238}Pu	87.74	17.1	152.8	6.4×10^6
			766.4	1.5×10^5
			1000.1	8.2×10^3
^{239}Pu	24119	0.0621	129.3	1.4×10^5
			375.0	3.6×10^4
			413.7	3.5×10^4
^{240}Pu	6564	0.228	160.4	3.5×10^4
			642.3	1.2×10^3
^{241}Pu	14.35	103.4	148.6	7.3×10^6
^{242}Pu	3.763×10^5	0.0039	none	
^{241}Am	433.6	3.42	368.6	2.6×10^5
			662.4	4.4×10^5

B. Scintillation Spectroscopy

1. Enrichment Meter. Figure 2 shows a microprocessor-based multichannel analyzer (MCA) with a sodium iodide (NaI) detector (typically 1.27 cm thick by 3.81-cm diameter). A typical pulse-height spectrum obtained with a uranium sample using this instrument is shown in Fig. 3. This device and similar types of instruments built by other manufacturers can accurately measure uranium enrichment. For samples that are thick relative to the penetrating depth of the 186-keV U-235 gamma ray and for fixed detector-sample geometry, the count rate due to 186-keV gamma rays is proportional to enrichment; this linear relationship between enrichment and count rate is referred to as the enrichment meter principle.[7] Calibration of enrichment meters is accomplished using two or more enrichment standards having container walls similar or preferably identical to those of the unknown samples.[7-9]

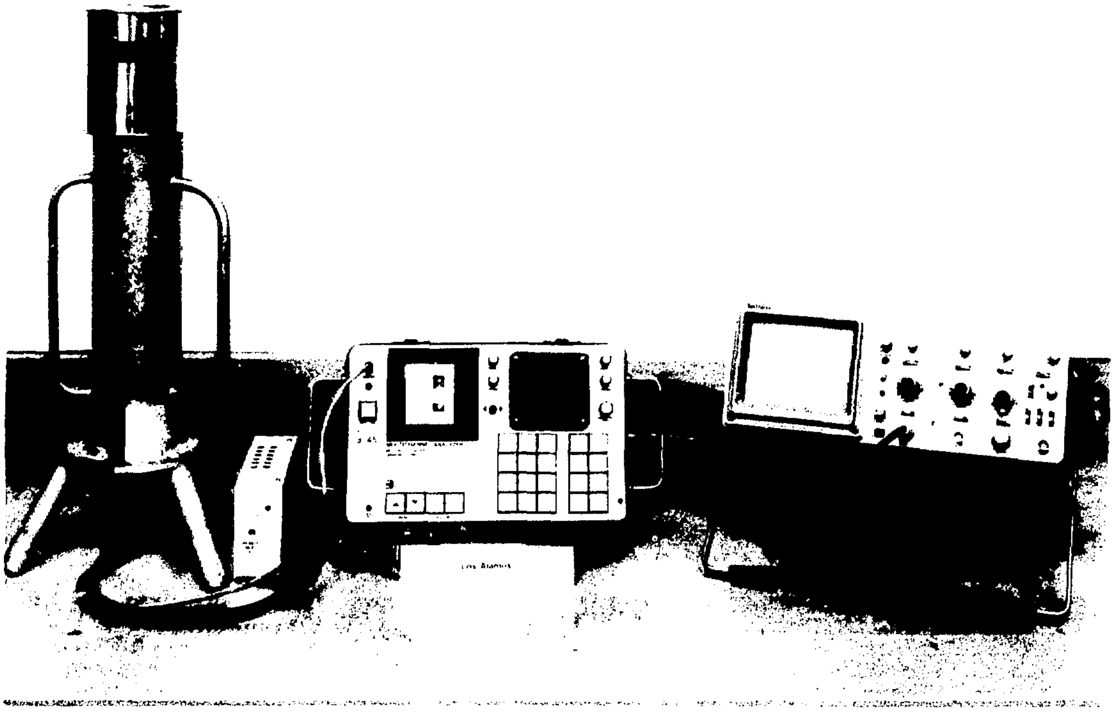
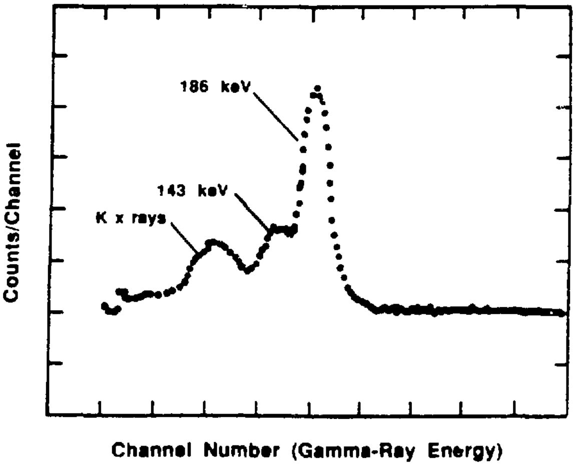


Fig. 2.
Arrangement for measuring ^{235}U enrichment of UO_2 powder in cans. A Davidson portable MCA unit is used with a NaI photomultiplier detector mounted vertically under the sample can.

Fig. 3.
Characteristic pulse-height spectrum obtained with a Davidson MCA and a NaI detector viewing a ^{235}U sample.



2. <u>Other Applications</u>. Although the enrichment meter is perhaps the most well known, gamma-ray instruments using sodium iodide and other scintillation detectors are used for many other applications in safeguards, such as assaying low-level waste, monitoring effluents, and estimating the holdup of nuclear material in processing plants (Fig. 4). Because they are portable, simple, and reliable, instruments employing scintillation detectors are also used as portal monitors and survey meters (Fig. 5).

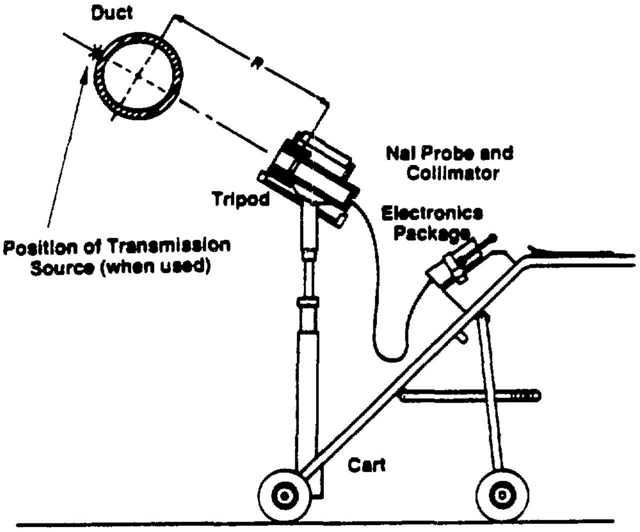


Fig. 4.
Holdup of nuclear material in process lines measured using portable scintillation detection equipment and microcomputers to analyze the data rapidly.

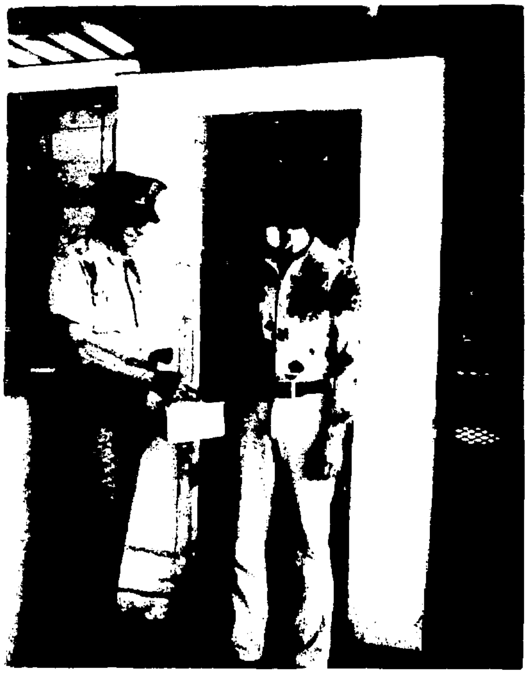


Fig. 5.
Scintillation detectors used in portal monitors and hand-held survey meters. The portable instrument shown was developed by Los Alamos Group N-2 and manufactured by the National Nuclear Corporation.

C. Semiconductor Spectroscopy

1. Methods Using Relative Efficiency Correction. High-resolution gamma-ray spectroscopy (HRGS) using semiconductor detectors, such as intrinsic germanium (Ge) and germanium-lithium [Ge(Li)], provides significantly better energy resolution than can be achieved using scintillation detectors, as is demonstrated by the two plutonium gamma-ray spectra shown in Fig. 6. Energy resolution (FWHM) for high-quality coaxial Ge detectors is on the order of 0.6 keV for 122-keV gamma rays and 1.5 to 1.6 keV for 1.33-MeV gamma rays. In the last few years, portable HRGS systems have become available through the advent of intrinsic Ge detectors (that can be transported at room temperature) and smaller multichannel analyzers (Fig. 7).

If one measures the photopeak areas of gamma rays from different isotopes, it may be possible to determine isotopic ratios using a technique known as the relative efficiency correction. The relative efficiency correction factor (Fig. 8) includes effects due to attenuation in the sample, attenuation in external absorbers, and the detector sensitivity, all of which vary as a function of gamma-ray energy and measurement geometry.

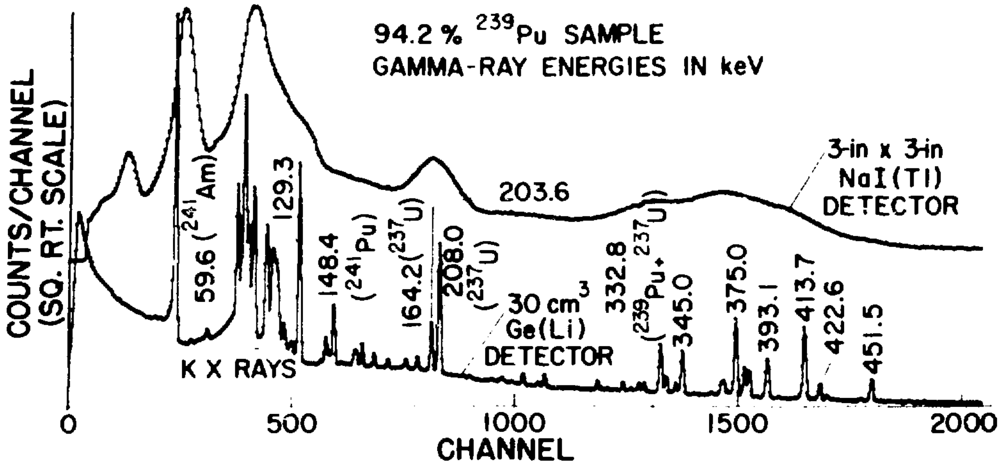


Fig. 6.

Illustration of plutonium gamma-ray spectra as measured with a NaI detector (upper curve) and a Ge(Li) detector (lower curve), showing the capability of high-resolution Ge spectroscopy to determine energies and relative intensities of individual gamma lines in complex spectra.

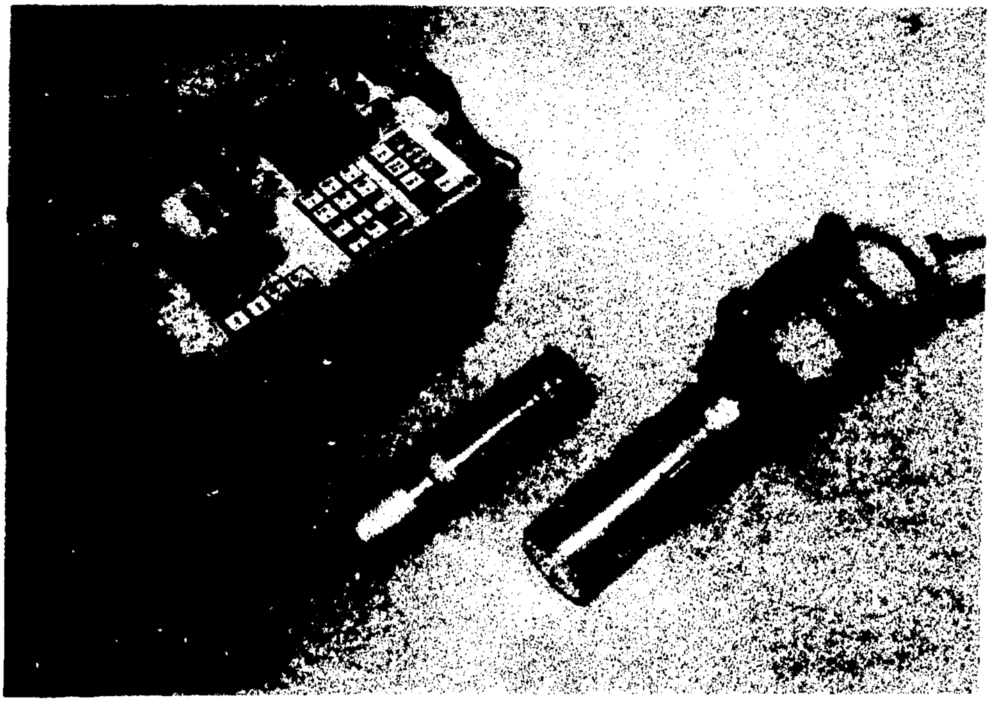


Fig. 7.

The battery-operated Davidson Portable Multichannel analyzer, shown with both a NaI (scintillation) detector (center) and a portable Ge spectrometer (right). This unit, in widespread use, is heavily utilized by the IAEA.

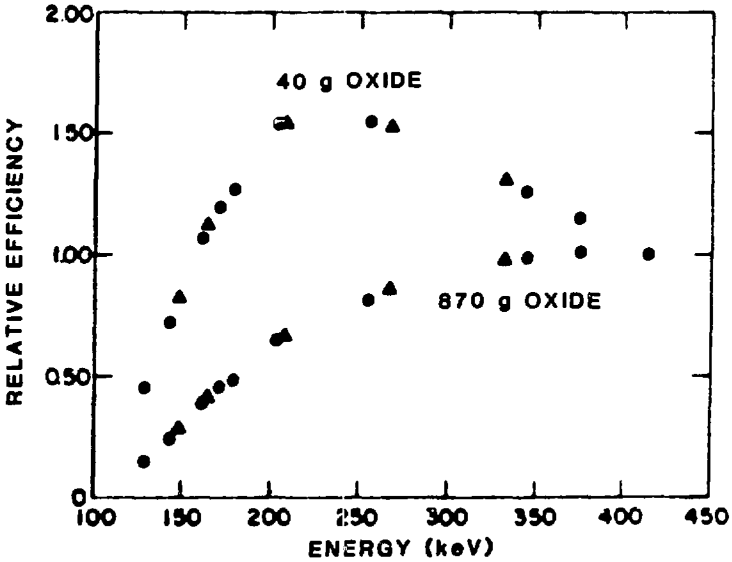


Fig. 8.
Relative efficiency curves taken with a 200-mm^2 × 10-mm-deep planar Ge detector, showing dependence on gamma-ray absorption in the sample. Circles are points from ^{239}Pu; triangles are from ^{241}Pu and ^{241}Pu-^{237}U. The points for each sample are normalized at 332 keV.

Isotopic ratios are calculated from the equation

$$\frac{I_1}{I_2} = \frac{A_1}{A_2} \frac{(BR)_2\lambda_2}{(BR)_1\lambda_1} \frac{\varepsilon_2}{\varepsilon_1} ,$$

where

I_1/I_2 = isotopic ratio,
A_1/A_2 = ratio of photopeak areas,
BR_n = branching ratio for particular gamma ray from isotope n,
λ_n = decay constant of isotope n, and
$\varepsilon_1/\varepsilon_2$ = relative efficiency correction factor for two gamma rays used in calculation.

The relative efficiency correction factor is experimentally determined from the above equation by using gamma rays of different energies from the same isotope and setting I_1/I_2 = 1. This technique has been successfully applied for measuring plutonium isotopic ratios and spent-fuel fission-product isotopic ratios[10,11] (see Figs. 6, 9, and 10). In these applications, a single gamma-ray spectrum contains the peak area data for both the relative efficiency correction and the determination of isotopic ratios.

The relative efficiency correction method works well when

- isotopes are uniformly distributed throughout the sample,
- at least one isotope in the sample has two or more prominent gamma rays in the appropriate energy range, and
- the objective is to determine isotopic ratios in a sample, as opposed to the total amount of an isotope present in a sample.

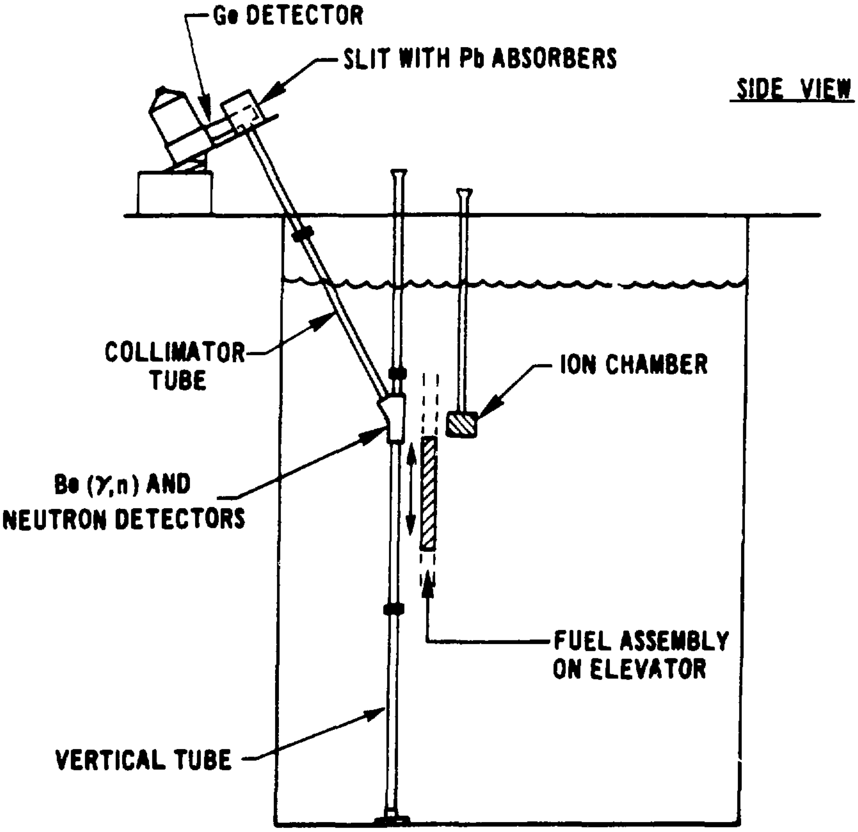


Fig. 9.
Arrangement of Ge detector and slant collimator pipe for observing fission-product gamma rays from spent-fuel assemblies stored underwater. Ion chambers and fission chambers are placed in the vertical pipes.

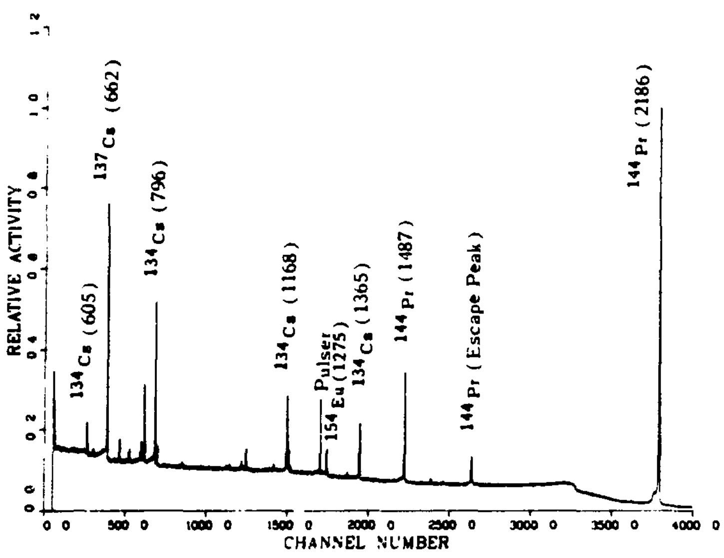


Fig. 10.
Characteristic gamma-ray spectrum observed with spent fuel. From fisson product isotopic ratios, it is possible to verify cooling time and burnup.

2. Methods Using External Sources to Correct for Sample Attenuation. To deal with situations in which the three conditions listed in the previous paragraph are not met, techniques have been developed to correct for gamma-ray absorption in the sample using external radiation sources. One such instrument, the segmented gamma-ray scanner (SGS),[12] was designed for assaying uranium and/or plutonium waste in a variety of container sizes and matrices (see Fig. 11). The idea is to divide the sample into a series of horizontal segments and to assay each segment, one at a time, with a self-absorption correction separately determined for each segment. For assaying ^{235}U using the 186-keV gamma ray, the SGS uses a ^{168}Yb external radiation source with gamma rays at 177 and 198 keV. For assaying ^{239}Pu, using the 414-keV gamma ray, the SGS uses a ^{75}Se external radiation source with gamma rays at 400 keV.

Other instruments that use external radiation sources to correct passive gamma-ray assays for absorption in the sample include the plutonium solution assay system (PUSAS),[13] uranium solution assay system (USAS),[14] and a new at-line solution assay system (ALSAS).[15] All of the instruments in this category give isotopic information. In size and complexity, they

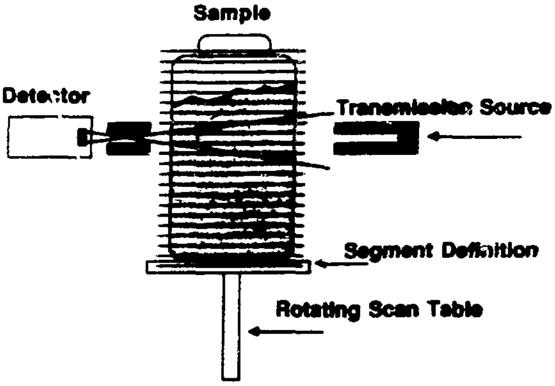


Fig. 11a.
In the segmented gamma scanner, the sample container stepped vertically past the fixed Ge detector and transmission source. A separate gamma-ray absorption correction is made for each vertical segment.

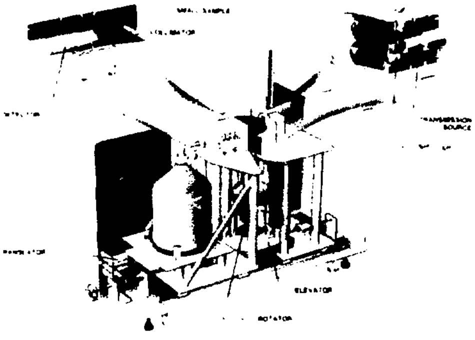
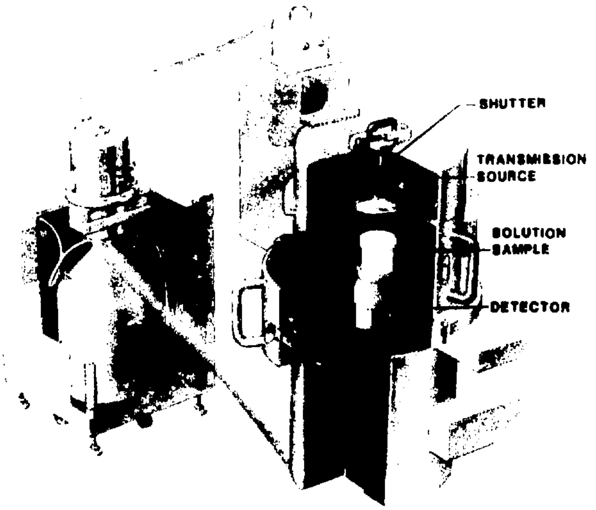


Fig. 11b.
Segmented-gamma-scanner systems, suitable for assaying a variety of container sizes. Developed at Los Alamos, some are now commercially available.

are comparable to some of the active interrogation instruments such as x-ray densitometers and active-well coincidence counters. The measurement station for the ALSAS is shown in Fig. 12.

Fig. 12.
The high-resolution gamma-ray detector looking up through small solution samples for the ALSAS. The heavily shielded measurement station also contains a ^{169}Yb transmission source, as shown. This instrument is capable of better than 0.2% measurement accuracy in approximately 1000 s of assay.



D. Gross Gamma-Ray Techniques

A few instruments used in safeguards applications measure gross gamma-ray fields (or dose rates), rather than individual gamma rays. The Cerenkov detector, shown in Fig. 13, is used to obtain an image from light produced by spent-fuel assemblies stored underwater. The detector consists of a telephoto lens coupled to an image intensifier tube that amplifies the Cerenkov effect, so that it is easily seen in a darkened fuel storage pond (Fig. 14). This instrument permits IAEA inspectors to verify that spent-fuel assemblies are intact and are highly radioactive, without placing any instrumentation underwater.[16]

Ion chambers are also used to measure the gamma-ray fields produced by spent-fuel assemblies. In particular, ion chambers are used to determine axial gamma-ray activity profiles, which closely resemble the burnup profiles of spent-fuel assemblies.[17]

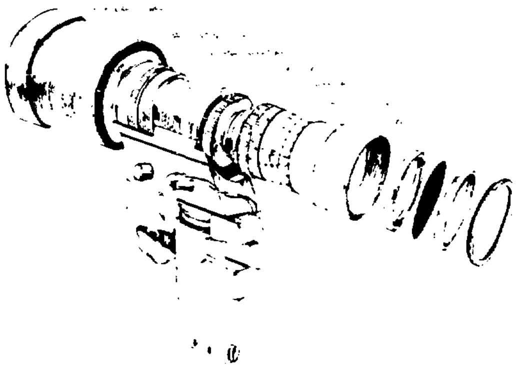


Fig. 13.
The hand-held Cerenkov detector developed by Los Alamos Group N-2 for the IAEA and used to observe light produced by irradiated fuel assemblies stored underwater. Later models permit the attachment of a film camera, so that the inspector has a permanent record.

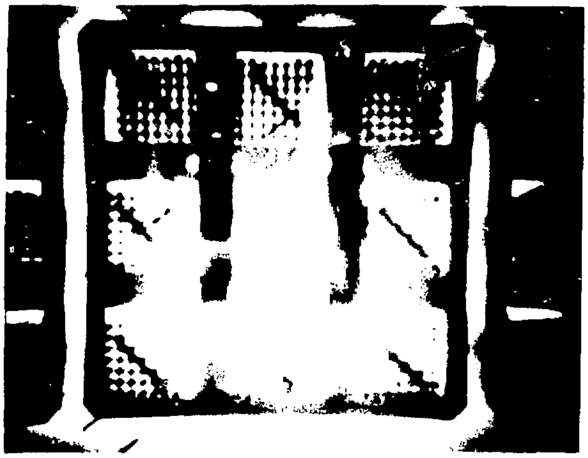


Fig. 14.
Image recorded by the Cerenkov detector while looking down into a storage pond from a bridge crane to observe boiling-water reactor (BWR) fuel assemblies.

III. PASSIVE NEUTRON METHODS

A. General Information

Neutrons originate in special nuclear materials primarily because of spontaneous fission and (α,n) reactions (see Tables II, III, and IV as well as Ref. 18). Passive neutron measurements are influenced by neutron multiplication in the sample and by the presence of neutron moderators, reflectors, and absorbers in or near the sample. Compared with gamma rays, neutrons are much more penetrating in high-Z materials; this characteristic makes passive neutron techniques invaluable for assaying large heterogeneous samples of plutonium.

TABLE II

SPONTANEOUS FISSION OF FISSIONABLE ISOTOPES

Isotope	Half-Life (yr)	Spontaneous Fission Half-Life (yr)	$\bar{\nu}$ (Spontaneous Fission)	Spontaneous Fission per g-s
^{232}Th	1.41×10^{10}	$\sim 10^{21}$		$\sim 10^{-8}$
^{234}U	2.47×10^{5}	2.0×10^{16}	~2	2.8×10^{-3}
^{235}U	7.04×10^{8}	1.9×10^{17}	~2	2.96×10^{-4}
^{236}U	2.40×10^{7}	2.0×10^{16}	~2	2.8×10^{-3}
^{238}U	4.47×10^{9}	9.86×10^{15}	1.95	5.64×10^{-3}
^{238}Pu	87.79	4.7×10^{10}	2.26	1.1×10^{3}
^{239}Pu	24119	5.5×10^{15}	2.2	1.0×10^{-2}
^{240}Pu	6564	1.17×10^{11}	2.17	4.71×10^{2}
^{241}Pu	14.35	5.0×10^{15}	2.2	1.1×10^{-2}
^{242}Pu	3.763×10^{5}	6.8×10^{10}	2.16	8.0×10^{2}
^{241}Am	433.6	2.0×10^{14}	2.3	0.27
^{242}Cm	0.4456	7.2×10^{6}	2.65	7.8×10^{6}
^{244}Cm	17.6	1.4×10^{7}	2.84	4×10^{6}
^{252}Cf	2.646	86	3.8	6.14×10^{11}

TABLE III

(α,n) YIELDS FROM OXIDES AND FLUORIDES

Material	Yield (neutron/s/g)
$^{234}UO_2$	~14
$^{234}UF_6$	5.8×10^2
$^{235}UF_6$	12.2×10^{-2}
$^{238}UF_6$	12.9×10^{-3}
$^{238}PuO_2$	1.4×10^4
$^{238}PuF_4$	2.1×10^6
$^{239}PuO_2$	45
$^{239}PuF_4$	4300
$^{240}PuO_2$	170
$^{240}PuF_4$	1.6×10^4
$^{241}PuO_2$	~10
$^{241}AmO_2$	3754
$^{242}PuO_2$	~10

TABLE IV

NEUTRON EMISSION RATES FOR PLUTONIUM METAL, PuO_2, AND PuF_4

		Neutron Rate for 100 g of Plutonium Metal (n/s)		
Isotope	Wt%	Metal (Spontaneous Fission)	PuO_2 (α,n)	PuF_4 (α,n)
^{238}Pu	0.3	746	4 200	630 000
^{239}Pu	75.6	2	3 400	325 080
^{240}Pu	18.0	18 400	3 060	288 000
^{241}Pu	5.0	~0	50	5 000
^{242}Pu	1.1	1 900	10	1 000
	Total	21 048	10 720	1 249 080

Whereas gamma-ray energies allow one to identify isotopic content, passive neutron energies contain no isotopic information. As a result, neutron assays involve counting rather than spectroscopy, and for this reason, passive neutron hardware is usually simpler than high-resolution gamma-ray hardware. The most commonly used neutron detector for NDA instrumentation is the gas proportional counter, typically ^{3}He or $^{10}BF_3$. This type of detector is chosen because of its relatively high efficiency for detecting thermal neutrons, its insensitivity to gamma rays, and its reliability and long-term stability.

B. Passive Methods (Including SNAP) That Detect Single Neutron Counts

The Shielded Neutron Assay Probe (SNAP), shown in Fig. 15, is used for assaying total plutonium when the chemical and isotopic composition are known and suitable standards are available.[19] In assaying plutonium, neutrons from both the spontaneous fission of the even plutonium isotopes and (α,n) reactions in the sample are measured. The SNAP detector consists of two ^{3}He proportional tubes in a cylindrical polyethylene moderator

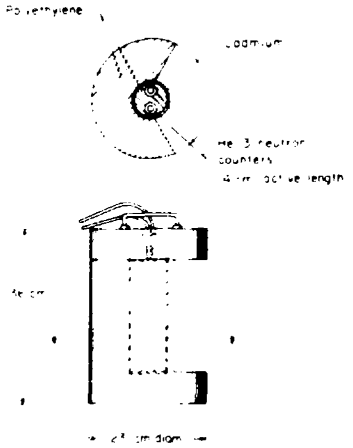


Fig. 15a.
Assembly drawing of the Shielded Neutron Assay Probe (SNAP), showing two ^{3}He proportional tubes inside a cadmium shield.

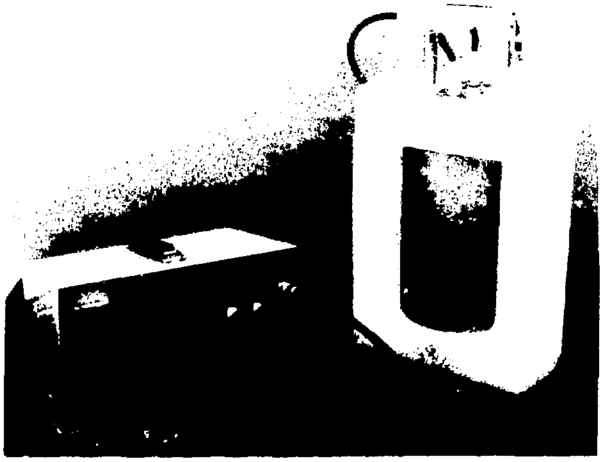


Fig. 15b.
The SNAP connected to the Eberline SAM-II electronics unit used on early safeguards instruments. The SNAP could be used to assay plutonium samples by counting both (α,n) and fission neutrons.

encased in a cadmium shield. To achieve directionality and reduce background, a 240° polyethylene shield is placed around the inner cylinder.

Neutron counting, using ^{235}U fission chamber detectors, has been applied to the assay of spent-fuel assemblies from light-water reactors (LWRs). These neutrons originate primarily from isotopes of curium and plutonium and can be correlated with burnup via a power law relationship.[17]

More specialized applications of single neutron counting include the measurement of ^{234}U enrichment (by observing α,n neutrons in UF_6) and the assay of total uranium in low-enriched scrap (based on the spontaneous fission of ^{238}U). These applications are considered special because, in general, passive neutron signals from uranium are too weak to give reliable assays.

C. Passive Methods That Detect Coincident Neutron Counts

The purpose of using coincidence counting for passive neutrons is to discriminate against single (α,n) neutrons, while detecting coincident neutrons due to spontaneous fission. For assaying plutonium, coincidence counting is generally better than singles counting because coincidence methods are less sensitive to variations in low-Z matrix materials and less sensitive to changes in neutron background.

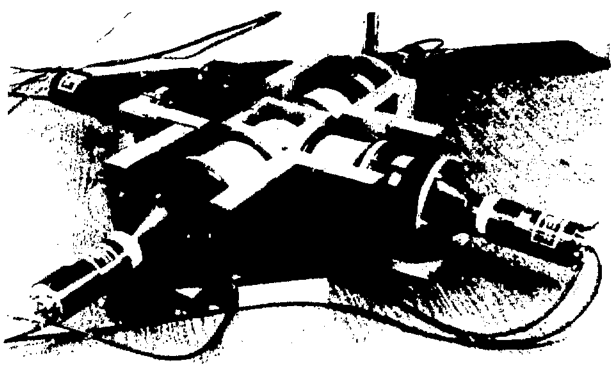
Since the efficiency for detecting coincidences is approximately equal to the square of the efficiency for detecting singles, coincidence counters are designed to achieve high singles counting efficiency by using well-counter geometry, that is, by surrounding the sample with detectors.

The newest version[20] of the High-Level Neutron Coincidence Counter[21] (HLNCC-II) shown in Fig. 16 is a compromise between the highest obtainable efficiency and portability.[13] This detector, designed for use by IAEA inspectors, consists of a ring of eighteen ^{3}He detectors in a cylindrical polyethylene shield. Larger, more efficient well counters are designed for other applications. The most recent work in this area focuses on the measurement of higher coincidence moments (threefold coincidences and higher). This is being explored with higher-efficiency well counters[22,23] (Fig. 17) and counters with fast coincidence resolving times[24] (Fig. 18). These additional coincidence data allow the determination of additional sample properties, such as (α,n) neutron production rate or the self-multiplication rate in the sample.

Fig. 16.
The High-Level Neutron Coincidence Counter Model II (HLNCC-II). This newest version of the traditional well-counter design incorporates fast electronics and ^{3}He proportional tubes in a cylindrical polyethylene moderator. Coincidence counting allows the detection of fission neutrons from ^{240}Pu and other even isotopes, while discriminating against (α,n) neutrons in the sample.

Fig. 17.
A prototype of the high-multiplicity neutron coincidence counter. The basic counter design is the same as that of the HLNCC-II. The larger counter diameter is to accommodate more than 120 ^{3}He proportional tubes (which achieves higher coincidence counting efficiency for better detection of higher-multiplicity coincidence events). With this counter, it is possible to determine additional sample properties, such as (α,n) production rate or neutron self-multiplication.

Fig. 18.
Assay chamber and form-detector head of the liquid-scintillator fast-neutron counting system under development for the assay of plutonium content in samples with unknown self-multiplication and unknown (α,n) yields. The liquid scintillators give the system faster coincidence resolving time, which allows effective measurement of threefold and higher neutron coincidences.



Well counters are used to assay ^{240}Pu effective, a quantity defined by the equation

$$^{240}\text{Pu eff} = 2.52\,^{238}\text{Pu} + {}^{240}\text{Pu} + 1.68\,^{242}\text{Pu} \quad .$$

To obtain a complete plutonium assay, well-counter measurements are frequently made in conjunction with isotopic ratio measurements using gamma spectroscopy (Fig. 19).

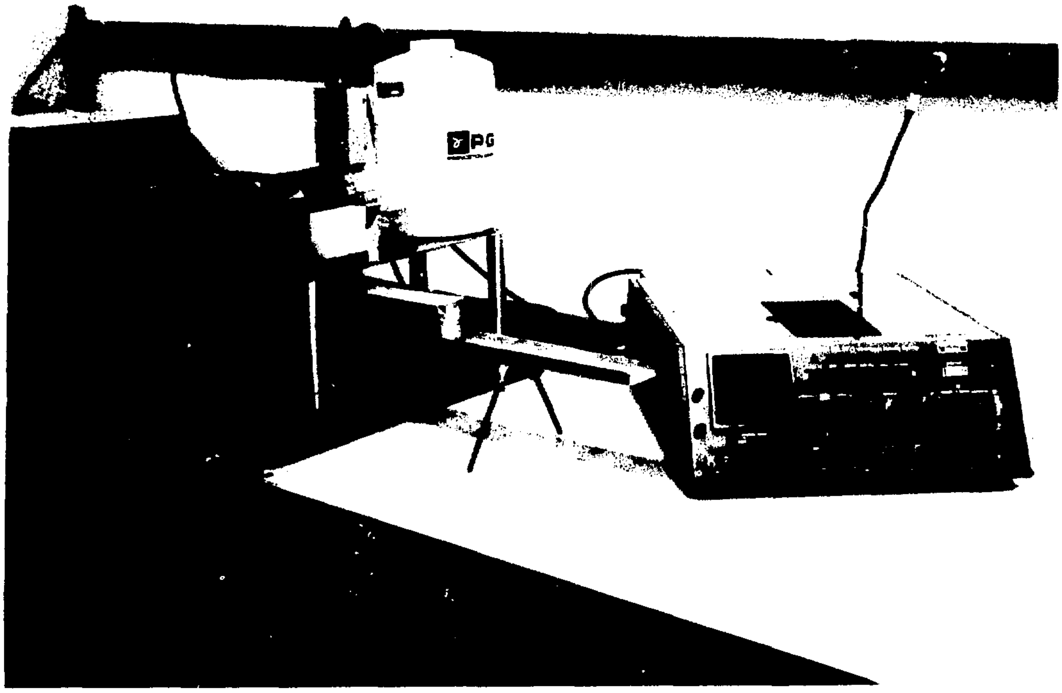


Fig. 19.
Plutonium assays using the HLNCC and depending on knowledge of plutonium isotopic ratios. Here, an HLNCC measurement is made on a zero power reactor fuel drawer, while isotopic ratios are being determined using an intrinsic Ge detector.

One of the more important improvements in neutron well-counter technology came about through the development of shift-register coincidence circuitry.[21] This technique, which allows higher coincidence counting rates than are possible with conventional coincidence circuits, can be used to assay very large plutonium samples, with minimum deadtime correction.

Passive coincidence counters have also been built using plastic scintillators that detect both fast neutrons and gamma rays from spontaneous fission. Although this approach has advantages in certain applications (see Ref. 24 and Fig. 18), well counters are more widely accepted for precise assays of plutonium because of their insensitivity to gamma rays and their long-term stability.

IV. CALORIMETRY

The heat generated by natural radioactive decay is the basis of one of the most precise methods for assaying plutonium. Almost all of the power generated in typical plutonium samples comes from alpha decay, with minor amounts coming from beta decay and spontaneous fission. Table V gives the specific power (watts per gram) for the plutonium and americium isotopes of interest to calorimetry measurements.[25] For "reactor grade" plutonium, the specific power is about 15 mW/g, which is sufficient to allow calorimetric measurements of even subgram samples.

One of the unique advantages of calorimetry compared with other NDA methods is that absolute calibration can be performed using electrical standards; the precision obtainable under laboratory conditions is 0.1 to 0.2%, which is difficult to achieve by most other methods. On the other hand, for large samples of PuO_2, the measurement time is long, approximately two to four hours, due to the thermal properties of the sample material itself. Furthermore, calorimetry requires accurate knowledge of isotopic content, and absolute accuracy of total plutonium is typically limited to about 1% by the uncertainties in determining the fraction of ^{238}Pu and ^{241}Am. Calorimeters are designed to give optimum performance (in terms of precision and measurement time) for a particular sample size, shape, and weight, and have lower precision when applied to other types of samples.

TABLE V

SPECIFIC POWERS OF PLUTONIUM AND AMERICIUM

Isotope	Half-Life (yr)	Specific Power (W/g)	Uncertainty in Specific Power (%, 1σ)
^{238}Pu	87.74	5.6757×10^{-1}	0.10
^{239}Pu	24 119	1.9288×10^{-3}	0.27
^{240}Pu	6 564	7.0824×10^{-3}	0.2
^{241}Pu	14.35	3.412×10^{-3}	0.06
^{242}Pu	376 300	1.1594×10^{-4}	--
^{241}Am	433.6	1.1423×10^{-1}	0.14

Figure 20 shows an instrument developed at Mound Laboratory for simultaneously measuring both plutonium isotopic ratios (using gamma-ray spectroscopy) and the power generated in the sample due to radioactive decay.[26,27] The calorimeter consists of a constant-temperature water bath that contains the sample well and temperature sensors. When a plutonium sample is placed in the calorimeter, the sample comes to an equilibrium temperature that is measurably different from the reference temperature. Mound quotes an uncertainty in assaying grams of plutonium of 1% for 11-cm-diameter containers with a measurement time of four hours.

Portable calorimeters were developed at Argonne for use by the IAEA.[28] The design consists of a series of concentric aluminum cylinders, each separately insulated and temperature controlled (Fig. 21). When placed in the innermost cylinder, a plutonium sample reduces the electrical power required to maintain constant temperature. These instruments have a precision of about 1% and an equilibrium time of 20 minutes for samples of a few grams.

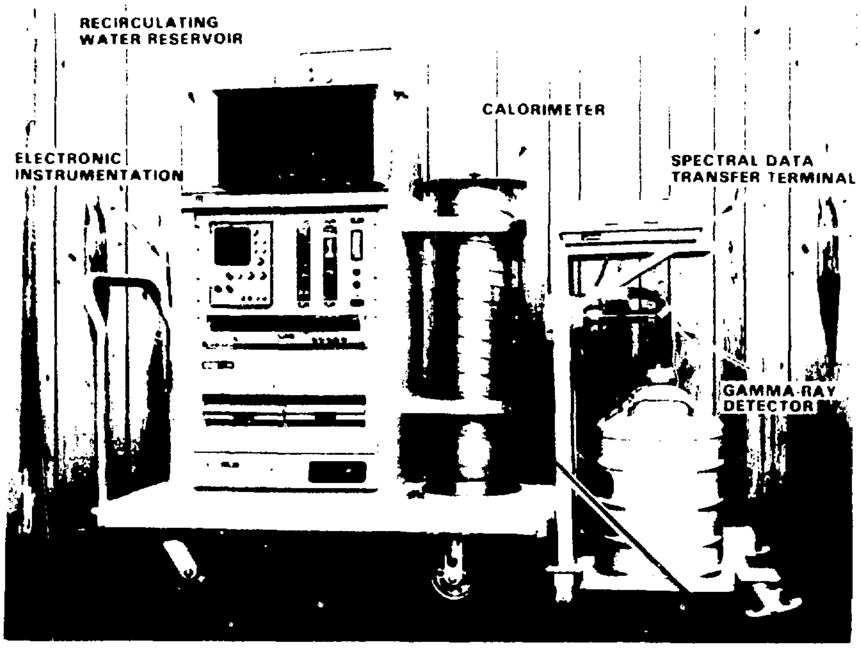


Fig. 20.
Mound Laboratory instrument for assay of plutonium. The calorimeter measures power in watts, while the Ge spectrometer determines watts per gram based on plutonium isotopic ratios.

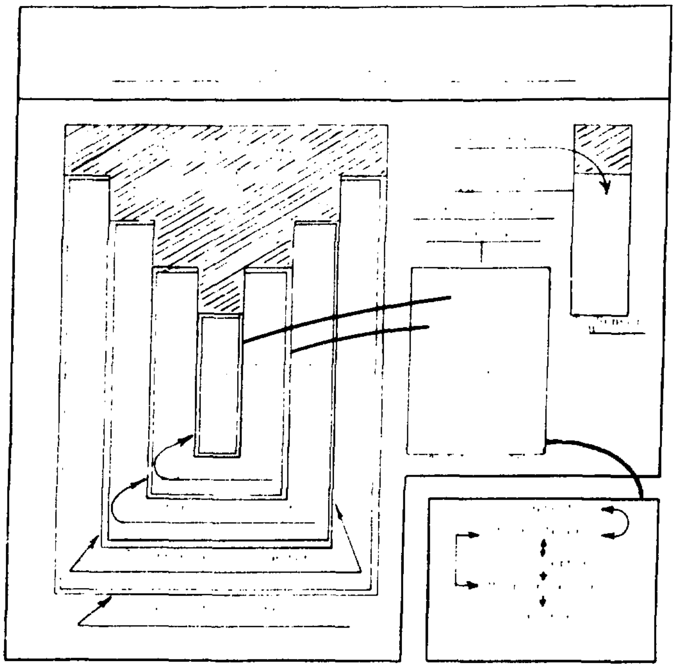


Fig. 21.
Argonne design of a portable small-sample calorimeter for the IAEA that uses concentric aluminum cylinders, each with precise temperature control.

V. ACTIVE GAMMA-RAY AND X-RAY METHODS

A. Absorption Spectrometry (Including X-Ray Densitometry)

Active gamma-ray and x-ray methods can be further divided into absorption spectrometry (absorptiometry) and induced active response techniques (see Fig. 1).

Gamma-ray absorption measurements are not commonly used as a standalone assay technique in nuclear safeguards, as they are capable of little more than verifying the amount of high-Z material in a sample. However, gamma-ray absorption techniques are widely used in many nonsafeguards applications, such as in thickness gauges.

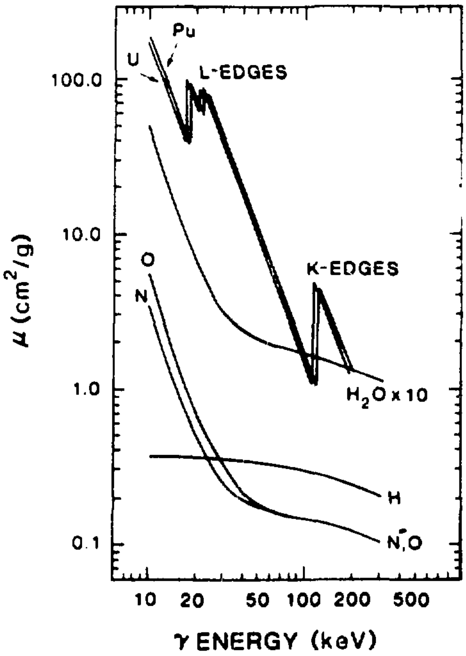
By contrast, x-ray absorption techniques are finding increasing application in safeguards, based largely on work at Los Alamos, where both K-edge and L-edge x-ray densitometers were developed.[29-33] X-ray densitometers are used to determine the amount of elemental uranium or plutonium in a sample by measuring the transmission of the sample at photon energies just above and below either the K or L absorption edge (see Table VI and Fig. 22). Measurements are made with a high-resolution gamma-ray detector, external radiation sources, and suitable collimators for viewing the sample. For a K-edge assay of plutonium concentration, the sample transmission is measured at 121.1 keV (^{75}Se) and 122.1 keV (^{57}Co) (see Fig. 23). Plutonium concentration (grams per liter) is calculated from the following equation:

TABLE VI

L_{III} AND K ABSORPTION EDGE ENERGIES FOR URANIUM AND PLUTONIUM

Absorption Edge	Element	Edge Energy (keV)	$\Delta\mu$ (cm^2/g)
L_{III}	Uranium	17.17	54.60
	Plutonium	18.05	51.90
K	Uranium	115.60	3.65
	Plutonium	121.76	3.39

Fig. 22.
The X-ray mass absorption coefficients for uranium, plutonium, and typical low-Z matrix materials. X-ray densitometers were designed that use both the K-edge and L-edge regions to determine elemental concentrations of uranium and plutonium.



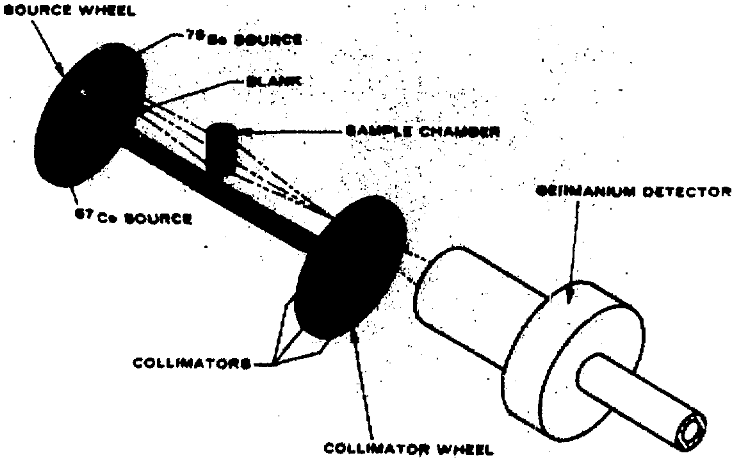


Fig. 23.
A ^{75}Se source positioned to measure the transmission at 121.1 keV. In the K-edge densitometers installed at the Tokai Reprocessing Plant in Japan and at the Savannah River Plant in the U.S., isotopic sources and collimators are automatically rotated into position to measure x-ray attenuation of the sample just above and below the plutonium K-edge.

$$\rho = \frac{-\ln(T_2/T_1)}{\Delta\mu x} ,$$

where

T_2/T_1 = ratio of sample transmission at 122.1 keV and 121.1 keV,

$\Delta\mu$ = difference in mass attenuation coefficient at 122.1 and 121.1 keV, and

x = sample thickness.

Precisions on the order of 0.5% can be obtained in a 30-minute assay.

Most of the K-edge instruments were designed to measure discrete liquid samples of a few milliliters;[30,31,33] however, an in-line instrument was installed and tested successfully at the Savannah River Plant (Fig 24). (See Ref. 32.)

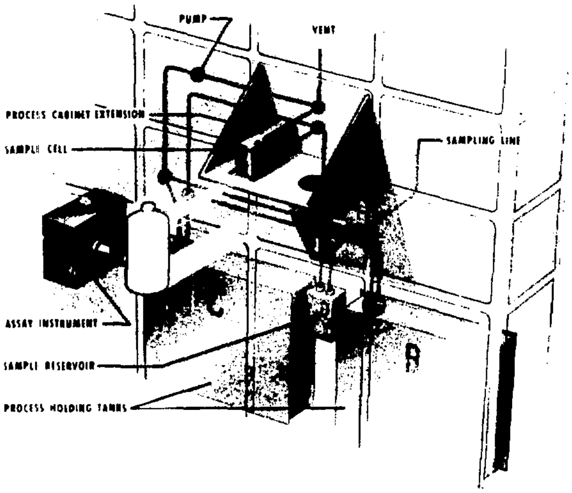


Fig. 24.
The in-line K-edge densitometer installation at the Savannah River Reprocessing Plant. Plutonium product solution can be pumped from either of the process holding tanks through the sample cell, which is contained in a small extension of the process cabinet. The assay instrument sits on a shelf outside the process cabinet, allowing transmission measurements of the sample cell.

For solutions having plutonium densities below 20 g/ℓ, the sample thickness required to perform accurate K-edge assays becomes impractically large. Table VI shows that the values of $\Delta\mu$ at the L_{III} edge are about 15 times greater than $\Delta\mu$ at the K-edge, allowing sample thicknesses to be reduced accordingly for L-edge assays.

L-edge densitometers use the bremsstrahlung from low-energy x-ray generators to determine the sample transmission as a function of energy across the absorption edge (Fig. 25). The use of a continuous x-ray spectrum provides a complete assay in one measurement, and the same x-ray machine can be used for assaying plutonium, uranium, and mixed uranium-plutonium solutions (Fig. 26). Unlike K-edge assays, L-edge assays are sensitive to low-Z matrix constituents because of the rapidly changing photoelectric and Compton cross sections of low-Z materials in this energy region. A portable version of the K-edge densitometer was also developed for use by the IAEA to verify densitometry measurements independently at Tokai-Mura (Fig. 27). (See Refs. 31 and 33.)

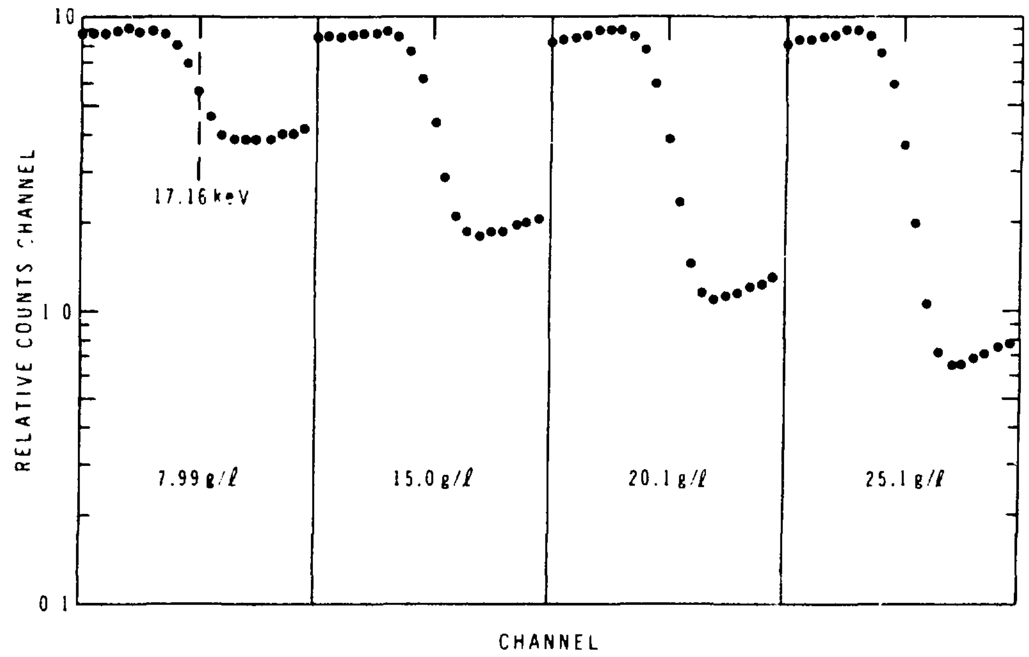


Fig. 25.
The X-ray transmission spectra for 2-cm-thick uranium solutions near the L_{III} absorption edge of uranium (17.16 keV), taken with the instrument shown in Fig. 26.

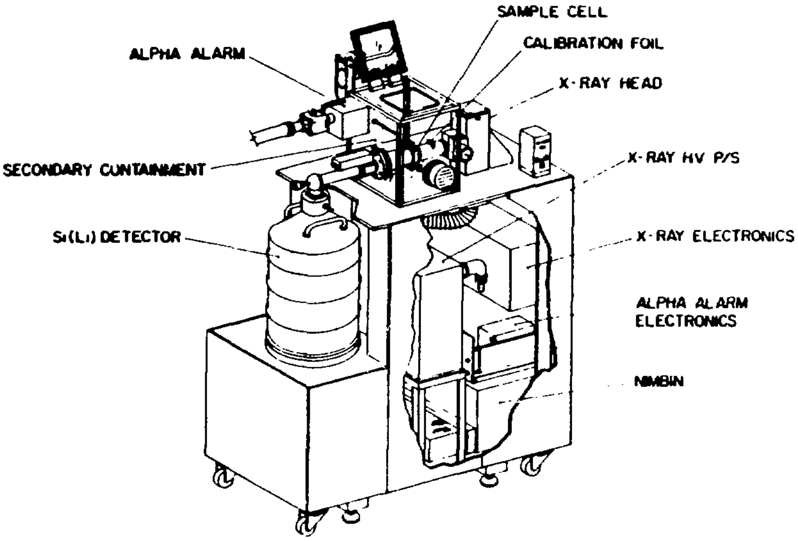


Fig. 26.
The L-edge densitometer designed for measuring uranium or plutonium concentrations in low-density solutions. The secondary containment box that encloses the sample cell is designed to be mounted to the rear of the glovebox, and solution from the glovebox is piped into the sample cell.

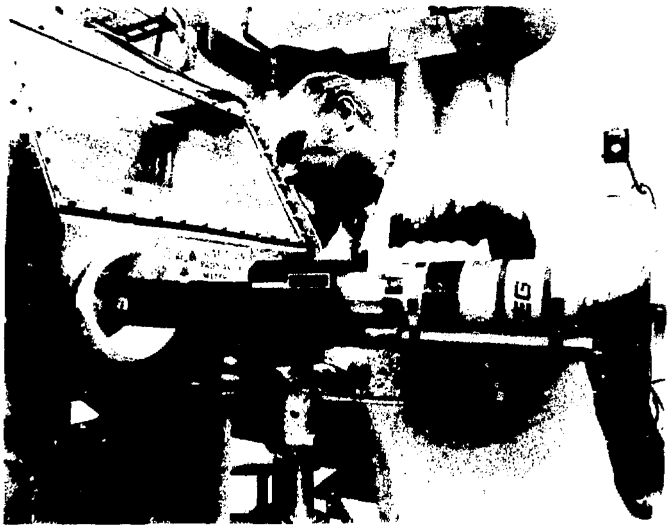


Fig. 27.
A portable version of the K-edge densitometer. A small Ge gamma-ray spectrometer and a portable Davidson MCA are used for data acquisition. The entire instrument remains outside the glovebox and views the plutonium solution samples through the gloves. With this design, the IAEA inspector can verify independently the at-line densitometry measurements on the same solution samples measured and declared by the facility operator without the necessity of breaking containment.

B. Induced Active Response (Including X-Ray Fluorescence)

Active interrogation methods using gamma-ray or x-ray sources are not widely used in safeguards today, although one method was utilized in the past and another method looks promising for the future. In the early 1970s, IRT Corporation developed a barrel scanner using bremsstrahlung from a 10-MeV electron linac to cause photofission in ^{235}U, ^{238}U, and ^{239}Pu (see Ref. 34). Between each linac pulse, neutrons from the sample were moderated and counted with BF_3 counters. Although this technique gives fairly accurate assays of scrap materials, it is largely replaced by active neutron methods.

A method that holds promise for future safeguards applications is x-ray fluorescence. Because x-ray energies depend on atomic number, x-ray fluorescence was long used as a laboratory tool for chemical analysis. Most previous applications used electron bombardment to produce the characteristic K or L x rays; hence, careful sample preparation was required, much as is the case for alpha counting. More recently, low-energy gamma rays from isotopic sources are used as the exitation source,[35] allowing measurement of plutonium and uranium in their existing containers (Fig. 28).

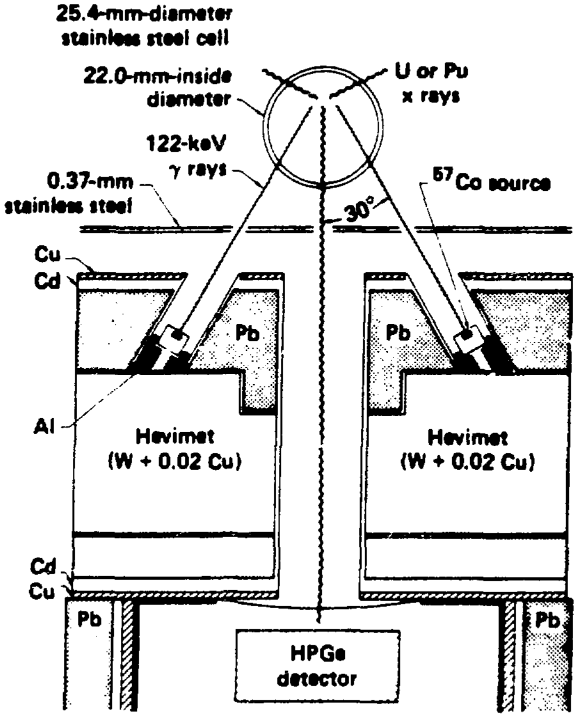


Fig. 28.
Arrangement of ^{57}Co excitation sources and Ge detector used by Camp and Ruhter[35] for x-ray fluorescence measurement of uranium and plutonium solutions contained in a cylindrical (pipe) geometry.

X-ray fluorescence has high precision over a wide dynamic range of uranium and plutonium concentrations. In mixed uranium-plutonium solutions, the method is capable of giving an accurate determination of the ratio of plutonium to uranium. However, to give accurate assays of individual concentrations of uranium and plutonium, techniques must be developed to correct for absorption in the sample of both the excitation gamma rays and the fluorescent x rays.

VI. ACTIVE NEUTRON METHODS

A. General Information

Because active neutron methods constitute one of the most powerful techniques for the assay of fissionable materials, the number of active neutron instruments used in safeguards grew rapidly during the 1970s. Initially, active neutron assays were performed using reactors and positive ion accelerators as the source of neutrons; these methods are still used when the ultimate in sensitivity is needed for small sample assay. However, for most safeguards applications, instruments that use isotopic neutron sources are preferred because of improved size, cost, and reliability. Characteristics of the most commonly used isotopic neutron sources are shown in Table VII (see Ref. 1).

TABLE VII

COMMON ISOTOPIC NEUTRON SOURCES

Source	Approximate Average Energy	Half-Life	Maximum Typical Strength (n/s)
^{252}Cf	Fission (2 MeV)	2.6 yr	5×10^9
^{238}Pu-Li(α,n)	0.5 MeV	88 yr	2×10^6
^{238}Pu-Be(α,n)	5 MeV	88 yr	10^6
^{241}Am-Li(α,n)	0.5 MeV	434 yr	5×10^5
^{124}Sb-Be(γ,n)	23 keV	60 days	5×10^8

The primary instrument design problem in active neutron interrogation is discriminating against source neutrons, while detecting neutrons produced by induced fissions in the sample. As shown in Fig. 1, the three methods used for discriminating against source neutrons are

- coincidence discrimination,
- time discrimination, and
- energy discrimination.

In the following sections, instruments are discussed that employ each of the above techniques.

B. Coincidence Discrimination (Random Driver, AWCC, NCC)

The random driver (Fig. 29) was one of the first active neutron assay instruments developed specifically for safeguards. The Los Alamos design[36] uses an americium-lithium neutron interrogation source of about 5×10^5 n/s and large plastic scintillator neutron detectors, shielded from the sample with lead to reduce gamma-ray sensitivity. By demanding that two neutrons be counted with a 50-ns coincidence resolving time, single neutrons from the americium-lithium source are discriminated against, while multiple neutrons from induced fission in the sample are detected. Other random driver designs that omit the lead shielding can assay samples of

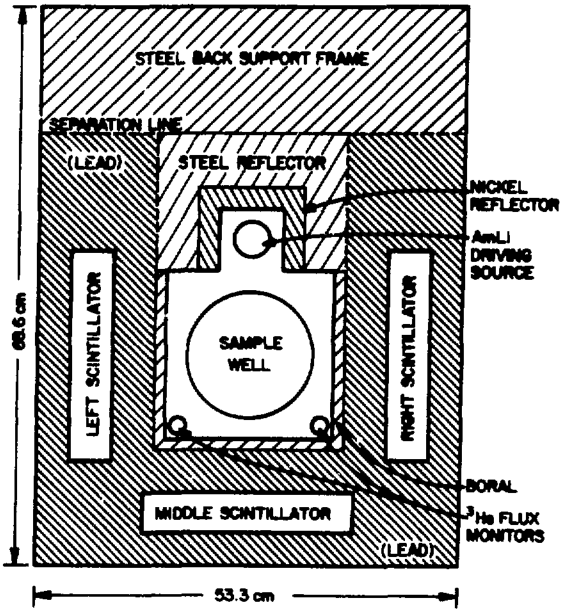


Fig. 29.
Random driver of recent design used by Los Alamos for assay of plutonium samples. One of the first active neutron instruments designed for safeguards applications, random drivers are widely used for the assay of uranium scrap materials in fuel fabrication facilities.

approximately 0.1 g of ^{235}U, but are also sensitive to gamma-ray attenuation in the sample. Random drivers, widely used for assaying uranium scrap and waste materials, are designed to accommodate a variety of container sizes, ranging from a few liters to 200-liter waste barrels.

Most random driver designs incorporate ^{3}He detectors to correct the assay for hydrogenous-moderating material in the sample and for rotating the sample to provide more uniform neutron irradiation. Some random drivers also use temperature sensors to correct for detector temperature dependence. Although the smaller random drivers are suitable for van installations, their basic design using large scintillator detectors and lead shielding does not lend itself to portability.

The Active-Well Coincidence Counter (AWCC) was designed as a simpler, more easily transported replacement for the random driver (Figs. 30, 31). The design of the AWCC is very similar to passive neutron well coincidence counters (Section III.C), except that two small americium-lithium neutron sources (approximately 5 × 10^4 n/s) are placed in end plugs above and below the sample well.[37] A shift-register coincidence unit effectively

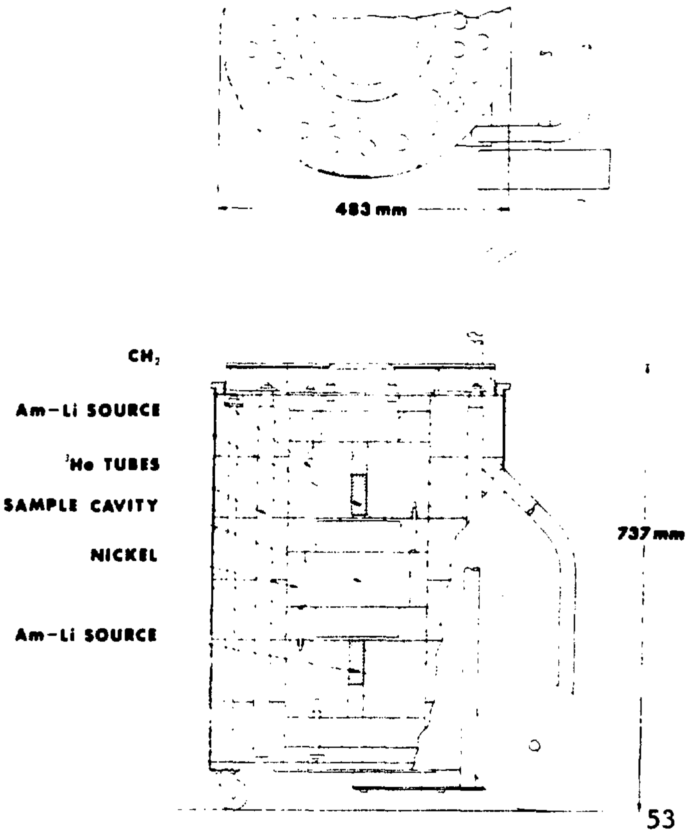


Fig. 30.
Cross section of Active-Well Coincidence Counter, showing location of neutron sources in end plugs above and below the sample well.

Fig. 31.
The Active-Well Coincidence Counter designed as a transportable instrument for IAEA use in assaying uranium samples.

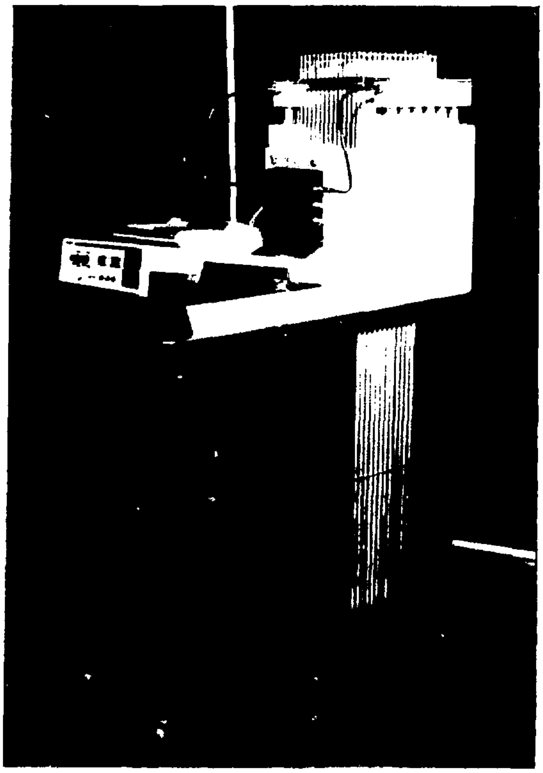
discriminates against single neutrons from the americium-lithium sources while detecting coincident neutrons from fissions in the sample. Compared with the random driver, the AWCC is less accurate for small samples and slightly more expensive; but it is far more portable, rugged, and reliable and, for these reasons, more suitable for IAEA applications.

An instrument based on the same principles as the AWCC was designed to assay fresh LWR fuel assemblies (Fig. 32). All of the instruments in this class can be used in the passive mode (by removing the americium-lithium neutron sources) to assay plutonium.

C. Time Discrimination (Californium Shuffler)

One of the oldest techniques for assaying fissionable materials involves irradiating samples with neutrons from reactors or particle accelerators and then counting either delayed neutrons or gamma rays from the sample. Delayed neutrons are emitted by neutron-unstable fission products with half-lives ranging from 0.25 to 56 s. For ^{235}U, the ratio of delayed neutrons to prompt neutrons is about 1/120, and for ^{239}Pu, about 1/335. Delayed gamma rays are emitted by many different fission products with half-lives ranging from seconds to years.

Fig. 32.
Active neutron instrument for the assay of fresh fuel assemblies. It uses a single americium-lithium neutron source on one side of the fuel assembly and six ^{3}He detectors in polyethylene slabs on the other three sides of the assembly. The electronics package is the same for this instrument, the Active-Well Coincidence Counter, and the High-Level Neutron Coincidence Counter.



With the production of large ^{252}Cf sources in the late 1960s, it became possible to use isotopic sources in delayed neutron and gamma-ray assay instruments. The californium shuffler (Figs. 33-35) uses a 1 mg ^{252}Cf source (approximately 2.5×10^{9} n/s), a U-shaped source transfer tube, and ^{3}He proportional counters around the sample well.[38] A motor-driven cable moves the source into position where it irradiates the sample for a few seconds, then quickly withdraws the source to a shielded position. With the source removed, the ^{3}He detectors are gated on to count delayed neutrons, and the whole cycle is then repeated many times for an assay. Typical irradiation and counting cycles are about 10 s each, although optimum times may vary depending on sample characteristics.

Californium shufflers are among the most sensitive assay instruments, capable of measuring 1 mg of ^{235}U in small containers, with an assay time of approximately 30 min. Using source-tailoring techniques such as nickel reflectors and CH_2 moderators, one can adjust the energy spectrum of the interrogating neutrons to obtain either a thermal or a fast-neutron assay. Shufflers are designed for a wide range of material types, including ^{235}U

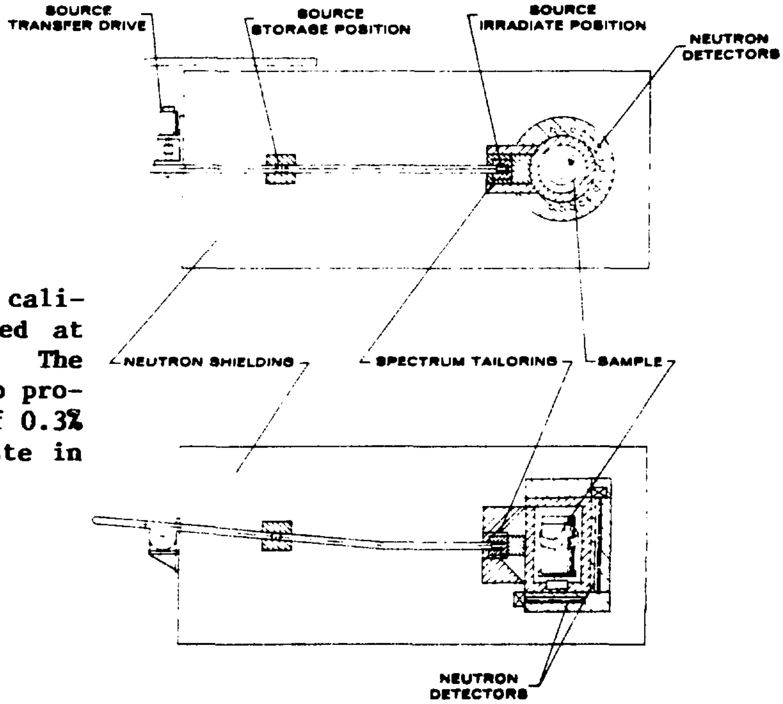


Fig. 33.
Top and side views of the californium shuffler installed at the Savannah River Plant. The instrument was designed to provide an assay precision of 0.3% for uranium scrap and waste in 18-cm x 30-cm cans.

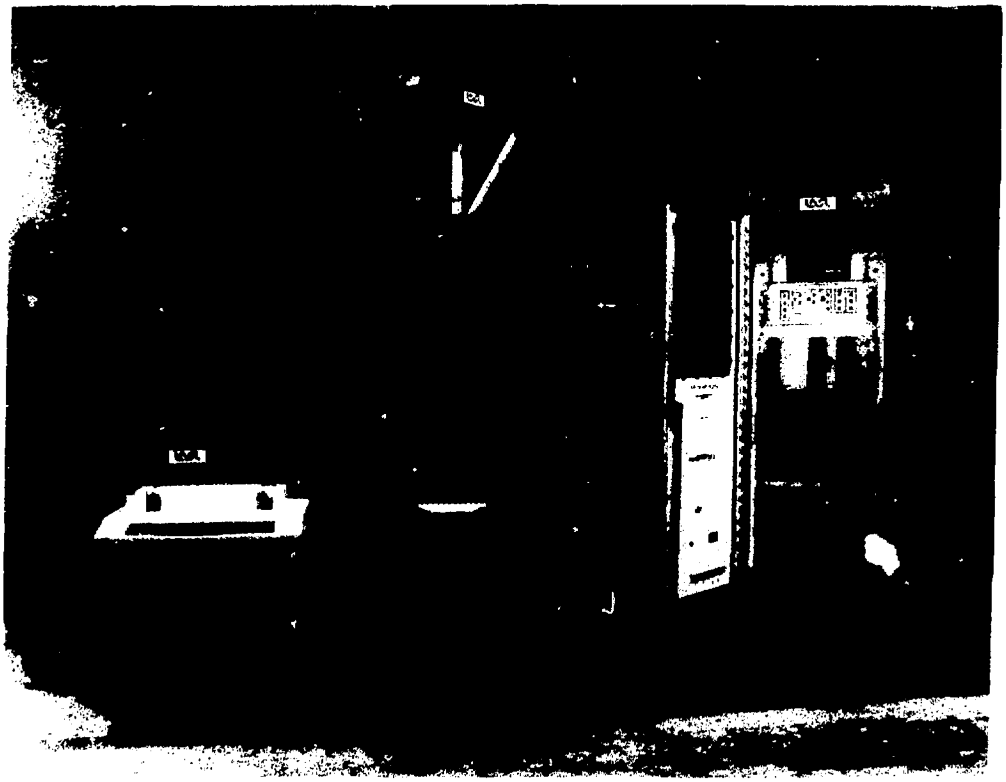
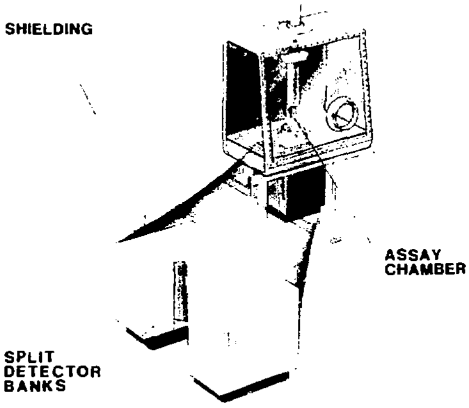


Fig. 34.
Complete Savannah River californium shuffler showing terminals, electronics rack, and hoist for lowering samples into the measurement well.

Fig. 35.
An in-line shuffler for measurement of high-density, in-process scrap and waste. The smaller shuffler design incorporates all of the traditional features, with the sample being lowered into the assay well in a downward extension of the glove-box floor.



scrap from fuel fabrication facilities, hot waste barrels containing uranium and plutonium, and highly enriched spent-fuel elements and waste canisters (Fig. 36). For measuring spent fuel, the californium source must be large enough to overcome neutron background from plutonium and curium isotopes in the sample.[39]

Another type of instrument using ^{252}Cf neutron irradiation was developed for assaying fast breeder reactor fuel rods (Fig. 37). Here the technique is to continuously move a fuel rod through a shielded neutron irradiator, past a NaI detector where delayed gamma rays are counted. Individual fuel pellets are scanned and total fissile content accurately measured for both materials accounting and quality control.[40]

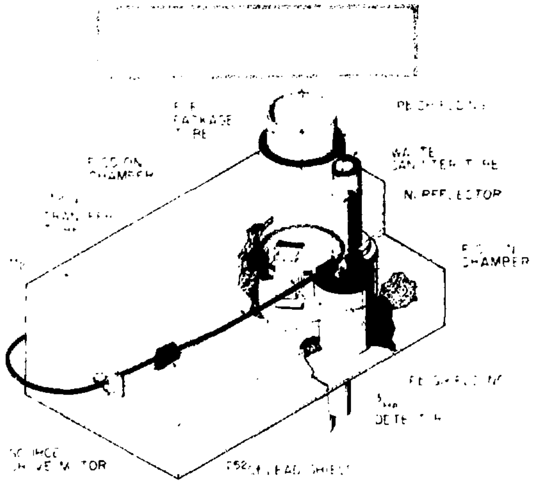


Fig. 36.
Large californium shuffler system for the assay of either spent-fuel assemblies or waste canisters. To achieve a more uniform assay of assemblies, the californium source moves around the fuel package tube during the irradiation cycle. This instrument is installed in the Florinel and Storage (FAST) Facility at the Idaho Chemical Processing Plant.

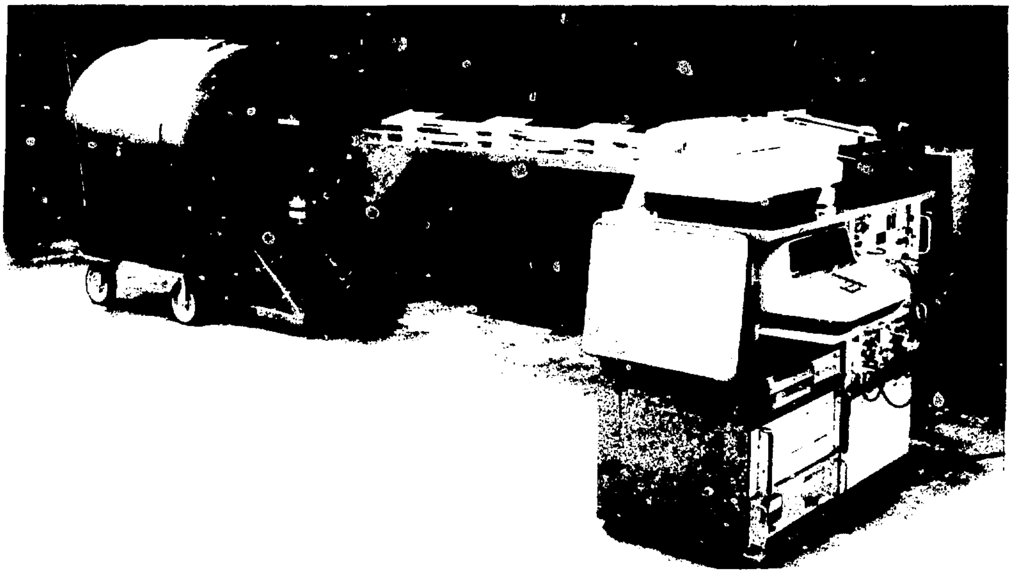


Fig. 37.
Fuel-rod scanner developed for the Fast Flux Test Facility (FFTF) at Hanford, Washington. The hybrid assay instrument uses a californium source for fast neutron interrogation and measures delayed gamma rays with two large NaI detectors. The system determines plutonium fissile content in a fuel rod to better than 0.5% accuracy and has been used to assay many thousands of rods.

D. Energy Discrimination (Spent-Fuel Assay System)

Several active neutron instruments were designed that discriminate against source neutrons on the basis of neutron energy. One example[41] is an instrument designed at Oak Ridge for the assay of spent-fuel from breeder reactor subassemblies. It uses four large ^{124}Sb-Be photoneutron sources, each of which produce about 10^9 n/s. Detectors are methane-filled, proton-recoil proportional counters, capable of discriminating against the 23-keV neutrons from the sources while detecting the more energetic neutrons from induced fissions in the spent fuel. Developed for performing assays at the head end of a reprocessing plant, the system is capable of 5% precision in a 20-min measurement time. The technique of energy discrimination against source neutrons was also applied by Los Alamos in instruments for assaying fresh LWR fuel assemblies and for well logging uranium ore formations.

VII. CONCLUSIONS

The interpretation of essentially all assays depends on having information, other than the quantity being measured, about the sample. Usually, the more well characterized a sample is from a physical and chemical standpoint, the more accurately it is assayed, either destructively or nondestructively.

The selection of one NDA technique over another commonly depends on what one knows and does not know about the characteristics of the sample material. From the standpoint of NDA, the most important characteristics of a sample are its spatial properties (size, shape, uniformity, etc.), its isotopic properties (ratios of fissionable isotopes), and its matrix properties (atomic numbers, density, unusual nonfissioning isotopes, etc.).

If a sample to be assayed has well-determined isotopic properties but poorly defined spatial properties, then a neutron method or calorimetry is likely to provide the best assay. Consider, as examples, the dependence of passive neutron and calorimetric assays on precise knowledge of plutonium isotopic content, but their relative independence of sample uniformity.

When neither spatial nor isotopic properties are well known, a combination of gamma-ray spectroscopy and active neutron methods is likely to provide the most accurate assay and greatest level of confidence.

Variations in high-Z or high-density matrix materials (that are not properly corrected for) increase the uncertainty in gamma-ray assays more than in neutron assays. Variations in low-density matrix materials, such as water, oxygen, and fluorine, increase the uncertainty in neutron assays more than in gamma-ray assays. Thus, a high-density matrix tends to favor neutron assay; a low-density matrix, gamma-ray assay.

The relationship between gamma-ray assay, neutron assay, and calorimetry is complementary in nature. When the characteristics of a sample (spatial, isotopic, or matrix) limit the accuracy of one NDA approach, another approach is generally used with a high degree of confidence.

Many NDA instruments developed over the past decade are now commercially available. Future development is expected to produce a new generation of NDA equipment that will ease the tasks of independent calibration, operation, and maintenance, and lead to new approaches for potential problem areas, such as large bulk-processing facilities.

Table VIII summarizes points discussed above. For the first example, gamma-ray scattering and absorption parameters are measurable or known, but isotopic composition of fissionable and matrix materials is unknown. In this case, several different gamma-ray techniques give the typical assay results indicated. For the second example, isotopic composition of fissionable and matrix materials is known, but gamma-ray scattering parameters of the sample are not known. In this case, passive or active neutron techniques and calorimetry are applicable. For the third example, neither gamma-ray scattering parameters nor isotopic composition of the sample are

TABLE VIII

CONDITIONS UNDER WHICH VARIOUS NDA METHODS ARE USEFUL

Example	Measurable or Known Sample Characteristics	Useful NDA Methods	Typical Assay Results
I	Key gamma-ray scattering/absorption characteristics	Passive gamma	Enrichment, isotopic ratios, isotopic content
		X-ray	Plutonium, uranium concentration
		Passive gamma & passive neutron	Plutonium mass
		Passive gamma & calorimetry	Plutonium mass
II	Isotopic composition	Passive neutron	Plutonium mass
		Calorimetry	Plutonium mass
		Active neutron	U-235 mass, plutonium mass
III	Nil	Passive gamma	Presence of certain isotopes
		Active neutron	Effective fissile

known. In this case, high-resolution gamma-ray spectroscopy can detect the presence of certain isotopes, and active neutron methods may give an estimate of effective fissile content.

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CHAPTER IV

PART ONE: STATISTICAL CONCEPTS

by

R. R. Picard and K. Campbell

I. VARIABILITY

At the core of any materials accounting system are the individual measurements that are combined to produce accountability information. Inherent in most such measurement data is variability; that is, measured values contain error and repeated measurements of the same quantity often yield different results. Proper evaluation of accountability data requires an understanding of the role of variability.

As an example, consider the data listed in Table I, which were obtained from the records of the Los Alamos Plutonium Facility. An electronic balance with 0.1-g readout was used to weigh a particular standard repeatedly. One hundred weighings were conducted over a 20-week period, and measured values ranged from 4001.2 g to 4001.9 g.

There are a number of potential causes of the observed variability. The balance may be affected by environmental conditions, such as vibration, temperature, and humidity. It may be impossible to reproduce exactly the measurement process, as when a person places the standard at different locations on the balance pan or when one person cannot duplicate the actions of another. Still more sources of variability may exist, as described in Chap. XI, Survey of Chemical and Bulk Measurement Methods.

As a consequence, many statements based on accounting data (such as "there has been no diversion of material") are not made with certainty. Such statements must account for the variability present in the measurements, and decisions are necessarily probabilistic in nature.

Because measurement errors are facts of life, it is important to find a rational way to deal with them. One step toward understanding variability in a particular measurement setting involves examination of the empirical distribution (sometimes called the sampling distribution) of the data generated by the measurement process. The empirical distribution can be displayed in a histogram, which plots the observed measured values

TABLE I

MEASUREMENT DATA FROM AN ELECTRONIC BALANCE

(Values in Grams)

Measurement i	Value x_i	Measurement i	Value x_i	Measurement i	Value x_i	Measurement i	Value x_i
1	4001.5	26	4001.5	51	4001.5	76	4001.6
2	4001.4	27	4001.4	52	4001.5	77	4001.3
3	4001.4	28	4001.4	53	4001.6	78	4001.7
4	4001.6	29	4001.5	54	4001.6	79	4001.8
5	4001.7	30	4001.8	55	4001.7	80	4001.6
6	4001.3	31	4001.6	56	4001.5	81	4001.6
7	4001.7	32	4001.6	57	4001.7	82	4001.5
8	4001.8	33	4001.5	58	4001.6	83	4001.6
9	4001.9	34	4001.7	59	4001.7	84	4001.7
10	4001.4	35	4001.6	60	4001.7	85	4001.7
11	4001.7	36	4001.3	61	4001.5	86	4001.4
12	4001.8	37	4001.5	62	4001.7	87	4001.6
13	4001.8	38	4001.6	63	4001.5	88	4001.3
14	4001.6	39	4001.7	64	4001.7	89	4001.3
15	4001.8	40	4001.7	65	4001.5	90	4001.5
16	4001.8	41	4001.7	66	4001.3	91	4001.6
17	4001.6	42	4001.8	67	4001.5	92	4001.5
18	4001.5	43	4001.6	68	4001.6	93	4001.6
19	4001.4	44	4001.6	69	4001.3	94	4001.7
20	4001.2	45	4001.8	70	4001.4	95	4001.7
21	4001.5	46	4001.5	71	4001.6	96	4001.4
22	4001.5	47	4001.3	72	4001.7	97	4001.6
23	4001.6	48	4001.8	73	4001.7	97	4001.7
24	4001.7	49	4001.6	74	4001.6	99	4001.6
25	4001.5	50	4001.3	75	4001.5	100	4001.3

against their frequencies of occurrence. The histogram for the balance data is given in Fig. 1. Of the 100 measurements, the value 4001.2 g is observed once, the value 4001.3 g is observed ten times, and so on. In Fig. 1, the term "relative frequency" refers to the proportion of observations having a given value. A relative frequency of 0.1 is plotted for the value 4001.3 g because 10 of the 100 measurements had that value. The most frequently obtained value is 4001.6 g; generally speaking, the farther from 4001.6 g a value is, the less often the value tends to be observed.

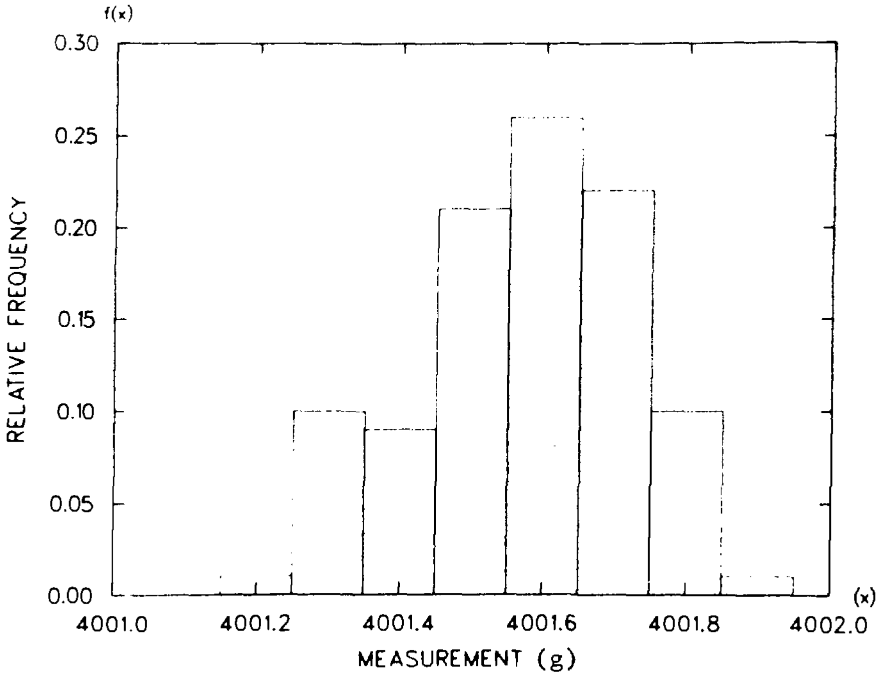

Fig. 1.
Histogram for the data from the electronic balance.

II. THE MEAN AND STANDARD DEVIATION

In the balance data of Table I, each observed value is the result of a complete repetition of the measurement process. Suppose that the standard were soon to be weighed on the balance once more. What is the probability that this weighing would result in the value 4001.6 g? The answer to this question is unknown and unknowable. Because 26 of the 100 observations resulted in the value 4001.6 g, a reasonable estimate of the probability of interest is 26%. A clear distinction exists between the actual quantity, which is unknown, and its estimate, which is based on observed data. This very important distinction should be kept in mind throughout this chapter.

If the actual probabilities for the possible values were known, they would define the probability distribution for the next observed value. Two properties of probability distributions, the mean and the standard deviation, are very useful in safeguards work. Generally, the mean reflects the typical size of an observation having a given probability distribution, whereas the standard deviation is a quantitative measure of variability.

More specifically, the mean is defined as the average value. The actual mean of a distribution is usually unknown, as is the distribution itself. The sample mean, or mean of the empirical distribution, is often used to estimate the actual mean. Common statistical notation denotes the i^{th} observed measured value by x_i and the sample mean by $\bar{x}$. If the observed data contain n measurements, the sample mean is computed by the formula

$$\bar{x} = \sum_{i=1}^{n} x_i/n \quad . \tag{1}$$

In other words, the sample mean is the average value of the observed measurements. For the balance data of Table I, the sample mean is 4001.572 g.

The standard deviation is defined as the square root of the variance, which in turn is defined as the average squared difference between an individual observed value and the actual mean. Though usually unknown, the standard deviation can be estimated from observed data by the sample standard deviation, commonly denoted s and computed as

$$s = \sqrt{\sum_{i=1}^{n} (x_i - \bar{x})^2/(n - 1)} \quad . \tag{2}$$

In other words, squared differences between the observed measurements and the sample mean are used to estimate the true standard deviation. If much variability exists in the observed data, the estimate s from Eq. (2) will be large. For the balance data, the sample standard deviation is 0.151 g.

Here $\bar{x}$ and s are statistics, or functions of the observed data. Their corresponding true values, usually denoted by μ and σ, respectively, are often referred to as parameters.

III. PRECISION, ACCURACY, AND BIAS

Three widely used terms are the subjects of this section. Precision is often used in (vague) reference to the repeatability of a measurement process. Precision is very important; poor precision means that experimental results can not be adequately duplicated, and the integrity of experimental conclusions suffers considerably. For example, if three consecutive measurements of the same standard yielded values of 4000 g, 6500 g, and 3000 g (possible using a very erratic balance), any experimenter would be hard pressed to place much faith in other measurements made using this balance. The standard deviation is a quantitative measure of repeatability, and it is frequently mentioned in relation to "precision."

The sample mean of the 100 measurements listed in Table I is $\bar{x}$ = 4001.572 g, and the sample standard deviation is s = 0.151 g. To many people, the size of this standard deviation might reflect satisfactory precision; however, few would be happy if the actual mass of the standard turned out to be 3000 g. Thus, precision is not the only important consideration.

Although the actual mass of the standard is unknown and unknowable, the National Bureau of Standards, presumably after much work with high-quality instrumentation, has provided the value 4001.566 g, as compared to the sample mean $\bar{x}$ = 4001.572 g. The term bias is defined as the difference between the mean of the distribution of a measured value and the actual mass of the standard. The actual bias is, of course, unknown and could be estimated using available information by

$$4001.572 \text{ g} - 4001.566 \text{ g} = 0.006 \text{ g} \quad .$$

Whether this result is "significant" is discussed in Sec. VII.

The term accuracy is used in two different contexts. The accuracy of an individual measured value is simply the difference between that value and the corresponding actual value. If the standard, whose actual weight is "known" to be 4001.566 g, were placed on the balance and the measured value 4001.7 g obtained, then the accuracy of that value would be easily quantified.

When an item is measured whose actual value is "unknown," accuracy as described above cannot be quantified. In the second and more useful context, accuracy is the property of an instrument, such as the electronic balance. For the measurement control data, the estimated precision and bias summarize how accurately repeated measurements reflect the standard weight, "on the average." It is often reasonable to assume that the precision and bias for measurement of an item of unknown weight are the same as for measurement of the standard. In such cases, the accuracy of the electronic balance--on the average--is often mentioned in connection with individual measured values.

The proper expression of measurement results is related to the concepts of accuracy. Above, the sample mean of the measurement control data, $\bar{x} = 4001.572$ g, is expressed to three decimal places. It might also be written as $\bar{x} = 4001.57$ g or $\bar{x} = 4001.5720$ g, in the event that expression to two or four decimal places were desired. As a general rule, the number of decimal places that should be used depends on whether the result is a "final" one or whether it is part of an intermediate-stage calculation. Because it is a good idea to minimize the introduction of rounding errors into intermediate calculations, those calculations should be performed to as many decimal places as is practical. When citing a final result, however, the presence of meaningless digits is often distracting and sometimes misleading. Expression of a final result to decimal places well beyond the accuracy of that result should be avoided.

In this chapter, most results, such as $\bar{x}$, are used for both "intermediate" and "final" purposes. For the sake of consistency, expression to three decimal places is used throughout, though the reader should keep in mind that this is not necessary.

IV. THE NORMAL DISTRIBUTION

Repeated measurements in many experimental settings result in bell-shaped empirical distributions, such as the one displayed in Fig. 1. A continuous (smooth) probability distribution called the normal distribution is often used to model experimental data. Although instances exist where use of the normal distribution is inappropriate, the widespread applicability of this distribution for purposes of deriving probability statements motivates further discussion.

The normal distribution is characterized by a probability density function,

$$f(x) = \frac{1}{\sigma\sqrt{2\pi}} e^{-(x - \mu)^2/2\sigma^2} \quad , \tag{3}$$

where the parameter μ denotes the actual mean of the distribution and the parameter σ denotes the actual standard deviation. In Fig. 2, a curve of this form, for μ and σ equal to $\bar{x}$ and s, respectively, is superimposed on the histogram for the balance data. It is seen that f(x) is a continuous approximation to the empirical distribution.

The continuous aspect of the normal distribution implies that if the next measured value, m, from the electronic balance were normally distributed, any given number (such as -2.481) might be observed. Because the balance provides only nonnegative values to the nearest tenth of a gram, it is clear that--strictly speaking--the next measured value is not normally distributed. The same is true for data from virtually any experimental setting.

Nonetheless, in modeling, the normal distribution is quite useful. Probabilities derived under the assumption that the next measured value is normally distributed often closely parallel those from the empirical distribution. For example, the area under the normal curve in Fig. 2 between 4001.55 g and 4001.65 g corresponds to the probability that the associated normally distributed value is between 4001.55 g and 4001.65 g. This area is 0.255, which compares well with the empirical probability of the reading 4001.6 g, or 26/100.

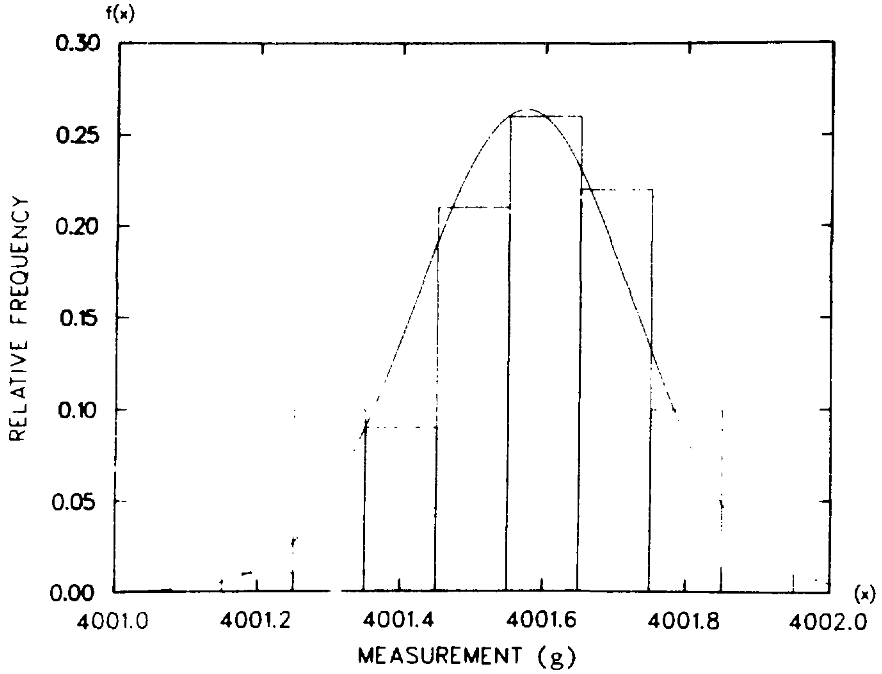

Fig. 2.
Histogram for the data from the electronic balance, with a superimposed curve from a normal probability density function.

There exists much theory, such as the central limit theorem and related results that can be found in many statistical texts (see Ref. 1), demonstrating that the normal distribution closely approximates distributions of many real phenomena. Such theory is at the heart of the widespread, successful use of the normal distribution in many areas of science. Figure 2 illustrates historical evidence to this end with respect to the balance data.

In other measurement situations, the assumption of approximate normality should not be made blindly. On occasion, the normal distribution may not be appropriate and alternatives must be considered. Adequate treatment of formal tests for normality and a discussion of specific alternatives is beyond the scope of this presentation, and the reader is advised to consult the literature.

All probability statements (e.g., "the measured value is significantly different from the NBS-certified mass of the standard") are based on underlying assumptions concerning the variability in the measurements. Such assumptions should be made explicit to allow the probability statements to be properly interpreted. Assuming that the underlying distribution of the measured values is normal permits the derivation of useful results, as discussed in the sections to come.

V. CONFIDENCE LIMITS AND CONFIDENCE INTERVALS

The most common type of probability statement arising in safeguards is related to the notion of confidence limits. The term "limit of error" is often used in this context.

The purpose of much statistical work is to make probability statements about unknown actual values. For example, it might be desired to make such a statement about the actual mean of the distribution of the measured values obtained by weighing the standard on the electronic balance. Using available data, a range of values bounded by confidence limits, or a <u>confidence interval</u>, is constructed. The specific interval obtained depends on the specific data observed. If an experimenter duplicated the entire procedure (i.e., if he had placed the same standard on the same balance, repeating the same measurement process to acquire his own set of results and then used the same method to derive a confidence interval from his own data), that experimenter would obtain a confidence interval different from the one based on the data of Table I.

Whether the specific interval derived from a given set of data contains the actual mean cannot be determined with certainty because the actual mean is unknown. What can be said, however, is that the overall procedure has a good track record. In other words, if a large number of such intervals were generated by different experimenters using the same method on their own data sets, the proportion of those intervals containing the actual value would be large.

The term <u>confidence level</u> refers to the proportion of such intervals containing the actual value. Thus, a 95% confidence interval is one that is obtained using a method that, when applied to a large number of data sets conforming to the stated assumptions, generates an interval containing the actual value in 95% of those applications. This is not quite ideal because each experimenter is primarily interested in whether his own interval contains the actual value, but it is important that the method has good overall qualities.

Suppose it is desired to derive a 95% confidence interval for the actual mean μ of the distribution of the measured values generated by weighing the standard on the balance. The procedure described for doing this is generally* valid if either of two conditions hold:

(1) the common distribution underlying each individual measurement is approximately normal and the sample mean $\bar{x}$ is based on a sample of moderate size (say, $n = 15$ or more) or

(2) $\bar{x}$ is based on a sample of large size (say, $n = 50$ or more).

For the balance data, Fig. 2 indicates the first condition is reasonable; the second condition clearly holds.

Neglecting mathematical details, it can be shown that a confidence interval whose approximate confidence level is $1 - \alpha$ (α is a number between 0 and 1/2) is

$$(\bar{x} - z_{\alpha/2}\, s/\sqrt{n} \quad , \quad \bar{x} + z_{\alpha/2}\, s/\sqrt{n}) \quad , \tag{4}$$

where $z_{\alpha/2}$ is the upper $100(1 - \alpha/2)$ percentile** of the standard normal distribution and s is the sample standard deviation. For 95% confidence

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*If exact normality is assumed, confidence intervals are obtained using the t distribution (see elementary statistical texts, which include Refs. 1-4; see also Ref. 5 for a synopsis of useful texts), and results are comparable to the above. The second condition arises from the central limit theorem (again see standard texts), which assumes that the underlying distribution has finite variance. The reader is cautioned that isolated situations exist where other methods for deriving confidence intervals should be considered.

**The upper $100(1 - \alpha/2)$ percentile of the standard normal distribution is the number $z_{\alpha/2}$ that solves the integral equation

$$1 - \alpha/2 = \int_{-\infty}^{z_{\alpha/2}} \frac{1}{\sqrt{2\pi}} e^{-x^2/2}\, dx \quad .$$

intervals, probably the most commonly used intervals, $\alpha = 0.05$, and it can be shown that $z_{\alpha/2} = 1.96$. As a rule of thumb, the value 2 is often substituted for 1.96, so that an approximate 95% confidence interval for the actual mean μ extends roughly $2s/\sqrt{n}$ to either side of the sample mean $\bar{x}$.

For the balance data, substituting $\bar{x} = 4001.572$ g, $s = 0.151$ g, and $n = 100$ into the interval expression (4) gives

$$[4001.572 - 2(0.151)/\sqrt{100} \quad , \quad 4001.572 + 2(0.151)/\sqrt{100}]$$

or

$$[4001.542 \text{ g} \quad , \quad 4001.602 \text{ g}] \quad .$$

That is, an approximate 95% confidence interval for the mean, μ, consists of all values between the confidence limits 4001.542 g and 4001.602 g.

The <u>limit of error</u> of an estimated quantity has been traditionally defined (see Ref. 6, p. 285) as two times the estimated standard deviation associated with the estimated quantity. For example, the estimated standard deviation of $\bar{x}$ is $s/\sqrt{n}$ and the limit of error of $\bar{x}$ is $2s/\sqrt{n}$. In most cases, such as with the balance data, assumptions of normality are reasonable, and the limit of error corresponds directly to the construction of a 95% confidence interval. Above, the sample mean plus or minus its limit of error is one example.

The term "limit of error" has been abused over the years. It has acquired conflicting official definitions from sources such as the Code of Federal Regulations and the American National Standards Institute.[7] Usage of the term has at times been very careless (Ref. 8, pp. 293-294, discusses such carelessness), and some have suggested (e.g., Ref. 9) that limit of error should be banned altogether. Because of its colorful history, the term should be used with great care, if at all.

VI. MEASUREMENT ERROR MODELS

As mentioned in Sec. I, measurement errors have a number of sources. The first step in a statistical approach to dealing with error is to build a model, or a mathematical expression describing each measured value as a function of effects that may influence that value. Consider building a model for the next measured value, m, to be obtained by weighing the standard on the electronic balance.

Begin with the expression

$$m = t + b \quad , \tag{5}$$

where t is the mass of the standard and b is the actual bias of the balance (that is, the mean of the distribution of m minus the actual mass of the standard). Although Eq. (5) is an expression incorporating important effects t and b that influence the next measured value, it does not adequately describe m. Because of the many other effects that cause repeated measurements of the standard to differ in value, Eq. (5) is incomplete. Lumping the remaining effects into a single term e means that Eq. (5) can be revised to give

$$m = t + b + e \quad . \tag{6}$$

The next step for developing a statistical model is to add probabilistic assumptions describing the behavior of m. Such assumptions should reflect available knowledge; for example, the probability that the next measured value m will be 4001.6 g, based on the model's assumptions, should not be inconsistent with historical evidence concerning the balance. It could be assumed that t and b are unknown parameters (or "actual" values) and that e has a normal distribution with mean zero and unknown standard deviation σ, written

$$e \sim N(0,\sigma^2) \quad .$$

As described in Sec. IV, the assumption of a normal distribution for e is a reasonable approximation for measurement behavior and permits the derivation of probability statements. Of course, nonnormal distributions can be incorporated into modeling assumptions when warranted by the situation.

Based on the model in Eq. (6), there are two error terms, b and e, that allow m to be different from t. The term e is sometimes called a random error because it is unique to the measured value m. That is, if yet another measurement, m*, were to be obtained, an appropriate model for m* would be

$$m^* = t + b + e^* \quad ,$$

where the random error $e^* \sim N(0,\sigma^2)$. Random errors cause repeated measurements to take on different values. The term b in Eq. (6) is sometimes called a systematic error because it affects more than one measurement. Above, b affects both m and m*.

To this point, the term b has been treated as a fixed, unknown constant, and the corresponding model in Eq. (6) is an example of a fixed effects model. Occasionally, another approach is taken. Suppose the above balance has been selected at random from a group of balances. Each balance in the group has its own individual bias term and the set of biases, say $\{b_i\}$, has an empirical distribution, just as the observed measurements $\{x_i\}$ of Table I have such a distribution. The distribution of $\{b_i\}$ often is approximated by a normal distribution with mean zero and standard deviation σ_b. The term b in the model is written accordingly, that is $b \sim N(0,\sigma_b^2)$. Equation (6) together with the probabilistic assumptions that both the systematic error b and the random error e are normally distributed form a random effects model.

The term "systematic error" has been used in conjunction with both fixed effects models and random effects models. Because in one case b is assumed fixed and in the other it is assumed normally distributed, the term systematic error has created more than its share of confusion (see Refs. 10 and 11). Use of the terms "bias" and "random effect" when appropriate instead of the catch-all term systematic error would avoid such confusion.

In any event, Eq. (6) together with a set of probabilistic assumptions form an additive model for m. In other measurement problems, effects such as b and e do not always enter the model in a purely additive fashion. Errors may be expressed on a relative basis (this is common for some instruments, less so for electronic balances), and one model for a measured value m is

$$m = t(1 + b + e) \quad , \tag{7}$$

where again t is the actual value, e is the relative random error, and b is either a relative bias or a random effect. When probabilistic assumptions are incorporated, a model of Eq. (7) is called a multiplicative model.

Different models--for example, additive and multiplicative--are necessary because no single model adequately describes all types of measurement behavior encountered in safeguards. The existence of different models can sometimes be a problem. With respect to the usage of certain terms, such as "random error," that implicitly refer to components of models, it is important that the specific model be clearly understood when the term is mentioned.

VII. HYPOTHESIS TESTING

Much of the decision making based on accountability data concerns the subject of hypothesis testing. For example, suppose it is of interest to determine if the electronic balance used to obtain the data of Table I is biased. Such a determination cannot be made with certainty, but a quantifiable assessment is possible.

To make this assessment, a statistical model for measured values produced by the balance is developed. Based on historical evidence, an additive model with fixed effects and a normally distributed random error reflects measurement behavior, as discussed in the previous section. For simplicity, it is now also assumed that the mass, t, of the standard is 4001.566 g--the value supplied by the National Bureau of Standards. The model for a measured value m satisfies

$$m = 4001.566 + b + e \quad , \tag{8}$$

where b is the bias of the balance (possibly equal to zero) and e is the random error.

A hypothesis is a statement about a model. Two hypotheses about the model for balance data are

$$H_0: b = 0 \quad \text{and} \quad H_1: b \neq 0 \quad .$$

The "null" hypothesis, H_0, states that the bias of the balance is zero; the "alternative" hypothesis H_1, that it is not.

Based on observed data, a decision is to be made. In general terms, that decision will quantify how well the null hypothesis, H_0, agrees with the data. It cannot be determined with certainty whether H_0 is true or false, but it is possible to evaluate how consistent H_0 is with the available information.

Suppose that the 100 measured values listed in Table I are used to evaluate the null hypothesis. Under H_0, the actual mean of the distribution of a measured value is 4001.566 g, and the actual standard deviation of the distribution is unknown. As stated in Sec. II, the sample mean of the data is $\bar{x}$ = 4001.572 g, and the sample standard deviation is s = 0.151 g. Neglecting mathematical details as in Sec. V, it can be shown that the test statistic

$$(\bar{x} - t)/(s/\sqrt{n}) \quad , \tag{9}$$

which for the data of Table I is

$$(4001.572 - 4001.566)/(0.151/\sqrt{100}) = 0.397 \quad ,$$

may be interpreted relative to percentiles* of the standard normal distribution. For example, if the test statistic were less than -1.96 or greater than +1.96, then the test would be** significant at the 5% level. The estimated bias here is not significant, and the data are consistent with the null hypothesis.

The term significant merits further explanation. A test is based on a specific set of data. If an experimenter were to repeat the entire measurement and testing procedure (collecting 100 repeated measurements from the balance and computing a test statistic based on his own data), that experimenter would almost surely obtain a value for his statistic different from the value 0.397 based on the data of Table I. If the null hypothesis, H_0, is in fact true, the probability that such an experimenter's test would be significant at the 5% level is 5%.

When a test of the hypothesis, H_0, is significant at the 5% level, then either

(a) the hypothesis H_0 is true and the test result obtained is an unusual one or

(b) the hypothesis H_0 is false.

The word "unusual" in (a) can be quantified--relatively few experimenters (5%) repeating the measurement procedure would obtain data as inconsistent with the hypothesis as the data producing the significant result.

A definitive judgment often is required regarding a hypothesis. Even though it cannot be determined with certainty whether the hypothesis should be accepted as true or rejected as false, a judgment to that effect must

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*See the second footnote, Sec. V.

**Because the data do not conform exactly to a normal distribution, the values ±1.96 will closely (but not exactly) correspond to a 5% significance. When exact normality can be assumed, the test statistic [Eq. (9)] has a number of desirable properties (see elementary statistical texts) and is in some sense the "best" test of the hypothesis.

be made. In realistic situations, a probability exists that such a judgment is wrong. When a hypothesis rejected as false is, in fact, true, a false alarm occurs, and the associated probability is called a false-alarm probability. For example, when a test is used as the basis for the decision and the hypothesis is rejected as false when the test statistic is significant at the 5% level, then the false-alarm probability is 5%. A different error in judgment occurs when a hypothesis accepted as true is, in fact, false; this is called nondetection.

VIII. MEASUREMENT CONTROL AND CONTROL CHARTS

Put most simply, the primary goal of a measurement control program is to provide assurance that the instrumentation and procedures used to provide accountability information are working properly. For instance, before the electronic balance used to generate the data of Table I is used to weigh an item for accountability, the operator should have confidence in the measured values produced. A secondary goal of a measurement control program is to provide data useful for error propagation.

Not only does common sense dictate periodic checks on instrument performance, but regulations (such as DOE Order 5633.3) require that measurement control programs be in place. The most common tool for documenting and displaying the resulting data is called a control chart. Use of control charts began in the 1930s, became more popular in conjunction with the manufacture and testing of items for World War II, and is now a major component of industrial quality control programs. References 12 and 13 are standard texts on this subject.

Consider developing and using a control chart for the electronic balance. Control charts are based on statistical models, and their use is related to hypothesis testing. For a measured value, m, of the standard, the model on which the control chart is based is

$$m = 4001.566 + e \quad , \qquad (10)$$

where e ~ $N(0,\sigma^2)$ and σ is the unknown actual standard deviation of the random error e. The value 4001.566 is the presumed actual mass of the standard, and the balance is presumed unbiased as per the hypothesis test of the previous section.

The points plotted on a control chart indicate when measurement control data are collected and what the associated measured values are. Construction of a control chart requires the determination of a central line and control limits. The central line, or line about which plotted points should fall when the balance is operating properly, is drawn at the level 4001.566 g (see Fig. 3). The control limits, designated by dashed lines, are typically drawn three standard deviations* above and below the central line. As the actual standard deviation σ of a measured values is unknown, the estimate s = 0.151 g is used as a substitute. (In practice, it should be checked that the balance is "in control" when collecting data to derive s.) Thus, the control limits are plotted at the levels

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*The value "three" is somewhat arbitrary, but it is commonly used. Some control charts plot so-called warning limits at two standard deviations above and below the central line and so-called action limits at three standard deviations.

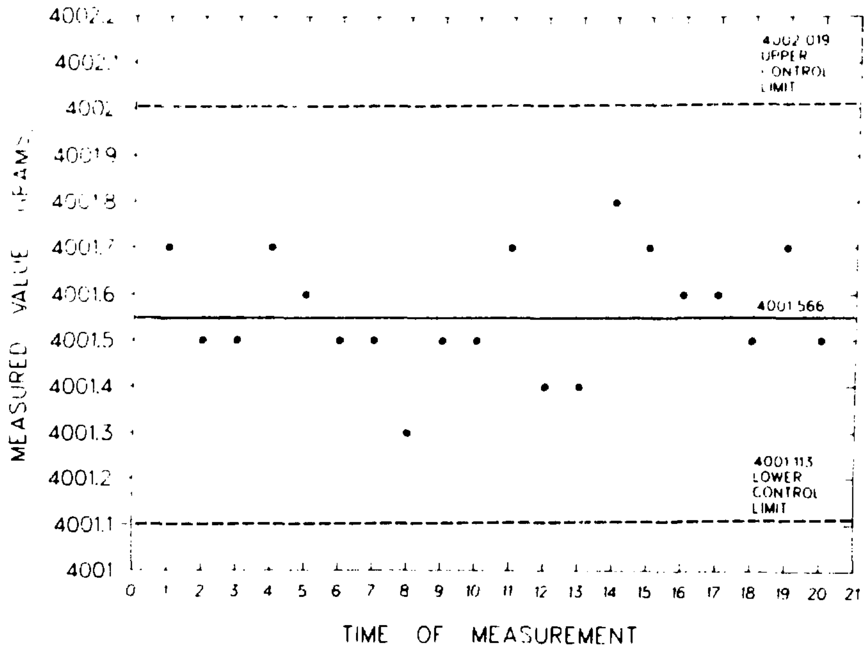

Fig. 3.
An example of a control chart.

$$4001.566 + 3(0.151) = 4002.019$$

and

$$4001.566 - 3(0.151) = 4001.113 \quad .$$

If the balance continues to function properly, it is highly unlikely that an individual measurement of the standard would be plotted outside the dashed lines. Based on the model in Eq. (10), fewer than 1 in 100 values would be expected to fall outside the control limits. Even if random errors do not behave in accordance with the normal distribution postulated by the model, it can still be shown* that for "unimodal" error distributions (those whose probability density functions decrease from their maximum values) that fewer than 5 in 100 future measurements would be expected to fall outside the control limits. Consequently, control charts are also quite useful when normal models are inappropriate.

Once the control chart has been constructed, future measurement control data are plotted on it. It is very important that those future data be obtained by faithfully reproducing the entire measurement process to be used when items are actually measured for accountability. Otherwise, behavior of the plotted values may fail to adequately reflect behavior of the accountability measurements, rendering the control charting exercise pointless.

From the records of the Los Alamos Plutonium Facility, 20 measured values listed in Table II (acquired from once-daily weighings of the standard immediately following collection of the data in Table I) were obtained and are plotted in Fig. 3. When the balance is working properly, such plots should contain very few points outside the control limits and the chart should not exhibit discernable trends. For example, there should be no sudden change in measurement behavior, nor should any predictable drift in measured values be apparent. When large discrepancies between the measured values and the mass of the standard or other anomalies are detected, action to rectify the situation (for example, balance recalibration) should be taken.

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*This is done using the Camp-Meidel extension of Chebyshev's Theorem (see standard quality control texts, such as Ref. 12).

TABLE II

MORE MEASUREMENT DATA FROM AN ELECTRONIC BALANCE

(Values in Grams)

Measurement i	Value x_i	Measurement i	Value x_i
101	4001.7	111	4001.7
102	4001.5	112	4001.4
103	4001.5	113	4001.4
104	4001.7	114	4001.8
105	4001.6	115	4001.7
106	4001.5	116	4001.6
107	4001.5	117	4001.6
108	4001.3	118	4001.5
109	4001.5	119	4001.7
110	4001.5	120	4001.5

Another aspect of the use of control charts is that control limits should be updated periodically based on recently accumulated information. In the example at hand, the true standard deviation σ could be re-estimated based on all 120 measured values, and new limits for future measurement control could be obtained.

There are many types of control charts other than the one displayed in Fig. 3. Cusum charts, which plot the cumulative sum of differences between individual measured values and the central line value, are often helpful in detecting trends. For monitoring potential changes in variability over time, s charts are sometimes used. Charts involving moving averages of important quantities may also be constructed. Moreover, separate charts could be kept for each person operating the balance, each different standard that is weighed, and so on. Proper use of such charts cannot be adequately covered in a few paragraphs, and the reader is advised to consult the literature (see Refs. 12-14 and also the bibliography given in Ref. 15).

In any situation, some discretion is involved in establishing the amount of measurement control activity, number of control charts, and other related efforts. At one extreme, a complete lack of any checks on instrument performance leads to obvious problems. At the other extreme, productivity decreases when too much time and manpower are devoted to obtaining measurement control data and maintaining numerous control charts instead of being devoted to other work. Indeed, if the instrument is functioning properly and operating personnel know it, a great deal of measurement control is unnecessary. Finally, the time spent using control charts and similar tools to identify that an instrument is not functioning properly represents only a portion of the overall program--still more time may be required to isolate the cause(s) of the trouble and to make needed adjustments or repairs.

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CHAPTER IV

PART TWO: ERROR PROPAGATION

by

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I. EXACT RESULTS

Estimated values, such as a measured weight of a standard, are often composed of a single measurement. Many important quantities, however, are the result of combining several measurements. For example, an NDA-based estimate may require two count rates (one for the source plus background and another for the background alone) and a calibration constant (to convert the observed net count rate to an estimated value). Other simple examples include quantities obtained by multiplying measured volumes by measured concentrations and net weights determined by subtracting tare weights from gross weights. More generally, a facility materials balance is a combination of a large number of measurements. Uncertainties attached to complex estimates are functions of the uncertainties in the individual measured values that are combined.

To illustrate some of the issues involved, consider an NDA-based estimate, M_1, that is obtained as

$$M_1 = (s_1 - b_1)/c \quad ,$$

where s_1 is the observed count rate of the source plus background, b_1 is the observed count rate of the background alone, and c is the estimated calibration constant. Errors in s_1, b_1, and c all contribute to the error in M_1.

Suppose now that another item is counted and a second estimate M_2 is obtained as

$$M_2 = (s_2 - b_2)/c \quad ,$$

where s_2 and b_2 are count rates of this source plus background and background alone, and c is the same estimated calibration constant used in M_1 above. The effect of M_1 and M_2 both depending on c is to induce a tendency for M_1 and M_2 to both exceed or to both fall short of their "true" values. To illustrate the point, suppose that the net count rates can be obtained exactly and that the only source of error is in estimation of the calibration constant. If the error in the estimate c is such that c exceeds the actual calibration constant, then both M_1 and M_2 will be less than their actual values. Conversely, if the error in c is in the opposite direction, both M_1 and M_2 will exceed their actual values.

In actuality, errors in the count rates s_1, s_2, b_1, and b_2 also contribute to errors in M_1 and M_2, so that it is possible for one of the measured values to exceed its actual value while the other does not. Nonetheless, a tendency for both to behave similarly exists, and this tendency affects accountability decisions. For example, suppose that it were of interest to assess the sum $M_1 + M_2$ of the two measured values. Because of the positive correlation between M_1 and M_2, the individual errors in M_1 and M_2 cannot be expected to "cancel" each other to the same extent as would be the case if the measurements were unrelated. It follows that the standard deviation of $M_1 + M_2$ is larger in the presence of positive correlation than otherwise.

In the above example, M_1 and M_2 varied together in such a way that both tended to exceed or fall short of their true values. In general, a quantitative measure of the degree to which two measurements vary together is the covariance. If μ_1 and μ_2 are the actual means of the distributions of generic measured values m_1 and m_2, respectively, the covariance σ_{12} between m_1 and m_2 is defined as the mean of the distribution of the product $(m_1 - \mu_1)(m_2 - \mu_2)$. In the above (hypothetical) example involving NDA-based measurements M_1 and M_2, $(M_1 - \mu_1)$ and $(M_2 - \mu_2)$ tend to be either both positive or both negative because of the dependence on the same calibration constant c, so that the product $(M_1 - \mu_1)(M_2 - \mu_2)$ tends to be positive, and it follows that the covariance is positive also.

In general, the mean and standard deviation of a function of measured values m_1 and m_2, such as the sum, $m_1 + m_2$, or product, $m_1 m_2$, may depend on the covariance, denoted σ_{12}. Methods of formally calculating means and standard deviations of several functions of m_1 and m_2 are outlined below, and specific examples are subsequently given. Extensions of the stated results to functions of more than two measured values are provided in the Appendix.

The formulas presented are primarily useful in estimating means and standard deviations of functions of m_1 and m_2. Though such formulas involve the actual means and standard deviations of m_1 and m_2, estimates of these quantities can be substituted into the formulas to yield estimated results for functions of interest. Also, the effects of improving the precisions of underlying measurements can be quantitatively evaluated with respect to the overall reduction of variability in the final estimate.

Mathematical formulas of interest are now derived and are followed by several examples illustrating their use. The following notation is used:

The distribution of m_1 has mean μ_1 and standard deviation σ_1.
The distribution of m_2 has mean μ_2 and standard deviation σ_2.
The covariance between m_1 and m_2 is σ_{12}.

Exact Formulas for Means and Standard Deviations

E1. For c_1 and c_2 specified constants, the mean of the distribution of $c_1m_1 + c_2$ is

$$c_1\mu_1 + c_2 \quad ,$$

and the standard deviation is

$$\sqrt{c_1^2\sigma_1^2} \quad .$$

E2. For c_1 and c_2 specified constants, the mean of the distribution of $(c_1m_1 + c_2m_2)$ is

$$(c_1\mu_1 + c_2\mu_2) \quad ,$$

and the standard deviation is

$$\sqrt{c_1^2\sigma_1^2 + c_2^2\sigma_2^2 + 2c_1c_2\sigma_{12}} \quad .$$

E3. For c_1, c_2, k_1, and k_2 specified constants, the covariance between $(c_1m_1 + c_2m_2)$ and $(k_1m_1 + k_2m_2)$ is

$$c_1k_1\sigma_1^2 + c_2k_2\sigma_2^2 + \sigma_{12}(c_1k_2 + c_2k_1) \quad .$$

E4. The mean of the distribution of the product m_1m_2 is

$$\mu_1\mu_2 + \sigma_{12} \quad .$$

E5. For c_1, c_2, and c_{12} specified constants, the mean of the distribution of $(c_1m_1^2 + c_2m_2^2 + c_{12}m_1m_2)$ is

$$c_1(\mu_1^2 + \sigma_1^2) + c_2(\mu_2^2 + \sigma_2^2) + c_{12}(\mu_1\mu_2 + \sigma_{12}) \quad .$$

E6. If m_1 and m_2 are "independent," the standard deviation of the distribution of the product m_1m_2 is

$$\sqrt{\mu_1^2\sigma_2^2 + \mu_2^2\sigma_1^2 + \sigma_1^2\sigma_2^2}$$

(if m_1 and m_2 are jointly normally distributed, independent means that $\sigma_{12} = 0$; for a definition of independence when nonnormal distributions are involved, see standard statistical texts as cited in Part One: Statistical Concepts).

Simple Examples of Exact Formulas

(a) Suppose that the mean and standard deviation of m_1 are 4001.566 g and 0.151 g, respectively. Conversion to kilogram units is accomplished through use of a scale factor. Applying Formula E1 with $c_1 = 0.001$ and $c_2 = 0$, the mean and standard deviation are 4.001566 kg and 0.000151 kg.

(b) The mean and standard deviation of the distribution of the sum $m_1 + m_2$, obtained using Formula E2 with $c_1 = c_2 = 1$, are $\mu_1 + \mu_2$ and $\sqrt{\sigma_1^2 + \sigma_2^2 + 2\sigma_{12}}$. The mean and standard deviation of the distribution of the average $(m_1 + m_2)/2$, obtained using Formula E2 with $c_1 = c_2 = 1/2$, are $(\mu_1 + \mu_2)/2$ and $(\sqrt{\sigma_1^2 + \sigma_2^2 + 2\sigma_{12}})/2$.

(c) Suppose that in measuring a certain item, m_1 is the measured volume of the item and m_2 is the measured concentration of a certain element. Then the product m_1m_2 estimates the total quantity of the element in the item and, because m_1 and m_2 are reasonably presumed independent, Formulas E4 and E6 imply that the mean and standard deviation of the distribution of the product m_1m_2 are $\mu_1\mu_2$ and $\sqrt{\mu_1^2\sigma_2^2 + \mu_2^2\sigma_1^2 + \sigma_1^2\sigma_2^2}$.

(Important note. If only a portion of the item is sampled and its concentration measured, then sampling errors may be present. That is, if the material in the item is not perfectly homogeneous, the actual concentration of the portion sampled may not equal the actual overall concentration for the item. Even if the sample could be measured exactly, the estimated quantity for the entire item would not be exact. When using a sample's measured concentration to estimate the item's concentration, it is necessary to incorporate sampling error into the standard deviation of the concentration estimate of the item.)

(d) Suppose $\mu_1 = \mu_2$ and $\sigma_1 = \sigma_2$, so that the distributions of m_1 and m_2 have the same mean and standard deviation. This situation is common if m_1 and m_2 correspond to repeated measurements of a specific item.

Letting $\bar{m} = (m_1 + m_2)/2$ denote the average value, application of the formula for the sample variance (see Part One: Statistical Concepts) gives

$$s^2 = \sum_{i=1}^{2} (m_i - \bar{m})^2/(2 - 1) = (m_1^2 + m_2^2 - 2m_1m_2)/2 \quad .$$

Applying Formula E5 establishes that the mean of the distribution of this function is $\sigma_1^2 - \sigma_{12}$. (This result also holds for a sample variance computed from $n > 2$ measurements with common variance and covariance.) If $\sigma_{12} = 0$, the mean value is the common variance σ_1^2, so that s^2 is an unbiased estimate of σ_1^2.

II. PROPAGATION OF ERROR FOR A SINGLE MEASURED VALUE

The previous section examined variance calculations for certain functions of one or two measured values. For other functions of measured values, it is often impractical or inconvenient to calculate variances exactly. The mathematics of certain nonlinear functions can be cumbersome, and exact results may depend on specific distributional assumptions (for example, whether the distribution of m_1 is normal), unlike the Formulas E1-E6 that apply to normal and nonnormal distributions. In such circumstances, propagation of error formulas are useful in approximating mean and standard deviations. The term "error propagation" is not widely used in the statistics world; commonly used names for this procedure include "the delta method," "the method of statistical differentials," "the Taylor method," and "the infinitesimal jackknife." Some elementary references on uncertainty estimation include Refs. 1-4.

Statistical theory underlying error propagation for a single measured value is reviewed in this section. As before, begin with the following notation regarding the measured value m_1:

The distribution of m_1 has mean μ_1 and standard deviation σ_1.

The basic problem of error propagation is to approximate the mean and standard deviation of some function $f(m_1)$. In other words, it is desired to determine how uncertainty in m_1 "propagates" into uncertainty in some function of m_1.

The conventional approach to this problem invokes the Taylor series expansion. That result, common to elementary calculus, says that if a continuously differentiable function f(x) satisfies certain boundedness constraints, then f(x) can be written as

$$f(x) = f(x_o) + f'(x_o)(x - x_o) + f''(x_o)(x - x_o)^2/2 + \dots + f^{(n)}(x_o)(x - x_o)^n/n! + \dots \quad , \tag{1}$$

where x_o is a given value, f' is the first derivative of f, f'' is the second derivative of f, and so on. (Because functions that are not differentiable are rarely of safeguards interest, they are not considered here.)

Error propagation uses the representation of Eq. (1) and approximates the function f ignoring higher-order terms. That is, the function $f(m_1)$ is expanded about the mean μ_1 of m_1, giving

$$f(m_1) \simeq f(\mu_1) + f'(\mu_1)(m_1 - \mu_1) \quad . \tag{2}$$

The approximation [Eq. (2)] uses the first two terms of the Taylor series expansion--the two most important terms. Given this approximation, the rationale is straightforward: if $f(m_1)$ is approximately equal to $f(\mu_1) + f'(\mu_1)(m_1 - \mu_1)$, then the mean and standard deviation of $f(m_1)$ are approximately equal to the mean and standard deviation of $f(\mu_1) + f'(\mu_1)(m_1 - \mu_1)$. Thus follows the general rule as expressed in Formula A1.

Approximate Formula for the Mean and Standard Deviation

A1. The mean of the distribution of $f(m_1)$ is approximately $f(\mu_1)$ and the standard deviation is approximately $\sigma_1\sqrt{[f'(\mu_1)]^2}$.

Simple Examples of the Approximate Formula

(a) Similar to example (a) for the exact formulas of the previous section, let $f(m_1) = cm_1$, where c is a specified constant. Then $f'(\mu_1) = c$, and, by Formula A1, the mean of the distribution of $f(m_1)$ is approximately $f(\mu_1) = c\mu_1$, and the standard deviation is approximately $\sigma_1\sqrt{c^2}$. By formula E1, it is seen that these approximations are, in this instance, exact.

(b) Let $f(m_1) = m_1^2$, so that $f'(\mu_1) = 2\mu_1$. By Formula A1, the approximate mean of $f(m_1)$ is μ_1^2, and the approximate standard deviation is $\sigma_1\sqrt{(2\mu_1)^2} = 2\sigma_1\sqrt{\mu_1^2}$. By Formula E5 with $c_1 = 1$ and $c_2 = c_{12} = 0$, the exact mean of $f(m_1)$ is $\mu_1^2 + \sigma_1^2$, which is close to the approximate result when σ_1 is small relative to μ_1. If the distribution of m_1 is normal, it can be shown that the exact standard deviation of $f(m_1)$ is $2\sigma_1\sqrt{\mu^2 + \sigma_1^2/2}$. Again, the approximation is good if σ_1 is small relative to μ_1.

(c) Suppose that the mean μ_1 of the distribution of m_1 is written μ_1 = actual value + bias. Then the approximate mean of the distribution of $f(m_1)$ is f(actual value + bias), and the approximate bias in $f(m_1)$ is f(actual value + bias) - f(actual value). In this way, it is possible to "propagate bias" for nonlinear functions f.

(d) Let $f(m_1) = 1/m_1$, so that $f'(\mu_1) = -1/\mu_1$. Using Formula A1, the mean of the distribution of $1/m_1$ is approximately $1/\mu_1$, and the standard deviation is approximately σ_1/μ_1. If the distribution of m_1 is normal, it can be shown that neither the mean nor the standard deviation of $1/m_1$ is finite. In some sense, the approximations are poor, although in many cases the derivation of confidence limits using propagated results is still justified. The result is implicitly used in the derivation of confidence intervals for many calibrated values--e.g., when m_1 corresponds to a calibration constant that is used to convert an observed net count rate to a measured value.

As indicated in the examples, the closeness of error propagation results from Formula A1 to exact results can vary. Three important factors in this regard concern the relative standard deviation σ_1/μ_1 of m_1, the form of the function f involved, and the particular distribution of m_1. As a general rule, the approximations using error propagation are best when

(1) the relative standard deviation is small,

(2) the function f is "smooth" in a neighborhood of $m_1 = \mu_1$, and

(3) the distribution is well behaved (for example, approximate normality qualifies).

Because conditions (1), (2), and (3) are usually satisfied in most safeguards applications, propagation of error is a very useful technique for estimating means and standard deviations.

A geometric interpretation is useful with respect to conditions (1) and (2). Consider drawing a graph of $f(m_1)$; one such example is given in Fig. 1. The function f can be thought of as tracing out a curve. The right-hand side of Eq. (2) represents the tangent line to the curve. That line intersects the curve at the point $(x,y) = (\mu_1, f(\mu_1))$ and has slope $f'(\mu_1)$. The region of interest, or range of measured values that would be anticipated, falls within $2\sigma_1$ or $3\sigma_1$ of $x = \mu_1$. When condition (1) holds, as in most applications, σ_1 is small relative to μ_1, so that the tangent line closely approximates the smooth curve over the relatively narrow region of interest; thus propagated means and standard deviations closely approximate their exact counterparts.

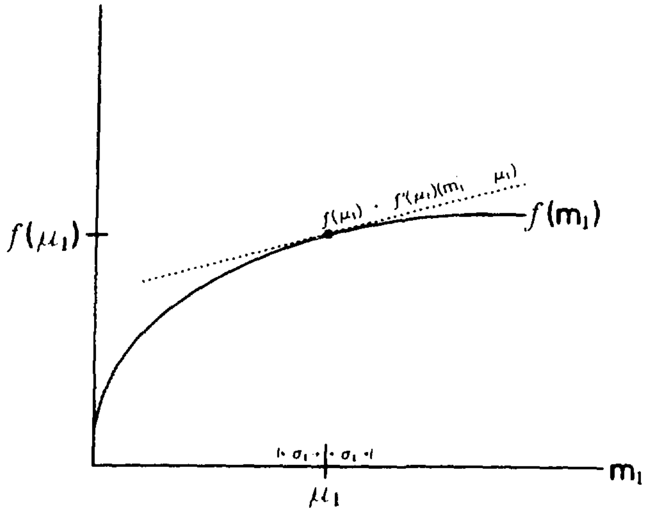

Fig. 1.
Tangent approximation to a continuous function $f(m_1)$.

III. PROPAGATION OF ERROR FOR SEVERAL MEASURED VALUES

The principles underlying propagation of error for a single measured value extend directly to propagation of error for two or more measured values. A function of several measured values can be represented using the multivariate version of the Taylor expansion and the mean and standard deviation of the first-order approximation computed.

Error propagation results have several uses. The first is to provide estimates of uncertainty, which are commonly pursued by direct substitution of estimated values into the formulas to follow. By substituting the observed measured values $\{m_i\}$ for their corresponding means $\{\mu_i\}$ and inserting estimates for the standard deviations $\{\sigma_i\}$ and covariances $\{\sigma_{ij}\}$, an estimate of the standard deviation of $f(m_1,m_2,\ldots m_n)$ is obtained. Because this substitution is prone to the GIGO ("garbage in, garbage out") phenomenon, it is important that the substituted values be of good quality. Resulting uncertainty estimates often have a very slight bias but are nonetheless quite useful.

The second use of error propagation provides uncertainty estimates for uncertainty estimates. Substitution of estimated values into the formula for the approximate standard deviation of $f(m_1,m_2,\ldots m_n)$ simply defines another function, say, $g(m_1,\ldots,m_n,\hat{\sigma}_1,\ldots,\hat{\sigma}_n,\ldots,\hat{\sigma}_{ij}\ldots)$. By applying the aforementioned theory to the function g, the standard deviation of an estimated standard deviation can be quantified.

The third use of error propagation is for sensitivity studies. Once the standard deviation of a function is expressed in terms of the individual measurement uncertainties, it is possible to determine which individual uncertainties have the greatest impact on the overall uncertainty. The potential value of working to reduce specific individual uncertainties can then be examined.

To develop specific results, the following notation is used. For a function $f(m_1,m_2,\ldots,m_n)$ of the measured values $\{m_i\}$, the first-order Taylor series approximation is

$$f(m_1,m_2,\ldots,m_n) \simeq f(\mu_1,\mu_2,\ldots,\mu_n) + \sum_i d_i(m_i - \mu_i) \quad , \tag{3}$$

where

$$d_i = \partial f(\mu_1,\mu_2,\ldots,\mu_n)/\partial\mu_i \quad .$$

Equation (3) generalizes Eq. (2) of the previous section, where propagation of error for a single measured value was considered. The propagated mean and standard deviation of $f(m_1,m_2,\ldots m_n)$ are obtained using the right-hand side of Eq. (3), giving the general rules.

Approximate Formulas for the Mean, Standard Deviation, and Covariance

A2. The mean of the distribution of $f(m_1,m_2,\ldots m_n)$ is approximately $f(\mu_1,\mu_2,\ldots\mu_n)$, and the standard deviation is approximately

$$\sum_{i=1}^{n} d_i^2\sigma_i^2 + \sum_{\substack{i=1 \\ i\neq j}}^{n} \sum_{j=1}^{n} d_i d_j \sigma_{ij} \quad .$$

A3. Given another function $\tilde{f}(m_1,m_2,\ldots m_n)$ corresponding to partial derivatives $\{\tilde{d}_i\}$, where

$$\tilde{d}_i = \partial\tilde{f}(\mu_1,\mu_2,\ldots,\mu_n)/\partial\mu_i \quad ,$$

it follows that the covariance between $f(m_1,m_2,\ldots m_n)$ and $\tilde{f}(m_1,m_2,\ldots m_n)$ is approximately

$$\sum_{i=1}^{n} d_i\tilde{d}_i\sigma_i^2 + \sum_{\substack{i=1 \\ i\neq j}}^{n} \sum_{j=1}^{n} d_i\tilde{d}_j\sigma_{ij} \quad .$$

This result is equivalent to finding the exact covariance between the first-order approximations of f and $\tilde{f}$.

Simple Examples of Approximate Formulas

(a) Let $f(m_1) = m_1$ and $\tilde{f}(m_1) = m_1^2$, so that $d_1 = 1$ and $\tilde{d}_1 = 2\mu_1$. By Formula A3, the covariance between $f(m_1)$ and $\tilde{f}(m_1)$ is $2\mu_1\sigma_1^2$. If the distribution of m_1 is normal, it can be shown that the approximation is exact.

(b) Let $f(m_1,m_2) = m_1m_2$, so that $d_1 = \mu_2$ and $d_2 = \mu_1$. By Formula A2, the distribution of m_1m_2 has mean approximately equal to $\mu_1\mu_2$ and standard deviation approximately equal to

$$\sqrt{\mu_1^2\sigma_2^2 + \mu_2^2\sigma_1^2 + 2\mu_1\mu_2\sigma_{12}} \quad .$$

By Formula E4, the mean is exactly $\mu_1\mu_2 + \sigma_{12}$. By Formula E6, if m_1 and m_2 are independent, then the standard deviation of m_1m_2 is

$$\sqrt{\mu_1^2\sigma_2^2 + \mu_2^2\sigma_1^2 + \sigma_1^2\sigma_2^2} \quad .$$

When the $\{\sigma_i\}$ are small relative to the μ_i, the approximation is quite good.

(c) Suppose m_2, a tank volume, is the quantity of interest but m_1, a monometer reading, constitutes the observed measurement. A calibration determines m_2, the relationship being

$$\begin{aligned} m_1 &= g(m_2,a,b,c) \\ &= am_2^2 + bm_2 + c \quad , \end{aligned}$$

where a, b, and c are calibration constants. Then $m_2 = g^{-1}(m_1,a,b,c)$, where g^{-1} inverts the calibration function g and expresses m_2 as a function of m_1, a, b, and c. Applying Formula A2 for the function f taken to be $g^{-1}(m_1,a,b,c)$ leads to the propagated mean and standard deviation for the estimated tank volume m_2.

Unfortunately, this is somewhat complex mathematically. In the present example,

$$0 = am_2^2 + bm_2 + c - m_1 \quad ,$$

and inversion using the quadratic formula for the desired (greater) root gives

$$\begin{aligned} m_2 &= (1/2a)(-b + \sqrt{b^2 - 4ac + 4am_1}) \\ &= g^{-1}(m_1,a,b,c) \quad . \end{aligned}$$

Differentiation of g^{-1} with respect to m_1, a, b, and c can be pursued in a straightforward fashion. For example,

$$\frac{\partial g^{-1}(m_1,a,b,c)}{\partial a} = \frac{b}{2a^2} + \frac{(m_1 - c)}{a\sqrt{b^2 - 4ac + 4am_1}} - \frac{\sqrt{b^2 - 4ac + 4am_1}}{2a^2} \quad . \tag{4}$$

Calculations are simpler when viewed in a different light. Define the function

$$\begin{aligned} h(m_1,m_2,a,b,c) &= g(m_2,a,b,c) - m_1 \\ &= am_2^2 + bm_2 + c - m_1 \end{aligned} \tag{5}$$

to be the difference between the calibration function g and the measured value m_1. By construction, h is equal to a constant (zero), and the implicit function theorem from elementary calculus implies that

$$\frac{\partial m_2}{\partial a} = \frac{\partial g^{-1}(m_1,a,b,c)}{\partial a}$$

$$= - \frac{\{\partial h(m_1,m_2,a,b,c)/\partial a\}}{\{\partial h(m_1,m_2,a,b,c)/\partial m_2\}} \qquad (6)$$

$$= - \frac{m_2^2}{(2am_2 + b)} \quad , \qquad (7)$$

which is considerably easier to obtain than Eq. (4). Substitution of $m_2 = (1/2a)(-b + \sqrt{b^2 - 4ac + 4am_1})$ into Eq. (7) and some algebra can verify that Eq. (7) equals Eq. (4).

Derivatives of m_2 with respect to b, c, and m_1 can be computed similarly, for example,

$$\frac{\partial g^{-1}(m_1,a,b,c)}{\partial b} = - \left\{\frac{\partial h(m_1,m_2,a,b,c)}{\partial b}\right\} \bigg/ \left\{\frac{h(m_1,m_2 a,b,c)}{\partial m_2}\right\} \quad .$$

After evaluating such derivative at $m_1 = \mu_1$ and so on, Formula A2 can be implemented. (The implicit function theorem requires that the calibration function g satisfy certain regularity conditions, although this is not an obstacle in most applications.)

Importantly, construction of the function h, as in Eq. (5), allows for the derivative Eq. (6) of g^{-1} to be computed without (explicit) knowledge of the functional form of g^{-1}. For certain calibration functions involving higher-order polynomials or other nonlinearities, it may be difficult to explicitly determine the function's inverse and/or to differentiate it, and implicit differentiation as above is advised for error propagation in such cases.

Similar to propagation of error for a single measured value, the closeness of propagated standard deviations to their actual counterparts can vary. Generally, results are good when the tangent plane approximation in Eq. (3) is close to $f(m_1,m_2,...,m_n)$ over the region of measured values that would be anticipated. If the approximation using Formula A2 is not adequate, alternatives--such as computing the standard deviation of the second-order Taylor's series approximation instead of the first order approximation in Eq. (3) or else doing the theory exactly--exist. These alternatives are usually unnecessary but can be helpful in cases where the measured values have skewed distributions or where the function f is distinctly nonlinear over the region of interest.

At a somewhat more esoteric level, research into the subject of statistical curvature has led to evaluations of how well the usual Taylor series expansions work in more complicated settings. Although the details are beyond the scope of this presentation, curvature[5] is basically a quantitative measure of how "nearly linear" something is. As intuition suggests, the lower the curvature, the better the standard techniques based on first-order approximations perform. Work in the context of nonlinear regression[6] indicates that exceptions to the general rules exist, but such exceptions are extremely rare in safeguards applications.

IV. ERROR PROPAGATION FOR MATERIALS BALANCES

Return to the fundamental materials balance equation,

$$MB = BI + R - S - EI \quad , \tag{8}$$

where

MB denotes the materials balance,
BI denotes the beginning inventory,
R denotes the receipts or input transfers,
S denotes the shipments or output transfers, and
EI denotes the ending inventory.

Because each of the components of the materials balance equation appears to be obtained in a known fashion using measured values, the observed materials balance appears to be a known function of measured values. Thus, it is straightforward--in principle--to use the theory described in the previous section to propagate errors for MB for evaluation of potential loss. Although the magnitude of the computational problem can be large owing to the number of individual measured values in the MB of a facility, application of the theory is conceptually simple.

Unfortunately, such a conceptually simple approach often does not work well in practice. The main reason for this, aside from poorly quantified measurement uncertainties, involves the role of nonmeasurement contributors to the materials balance. At most facilities, each of the terms in Eq. (8) can be thought of as having measured and unmeasured components. For example, we could write

$$BI = BI_{meas} + BI_{unmeas}$$

and

$$S = S_{meas} + S_{unmeas} \quad .$$

The term BI_{meas} consists of all items measured for inventory, whereas the term BI_{unmeas} consists of other material, including process holdup or "hidden inventory." Similarly, unmeasured waste streams and, potentially, diversion are included in S_{unmeas}. Moreover, factors not generally considered as measurement errors per se (such as transcription errors, prior period book adjustments, and outright mistakes in bookkeeping) can also be viewed as nonmeasurement contributors to the MB.

Considering each of the terms of the MB equation as having measured and unmeasured components, substitution into Eq. (8) gives, after rearranging terms,

$$\begin{aligned} MB + (EI_{unmeas} - BI_{unmeas}) + (S_{unmeas} - R_{unmeas}) \\ = BI_{meas} + R_{meas} - S_{meas} - EI_{meas} \\ = MB_{meas} \quad , \qquad (9) \end{aligned}$$

where the MB_{meas} is defined as the collection of all components measured for inclusion in the materials balance. From Eq. (9), it is seen that even if all measurements could be made exactly, the observed materials balance would not equal the actual materials balance; rather, it would equal the MB plus effects of changes in facility holdup plus effects of unmeasured waste streams and so on.

The presence of measurement errors means the observed materials balance has the form

$$\begin{aligned} MB_{observed} = MB_{meas} + e \\ = MB + [(EI_{unmeas} - BI_{unmeas}) + (S_{unmeas} - R_{unmeas})] + e \quad , \qquad (10) \end{aligned}$$

where the term e denotes the combined effects of measurement errors. In the most idealistic case, the effects over time of the nonmeasurement contributors and of the measurement errors behave as stationary sequences independent of each other, and Eq. (10) can loosely be thought to imply that

$$\begin{aligned} \text{Variance } (MB_{observed}) = \text{Variance(effect of nonmeasurement contributors)} \\ + \text{Variance(effect of measurement errors)} \quad . \qquad (11) \end{aligned}$$

The major implication of Eq. (11) is that propagation of measurement errors alone frequently does not explain behavior of observed materials balances. Control limits for the MBs derived from measurement errors alone will be too narrow.

Derivation of meaningful control limits for materials balances is an important issue, and the proper treatment of nonmeasurement contributors has been a source of regulatory concern. The above discussion is not intended to judge the various prospective procedures for dealing with nonmeasurement contributors, but instead is designed to indicate the sources of difficulties in establishing control limits.

V. APPLICATION OF ERROR PROPAGATION TO AN EXAMPLE UF_6 CONVERSION PROCESS

This section illustrates application of the error propagation results for an example UF_6 conversion process. The standard deviation of the quarterly (3-month) materials balance is derived using error estimates for the terms in the balance equation. Error estimates as cited below are consistent with those given in the literature.[7] For purposes of demonstration, it is presumed that this process has negligible nonmeasurement contributions to the materials balance, so that propagation of measurement errors alone adequately describes observed behavior.

The materials balance equation here is written

$$MB = BI + \sum_{i=1}^{D} I(i) - \sum_{i=1}^{D} P(i) - \sum_{i=1}^{D} W(i) - EI \quad , \tag{12}$$

where

BI is the measured beginning inventory,

D is the number of days of processing in the quarter,

I(i) is the measured input for the i^th^ day of processing,

P(i) is the measured product for the i^th^ day of processing,

W(i) is the measured waste for the i^th^ day of processing, and

EI is the measured ending inventory.

Sometimes the "product" and "waste" terms are combined into a single "output" term, but this is not done here for reasons that will become apparent.

The first step in deriving the standard deviation of the distribution of the MB is to consider each term in Eq. (12) separately. The (multiplicative) model for the measured value of the beginning inventory is

$$BI = t_{BI}\,[1 + e(BI)] \quad , \quad \text{where } e(BI) \sim N[0,\, \sigma^2_{e(BI)}] \quad , \tag{13}$$

t_{BI} is the actual beginning inventory, and e(BI) is the relative measurement error. For the purpose of this example, the values

$$t_{BI} = 20 \text{ tons of uranium (U)} \quad \text{and} \quad \sigma_{e(BI)} = 0.2\%$$

are used. It follows that the standard deviation σ_{BI} of the measured beginning inventory is, using Formula E1 of Sec. I,

$$\sigma_{BI} = t_{BI}\,\sigma_{e(BI)} = 0.040 \text{ ton U} \quad . \tag{14}$$

In actuality, the model for the beginning inventory, Eq. (13), is a rough approximation, and the standard deviation σ_{BI} should be propagated using knowledge of properties of the individual measurements involved in the beginning inventory. Because that propagation is quite lengthy and often involves incorporation of so-called systematic errors, which largely cancel when the ending inventory is subtracted, the simplified approximation is used for illustrative purposes.

The second term in Eq. (12), the balance equation, is the sum of the measured daily inputs, $\sum I(i)$. The model for I(i) here is

$$I(i) = t_{I(i)}\,\{1 + \eta(I) + e[I(i)]\} \quad ,$$

where

$$\eta(I) \sim N[0, \sigma^2_{\eta(I)}] \quad \text{and} \quad e[I(i)] \sim N[0, \sigma^2_{e(I)}] ,$$

and $t_{I(i)}$ is the actual input for the i^{th} day of processing, $\eta(I)$ is the random effect, and $e[I(i)]$ is the relative random error. Summing the measured daily inputs gives

$$\sum_{i=1}^{D} I(i) = \sum_{i=1}^{D} t_{I(i)}[1 + \eta(I) + e(I(i)]$$

$$= \sum_{i=1}^{D} t_{I(i)} + \eta(I) \sum_{i=1}^{D} t_{I(i)} + \sum_{i=1}^{D} t_{I(i)}\, e[I(i)] \quad .$$

The standard deviation of $\eta(I) \sum t_{I(i)}$ is, using Formula E1 of Sec. I, equal to $\sigma_{\eta(I)} \sum t_{I(i)}$. The standard deviation of $\sum t_{I(i)} e[I(i)]$ is, using Formula E7 of the Appendix, equal to $\sigma_{e(I)}\sqrt{\sum t^2_{I(i)}}$. Because $\eta(I)$ and the random error terms, $\{e[I(i)]\}$, are uncorrelated, the standard deviation of the sum of measured inputs is, by Formula E2,

$$\sigma_{\sum I(i)} = \sqrt{\sigma^2_{\eta(I)}[\sum t_{I(i)}]^2 + \sigma^2_{e(I)} \sum t^2_{I(i)}} \quad . \tag{15}$$

For the purpose of this example, the values

$t_{I(i)} = 1$ ton U for all i, $D = 60$ days,

$\sigma_{\eta(I)} = 0.05\%$, and $\sigma_{e(I)} = 0.05\%$.

Substituting these values into Eq. (11) gives

$$\sigma_{\sum I(i)} = \sqrt{(0.0005)^2\ 60^2 + (0.0005)^2\ 60}\ \text{tons U}$$

$$= 0.030\ \text{ton U}\quad . \tag{16}$$

The third term in the balance equation is the sum of measured products, $\sum P(i)$. This term is treated similarly to the sum of measured inputs, and it follows [cf. Eq. (15)],

$$\sigma_{\sum P(i)} = \sqrt{\sigma^2_{\eta(P)}\ [\sum t_{P(i)}]^2 + \sigma^2_{e(P)}\ \sum t^2_{P(i)}}\ ,$$

where $t_{P(i)}$ is the actual quantity of product for the i^{th} day of processing, and $\sigma_{\eta(P)}$ and $\sigma_{e(P)}$ are defined in the same manner as the terms $\sigma_{\eta(I)}$ and $\sigma_{e(I)}$ of Eq. (15). Using the values $t_{P(i)} = 0.988$ ton U for all i, $\sigma_{\eta(P)} = 0.05\%$, and $\sigma_{e(P)} = 0.05\%$, the standard deviation of the distribution of $\sum P(i)$ is [cf. Eq. (16)],

$$\sigma_{\sum P(i)} = \sqrt{(0.0005)^2[60(0.988)]^2 + (0.0005)^2 60(0.988)^2}\ \text{ton U}$$

$$= 0.030\ \text{ton U}\quad . \tag{17}$$

The fourth term in the balance equation is the sum of measured wastes, $\sum W(i)$, and its distribution has a standard deviation equal to

$$\sigma_{\sum W(i)} = \sqrt{\sigma^2_{\eta(W)}\ [\sum t_{W(i)}]^2 + \sigma^2_{e(W)}\ \sum t^2_{W(i)}}\ ,$$

where all terms are defined analogous to the inputs and products. Taking the values $t_{W(i)} = 0.012$ ton U for all i, $\sigma_{\eta(W)} = 10\%$, and $\sigma_{e(W)} = 25\%$ implies

$$\sigma_{\sum W(i)} = \sqrt{(0.10)^2\ [60(0.012)]^2 + (0.25)^2 60(0.012)^2}\ \text{ton U}$$

$$= 0.076\ \text{ton U} \quad . \tag{18}$$

Here the waste is measured poorly relative to the other terms in the balance equation. The total quantity of waste, 0.8 ton U for the balance period, is large (the daily input was 1.0 ton U), and thus the errors in estimation of waste contribute the most to the variability in the observed material balance.

The final term in the balance equation is the measured ending inventory, EI. The model for EI is

$$EI = t_{EI}[1 + e(EI)], \quad \text{where} \quad e(EI) \sim N(0, \sigma^2_{EI})$$

for t_{EI} the actual ending inventory and e(EI) is the relative measurement error. As with the beginning inventory, the values

$$t_{EI} = 20\ \text{tons U} \quad \text{and} \quad \sigma_{e(EI)} = 0.2\%$$

are taken, giving

$$\sigma_{EI} = 0.040\ \text{ton U} \quad . \tag{19}$$

The standard deviation of the distribution of the materials balance can now be computed using the standard deviations of the individual terms. Recall from Eq. (12) that

$$MB = BI + \sum_{i=1}^{D} I(i) - \sum_{i=1}^{D} P(i) - \sum_{i=1}^{D} W(i) - EI \quad .$$

Because the five terms on the right hand-side of this balance are mutually uncorrelated in this example (i.e., the covariance between any pair of the terms is zero), it follows from Formula E7 of the Appendix and Eqs. (14), (16), (17), (18), and (19) that the standard deviation of the MB is

$$\sigma_{MB} = \sqrt{\sigma^2_{BI} + \sigma^2_{\sum I(i)} + \sigma^2_{\sum P(i)} + \sigma^2_{\sum W(i)} + \sigma^2_{EI}}$$

$$= \sqrt{(0.040)^2 + (0.033)^2 + (0.032)^2 + (0.076)^2 + (0.040)^2} \text{ tons U}$$

$$= 0.104 \text{ ton U} \quad .$$

This standard deviation, ~104 kg U, is roughly 0.17% of the quarterly throughput (60 tons U). For many UF_6 conversion processes, the standard deviation of the materials balance is on the order of 0.10% to 0.25% of throughput.

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APPENDIX

ADDITIONAL FORMULAS

The Formulas E1-E6 deal with means and standard deviations of functions of one or two measured values. This appendix extends those results to functions of an arbitrary number of measured values. Desirability of complete generality occasionally results in lengthy formulas.

Notation. There are n measured values, denoted m_1, m_2, ..., m_n. The distribution of m_i has true mean μ_i and true standard deviation σ_i, for i = 1, 2, ..., n. The covariance between m_i and m_j is σ_{ij} for $i \neq j$.

Exact Formulas for Means and Standard Deviations

E7. (Extension of E2). For c_1, c_2, ..., c_n specified constants, the distribution of

$$\sum_{i=1}^{n} c_i m_i$$

has mean

$$\sum_{i=1}^{n} c_i \mu_i$$

and standard deviation

$$\sqrt{\sum_{i=1}^{n} c_i^2 \sigma_i^2 + \sum_{\substack{i=1 \\ i\neq j}}^{n} \sum_{j=1}^{n} c_i c_j \sigma_{ij}} \quad .$$

E8. (Extension of E3). For $c_1, c_2, \ldots, c_n$ and $k_1, k_2, \ldots, k_n$ specified constants, the covariance between

$$\sum_{i=1}^{n} c_i m_i \quad \text{and} \quad \sum_{i=1}^{n} k_i m_i$$

is

$$\sum_{i=1}^{n} c_i k_i \sigma_i^2 + \sum_{\substack{i=1 \\ i \neq j}}^{n} \sum_{j=1}^{n} c_i k_j \sigma_{ij} \quad .$$

E9. (Extension of E5). For $c_{11}, c_{12}, \ldots, c_{1n}; c_{21}, c_{22}, \ldots, c_{2n}; \ldots; c_{n1}, c_{n2}, \ldots, c_{nn}$, a specified set of constants, the distribution of

$$\sum_{i=1}^{n} \sum_{j=1}^{n} c_{ij} m_i m_j$$

has mean

$$\sum_{i=1}^{n} \sum_{j=1}^{n} c_{ij} \mu_i \mu_j + \sum_{i=1}^{n} c_{ii} \sigma_i^2 + \sum_{\substack{i=1 \\ i \neq j}}^{n} \sum_{j=1}^{n} c_{ij} \sigma_{ij} \quad .$$

E10. (Extension of E6). If measured values $\tilde{m}_1, \tilde{m}_2, \ldots, \tilde{m}_n$ are independent of $m_1, m_2, \ldots, m_n$, if the distribution of $\tilde{m}_i$ has mean $\tilde{\mu}_i$ and standard deviation $\tilde{\sigma}_i$, and if the covariance between $\tilde{m}_1$ and $\tilde{m}_j$ is $\tilde{\sigma}_{ij}$, then the distribution of

$$\sum_{i=1}^{n} m_i \tilde{m}_i$$

has mean

$$\sum_{i=1}^{n} \mu_i \tilde{\mu}_i$$

and standard deviation

$$\left\{ \sum_{i=1}^{n} \mu_i^2 \tilde{\sigma}_i^2 + \sum_{\substack{i=1 \\ i \neq j}}^{n} \sum_{j=1}^{n} \mu_i \mu_j \tilde{\sigma}_{ij} + \sum_{i=1}^{n} \tilde{\mu}_i^2 \sigma_i^2 + \sum_{\substack{i=1 \\ i \neq j}}^{n} \sum_{j=1}^{n} \tilde{\mu}_i \tilde{\mu}_i \sigma_{ij} \right.$$

$$\left. + \sum_{i=1}^{n} \sigma_i^2 \tilde{\sigma}_i^2 + \sum_{\substack{i=1 \\ i \neq j}}^{n} \sum_{j=1}^{n} \sigma_{ij} \tilde{\sigma}_{ij} \right\}^{1/2} .$$

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CHAPTER V

STATISTICAL DECISIONS

by

R. R. Picard

I. HYPOTHESIS TESTS: AN INDIVIDUAL MEASUREMENT

The subject of hypothesis testing was introduced in Chap. IV, Statistical Concepts. Data concerning repeated measurements of a nominally 4-kg standard were used to test the hypothesis that the electronic balance was biased. The test was not significant at the 5% level, and the hypothesis of no bias was consistent with the observed data.

A canister of low-enriched UO_2, weighing roughly 4 kg, is now weighed on the electronic balance. Because the balance is presumed unbiased, a model for the measured value, m, to be obtained is

$$m = t + e \quad , \quad \text{where} \qquad e \sim N(0,\sigma^2) \quad , \tag{1}$$

and t is the unknown actual weight of the canister. The standard deviation, σ, of the distribution of the measurement error e is unknown, and it is estimated using measurement control data by s = 0.151 g. Suppose that someone claims the actual weight of the canister is exactly 4 kg, but upon weighing the canister on the balance, the value 3999.4 g is obtained. Should the claim be accepted as true?

Following the methodology discussed in Chap. IV, Part One, Sec. VII, the hypotheses of interest are

$$H_0\text{:} \quad t = 4000 \text{ g} \qquad \text{and} \qquad H_1\text{:} \quad t \neq 4000 \text{ g} \quad .$$

The value 3999.4 g can be viewed as the sample mean from a "sample" of $n = 1$ measurement. As in Chap. IV, Sec. VII, Eq. (9), the test statistic

$$(m - t)/(s/\sqrt{n}) = (3999.4 - 4000.0)/(0.151/\sqrt{1}) \tag{2}$$

$$= -3.97$$

is obtained. The value -3.97 is less than -2, and the hypothesis H_0 is rejected at the 5% level. Equivalently, the limit of error for m is twice the standard deviation σ, estimated by

$$LE(m) = 2s = 0.302 \text{ g} \quad .$$

The observed weight, 3999.4 g, is more than its limit of error from the claimed weight.

Thus, it is concluded that the observed measurement is inconsistent with the hypothesis, H_0; if the item truly weighed exactly 4 kg, fewer than 5% of measured values would be as far from 4 kg as the value observed (3999.4 g). The decision is made that the canister does not weigh 4 kg.

This decision is based on the available information--one measurement. If the canister were measured several times, a different decision might be reached. Or, the same decision might be reached again, and even greater confidence placed in it. Intuitively, it is obvious that a hypothesis test based on several measurements of the canister is better than the test above, which was based on only a single measurement. The degree of improvement can be quantified.

The test above can be described as follows: make a single measurement and, if the measured value is farther from 4 kg than 2s = 0.302 g, then reject at the 5% level the hypothesis, H_0, that the true weight is exactly 4 kg. If, in fact, the canister actually weighed 3999.7 g, the correct decision would be to reject H_0. What is the probability that the test above makes the correct decision?

Assuming the canister actually weighs 3999.7 g, the model [Eq. (1)] becomes

$$m = 3999.7 + e \ , \text{ where } \quad e \sim N(0, \sigma^2) \quad , \tag{3}$$

and, again, σ is unknown and is estimated by $s = 0.151$ g. Neglecting mathematical details, it can be shown that based on Eq. (3), the probability that m will be within 0.302 g of 4 kg and H_0 would be accepted is almost exactly 50%. Stated differently, if the canister actually weighed 3999.7 g, the nondetection probability, or the probability of a failure to detect that the canister did not weigh 4 kg, is 50%.

Because of the inability to make error-free measurements, it is impossible to eliminate completely the chance of incorrect decisions. However, by making more measurements (or better measurements), the chances of a mistake are reduced. For example, suppose it were decided at the outset to weigh the canister twice instead of once, and that the measured values to be obtained, m_1 and m_2, are independent. Denoting the average of m_1 and m_2 by $\bar{m} = (m_1 + m_2)/2$, the test statistic based on $\bar{m}$ is [cf. Eq. (2)],

$$(\bar{m} - t)/(s/\sqrt{n}) = (\bar{m} - 4000)/(0.151/\sqrt{2}) \quad . \tag{4}$$

If the test statistic is greater than 2 or less than -2, the hypothesis H_0 is rejected at the 5% level.

Recall that the test based on a single measurement would fail to reject H_0 50% of the time when the actual weight was 3999.7 g. How much does making two independent measurements improve matters? Again neglecting mathematical details, it can be shown that the above test statistic, Eq. (4), rejects H_0 79% of the time when the canister weighs 3999.7 g. In other words, the nondetection probability is reduced from 50% to 21%. For tests based on 3 and 4 measurements, respectively, the nondetection probabilities drop to 8% and 3%. It is seen that a "diminishing returns" effect sets in and that successive measurements mean smaller gains with respect to nondetection.

When implementing test procedures, the potential for false alarms and nondetection should be considered. As expected, improving the quality of decisions through more and/or better measurements increases costs associated with the test. This tradeoff (cost of testing vs quality of decisions) is an important one in safeguards.

II. HYPOTHESIS TESTS: AN INDIVIDUAL MATERIALS BALANCE

A common decision problem involves evaluation of an individual materials balance. The principles of hypothesis testing for a materials balance are much the same as indicated in the previous section, where an individual measurement of a canister of UO_2 was made.

A key aspect of the decision process entails estimation of the standard deviation, σ_{MB}, of the materials balance. This estimation is done via error propagation; for instance, the standard deviation of the quarterly materials balance for an example UF_6 conversion process is estimated using error propagation to be 0.104 ton of uranium (ton U) (see Error Propagation, Chap. IV). The hypothesis of interest is generally that the actual materials balance is zero, and the test statistic is simply the observed materials balance divided by its estimated standard deviation.*

If the test statistic is greater than 2 or less than -2, the MB is significantly different from zero; e.g., if the quarterly materials balance above is greater than 0.208 ton U or less than -0.208 ton U, the hypothesis that the actual balance is zero is rejected at the 5% level.

The sensitivity of any test procedure to potential loss of material is limited by the quality of measurements. As illustrated in the previous section, the nondetection probability can be large when the loss is small relative to measurement error. For the example UF_6 conversion process, if the standard deviation (0.104 ton U) for the quarterly materials balance does not provide sufficient sensitivity, this issue must be resolved

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*The test statistic here is of the same form as Eq. (2) of the previous section. Here, the actual value of the materials balance is zero under H_0, and the MB is a sample mean, where the "sample" has n = 1 measurement. Also, the MB is presumed approximately normally distributed as a consequence of the central limit theorem (see Chap. IV, Sec. IV).

before processing begins. Unlike the situation of the previous section, where a canister of UO_2 was weighed, several components of the materials balance (e.g., inputs and wastes) cannot be remeasured at the end of the inventory period should questions of potential loss arise.

III. HYPOTHESIS TESTS: A SEQUENCE OF MATERIALS BALANCES

A. Introduction

The hypothesis tests discussed in Secs. I and II, dealing with an individual measured value and with an individual materials balance respectively, involved only a single decision. All necessary information was first obtained, and a single test statistic was then computed in each case. Such tests are known as fixed-length tests.

Other situations, however, demand more than a single decision. For example, suppose materials balances are closed frequently and that MB(i) denotes the balance for the i^{th} inventory period. For present purposes, MB(i) is perhaps best thought of as a materials balance closed around some area of processing and covering a shorter time period, such as one week. Any comprehensive decision process requires the evaluation of all available information; i.e., not only the most recent materials balance must be considered but also those from previous time periods. Ideally, observed materials balances should fluctuate around zero, with positive and negative values being obtained. Thus, a long string of materials balances where each indicated a slight, apparent loss of material might be just as disturbing as a single materials balance indicating a sizable loss.

A series of individual tests, where each test is based on all information available at the time of testing, defines a sequential test. Decisions are made frequently (e.g., each time period), and with each decision comes the potential for a false alarm or for nondetection.

In recent years, safeguards applications of sequential testing have received increasing attention.[1-4] By analyzing materials balance data in near-real-time, prompt feedback can be obtained in the event of anomalous behavior. Moreover, analyses are not confined to a single MB(i) and, thus, are sensitive to long-term trends.

Many unique qualities of materials balance sequences preclude direct application of the usual sequential procedures, which are oriented toward analysis of independent and normally distributed data. Among the complications are the following.

(1) Distinct materials balances cannot be reasonably treated as statistically independent. Propagation of error for materials balance sequences has been discussed elsewhere and need not be elaborated here; the point is that an assumption of independence often poorly approximates the actual situation.

(2) Under some circumstances, materials balances may not be reasonably treated as normally distributed. Although the effects of measurement errors may yield a normally distributed component of the materials balance, the impacts of nonmeasurement contributors (for example, unmeasured holdup and mistakes in the recording of data) can lead to nonnormal behavior.[5]

(3) The covariance structure associated with a given materials balance sequence is estimated, as opposed to being known.

Item (1), nonindependence, can be treated by conversion of the materials balance sequence to the innovation sequence, which is discussed in detail in the next subsection. Because items (2) and (3) do not seriously affect many of the basic concepts of sequential testing, those concepts are introduced here for the idealized environment where normality and known covariance structure is assumed. Consequences of (2) and (3) in practical applications are then addressed as specific matters are raised.

B. The Innovation Sequence

Consider, as an example, a sequence of weekly materials balances occurring between two cleanouts for a particular unit process. To be specific, let MB(n) denote the n^{th} such materials balance and let $\underset{\sim}{MB}$ denote the vector of {MB(i)}. (The mathematical notation is included for completeness and to allow the mathematically minded reader to follow computational details; it is intended that the text is such that all substantive concepts are conveyed to a general audience.)

Once all information from the time between the cleanouts has been obtained, the variances associated with the materials balances, as well as the covariances between such materials balances, can be estimated. Thus, the error propagation produces the covariance matrix $\underset{\sim}{\Sigma}$ associated with $\underset{\sim}{MB}$. The problem of interest is to evaluate whether the observed data are consistent with the conjecture that no loss has occurred. If the degree of inconsistency is too great, an alarm is to be generated.

Because the weekly materials balances and respective variances become known in a sequential fashion, the importance of timely loss detection implies that the decisionmaking process should be sequential in nature. After each weekly materials balance is observed, it is assessed in the light of additional information from previous weeks and a near-real-time determination is made. This determination, in its simplest form, concerns whether or not an alarm should be generated.

To make such a decision, the methodology outlined here borrows an idea from standard time-series analysis. The sequence of materials balances is converted to a sequence of innovations.[6] In the safeguards literature, the innovation sequence is sometimes called the ITMUF sequence[3] or the sequence of MUF residuals.[7] Components of the innovation sequence are statistically independent--in contrast to the weekly materials balances, which are not--and thus the innovations are amenable to the application of sequential test procedures.

For illustration, suppose that the n^{th} weekly materials balance, MB(n), since the last cleanout of the unit process, has just been observed and that the corresponding error propagation has been completed. The n^{th} innovation, denoted by i(n), is computed by subtracting from MB(n) its predicted value assuming zero loss, where the prediction is based on previously observed materials balances and on all information from the error propagation. As one example, if materials balances were independent, then all such predicted values would be zero and the sequence of innovations would be the same as the sequence of the materials balances.

More concretely, consider the usual case examined in the safeguards literature where materials balances are treated as if normally distributed with known covariance structure and as if they have mean zero when no loss has occurred. For a unit process with negligible nonmeasurement contributors to error, these conventional assumptions are quite useful. Let the vector of materials balances through the n^{th} week since the last cleanout be denoted by

$$\underset{\sim}{MB}_n = \begin{bmatrix} MB(1) \\ MB(2) \\ \cdot \\ \cdot \\ \cdot \\ MB(n-1) \\ \hline MB(n) \end{bmatrix} = \begin{bmatrix} \underset{\sim}{MB}_{n-1} \\ \hline MB(n) \end{bmatrix} ,$$

and let the associated covariance matrix be denoted by

$$\Sigma_n = \left[\begin{array}{cccc|c} \sigma_{1,1} & \sigma_{1,2} & \cdots & \sigma_{1,n-1} & \sigma_{1,n} \\ \sigma_{2,1} & \sigma_{2,2} & \cdots & \sigma_{2,n-1} & \sigma_{2,n} \\ \cdot & \cdot & \cdots & \cdot & \cdot \\ \cdot & \cdot & \cdots & \cdot & \cdot \\ \cdot & \cdot & \cdots & \cdot & \cdot \\ \sigma_{n-1,1} & \sigma_{n-1,2} & \cdots & \sigma_{n-1,n-1} & \sigma_{n-1,n} \\ \hline \sigma_{n,1} & \sigma_{n,2} & \cdots & \sigma_{n,n-1} & \sigma_{n,n} \end{array}\right] = \left[\begin{array}{c|c} \Sigma_{n-1} & \underset{\sim}{a}_n \\ \hline \underset{\sim}{a}'_n & \sigma_{n,n} \end{array}\right] .$$

In other words, the known variance of the j^{th} weekly materials balance is denoted by $\sigma_{j,j}$, and the covariance between materials balances of the j^{th} and k^{th} weeks is denoted by $\sigma_{j,k}$. Under the assumptions, the n^{th} innovation, denoted by i(n), is computed using the formula

$$i(n) = MB(n) - \underset{\sim}{a}'_n \, \Sigma^{-1}_{n-1} (\underset{\sim}{MB}_{n-1}) \quad . \tag{5}$$

The variance of the n^{th} innovation is

$$v(n)^2 = \sigma_{n,n} - \underset{\sim}{a}'_n \, \Sigma^{-1}_{n-1} \, \underset{\sim}{a}_n \quad .$$

[The first innovation is $i(1) = MB(1)$ and has variance $v(1)^2 = \sigma_{1,1}$.] Some readers may recognize the expression $a_n \, \Sigma_{n-1}(\underset{\sim}{MB}_{n-1})$ as it relates to the conditional expectation for the multivariate normal distribution.

The n^{th} standardized innovation, $i(n)/v(n)$, is very useful for sequential testing, as discussed in the next subsection. When no loss has occurred, the sequence of standardized innovations behaves as an independent sequence of normally distributed random variables with mean zero and variance one. Such a sequence is sometimes referred to as "white noise." A time-sequence plot of the standardized innovations [that is, a graph of $i(n)/v(n)$ against n] should exhibit points with $i(n)/v(n)$ values fluctuating about zero and not exhibiting time trends.

If repeated loss has occurred, the behavior of the standardized innovation sequence differs from white noise. The specific behavior depends, of course, on the specific form of the recurring loss. As one example, consider an idealized steady-state model of the blending and packaging operation in a UF_6 conversion process, and suppose it is reasonable to compute the materials balances for the process on a daily basis. The error propagation for this situation is such that

$\sigma_{j,j} = 6.50\ kg^2$; that is, the variance associated with each daily materials balance is $6.50\ kg^2$ U; and

$\sigma_{j,k} = 2.02\ kg^2$ for $j \neq k$; that is, the covariance between distinct materials balances is $2.02\ kg^2$ U.

This covariance structure is unusual and stems from the negligible inventory at the time of balance closure.

Suppose there is no loss in the first 10 days, a loss of $\sqrt{\sigma_{j,j}} = 2.55$ kg U in each of days 11-30, and no loss thereafter. If all the observed materials balances were equal to the corresponding losses, the computed standardized innovations would be as in Fig. 1. Through the 10th day, materials balances and corresponding innovations are all zero. From the 11th through the 30th day, all the materials balances equal 2.55 kg and all innovations are positive, though not equal. From day 31 on, all materials balances are zero and innovations become negative. Plots analogous to Fig. 1 for a chemical separation process for plutonium have similar characteristics.[7]

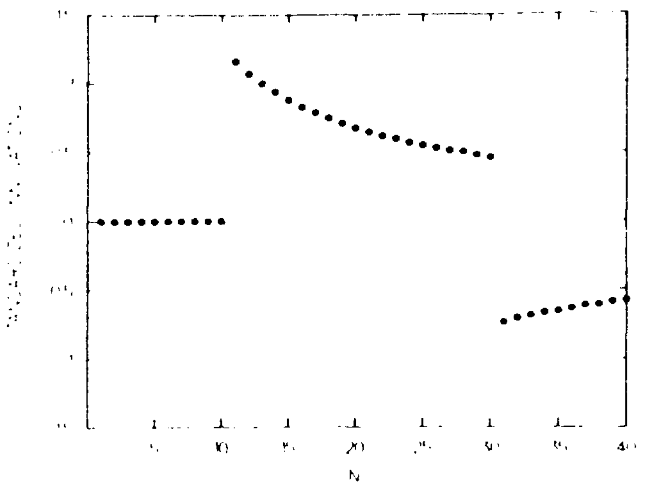

Fig. 1.
Standardized innovation sequence for the blending and packaging example.

In practice, an observed materials balance sequence can be thought of as being obtained by superimposing errors on the actual loss scenario. The impact of such errors on the computed innovations for the present example amounts to superimposing white noise on Fig. 1. As noted above, had no loss occurred, the standardized innovation sequence would behave as "pure" white noise, or white noise that is not superimposed on any pattern such as Fig. 1. Generally speaking, the sequential decision problem reduces to observing the standardized innovation sequence in near-real-time and deciding whether that sequence is consistent with pure white noise or whether there is an underlying loss.

Effects of the potential complications mentioned in the previous section, such as potential nonnormality of materials balances and the use of variance estimates in place of known values, do not greatly alter the fundamental concepts of sequential testing. If a nonnormal model were appropriate, then innovations might be computed using a formula other than Eq. (5) so as to evaluate the difference between MB(n) and its conditional expectation. Also, the uncertainty introduced through the use of variance estimates must be considered when computing performance measures, such as false-alarm rates. In any event, the innovations would have the same interpretation (namely, as errors of prediction), and the testing problem is one of evaluating in near-real-time whether the innovation sequence is consistent with a process of independent components having mean zero.

(Note that although nonnormality in $\underset{\sim}{\mathrm{MB}}$ impacts computation of the innovations, it may not seriously alter their testing. Because innovations are analogous to residuals in an ordinary regression, they may exhibit "supernormality"[8] and behave much like innovations from a normally distributed sequence. Note also that using variance estimates induces a slight dependence in the computed innovations.)

C. Sequential Decisionmaking

When considering sequential tests for loss detection, it is important to recognize that there does not exist a universally best test. Although tests can be designed to be very sensitive against specific loss scenarios, this usually results in poor sensitivity against many alternative scenarios. As one example, the long-term average of the standardized innovations serves as the basis for an effective procedure for detection of long-term losses and has been investigated in the literature.[7] Unfortunately, such a procedure is of much less value in other cases, such as when a recurring loss begins following a longer period of acceptable operation--leading to standardized innovations from the longer period dominating the long-term average and reducing sensitivity.

Because of these problems, two basic philosophies have evolved regarding sequential testing. The first philosophy addresses the case where the user has a very specific idea of the type of loss scenario of interest and/or specific ideas of the "costs" associated with various losses. A test can then be tailored to a specific loss scenario (or, somewhat more esoterically, to specific types of behavior of a potential diverter) using game theoretic[9] or Markov decision[10] approaches. In any event, underpinning this philosophy is the belief that poor performance against unanticipated occurrences is a worthwhile sacrifice to achieve very good results for the case(s) of interest.

The second philosophy emphasizes a test with relatively good properties against a wide class of recurring loss scenarios. When the user does not have a clear idea of the scenario of interest or when a potential diverter could adjust his behavior to avoid a specific scenario for which a test was designed, this philosophy is attractive. Near-optimal performance against a single scenario is sacrificed to some extent to achieve good performance in many other cases.

One test procedure in the spirit of the second philosophy is Page's Test. This test, proposed in its original form over 30 years ago,[11] has found much use in the area of quality control. More recently, safeguards applications have appeared in the literature,[3,12] which to some degree mimic earlier work[13] on conventional time-series problems. Page's Test is essentially a cusum procedure with a restart mechanism, where the restart allows for detection of both long-term, lower-level losses as well as shorter-term, higher-level losses.

To illustrate, consider the hypothetical example of the previous subsection where daily materials balances are obtained for the blending and packaging process. As before, let i(n)/v(n) denote the standardized innovation corresponding to the nth materials balance. Upon observation of i(n)/v(n), a one-sided Page's Test is based on the statistic

$$P(n) = \text{maximum of } [P(n-1) + i(n)/v(n) - k] \text{ and } 0 \quad ,$$

where $P(0) = 0$, and k is a threshold of the test. An alarm occurs whenever P(n) exceeds a specified threshold h. The thresholds h and k are jointly determined based on performance considerations, such as detection probabilities. (A two-sided version of Page's Test--that is, a test that is sensitive not only to apparent losses but also to apparent gains--exists.)

Consider the behavior of the test statistic P(n) for the threshold choice $k = 0$. If the sequence of standardized innovations is such that the cusum is always positive, then P(n) is equal to the cusum. If the cusum falls below zero, then P(n) "restarts," treating the cumulative sum as if equal to zero and beginning anew. For a threshold choice $k > 0$, a similar phenomenon occurs after subtracting the value k from each standardized innovation. In this way, the restart is designed to prevent a sequence of insignificant innovations, associated with a period of no loss immediately following a cleanout, from masking a recurring loss beginning at a later time, as could happen with the use of a long-term average.

Two considerations arise in the establishment of threshold values. The first involves a tradeoff in h and k. For the blending and packaging example with cleanouts assumed 60 working days (roughly 3 months) apart and materials balances assumed normally distributed with known covariance structure, any choice of (h,k) along the curve in Fig. 2 provides a sequential test with a 1/2% false-alarm rate. That is, the chance of a false alarm occurring at any time during the monitoring period is a 1/2%; this is not the same as a 1/2% false-alarm rate for each individual MB(n), which would lead to a high false-alarm rate over the sequence of materials balances. Generally speaking, low values of k are better for detection of longer-term, lower-level losses, while larger values of k are better for shorter-term, higher-level losses. Most implementations of Page's Test adopt something of a compromise, with values of k in the 0.3 to 0.5 range. See Ref. 14 for computational procedures related to derivation of threshold values.

A second consideration concerning thresholds involves side issues such as nonnormality and the use of variance estimates, which cannot be ignored when ensuring that stated objectives are met. As one example of the potential implications, the use of thresholds derived for the case where variances are known in a situation where variances are, in fact, estimated is likely to lead to more false alarms than originally anticipated.

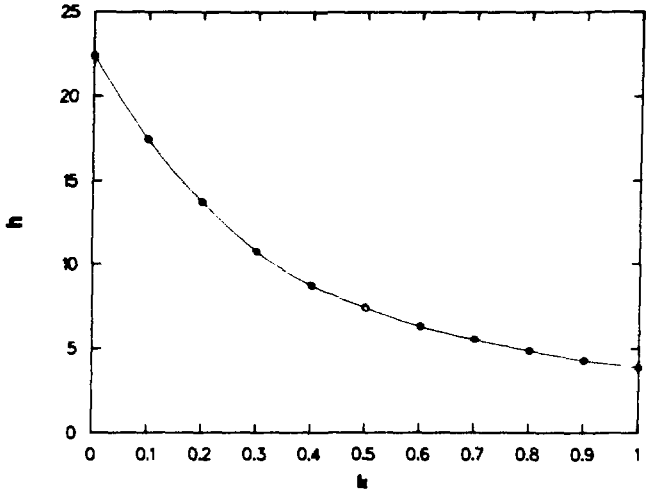

Fig. 2.
Threshold values for Page's Test (0.5% false-alarm rate) for the blending and packaging example.

D. Performance Measures

Because of the restart mechanism, Page's Test is somewhat sensitive to abrupt losses. Consider the example where weekly materials balances are obtained. It can be shown that Page's Test with thresholds (h,k) promptly detects with 99% probability a loss of L kilograms of material in the n^{th} week when the standard deviation $\sqrt{\sigma_{n,n}}$ (in kilograms) associated with the n^{th} weekly materials balance is such that

$$\sqrt{\sigma_{n,n}} < L/(h + k + 2.33) \quad . \qquad (6)$$

[Equation (6) assumes that materials balances behave as if normally distributed with known covariance structure.]

A simple interpretation of this result is that if the standard deviation $\sqrt{\sigma_{n,n}}$ is sufficiently small, then an abrupt loss is promptly detected. Although it may also be possible to arrange for Eq. (6) to hold by artificially establishing thresholds (h,k) such that h + k is sufficiently small, a test where h + k is too small will lead either to a large false-alarm rate or to poor sensitivity to longer-term, lower-level recurring loss. Thus, if $\sigma_{n,n}$ is too large, it is not practical to use Page's Test for abrupt loss detection.

To calculate abrupt loss detection probabilities for Page's Test, note that an alarm is always generated for the nth weekly materials balance when the nth standardized innovation i(n)/v(n) satisfies

$$i(n)/v(n) > h + k \quad .$$

Under the conventional assumptions of normality and known covariance structure, a loss of L kilograms in the nth week following a cleanout leads to (assuming no previous loss) i(n)/v(n) behaving as if normally distributed with mean L/v(n) and standard deviation 1. Using this, the probability that i(n)/v(n) exceeds h + k can be computed. Equation (6), for example, arises after noting that $v(n) < \sqrt{\sigma_{n,n}}$.

In contrast to the prompt detection of an abrupt loss, where the performance of a test can be summarized with a single number (the detection probability), performance measures in the presence of recurring loss can be more involved. A recurring loss is usually characterized by its loss scenario, or the specification of the "true" losses associated with the observed materials balances. The performance of any sequential test procedure depends on the underlying loss scenario.

Important qualities of tests for recurring loss are revealed through the run-length distribution. This distribution consists of the constants

$\{p_j\}$, where p_j denotes the probability that an alarm is generated upon observation of the j^{th} materials balance following the last cleanout of the unit process ($j = 1, 2, \ldots, N$, where N denotes the number of materials balances between cleanouts). Given a specific loss scenario for which a recurring loss begins during the time period corresponding to the k^{th} materials balance, the sum

$$\sum_{j=1}^{k-1} p_j$$

represents the probability of a false alarm for that scenario while the sum

$$\sum_{j=k}^{N} p_j$$

represents the detection probability. Timeliness of detection can be evaluated using the $\{p_j\}$. It is important to recognize that a run-length distribution depends on the underlying loss scenario through both the amount of material loss and the loss pattern.

To illustrate, again consider the hypothetical blending and packaging example of Subsection B, where materials balances are obtained daily for the materials control unit and assumed to behave as if normally distributed with the covariance structure described there. Suppose there are 60 working days between cleanouts for the process and that Page's Test with thresholds $(h,k) = (7.44,0.5)$ is implemented to provide timely feedback in the event the daily materials balances indicate an apparent anomaly. Recall from Fig. 2 that this choice of thresholds would provide for an ~1/2% probability of an alarm during the 60-day period if no loss were incurred. Lastly, suppose the loss scenario of interest is as depicted in Fig. 1, where no loss occurs for days 1-10 and days 31-60, but a recurring loss is present during days 11-30. For each of days 11-30, the amount of material loss is 2.55 kg U, equal to the standard deviation of each daily materials balance.

TABLE I

SIMULATION RESULTS[a]

Category	Empirical Probability (%)	Comment
False alarm	0.1	Alarm occurred before the initial loss on Day 11
Prompt alarm	3.7	Alarm occurred between Day 11 and Day 15
Alarm	17.5	Alarm occurred between Day 16 and Day 20
Delayed alarm	23.3	Alarm occurred between Day 21 and Day 35
Late alarm	0.0	Alarm occurred after Day 36
Nondetection	55	No alarm occurred during the inventory period

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[a] From 10 000 simulated materials balance sequences. Empirical probabilities add to 100% before rounding.

The run-length distribution (empirically determined from simulation of 10 000 materials balance sequences) is summarized in Table I. The nondetection probability for this loss scenario, involving a total loss of 51 kg U (~1.6 kg ^{235}U) for the process, using the sequential methodology, is ~55%. With roughly 20% probability, an alarm occurred within the first 10 days following the onset of the loss. Because such a small loss would rarely be detected from a plantwide balance closed quarterly, it is seen that much sensitivity is gained by closing balances frequently around individual process areas.

Similar calculations could be repeated for other loss scenarios. As a general rule, a recurring loss that begins immediately following a cleanout is less likely to be detected than one beginning later. This is partly because a loss beginning at a later time exhibits not only a departure from the anticipated zero-loss condition but also a change "internal" to the materials balance sequence. Oversimplifying somewhat, this phenomenon results from the presence of so-called systematic errors. A systematic error in a measured output, say, that transcends the time covering the materials balance sequence is indistinguishable from a recurring loss. When observed materials balances are consistent with either explanation, the sequential test must "decide" which explanation is true. A low false-alarm rate dictates that the benefit of the doubt often be given to the potential for systematic errors, thereby reducing sensitivity to small trickle losses.

If there were no systematic errors, the covariance structure for the materials balance sequence would resemble that for a first-order moving average process of conventional time series.[15] In such a case, a sequence of materials balances in which every balance reflected an apparent loss of material would be strong evidence of actual loss. Unfortunately, this argument breaks down in the presence of systematic errors, so that certain loss scenarios can be disguised. A more complete description of the impact of the loss scenario on detection is beyond the scope of this presentation, and the reader is advised to consult the literature.

The use of simulation to evaluate performance measures is quite common because deriving results analytically is often difficult. Most simulations are somewhat idealized; the one above, for example, presumes that each daily materials balance is a "clone" of every other materials balance, having exactly the same standard deviation, etc. Performance of the sequential methodology under more realistic conditions is only approximated to the degree that the actual materials balance behavior resembles the assumptions of the simulation.

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ABOUT THE AUTHOR

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CHAPTER VI

PROCESS HOLDUP OF SPECIAL NUCLEAR MATERIALS

by

K. K. S. Pillay and R. R. Picard

I. INTRODUCTION

Safeguarding special nuclear material (SNM) through materials control and accounting (MC&A) often encounters a variety of implementation problems. One of the insidious problems of materials accounting is due to unmeasured inventories. The primary source of unmeasured inventories in most bulk-handling facilities is the holdup or hidden inventory of materials within process equipment. In materials accounting terminology, hidden inventories are part of materials unaccounted for (MUF) of inventory difference (ID). The MUF or ID could be construed as loss or diversion. From a safeguards perspective, all these accounting differences are undesirable.

Holdup of materials in process equipment is not unique to SNM processing. But uncontrolled accumulation of materials within process equipment is both a safety and safeguards concern at nuclear material processing facilities. Because holdup of nuclear materials in process equipment offers unique challenges to MC&A, this topic is carefully explored in this chapter with special efforts to estimate process holdup at an example uranium conversion facility (discussed in the Appendix).

In recognition of the increasing importance of process holdup in materials accounting, a special workshop was organized in 1988 under the auspices of the Institute of Nuclear Materials Management to identify the major issues as well as to investigate them. Two major publications resulting from the above workshop are desirable references for those who wish to explore the subject in greater detail.[1,2]

II. HOLDUP (HIDDEN INVENTORY)

Nuclear materials are generally produced and used through complex chemical and manufacturing processes. Some of these processes lead to accumulation of sizable and often constantly increasing amounts of special nuclear material (SNM) in regions of poor circulation and complex structural features. From a materials accounting point of view, these residual accumulations of materials may be referred to as "hidden inventories."

A. Definition

One simple definition of holdup is the amount of residual materials remaining in a processing facility after the runout of bulk materials processed. Two distinct kinds of holdup are commonly identified as

(1) in-process holdup, which may be defined as

$$H_{t_1} = \int_0^{t_1} I_t - \int_0^{t_1} O_t - \int_0^{t_1} D_t \quad , \qquad (1)$$

where I_t = input(s), O_t = output(s), D_t = discard(s), and t_1 is the time of measurement of holdup and

(2) residual holdup, which may be defined by Eq. (1), when the input is zero and the output is a maximum.

B. Causes

The SNM can not only segregate in regions of processing facilities where there are cracks, pores, and zones of poor circulation, but also, under certain conditions, the chemical environment of SNM can react with components of process equipment and tenaciously adhere to them making these deposits extremely difficult to recover. These problems become acute where the piping runs are very long and surface areas are very large. The physical layout of structural components (such as transfer pipe lines, storage tanks, ductwork, and drain pipes) does influence SNM holdup in process facilities. In addition, some of the internal features of equipment, such as Raschig-ring-filled tanks, contribute to the severity of holdup problems. The nature of the process used at a plant and the physical conditions of intermediates, such as solutions, precipitates, and powders, are determining factors in the extent of holdup at a processing plant. Also, process upsets, such as incomplete precipitation and/or postprecipitation, lead to undesirable material depositions in process equipment.

C. Mechanisms

A mechanism of material accumulation in process equipment is the slow accumulation of fine particles of materials in regions of poor circulation and the eventual buildup of such materials over a long period. Other mechanisms of material accumulation in process vessels and facilities are important. Among them are

(1) slow but steady buildup of materials in designated areas, such as filters or sumps;
(2) unplanned buildup of materials in pipes and ducts caused by the layout and construction features of the physical plant;
(3) slow sedimentation and settling of materials on large surfaces, such as Raschig rings in storage tanks;
(4) coating of surfaces of precipitators and filtration devices in response to unique characteristics of certain chemical forms of SNM;
(5) electrostatic deposition and buildup of charged particulates in ductwork, surfaces of glove boxes, filter holders, etc.;
(6) postprecipitation from reactions in transfer lines of filtrates and other process liquid wastes;
(7) splashing of materials from unregulated chemical reactions in reaction vessels, furnaces, etc.;
(8) accumulation of materials in powder transfer lines resulting from poor design features;
(9) solid or liquid product formation from inadvertent reactions in the gas phase, such as hydrolysis of UF_6 to UO_2F_2 in gaseous diffusion plants; and
(10) coagulation and sedimentation in holding tanks and settling tanks used in process facilities.

D. Magnitude of Holdup

Holdup of SNM in process facilities can result from both normal and abnormal operations of the plant. From a detailed knowledge of the process chemistry and behavior of material forms, one can make reasonable predictions about regions of holdup as well as approximate magnitude of holdup during normal operations. However, it is extremely difficult to speculate on the magnitude of holdup during abnormal conditions resulting from process upsets and/or improper plant operations.

Plant layout, frequency of process upsets, quality of facility maintenance, operational skills of personnel, and plant throughput are factors causing the magnitude of holdup to vary significantly from one plant to another using the same process. During normal operations of a fuel material preparation facility (UF_6 conversion to UO_2), the pipelines used for transfer of solutions can have a steady-state holdup of about 1 g/m length of the pipe. Similarly, a batch precipitator used for the precipitation of ammonium diuranate (ADU) can normally have a holdup of about 1% of the batch throughput. However, on several occasions these holdup levels have changed drastically, blocking the flow in pipes transferring uranyl solutions and in precipitators--with 5-8% of batch throughput as holdup.

III. PROCESS HOLDUP AND MATERIALS ACCOUNTING

A. Past Efforts

The identification and measurement of process holdup of SNM was recognized as important to materials accounting very early in attempts to establish effective safeguard systems in the U.S.[3] For holdup measurements, in situ assay techniques are preferable to process-disruptive and time-consuming cleanout efforts. Although nondestructive assay (NDA) procedures are extensively used in materials accounting measurements, the accuracies of holdup measurements using these techniques are generally poor[4,5] because of the complexities of residue deposition patterns and irregularities in the geometries of equipment and facilities. So far, almost all attempts to measure holdup of SNM in processing facilities have been stimulated by the need to explain large inventory differences. Generally, they have been crude measurements done on process equipment or cleanout residues resulting in large uncertainties in the holdup data, although these efforts have been valuable in demonstrating to regulatory agencies the importance of holdup measurements to materials accounting. As a result of past efforts in estimating holdup, there have been several innovative suggestions to minimize obvious bias in standards and facility-specific calibration procedures for the measurement of holdup.[6-9]

Holdup can be measured nondestructively by both neutron and/or gamma-ray measurements. Generally gamma-ray techniques are used because of the ready availability of instruments at processing facilities and the ease of measurement. When the attenuation of gamma radiation and complexity of geometry become dominant factors, passive neutron measurements are attempted. The recognition of the difficulties associated with estimation of process holdup is reflected in proposals to use indirect methods of measurements using isotopic and radioactive tracer techniques.[10-15] In recognition of the influence of design features and layouts of plants to material holdup, the Nuclear Regulatory Commission (NRC) has proposed design considerations for process facilities to minimize holdup.[16]

B. Holdup and Inventory Difference

Location and recovery of SNM from hidden inventory (holdup) are generally very difficult. In most plants, these hidden inventories therefore remain unidentified losses. In such cases, the comparison of observed inventory difference (ID) with the value expected from propagation of measurement errors is not very useful if the former contains a substantial contribution from losses not correctly estimated. A positive ID (loss of material) incorrectly interpreted can be a diversion.

Where inventory differences are consistently positive, the existence of unidentified losses can be suspected. Experience indicates that production personnel are reluctant to take steps necessary to identify all significant losses and account for them accurately. This is understandable because explanations for these losses presume quantitative knowledge of losses from spills, fires, hidden inventories, equipment leakage, and various effluents that go up the stack or down the drain. Therefore, safeguards personnel have the responsibility to assure that reasonable estimates of all significant process losses are made. However, it should be emphasized that the estimation of hidden inventories is indeed a most difficult safeguards problem for which there is no simple solution.

IV. HOLDUP MEASUREMENTS AT PROCESSING FACILITIES

Holdup is characterized by materials that are difficult to locate, sample, identify, analyze, and quantify. In materials accounting, the inventory term associated with holdup is often ignored or improperly measured. Thus, holdup generally has adverse effects on the quality of physical inventories and on materials accounting programs.

As part of a recently completed investigation for the NRC, Los Alamos evaluated several types of data on holdup.[17] Holdup of uranium and plutonium at three processing facilities was examined as part of this investigation. The varied pieces of equipment involved in these holdup measurements were

(1) high-efficiency particulate air (HEPA) filters at the plutonium processing facilities of Los Alamos;
(2) several air filters and batch calciners, and a continuous precipitator and a rotary drum filter at the uranium scrap recovery facility at Los Alamos; and
(3) several air ducts at the High-Temperature Gas Reactor (HTGR) fuel fabrication facilities of GA Technologies, Inc., San Diego.

A. Plutonium on HEPA Filters

The holdup measurements of plutonium on HEPA filters were performed using a shielded and collimated NaI(Tl) detector installed on top of a glove box about 18 cm from the HEPA filter. A dedicated multichannel analyzer system was used to scan the gamma spectrum, and the 320- to 470-keV region was integrated to estimate the holdup on this HEPA filter. Calibration standards for this detector system were fabricated to resemble the filter being measured with known amounts of PuO_2 dispersed on the filter medium. Transmission and attenuation corrections were determined using a thin source of PuO_2. Confirmatory measurements were performed on the filters at the end of the experiment period using a neutron coincidence counter to determine the plutonium content. The coincidence counter measurement was within 8% of the in-place NDA estimates of the holdup of plutonium.

B. Uranium Holdup in Scrap Recovery Facility

The measurements were made with portable NaI(Tl) detectors using a two-channel stabilized assay meter (SAM-II). Combinations of point- and foil-type calibration sources were employed for different geometries of the various pieces of equipment (air filters, continuous precipitator, rotary drum filter, and batch calciners). Except for a few air filters, the uncertainty in holdup data for uranium from this location was very large, greatly limiting the value of data to predict holdup patterns in the equipment.

C. Holdup of Uranium in Air Ducts

This facility (of GA Technologies, Inc.) fabricates HTGR fuel pins and therefore contains large quantities of thorium associated with uranium holdup inventories. Measurements of holdup used an ^{241}Am-doped NaI(Tl) detector and a SAM-II. It is estimated that these measurements of uranium holdup in the ductwork had a precision of 25-75%; no efforts to determine the accuracies of the measured values have been reported.[18]

V. CONTROLLED STUDIES OF SNM HOLDUP

These controlled experiments were designed to measure uranium holdup in several unit processes common to nuclear reactor fuel fabrication lines. Three of these unit processes chosen for brief discussion here are

(1) a dust-generating operation at a highly enriched uranium (HEU) processing facility,

(2) an ammonium diuranate (ADU) precipitation and calcination process, and

(3) a solution loop system circulating uranyl solutions.

Total throughput of uranium through these experimental facilities ranged from 50 kg to about 100 tonne. The quality of measured holdup data during these controlled experiments was improved by at least an order of magnitude through the use of carefully selected radioactive tracers and specially designed calibration standards. Tracers, at concentration levels of about one part per billion, were homogeneously incorporated into the process materials. During these experiments, considerable attention was paid to fabricate instrument calibration standards compatible with the equipment measured and the distribution of holdup therein. This also contributed to improving the quality of holdup data from noninvasive NDAs by gamma-ray spectrometry using NaI(Tl) detectors. Complete details of the experimental facilities and experimental results are discussed elsewhere.[17] Some of the general features of the controlled experiments are summarized in Table I.

TABLE I

EXPERIMENTAL PARAMETERS OF CONTROLLED HOLDUP STUDIES

Involved Controlled Experiments	Material Forms Involved	Tracer Used	Experimental Parameters Varied	Equipment Used in Holdup Measurements
U dust generation	U_3O_8 powder and incinerator ash taining U_3O_8	^{95}Zr-Nb (Neutron-activated U_3O_8)	40- to 200-μm particle size, air flow rates from 5 to 100 cfm	Glove box, ducts, elbows, tee, prefilter
ADU precipitation and calcination	$UO_2(NO_3)_2$, ADU, and U_3O_8	^{46}Sc as Sc^{3+}	pH of solutions, mixing rates, calcination temperature	Dissolver, precipitation filters, calciner trays, calciner
U solution loop	$UO_2(NO_3)_2$ and UO_2F_2	^{46}Sc as Sc^{3+} and $(ScF_6)^{3-}$	Flow rates, materials of construction, pipe dimensions	Pump, pipes, elbows, tees, unions, valves, terminal valves

A. Uranium Holdup in a Dust-Generating Facility

A glove box with ventilation system (Fig. 1) using materials and designs similar to those used at the HTGR fuel fabrication plant was set up to generate uranium dust and <u>in-situ</u> holdup measurement. A mechanical dust-generating apparatus, designed and fabricated for this experiment, was allowed to generate U_3O_8 dust from various types of oxides and incinerator ash samples. The <u>in-situ</u> holdup of uranium was measured at 14 points (shown in Fig. 1) using a shielded portable NaI(Tl) detector and a Ludlum dual-channel analyzer. At the end of each experiment, the ventilation system and the glove box were cleaned out, and the cleanout measurements were conducted nondestructively using a sensitive gamma-ray spectrometry system.

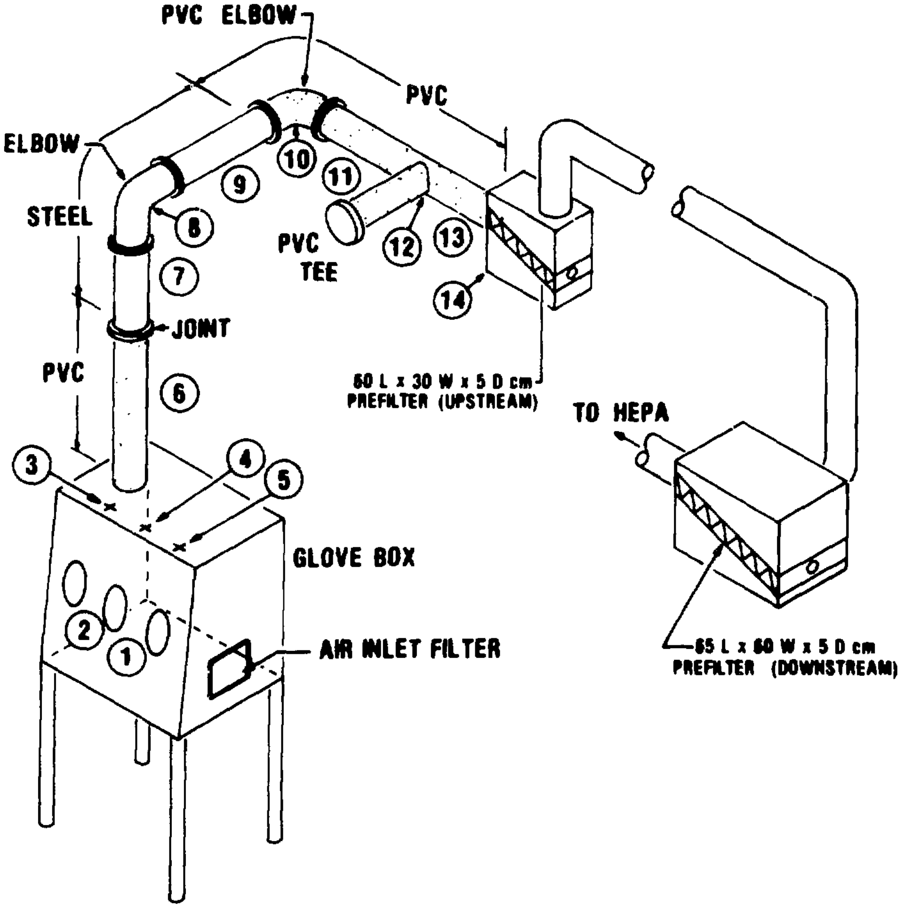

Fig. 1.
Isometric view of the controlled holdup study facility.

Seven such experiments involving 70 dusting cycles with a total throughput of about 70 kg of uranium were performed using this dust-generating system. The data obtained from these experiments were used to develop mathematical models of holdup for each of the 14 locations of the experimental facility.

B. Uranium Holdup During ADU Precipitation and Calcination

The ADU precipitation and calcination process is a major part of MBA-1 of the "Example Process" discussed in the Appendix of this chapter. This experimental study simulated the generic process involved in ADU precipitation and calcination and measured the holdup of uranium in a dissolver, a batch precipitator column, several filters, a calciner, and several calciner trays. The precipiation column used for this experiment was a tall stainless-steel cylinder (20-cm diam and 1 m high). This batch precipitator and the associated equipment used for precipitation are shown schematically in Fig. 2. Instead of UF_6, this controlled study utilized a feed makeup prepared by dissolving U_3O_8 in nitric acid. The important process steps are shown in Fig. 3.

For this experiment, U_3O_8 was used as the starting material. Each batch contained about 1 kg of uranium, which was dissolved in nitric acid, and to this a solution ^{46}Sc tracer (~10^8 Bq) was added as Sc^{3+}. The uranium nitrate solution was vacuum-transferred to the precipitation column and precipitated as ADU using NH_4OH, while the contents of the precipitation column were vigorously agitated by a circulation pump. The ADU was filtered using large Buchner filters, and the ADU cake was calcined in a

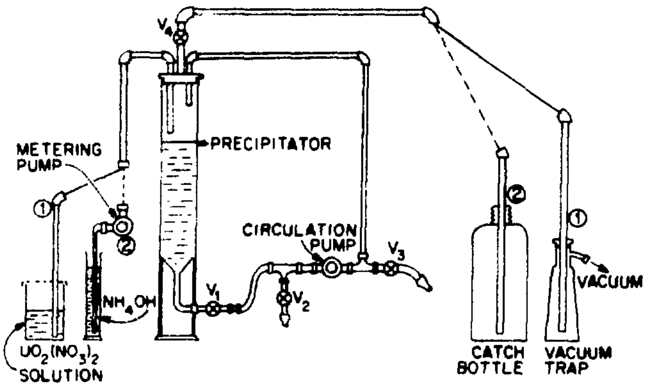

Fig. 2.
Schematic illustration of the ADU precipitation column and associated apparatus: (1) solution transfer and (2) ammonia addition.

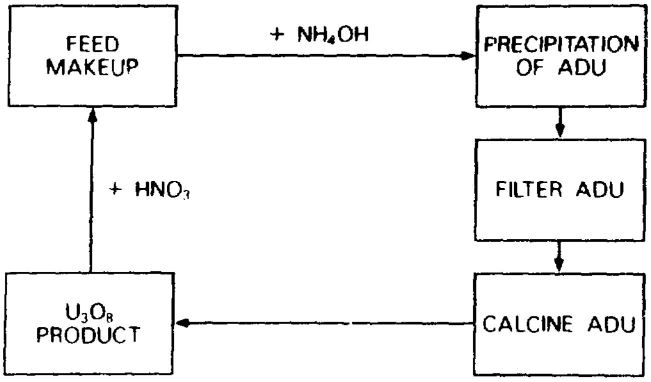

Fig. 3.
Process steps of ADU precipitation and calcination experiment.

Lindberg furnace at a temperature of 700-900°C. This process was repeated to have a total throughput of ~52 kg of uranium through the experiment system.

After each batch processing, the holdup of uranium in the dissolver, precipitator column, filters, calciner trays, and the calciner was measured nondestructively using a specially mounted NaI(Tl) detector-based gamma-ray spectrometry system. Several cleanout measurements were also performed during this series of experiments to confirm the NDA measurements of holdup. Some of the data obtained from NDA measurements are compared with cleanout measurements in Table II. The NDA measurement data were used to

TABLE II

COMPARISON OF NDA MEASUREMENTS OF HOLDUP WITH CLEANOUT MEASUREMENTS (in grams of uranium)

Equipment/Parts	NDA Measurement	Cleanout Measurement
ADU precipitation vessel (after Experiment 32)	12.6	14.6
ADU precipitation vessel (after Experiment 40)	8.8	9.8
ADU precipitation vessel (after Experiment 52)	9.3	10.5
Calcining furnace (after Experiment 52)	1.7	1.5
Calcining trays (after Experiment 52)	1.4	1.3
Filter funnels (after Experiment 52)	10.1	9.8

develop holdup models for the various pieces of equipment used in this study. A few examples of modeling using data from this study are presented in Sec. VI. Complete data and details of models developed for each piece of equipment are presented in a separate report.[17]

C. Circulation Loop System for Uranyl Solutions

In uranium processing facilities and scrap recovery operations, a variety of uranium solutions are transferred from one location to another, continuously and/or intermittently, using various types of pumps, tanks, valves, flowmeters, pipes, and pipe fittings. Because extensive piping and transfer systems are an essential part of a large processing facility, the residual amounts of HEU in these solution transfer systems can be an important part of the residual holdup of the plant. Because the accumulation of residues inside a solution loop is a relatively slow process, the measurement of the buildup of uranium in these components of the loop offered considerably more challenges than any of the other measurements undertaken during these experimental studies.

Two types of materials--stainless steel and chlorinated polyvinylchloride (CPVC)--were chosen for the construction of the solution loops. Because two types of solutions--uranyl nitrate and uranyl fluoride--are often found at HEU fuel materials preparation facilities, they were chosen for this experimental study. The circulating system (see Fig. 4) was designed and built incorporating a large storage tank, a surge tank, a pump, about 50 m of pipes of various dimensions, several valves and terminal valves, various pipe unions and clamps, two types of flowmeters, elbows, tees, and pressure relief valves.

The uranyl nitrate (or fluoride) solution contained about 100 g of uranium per liter with 4 moles of excess nitric (or hydrofluoric) acid per mole of uranium. The system was designed to change the flow rates from 1 to 2 kg of uranium per minute at a solution flow rate of approximately 10-20 L per minute. Other details of the loop components and experimental parameters are summarized in Table I. The loop throughput of uranium between holdup measurements was calculated from the known flow rates, the elapsed time, and the concentration of uranium solution in the feed tank.

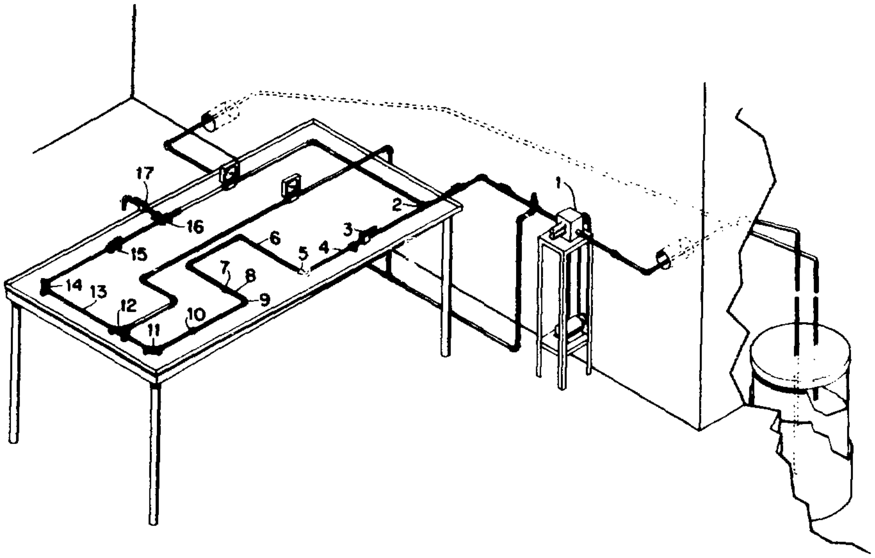

Fig. 4.
Isometric view of one of the solution loops for uranyl solution circulation.

Residual holdup of uranium in various components of the solution loop was measured at 17 locations (shown in Fig. 4) using a specially fabricated NaI(Tl) detector assembly. A set of cleanout measurements was conducted on selected components of the stainless steel loop before they were dismantled.

D. Results of Controlled Experiments

The primary objective of the controlled studies was to demonstrate that well-designed, controlled experiments carried out at large facilities combined with reliable measurements can be used to develop holdup estimation models. The quality of the holdup data being the key to the successful development of estimation models, it is important to invest sufficient effort to minimize measurement uncertainties. Data obtained from these controlled experiments were extremely satisfactory for holdup measurements. The accuracy of holdup measurements was within 3-12% of the "cleanout" values, and a majority of these measurements showed precisions of less than ±5%.

VI. MODELING APPROACHES

Although a body of literature has evolved around the important aspects of making holdup measurements, much less work has been done regarding the interpretation of the resulting data. In this section, many analytical principles are introduced, and their applications are illustrated using data from the controlled holdup studies described in the previous section.

Like many physical processes, the accumulation of holdup is often amenable to modeling. When a facility operation is stable, the holdup in a piece of equipment behaves as a smooth function of time, perhaps gradually increasing or remaining (nominally) constant. This aspect of "temporal continuity" in holdup behavior can be captured through modeling. A "spatial continuity" may exist as well. For example, holdup at a particular location may be very similar to that at locations nearby. A proper combination of all such relevant information (formalized through the use of a model) leads to holdup estimation much improved over reliance on a single measurement value. A lengthy discussion of holdup modeling is given in Ref. 19. The flow diagram (Fig. 5) shows the basic steps of an iterative process to build and update an estimation model.

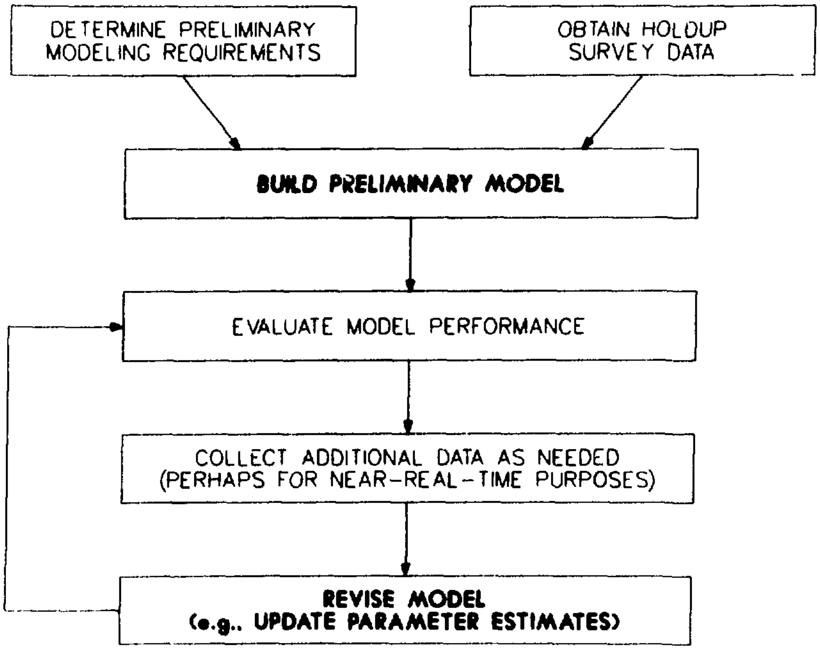

Fig. 5.
Typical model-building process.

A. Modeling with Respect to Time: Increasing Holdup

The data obtained from air filters used in the dust-generation experiment (Fig. 6) and the measurements at the plutonium facility (Fig. 7) are "best case" examples of the increase in holdup with time. Holdup in filters, like holdup in many other pieces of equipment, undergoes something of a life cycle. The initial condition of little or no holdup is followed by a gradual accumulation of material. Finally, the filter is replaced (or, more generally, the equipment is cleaned out) and the cycle begins anew.

Figure 7 displays data collected over a 6-month period from a filter at the Los Alamos plutonium facility and shows the temporal continuity described above. Figure 6 summarizes the results of three filters from uranium dust-generation experiments conducted in a glove box. In all these cases, holdup accumulation on filters is well represented by the model

$$h(t) = \alpha t + \beta t^2 \quad , \qquad (2)$$

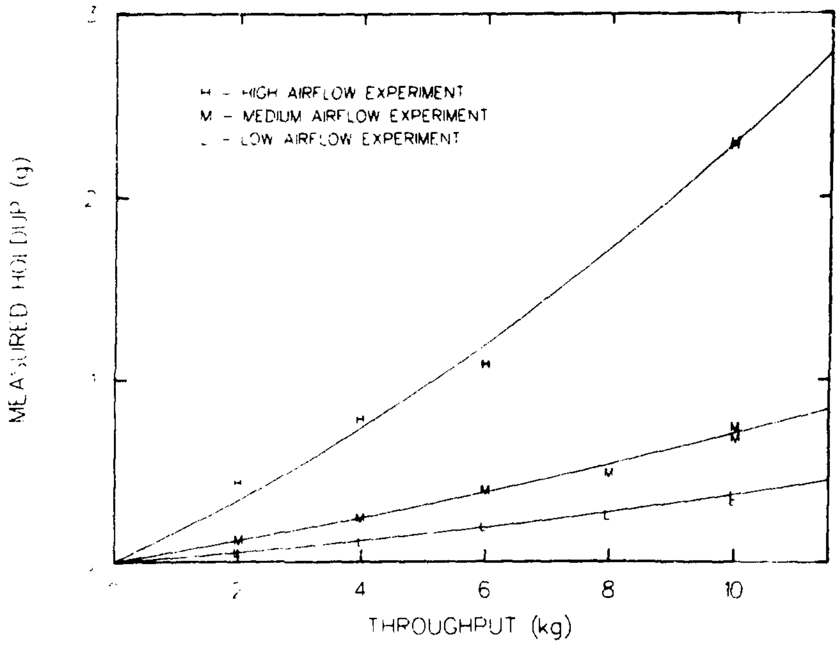

Fig. 6.
Change in the holdup of fine U_3O_8 as a function of throughput at the exhaust air filter of the glove box.

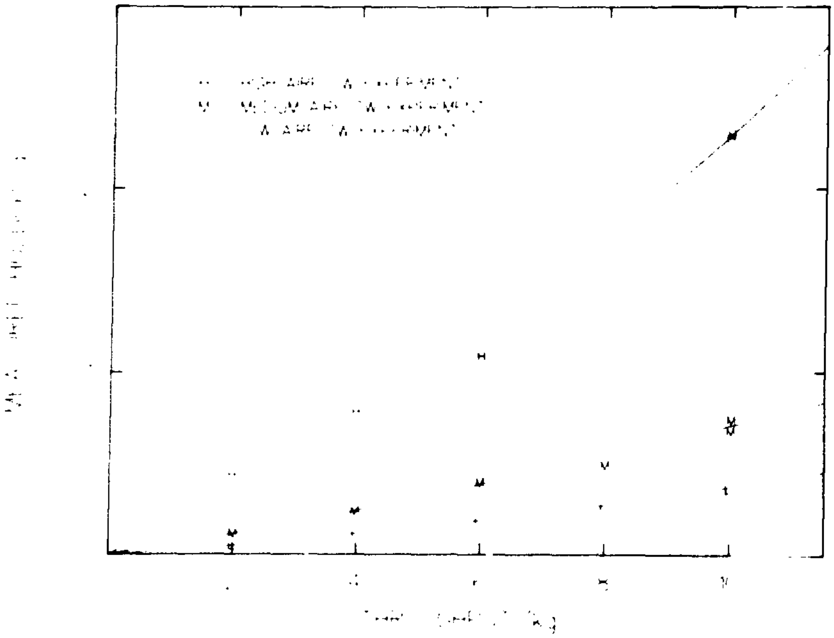

Fig. 7.
Measurement history of holdup of plutonium on an air filter at TA-55.

where h(t) is the amount of holdup on the filter when the throughput is t kg and α and ß are constants. Curves of these forms are superimposed on Figs. 6 and 7. The former figure clearly shows the dependence of the constants α and ß on the specific operating conditions involved and demonstrates that a model developed for one set of conditions may not apply under another.

Central to good predictability in these experiments are two factors: the high quality of measurement data and the stable operation of the process. The quality of data is important because large measurement errors can easily obscure the nature of material deposition and make difficult the extraction of a model. If measurements are obtained infrequently, problems are compounded. The second important factor concerns process operation. With respect to Fig. 6, it is not difficult to imagine the results of a hypothetical experiment, the first half of which would be conducted at low airflow; the second half, at high airflow. More generally, if the airflows were changed often, the increase in holdup would not be nearly as smooth as for the curves of Fig. 6.

These experiments indicate that holdup can be described very well through the use of models. But a caution should be added here: all the measurements carried out on air filters during this study did not provide data of high enough quality to allow the development of good mathematical models. The limitations in most cases were the poor signal-to-noise ratio from filters that were measured in place, with portable instruments.

When good predictability can be demonstrated, the use of models reduces the level of measurement effort otherwise needed to maintain good holdup accountability. Models allow the estimation of holdup for past times when no measurement was made (such as t = 9 kg in Fig. 6) and for a limited time into the future, provided the process remains (nominally) the same. Maintaining good estimation requires that periodic measurements be used to update the fitted model. The frequency of data collection depends on the desired accuracy of estimation.

B. Modeling with Respect to Time: Steady State

The data set from the calciner of the ADU experiment (Fig. 8) is a good example of the steady-state behavior of holdup with time. Holdup here does not follow the life-cycle behavior exhibited for the filters. Instead, beginning from a clean slate, a brief initial increase in holdup (or a "plating out" period) is followed by long-term fluctuations about steady-state conditions. This type of holdup behavior was evident in the controlled study of holdup in pipes and pipe fittings. Process variability plays a major role in estimation. Other information concerning the measured values indicates that observed differences in measurements during a steady-state period are not solely the consequence of measurement errors but that the actual amount is also changing.

Modeling of steady-state processes is not difficult and typically involves the use of Kalman filtering. A major benefit of the Kalman filtering is its ability to incorporate process variability; that is, variability in the actual amount of holdup over time. The measurement history from a poorly measured but stable process might resemble the history from a well-measured, unstable process. Thus, holdup estimation crucially depends on the relative magnitudes of measurement errors and normal process variability.

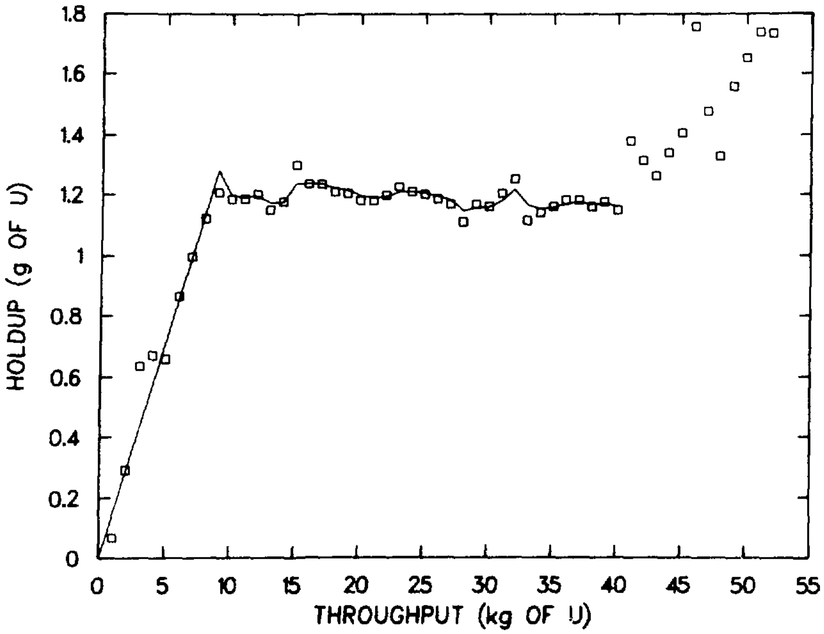

Fig. 8.
Uranium holdup data and model for the calciner.

The basis for the Kalman filter lies in the measurement and steady-state equations. For the i^{th} measured value, $m(t_i)$, obtained when the throughput is t_i kg, the measurement equation is

$$m(t_i) = h(t_i) + e(t_i) \quad , \tag{3}$$

where $h(t_i)$ denotes the actual holdup and $e(t_i)$ is the measurement error. Most models presume $e(t_i)$ is normally distributed with mean zero and standard deviation σ_m. Generally, σ_m can be estimated from measurement control information. The steady-state equation is

$$h(t_i) = h(t_{i-1}) + \varepsilon(t_i) \quad , \tag{4}$$

and reflects the steady-state character of the process. The difference, $h(t_i) - h(t_{i-1}) = \varepsilon(t_i)$, is the actual change in holdup between throughputs

t_{i-1}, and t_i is assumed to act as a random variable with mean zero and variance $(t_i - t_{i-1})\sigma_p$, where σ_p is the process variance. For the calciner, the measurements were obtained that were equally spaced. Had the measurements obtained been unequally spaced, some of the $\varepsilon(t_i)$ would have been more variable than others. More detailed discussions of Kalman filtering are found in the literature.[20]

The measured values $\{m(t_i)\}$ and the estimates of the measurement variability σ_m and the process variability σ_p are input to the Kalman filter, which produces the estimated holdup $\{h(t_i)\}$. For the calciner, these estimates are connected by the line segments in the steady-state portion of Fig. 7. When holdup in a piece of equipment is stable and process variability is small, that equipment need not be measured as frequently as other equipment where holdup is not stable or where the process variability is larger.

Note also in Fig. 7 that, following the steady-state portion of the data, a marked increase in holdup began after throughput t_{40} = 40 kg. This increase was caused by a change in experimental conditions; the calcining temperature was changed from 700°C to 900°C at that time. The resulting impact on holdup vividly illustrates how closely the nature of material deposition can relate to operating conditions.

C. Modeling with Respect to Space

For large pieces of equipment, such as pulse column in equilibrium or a batch precipitator after process runout, it is not possible to accurately estimate the holdup at a particular time based on a single nondestructive measurement. Other examples of this type include material accumulation on floors of glove boxes and sludge buildup in holding ponds. The accumulation of holdup can be nonuniform across space; for example, different sections along the length of a precipitator column can contain different concentrations of material. It is necessary to acquire measurements from different locations to estimate the holdup profile.

As an example, consider the precipitator used in the ADU experiment. At each of 17 locations along the column, concentration measurements (grams of uranium per unit length) were obtained. One such set of data is presented in Fig. 9, plotted for convenience in a logarithmic scale along the

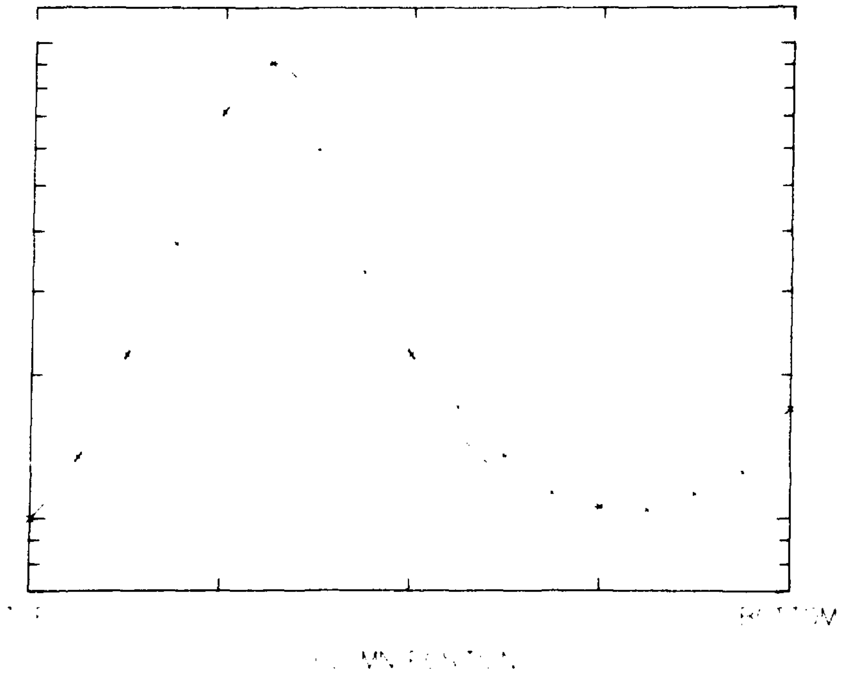

Fig. 9.
Holdup profile of ADU inside a precipitator column.

y-axis. It is clear that holdup is not uniformly distributed on the interior of the precipitator. Large accumulations in the upper regions of the column are caused by the violent chemical reactions that lead to phase changes when NH_4OH contacts the uranyl nitrate solution. Some of the ADU formed at this interface is splashed onto the interior surface above the liquid level. At the bottom of the column, the process of draining the ADU leads to the transport of material there and thus slightly increases residual holdup.

Once an estimate of the profile is obtained, mathematical integration of the profile provides the estimate of the holdup. The same approach can be easily extended to cover material deposited over large two-dimensional areas. Fitted contours of the profiles are developed and integrated to estimate holdup. This type of modeling is analogous to the response-surface methodology discussed in statistical texts.

Holdup can also be modeled with respect to both time and space. This requires estimation of the time-varying profile. Detailed illustrations of such modeling for holdup in glove box and ductwork are given in Ref. 15. Certain aspects of multivariate time-series analysis may be applied to such problems.

VII. SUMMARY AND CONCLUSIONS

The measurement of holdup of SNM in large processing facilities is a difficult problem; it will remain so because of its complexity and the inherent limitations of NDA techniques. One of the alternatives to NDA measurements is "cleanout" measurements using both destructive and nondestructive analyses. This approach is not only time-consuming and process disruptive; it can be extremely expensive as well. An inevitable reality at almost all processing facilities is the difficulty of assigning high priority for holdup measurements when other concerns seem to deserve higher priorities. It is important, however, for plant operators to recognize that knowledge of holdup problems can contribute significantly to plant safety, process efficiency, and nuclear material safeguards.

Statistical estimation models can assist plant operators in meeting regulatory requirements of holdup estimation as part of periodic inventory development. However, the development of useful prediction models of holdup hinges on the quality of data and the stability of process operations. The quality of measurements can be improved with better instrumentation and better calibration standards coupled with the application of carefully chosen secondary measurement techniques. Holdup estimation models require periodic updating to remain useful as facilities and process variables change. It is possible to carry out measurements for updating estimation models without seriously impacting or interfering with processing schedules. If the operating conditions are subject to frequent changes and/or the measurement errors are very large, it is unrealistic to expect the development of useful estimation models. On the other hand, if the process operation is stable and the holdup data gathered are of good quality, the models developed can be very valuable to making present and future estimations of holdup.

Improvements in holdup measurements and data development are most effectively accomplished if the problems of holdup can be addressed during facility design. Structural features can then be incorporated to make the holdup measurements with relative ease. It is possible to accomplish this without compromising process design, safety, or capital cost. The quality of holdup estimation in large facilities can be further improved if it is preceded by systematically developing a sampling plan--taking into account process details, facility layout, stratification of materials, degree of difficulty of measurements, and resource limitations.

The difficulties associated with holdup measurements at SNM-processing facilities are the results of both facility- and measurement-related problems. Neither of these has a simple short-term solution, although certain improvements can help to meet the objectives of nuclear material safeguards and accountability. Carefully designed measurements can be part of inventory records development. The judicious use of statistical prediction models is also vital.

There are several limiting factors to accomplishing the goals of regulatory requirements of holdup estimation. These impediments include the layout of the plant and equipment, the need for calibration standards, limitations of NDA instruments, and the lack of priorities for holdup measurement at special nuclear materials processing facilities. The layout of many of the existing facilities is a major hindrance to holdup measurement. Although major changes in existing facilities are difficult, layout should be considered in the design and construction of new facilities. The very considerable opportunity for innovations in the development of standards specially suited for materials holdup measurement can be stressed in regulatory guidelines on holdup measurements. Developments in NDA instrumentation of the last decade have not yet addressed the needs of holdup measurement. Thus, there is a dearth of specially designed NDA instruments that are readily adaptable to meet the needs of a variety of holdup measurements. Finally, and most vitally, an increased awareness of the importance of holdup measurements for materials accountability, process safety, and efficient plant operations can contribute significantly to meeting the goals of regulatory requirements of holdup estimations.

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APPENDIX

EXAMPLE PROCESS USED IN THE STUDY OF SNM HOLDUP (Low-Enriched Uranium Conversion and Fuel Fabrication)

by

K. K. S. Pillay

I. INTRODUCTION

The example process considered is an important part of the fuel fabrication technology for light-water reactors (LWRs). There are many commercially licensed facilities in the U.S. where a similar process is used to prepare enriched uranium fuel materials for a variety of reactors.[1] Two distinct segments of this example process are

(1) uranium hexafluoride conversion to uranium dioxide and

(2) fabrication of uranium dioxide pellets into fuel pins and assemblies.

These major processes at the example uranium conversion facility are schematically shown in Figs. A-1 and A-2, respectively. In Secs. II and III of this appendix, these two process segments are described in detail. In Sec. IV, some basic elements of materials accounting for this example process are considered with the objective of highlighting the role of "holdup" in materials accounting.

II. THE UF_6 CONVERSION TO UO_2

The chemical form of uranium commonly used in the preparation of fuel pellets is a highly sinterable UO_2. The sinterability (or ceramic activity) of UO_2 is related to its specific surface area. This special form of UO_2 can be prepared in many ways using various starting materials and processing details. Five common process routes for the conversion of UF_6 to UO_2 are (1) $UF_6 \rightarrow ADU \rightarrow UO_2$; (2) $UF_6 \rightarrow UF_4 \rightarrow UO_2$; (3) $UF_6 \rightarrow UO_4 \rightarrow UO_2$; (4) $UF_6 \rightarrow UO_2F_2 \rightarrow UO_2$; and (5) $UF_6 \rightarrow AUC \rightarrow UO_2$. (Note that ADU and AUC

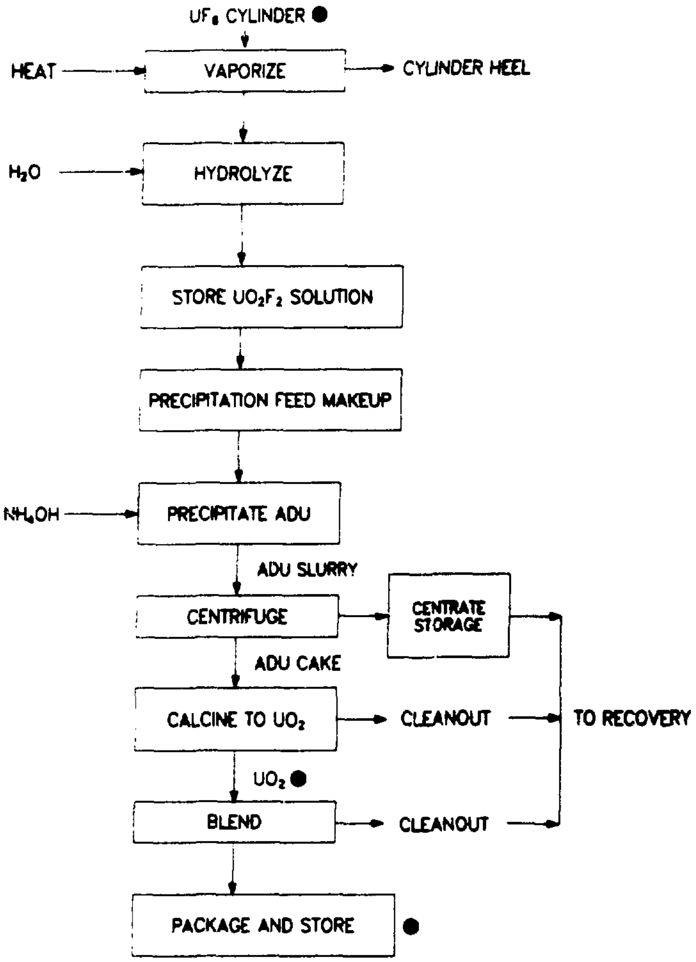

Fig. A-1.
The UF_6 to UO_2 conversion process. Key measurement points are indicated by •.

are ammonium diuranate and ammonium uranyl carbonate, respectively.) In the example considered here, the starting material, UF_6 of the desired enrichment, is converted to UO_2 through an intermediate step involving precipitation of uranium as ADU. This process is common to commercial LWR fuel fabrication plants in the U.S.

Desirable characteristics of uranium dioxide for reactor fuel element fabrication include its low thermal expansion and the high compressed density (~10 g/cm^3) of its fuel pellets. To produce such fuel pellets, the UO_2 powder should have low bulk density and high surface area. Uranium dioxide particles of about 0.3 micron with a bulk density of about

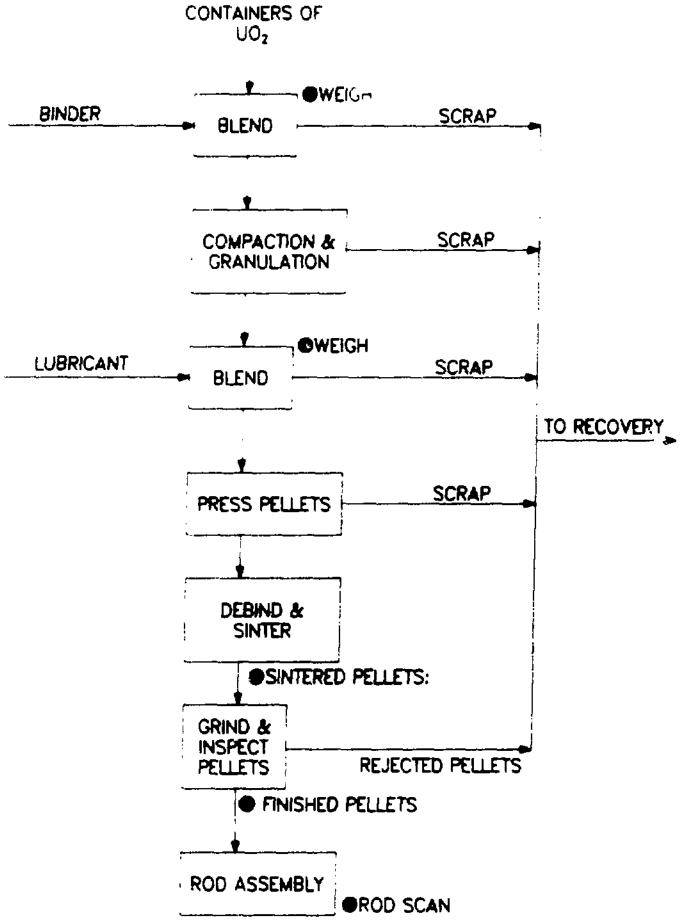

Fig. A-2.
Fabrication of LWR fuel from UO_2. Key measurement points are indicated by •.

1.8 g/cm^3 are considered desirable starting material. In the production of such UO_2 particles, an ADU cake with small crystalline size and large surface area is important so that the ADU reacts well during drying, calcination, reduction, and stabilization. Thus, ADU precipitation is an important step in the whole process of producing good quality fuel materials.

According to the Von Weimarn theory of the formation of small particles, the greater the initial rate of condensation into particles, the smaller the particles attained, and thus the greater the surface area.[2] Under ideal conditions, ADU precipitation produces particles with a surface area of up to 25 m^2/g. Numerous practical problems exist in producing this quality ADU cake in a large-scale production line. It is possible, however, to produce ADU with a surface area of up to 20 m^2/g routinely, which in turn can produce a fuel pellet of compressed density of about 10 g/cm^3.

Figure A-3 presents the process steps in the conversion of UF_6 to UO_2 via ADU precipitation.[3]

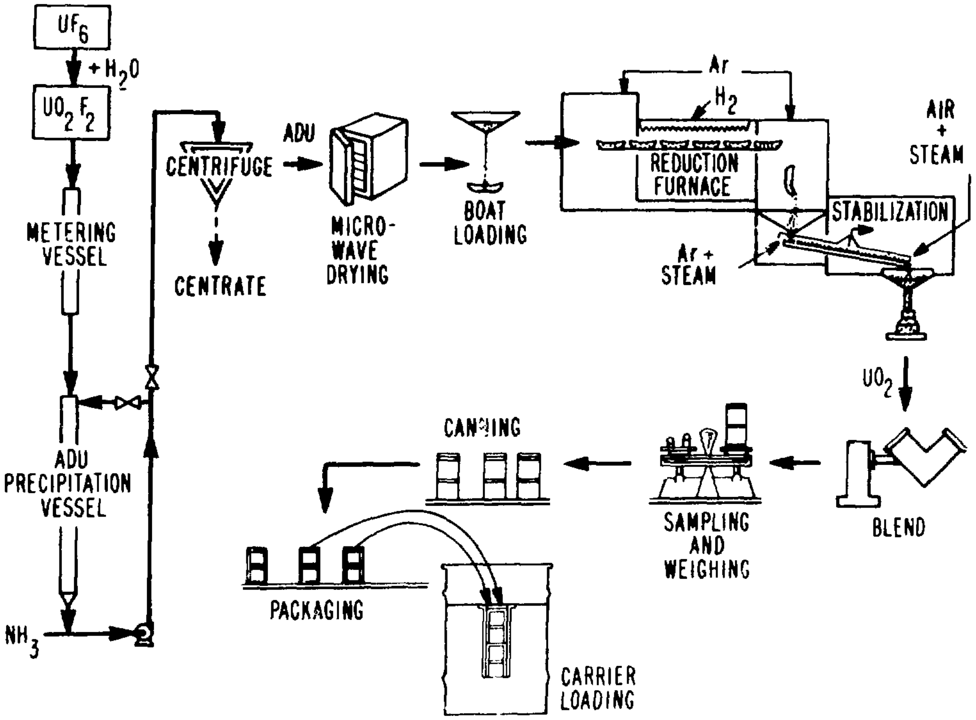

Fig. A-3.
Flow diagram of the $UF_6 \rightarrow UO_2$ conversion process.

A. Hydrolysis of UF_6

Uranium hexafluoride is a white crystalline solid that sublimes slowly at room temperature and normal atmospheric pressure. Under high pressure, the crystals melt to form a clear colorless liquid. When heated to 95°C with radiant heaters, UF_6 is vaporized directly from shipping cylinders, at about 4 atmospheres absolute. Chemically, UF_6 is highly reactive.

It reacts vigorously with water. The primary step in the conversion of UF_6 to UO_2 is its hydrolysis to uranyl fluoride, as represented by the equation

$$UF_6\ (g) + 2H_2O\ (l) = UO_2F_2\ (aq) + 4HF\ (aq) \quad .$$

This chemical reaction is sufficiently exothermic (50.2 Kcal/mole) to produce a consequent rise in the temperature of the system.

B. Precipitation of Uranium from Aqueous Solution

Uranium in uranyl fluoride solution is precipitated as ADU by the addition of ammonia. The ADU is a nonstoichiometric compound with an approximate composition represented by the formula $(NH_4)_2U_2O_7$.

$$2UO_2F_2\ (aq) + 6NH_4OH\ (aq) = (NH_4)_2U_2O_7\ (s)$$
$$+ 4NH_4F\ (aq) + 3\ H_2O\ (aq) \quad .$$

Because this reaction is also exothermic, it is desirable to keep the system temperature around 30-40°C during the ADU precipitation. Theoretically, 1 mole of uranium requires 3 moles of NH_4OH. As the UO_2F_2 solution contains 4 moles of hydrogen fluoride per mole of uranium, a total of 7 moles of NH_4OH is required theoretically to precipitate 1 mole of uranium from UO_2F_2. In practice, about 9 to 10 moles of NH_4OH are required to completely precipitate 1 mole of uranium from this solution. Although excess NH_4OH in the mixture improves the quality of the ADU precipitate by increasing its surface area, an extremely large excess of NH_4OH makes the precipitate impossible to filter. Considering both filtration and sintered product characteristics, the recommended molar ratio of NH_4OH to UO_2F_2 is about 26:1 (Ref. 2).

C. Separation of ADU from Slurry

The ADU can be separated from the reaction mixture by various filtration and centrifugation techniques. The centrifuge, which is efficient, does not adversely impact the quality of ADU cake. Centrifuging at about 1000 g provides a rapid method for separating ADU from the mother liquor. The centrifugate (or centrate) generally contains extremely low levels of uranium. The centrate, normally collected in large storage tanks of known volume, is sampled for analysis before its dumping into waste lagoons.

D. Drying the ADU

The moisture-laden ADU from the centrifuge is placed in shallow trays and dried in a microwave oven at ~100°C.

E. Reduction of ADU to UO_2

Shallow calcining boats, made of Hastalloy-C or nickel, are loaded with the dry ADU cake to a height of not more than 1 inch then placed in a reduction furnace maintained at 650-700°C. The furnace is filled with argon at the time of loading to maintain an inert atmosphere. Hydrogen is introduced then to maintain its high concentration in the furnace; calcination and reduction continue for about 10-14 h.

F. Stabilization of UO_2

Exposing freshly reduced UO_2 to the air causes immediate chemisorption of a monolayer of oxygen, which, in turn, causes heat evolution and eventual ignition of UO_2, after which it burns, forming U_3O_8 (Ref. 4). The freshly reduced UO_2 is therefore cooled in an environment of steam and argon before exposure to air. This process changes the pyrophoric characteristics of the UO_2 and stabilizes it against oxidation without reducing the surface area of the powder.

III. FUEL FABRICATION

Figure A-4 shows the process steps of fuel fabrication subassembly.[5] The UO_2 from the conversion line is first blended and milled to a uniform consistency. Binder materials, which serve to control the final

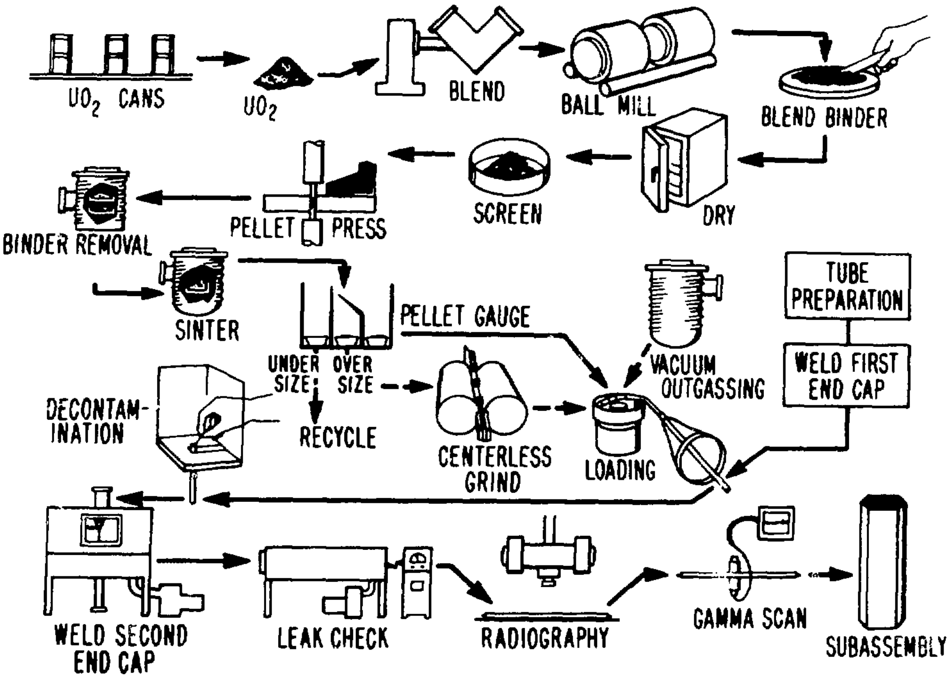

Fig. A-4.
Flow diagram of an LWR fuel fabrication line.

porosity of the pellets, are added to the blended UO$_2$. This mixture is dried, granulated, and screened to retain granules of -20 to +100 mesh (or 150-850 microns). These granules are blended with a lubricant before being placed in pellet presses operating at about 30 000 to 60 000 psi. The binder is removed from the green pellets by heating them (in a furnace) to 650°C in an atmosphere of argon mixed with about 8% hydrogen. These pellets are then sintered in a similar inert reducing atmosphere at 1600-1750°C. The sintered pellets, cooled to room temperature in an inert atmosphere of argon, are finally sorted and ground (in centerless grinding machines) to tolerances that meet the fuel pellet specifications. Thereafter, the pellets are individually inspected.

The finished pellets, stacked and weighed as UO$_2$ before canning, are outgassed at elevated temperatures to remove final traces of moisture and organic residues before they are loaded into clean cladding tubes with one end cap welded in place. The loaded tubes are inspected, decontaminated, evacuated, and filled with inert gas before the second end cap is welded. The sealed tubes are leak tested, radiographed, and subjected to a fissile loading assay by nondestructive assay (NDA) techniques before their use in fuel subassemblies.

IV. ELEMENTS OF MATERIALS ACCOUNTING AND THE EXAMPLE PROCESS

No attempt is made here to consider deeply the aspects of materials accounting that are rigorously considered in other chapters. Some elementary, but important, aspects of materials accounting applicable to the example process are briefly discussed in the following paragraphs.

A. Materials Accounting

Nuclear materials accounting is based on a system of measurements and reports that document the flow and disposition of SNM. Some of the key measurement points of the conversion process MBA and the fabrication process MBA are identified in Figs. A-1 and A-2. However, materials flow identification for process control and inventory measurements for materials accounting may require additional measurements of SNM at other points of the process. The actual number of measurement points for materials flow identification and inventory measurements are variable depending on the facility, its process streams, and the administrative controls.

Materials balances can be drawn around the MBAs of this example process by interrupting the plant operation, cleaning the equipment, and measuring all components of the in-process inventory. There are inherent limitations to this approach in sensitivity and timeliness. The sensitivity is limited by measurement uncertainties that may conceal losses of significant quantities of materials in large plants. The timeliness is limited by the frequency of physical inventories. Both sensitivity and timeliness are improved by implementing dynamic materials accounting (or near-real-time accounting). This approach combines conventional analyses and measurements with on-line, NDA instrumentation to provide rapid and accurate assessment of the locations and amounts of nuclear material in a facility. Materials balances are drawn without plant closure; in-process inventories are measured, or otherwise estimated, while the plant is operating.

To implement this approach, the plant is divided into several discrete accounting areas. Each includes one or more chemical or physical processes chosen on the basis of process logic and the ability to draw a materials balance. By measuring all materials flows in each area separately, quantities of material much smaller than the plant inventory are controlled on a timely basis, and any discrepancies are localized to the portion of the process contained in the accounting area.

Near-real-time accounting is not a necessary approach for complying with the current regulatory requirements of low-enriched uranium fuel fabrication facilities but is desirable for processing facilities handling large quantities of plutonium and/or highly enriched uranium.

B. The MBAs and ICAs

An important aspect of any materials accounting system is the designation of MBAs and ICAs. Of these, MBAs are more important to materials accounting and safeguards. Because materials balance areas have defined physical boundaries, each MBA represents a natural grouping of related processing and handling operations. The natural flow of materials between MBAs involves the transfer of discrete measurable items. There is no requirement that a facility be divided into any particular number of MBAs. However, a greater number of MBAs will improve the localization of materials loss, although the degree of improvement in overall sensitivity may be rather small and dependent on the quality of transfer measurements. The MBAs should be established so that they provide useful information while retaining adequate internal control of SNM.

In the example process discussed, at least two MBAs are easily designated. The process areas represented in Figs. A-1 and A-2 represent two distinct MBAs. In MBA-1, the UF_6 is converted into UO_2. This material is transferred to MBA-2 as discrete and measured items (known weights of UO_2 in cans). The UO_2 is fabricated into fuel pellets and eventually into fuel pins and subassemblies. The boundaries of these two MBAs, shown in Fig. A-5, are representative of most processing facilities. If there are shipper-receiver differences between the two MBAs, they may be caused by uncertainty in moisture content of the UO_2 powder. Because of lower

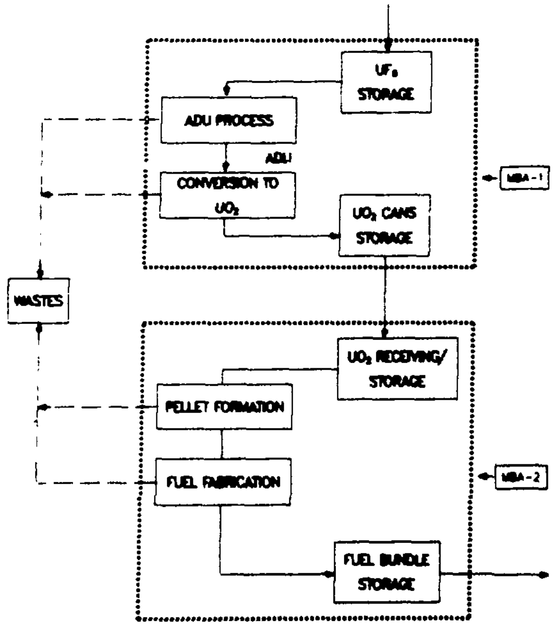

Fig. A-5.
Boundaries of the two MBAs of the example process.

levels of measurement uncertainties, materials accounting in the conversion facilities (MBA-1) may better detect materials losses than materials accounting in the fabrication line (MBA-2).

The ICAs are designed to provide maximum control over all materials not in an immediate processing status. Figure A-6 shows five distinct ICAs for our example process: the UF_6 storage area, the UO_2 can storage/transfer area in MBA-1, the UO_2 receiving/storage area in MBA-2, the fuel bundle storage area, and the waste barrel storage area common to both MBAs.

C. Uncertain Inventories

Waste streams and materials held up in equipment as hidden inventories are often difficult to measure or estimate. The potential areas of waste and holdup accumulation in the two MBAs of our example processes are shown in Figs. A-7 and A-8. A detailed examination of holdup problems in materials control and accounting is presented in Chap. IX.

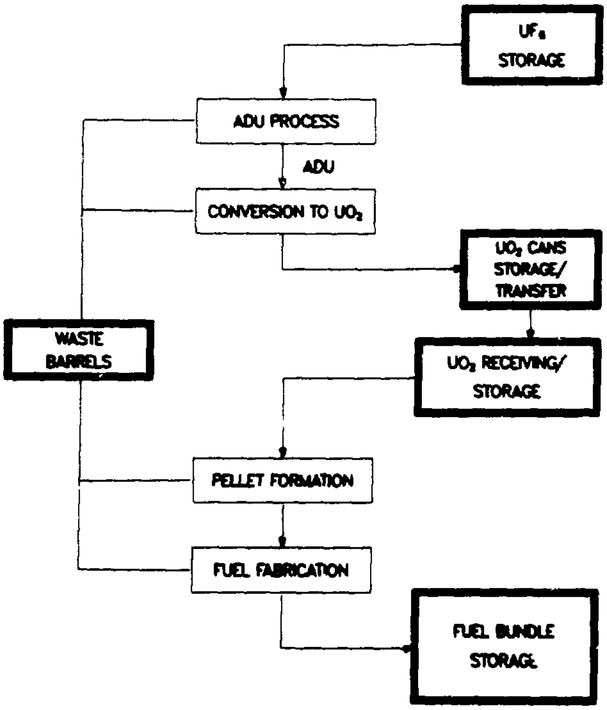

Fig. A-6.
Five distinct ICAs of the example process.

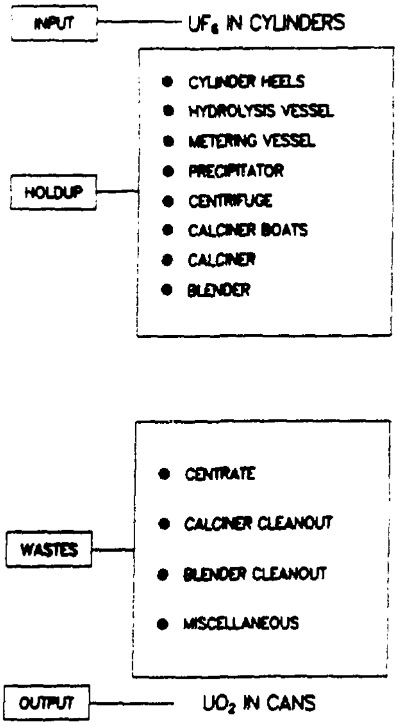

Fig. A-7.
Areas of holdup and sources of waste of the UF_6 conversion segment of the example process (MBA-1).

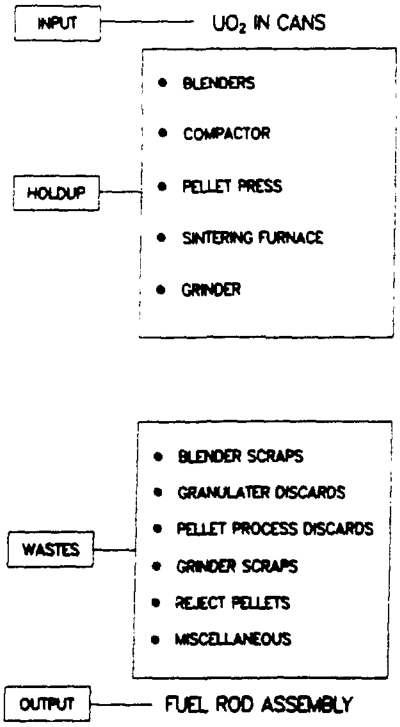

Fig. A-8.
Areas of holdup and sources of waste of the fuel fabrication line of the example process (MBA-2).

D. The MBA Subsystems

Materials balance data for a process facility are usually collected from several MBAs. Each MBA should have the subsystems shown in Fig. A-9 to enable the facility operator to identify correctly any materials lost or diverted as well as the point of that loss or diversion. These subsystems are subjects of in-depth discussion in other parts of this document.

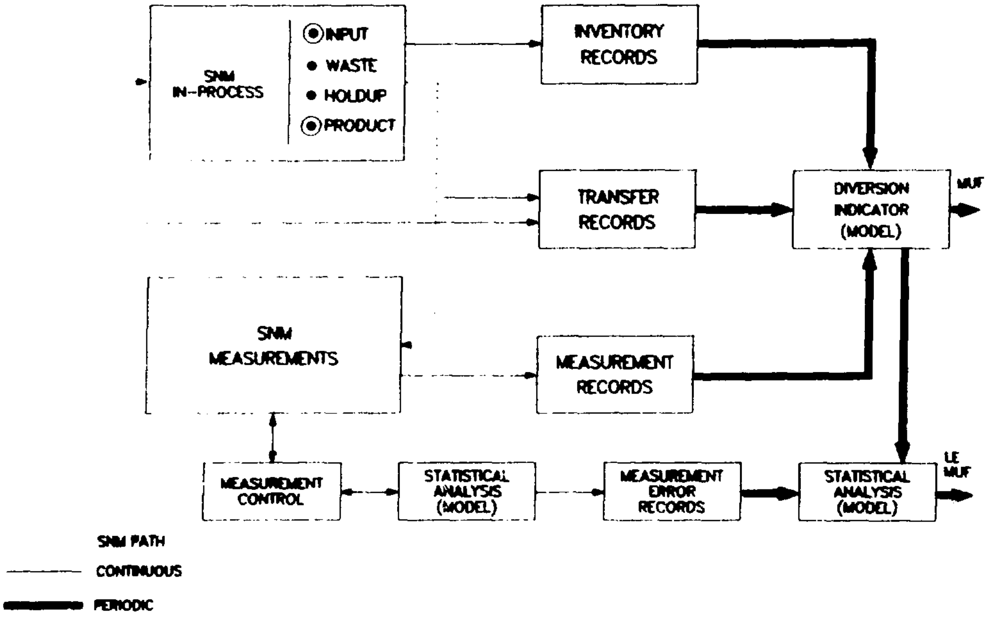

Fig. A-9.
The MBA subsystems and relationships.

In some formal discussions of materials accounting, materials balances are drawn around block diagrams without much consideration to process details. The components of a materials balance equation are initial inventory, final inventory, input transfers, and output transfers, as represented in the following equation.

$$MB = I_i + \sum I_t - I_f - \sum O_t \ ,$$

where I_i is the initial inventory, I_f is the final inventory, $\sum I_t$ is the sum of all input transfers, and $\sum O_t$ represents all output transfers during the inventory period.

In the context of materials accounting, these quantities are assumed measurable irrespective of the nature of the process or the complexity of the facility layout. In practice, materials inventory in process vessels, in-plant holdup, and waste streams is difficult to measure. Although the absolute values of holdup and wastes are not a large part of the plant inventory, the variations in these components can affect materials balances. It is therefore prudent to develop better estimates of these two components to improve the overall sensitivity of the materials accounting system.

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CHAPTER VII

MEASUREMENT CONTROL AND QUALITY ASSURANCE

by

R. G. Gutmacher

I. INTRODUCTION

Measurements of weight and volume, chemical and isotopic composition, and physical properties of materials are made to control a process, certify that products meet specifications, and provide regulation and accounting of special nuclear materials. It is vital that these measurements be of consistent and acceptable quality. In a processing plant, faulty data can cause incorrect decisions, loss of materials, rejected product, equipment failure, and operational errors.[1]

In safeguards, the effectiveness of the materials balance accounting system hinges directly on the accuracy and precision of the measurements that are used to calculate the materials balances. Erroneous data can lead to incorrect decisions regarding the loss or diversion of nuclear material. Large measurement errors and known sources of bias must be detected and eliminated. The design and evaluation of a safeguards system requires knowledge and control of the inherent random and systematic errors of all measurements that go into the materials balance. Using an effective quality assurance program helps assure the quality of measurement data.

The quality of measurement data depends on the validity, integrity, preservation, and retrievability of the data. Data are valid when they are obtained by technically sound methods; they have integrity when the measurement methods are correctly practiced; they are preserved when protected against loss and physical damage or destruction; and data are retrievable when they are readily obtained as needed.[1]

Providing quality data depends on how well measurement activities are planned and executed to minimize problems that adversely affect those four factors. Some examples of such problems are improper use of procedures or instruments, poorly trained technicians or operators, misinterpretation of data, and inadequate data recording systems. To ensure success, control must be established over sources of problems throughout the lifetime of any measurement activity.

Measurement control is part of the larger discipline of quality assurance. Quality assurance has been defined as "all those planned and systematic actions necessary to provide adequate confidence that a structure, system, or component will perform satisfactorily in service."[2] The key phrase in this definition is "planned and systematic actions" because quality assurance helps to provide a disciplined approach in planning, organizing, and carrying out work tasks. Quality assurance integrates technical and administrative practices.

Quality assurance has two distinct but related activities:

(1) quality (or measurement) control--those procedures and activities developed and implemented to produce a measurement of requisite quality and

(2) quality assessment--those procedures and activities utilized to verify that the quality control system is operating within acceptable limits and to evaluate the quality of the data.[3]

The key to the proper use of quality assurance is to apply it only to the extent needed to achieve effective control. Too much control wastes time, money, and people and can lead to nonacceptance of quality assurance by those responsible for carrying out project activities. Too little control can be wasteful also.[1] Inadequate control can result in losses, failures, incorrect decisions, and additional work to resolve discrepancies.

In this chapter, we discuss the technical and administrative elements of a quality assurance program for measurements. We also examine the qualification of measurement methods, the identification of sources of errors in various types of measurements and control procedures, the acquisition of measurement uncertainty estimates, and the use of control charts.

II. REGULATORY REQUIREMENTS

Two orders by the Department of Energy (DOE) pertain to quality assurance and measurement control. The DOE Order 5700.6B (April 1984) addresses quality assurance programs and states that the following elements must be included, as a minimum:

(1) assignment of organizational responsibility and authority for activities affecting quality and activities to assure quality achievement,

(2) definition of quality and quality assurance objectives and requirements,

(3) implementation of procedures and work instructions,

(4) independent verification of quality attainment and quality assurance program effectiveness, and

(5) early detection and correction of deficiencies.

DOE Order 5633.3 (February 1988) states

> ...each facility shall implement measurement control programs for all measurement systems used for the accountability of special nuclear material (SNM). These programs shall be consistent with a graded safeguards system and shall be referenceable to and validated by a national measurements and standards program, where practicable, and shall include:
>
> 1. scale and balance program;
> 2. analytical quality control program;
> 3. sample variability control program;
> 4. control program for volume, temperature, and pressure measurements;
> 5. calibration program for nondestructive assay measurements; and
> 6. sample exchange program.
>
> Measurement control programs for the other nuclear materials shall be developed to maintain adequate accountability consistent with the intrinsic and management value of these materials.

The Nuclear Regulatory Commission's requirements for a measurement control program for SNM are contained in the Code of Federal Regulations, Title 10, paragraph 70.57. We quote selected sections later in this chapter.

III. ELEMENTS OF A QUALITY ASSURANCE PROGRAM FOR MEASUREMENTS

Quality assurance should begin early in the planning process for a new or upgraded process or facility. The earlier in the planning process that measurement requirements, measurement and sampling points, and methods and instruments can be established, the greater the probability that the process and the measurements will be well integrated and that both safeguards and process needs will be met. If quality assurance is to be introduced into an existing process or laboratory, the existing measurement practices should be evaluated. Existing practices are modified or new practices are implemented only when the evaluation shows inadequacies in the current operations.

Two reports[1,4] and an American Society for Testing and Materials (ASTM) Standard Guide[5] provide excellent counsel in the establishment of quality assurance for measurements in the nuclear industry. Reference 3, while devoted primarily to the correct use of standard reference materials, also discusses quality assurance in general. Anyone who is responsible for or concerned with the quality of measurements would find these sources useful. We borrow liberally from them in this chapter.

Nine elements of quality assurance are identified in Refs. 1 and 5, and recommended practices are given for each. These elements are

- organization,
- quality assurance program,
- training and qualification,
- procedures,
- measurement records,
- control of records,
- control of equipment and materials,
- control and review of measurement methods, and
- periodic program reviews.

We discuss each of these briefly; the original sources should be consulted for details.

A. Organization

The effective administration of a quality assurance/measurement control program requires an organization with adequate skills, dedication, and authority to carry out the prescribed functions. The place of this organization within the facility should be clearly defined. For all personnel engaged in measurement activities, the functional responsibilities and levels of authority should be clearly established. Functional responsibility defines how work is accomplished in terms of who does it, where it is done, and who is ultimately responsible for the results. Authority includes decisionmaking and approval of actions, extending from the working level up to management.

The primary responsibility for planning, developing, coordinating, and administering the program should be assigned to an individual who holds a position at an organizational level that permits independent and objective action. That person should not have responsibilities of an operational nature that may result in conflicting goals. The administrator, who needs good knowledge of and experience with measurement operations, should have sufficient authority to enter work areas and inspect records and activities to obtain all of the information needed to monitor and evaluate measurement quality. Prescribing corrective actions if measurement quality becomes inadequate and ascertaining whether the actions have been taken are further responsibilities. The administrator needs direct access to and full support of top levels of management. The staff of the administrator will assist in the collection of data and in statistical evaluation, the performance of internal audits, assessments of the program, and assistance to laboratory and other personnel engaged in measurement activities.

B. Quality Assurance Program

Quality assurance becomes a formal, visible program when a document is prepared and approved that prescribes the quality assurance requirements applicable to measurement operations and that describes how those requirements are to be met. The description of the program should identify the measurements and other activities that must be monitored in order to evaluate and control measurement quality. These include calibration and standardization procedures and schedules as well as data control and statistical evaluation procedures. The document will describe those procedures used to monitor measurement facilities, equipment and instruments, measurement procedures, personnel, and information systems, to ensure their effective contributions to the quality assurance program.

Once the documentation has been prepared and approved, all measurement personnel should be instructed in the overall contents of the program. New or modified practices should be implemented by training personnel in their use.

C. Training and Qualification of Personnel

The quality of measurements used in nuclear materials control and accounting is affected by the knowledge, skill, and care of the persons who perform the measurements. It is important that sampling, bulk measurements, chemical analyses and nondestructive assay, and equipment calibrations be performed only by individuals who adequately qualify for these jobs. Procedures for selecting, training, and periodically evaluating such persons should be planned and carried out to ensure that performance is consistent, uniform, and of acceptable quality. When an evaluation indicates that a person is not performing a measurement task adequately, the situation can be corrected by either retraining or reassigning the individual.

A guide for developing training programs in the nuclear industry is available.[6] Establishment and operation of an analyst qualification program is described in Ref. 7.

D. Procedures

Measurements are carried out in a planned, systematic, and controlled manner, so that the results will be valid, that is, based on sound technology. To control measurements and avoid errors leading to unsatisfactory results, procedures are written for those doing the work. Written procedures also provide information for training analysts, establish the technical bases of the methods, and document the processes used in the measurements. Procedures must be well written, complete, and correct.

E. Measurement Records

Measurement records are of two kinds: those used to document measurements made in the laboratory or in the plant and those associated with the measurement control program. A laboratory record system provides documentation for the following functions: receive sample information from the submitter, provide sample identification, transmit information and data through the laboratory, provide a record of data and information generated in the course of the measurements, and report the results of measurements. Records associated with the measurement control program should include all data, information, reports and documents generated by the program, and summaries of the measurement control data used in the limit-of-error calculations for each materials balance period. Examples of data included in these records are

- equipment calibrations,
- measurements of standards and replicate measurements of process material and evaluations of the data,
- preparation and calibration of standards,
- bias corrections,
- statistical analyses of measurement data,
- test results for the approved bulk material mixing and sampling procedures, and
- designs, specifications, and preoperational tests of measurement equipment and methods.

F. Control of Records

An effective system of control must provide records that are identifiable and retrievable. Records provide direct evidence and support regarding the quality of measurement data that may be needed for future reviews and evaluations, particularly if regulatory or legal questions are raised. If a computer is used, the computer program must be verified and validated, and protection must be provided to prevent loss, tampering, or damage of the computer and the data. Recommended practices for the identification, distribution, storage, retrieval, and retention time of records are given in Refs. 1, 4, and 5.

G. Control of Equipment and Materials

1. Measurement Facilities and Equipment. The quality of materials accounting measurements can be limited by features of facility design. For example, if there is not sufficient accessibility to in-plant measurement equipment, recalibration may not be feasible. Unless the proper environment is provided, measurement equipment may be exposed to corrosive vapors, excessive temperatures, or undesirable vibrations. Unless adequate design specifications have been set, measurement equipment may lack the necessary sensitivity or reproducibility. Consideration of measurement system requirements during design, construction, or modification of nuclear process facilities and during the preparation of design or purchase specifications can reduce subsequent measurement control problems.

The design, specifications, and planned usage of all facilities and equipment that may impact on measurement quality should be reviewed prior to the final design or purchase commitments. At a minimum, the reviews should ensure that

(a) sufficient consideration is given to design and installation features that would provide acceptable measurement and sampling capabilities in the facility;

(b) measurement and sampling equipment and instruments can be properly calibrated, tested, and maintained after startup;

(c) all criteria and conditions necessary for achieving acceptable measurement quality are specified in purchase orders, design drawings, and instructions; and

(d) all special services and environmental conditions needed for successful operation of the measurement systems are provided, such as stabilized power sources and protection of instruments from corrosive vapors, vibration, and extremes of humidity and temperature.

Before use, new or modified measurement and sampling facilities and equipment should be tested for operability and compliance with specifications. The test results should be reviewed by the quality assurance personnel.

Instruments, equipment, and measurement systems should be controlled through a calibration program. The program should identify the specific items included, define calibration requirements, and designate calibration standards and frequency for each item. The program should identify the calibration status of each item on a continuing basis and control the use of out-of-calibration equipment. After calibration, the data should be reviewed to verify that (1) the calibration range is adequate; (2) the equipment meets performance criteria expressed as range, sensitivity, drift rate, and stability; and (3) the calibration and test data are adequate to establish acceptable operating procedures and to yield a sufficiently small standard deviation for the calibration curve. Complete records of designs, specifications, fabrication, and test data should be retained at least five years to permit retracing the performance history of facilities and equipment that affect measurement quality.

2. Reagents and Standards. The quality of chemicals used to prepare reagents and reference materials should be specified. Data on labels should include name; concentration; solvent if other than distilled water (for liquids); matrix if a solid; date prepared; and special limitations on storage, use, and age. Unlabeled, improperly labeled, or outdated material should be discarded.

Physical standards, such as calibration weights, must be properly stored and carefully handled to protect them from damage. Storage containers should protect materials from contamination by impurities and from change in concentration. Storage conditions should meet special requirements, such as control of exposure to light or humidity.

3. Samples. Loss of sample integrity can occur from inadequate sampling procedures and from improper control and handling practices once the samples have been taken. Proven sampling methods should always be used when possible and sampling responsibility should be clearly established. We discuss sampling and its contribution to measurement uncertainty in Sec. V. Recommended practices for sample receipt and inspection, identification, handling, and disposition are given in Refs. 1 and 5.

H. Control and Review of Measurement Methods

The choice of a measurement method often requires a compromise among such desirable characteristics as accuracy, precision, range of application, freedom from interferences, rapidity, and economy. We discuss the choice and validation of a measurement method in Sec. IV.

Formal review and approval procedures should be established and maintained for in-plant measurement, sampling, nondestructive analysis, and laboratory analytical methods. Each method should be documented, following the guidelines of Sec. III.D. Documentation should specify the reference materials to be used, the required frequency of use, any special instructions for obtaining reliable calibration or control data, and the required treatment of data. Criteria that indicate when a method is uncontrolled should be given, along with requirements to return the method to control. Instructions for preparation of reference materials should be included when appropriate. When possible, reference materials should be traceable to NBS Standard Reference Materials (SRMs) or other nationally recognized reference materials.

A formal procedure for review and approval of measurement methods serves several purposes:

(1) to adequately consider the needs of SNM control and accounting as well as process and product quality control (many measurement methods serving more than one purpose);

(b) to review, by responsible personnel, planned changes in procedures for measurement quality control before the changes are made; and

(c) to assure that application of the measurement procedures will be consistent; measurement control data, more stable and predictable.

Measurement performance is monitored and evaluated using data obtained from calibrations, replicate measurements, comparative measurements, and other techniques Evaluation includes calculating biases and random error standard deviations, deriving calibration curves, setting control limits, testing for outliers, and monitoring error trends both by control charts and by statistical hypothesis testing. These aspects are further discussed in Secs. V and VI.

I. Periodic Program Reviews

Management should review the measurement quality assurance program annually, to ensure that program procedures are not obsolete or irrelevant. The major emphasis of the review centers on how effective the program has been in meeting its goals and objectives. The responsibility for conducting the review should be assigned to a person with no direct responsibility for any measurement quality assurance functions. This person should have administrative and auditing experience and sufficient knowledge of quality assurance and measurement technology to ensure competent and objective judgments of the effectiveness of the program. Some objective indicators of the state of nuclear materials control and accounting that are most directly affected by the measurement quality assurance program and that can be used to evaluate its effectiveness are

(1) the magnitude of the historical inventory differences (IDs) and their randomness,
(2) comparisons of the standard deviations of the IDs derived by propagation of measurement error data and those calculated from historical IDs,
(3) comparisons between the measurement standard deviations being achieved and the current state-of-the-art information for similar applications, and
(4) comparisons of shipper and receiver data.

The reviewer should issue a report to management, describing procedures, results, and recommendations. When the review discloses discrepancies between performance and requirements, management should promptly act to correct any deficiencies. The program administrator should review the discrepancies, recommend actions to minimize the probability of subsequent failures or deficiencies, assign responsibility for carrying out the remedial actions and establish a schedule, and later confirm that required actions have been taken and that the responsible and involved technical and managerial personnel have been fully informed.

IV. SELECTION AND VALIDATION OF MEASUREMENT METHODS

A prerequisite for method selection and validation is the establishment of firm requirements for the data that the measurement method is to provide. These requirements may be stated in terms of bias, precision, and range. When data requirements are poorly defined, measurements can be unnecessarily expensive or time-consuming if the method chosen is more accurate than required, inadequate if the method is less accurate than required, or completely futile if the accuracy of the method is unknown.[8] To validate the method, the performance parameters of the method are compared with the requirements for the data. A guide for validation of measurement methods is available from the American Society for Testing and Materials (ASTM).[9] We borrow freely from it in this section.

When selecting a method for a particular application, four technical factors must be evaluated:

(1) is the method actually capable of providing the specific measurement or analysis required;

(2) is the method free of interferences;

(3) does the method have adequate sensitivity and range for the materials that will be measured; and

(4) is the method able to produce data that will meet established bias and precision requirements?

Each element must be answered in the affirmative for the chosen method.[9] Other factors may enter into the decision: cost, number of measurements required in a day, and how quickly results must be available.

The selection of a method should be based on the following criteria. The method must

(1) be based on sound technology, with proven techniques used in recognized and accepted ways;

(2) not be adversely affected either by other components in the material to be measured or by potential interferences, such as environmental or electrical/electronic conditions;

(3) be capable of responding adequately over the range of concentration levels encountered for the constituent measured, with adequate discrimination between concentration levels and clear establishment of the lowest concentration levels that can be measured reliably; and

(4) be capable of producing data, under the expected conditions of use, that meet the bias and precision requirements established for the measurement.

Once a method has been selected based on the above criteria, it must be demonstrated that the method is in fact applicable to the material to be analyzed and that acceptable data can be produced under operating conditions, not ideal test conditions. If modifications in the method are required, the validation process will provide the necessary technical information. Validation also provides the experience and information needed to write a detailed procedure. The validation process results either in the rejection of a proposed method or in the confidence that it is acceptable for use as intended.

The performance requirements should be used to establish the conditions required for validation of the method. Such conditions may require a statistically designed experiment to allow for other sources of variability, such as the number of analysts or instruments as well as the concentration range of interest. The test materials should be as similar as possible to the material that will be analyzed. Whenever possible, the composition or properties of test materials should be defined by measurements traceable to certified reference materials. Sufficient tests must be made to evaluate the method for the variety of matrices and ranges of composition expected. It is generally best to include at least three levels of concentration, namely, the extremes and the mid-range of compositions expected. Statistical considerations suggest that at least seven measurements should be involved at each decision point.[8]

During the validation, it must be shown that the measurement system is under statistical control. Statistical control may be defined as the attainment of a state of predictability. Under such a condition, the mean of a large number of measurements will approach a limiting value (limiting mean), and the individual measurements should have a stable distribution, described by their standard deviation. Under statistical control, the limits within which any new measured value would be expected to lie can be predicted with a specified probability, the confidence limits for a measurement or mean of a set of measurements can be calculated, and the number of measurements required to obtain a mean value with a given confidence can be estimated.[3]

The precision of the measurement method can be determined by repeated measurements of the test material. For evaluation of bias, reference materials whose composition or properties are well known are required. The results of a sufficient number of measurements are compared to the expected or certified values. A detailed discussion of the use of reference materials is given in Ref. 3.

When a measurement system is altered or disturbed, the new or modified measurement system may result in a limiting mean or standard deviation or both that differ from the previous values. Whenever changes are made in instrumentation or procedures, the method should be revalidated. Similarly, if a method has not been used for a specified time and no control standards have been measured, the method should be revalidated.

Once a method has been selected and validated and a detailed procedure has been written, the method is ready for routine use. However, there should be a continuing effort to ensure the acceptability of the data produced as the method is used over time. A well-designed measurement control program will provide that assurance.

V. DETERMINING AND CONTROLLING MEASUREMENT ERROR

The principal measurements involved in nuclear materials accounting systems are those of weight and volume, sampling, laboratory analyses, and nondestructive assay. The uncertainties in each of these operations contribute to the uncertainty of the materials balance through the measurements of inputs (receipts), outputs (products, scrap, and measured discards), and inventories. The sources of data for estimating the errors associated with these operations are, primarily, analyses of reference materials, calibrations, special measurement tests, mixing and sampling tests, replicate measurements of bulk material quantities, replicate analyses of samples, and analyses of replicate samples.

A formal plan is needed for the collection of these data, so that random error standard deviations can be calculated and biases and the standard deviations of the bias estimates for all measurement systems used in SNM accounting can be estimated. Basic requirements of the plan are that all sources of measurement error that affect the limit of error of an inventory difference (LEID) are accounted for and that the random error and bias are separable in the data. The plan also affords the acquisition of data for setting control limits used in routine monitoring of measurement system performance.[4]

The data obtained from the sources above should be analyzed by statistical methods such as the analysis of variance to identify significant sources of random error and bias and to estimate the variance components. To ensure that the data can be analyzed effectively, statistical experimental design methods should be used in designing the data collection plan, sampling plans, or special method tests.

Neither the random errors nor the biases of sampling and measurements are likely to be constant over long periods of time. Therefore, it cannot be assumed that data collected in the past are applicable to current measurements. Sufficient measurement control data from each materials balance period are needed to permit independent calculation of the measurement errors for that period. The measurement data collection plan should be flexible to accommodate changes in material composition, equipment used for sampling or measurements, personnel, and procedures. Continuous evaluation of data requirements can ensure that current needs are being met and that no unneeded data are being collected.

Generally, the estimate of the standard deviation for a measurement process should be based on at least 15 replicate measurements, but if individual sources of error, such as operator, instrument, and sample effects are to be estimated, more data are needed. The amount of data needed for each measurement system should be determined using experimental design techniques found in many statistical texts. Replicate measurements used to estimate standard deviations should be made independently and include all routine procedural steps. It may be advisable to separate the replicate measurements in time or have them made by different persons.

Routine accuracy checks using appropriate reference materials or physical standards should be performed sufficiently often for each measurement method to verify independently its calibration or to calculate a bias correction factor. Generally, no fewer than two measurements of reference materials should be made each week for each material type and each measurement method, but no general rule is adequate for all cases. Some measurement methods may need to be checked daily; others that have very stable calibrations, only infrequently. The frequency of calibration checks should be determined from an analysis of historical information on calibration stability and the sensitivity of the materials balances to biases in the particular measurement process and to the standard deviation of the calibration.

We now discuss factors that affect particular measurement operations and how errors can be determined and controlled.

A. Mass Measurements

Weighing nuclear material usually involves the measurement of gross and tare weights. The errors of both contribute to the error associated with the net weight. The common sources of error in mass measurements are the random variations due to the inherent limits of reproducibility of the scale or balance; variations between operators in reading, rounding, and recording data; and environmental effects such as vibration, electrostatic charges, and temperature changes. These errors are usually random. Bias can occur if the environmental conditions that prevail during routine use are different from those during calibration. Buoyancy effects can also cause bias if a correction is not applied.

Weighing errors can be controlled by a program of periodic calibrations, routine monitoring of scale performance, and regular maintenance of the scales/balances and the standard weights. Scales in routine use should be tested daily with calibrated check weights to ensure continued accuracy. The tests should be made in the same way that process material is weighed. If scale readings for the check weights fall outside preestablished control limits, the scale should be removed from service until repair and recalibration are complete. Reference 10 recommends procedures for calibrating test weights and weighing devices.

The standard deviation of weight measurements due to random error can be estimated from replicate weighings of process materials. The standard deviation should be monitored for each scale by reweighing process items at different times by different operators to include all potential sources of error. Data from reweighing process items are more likely to represent routine weighing performance than are replicate weighings of standard weights or test weights.

B. Measurement of Liquid Volumes

Volume measurements are made in calibrated tanks equipped with instruments for determining the liquid level and density. Typical instruments and their associated problems are described in Chap. III, "Survey of Chemical and Bulk Measurements." A recommended tank calibration procedure is described in an American National Standards Institute (ANSI) standard.[11] Reference 4 offers a good discussion of biases and random errors in volume measurements.

The quality of volume measurements should be controlled by a program of recalibrations, monitoring of measurement performance, and regularly scheduled testing and maintenance of the volume measurement instrumentation. The random error variance of volume measurements should be monitored by repeating measurements frequently. The duplicate measurements should be independent of each other, and each should include all normal measurement steps, such as mixing the tank's contents, manometer and temperature readings, and specific gravity determination, with different operators making the second measurement at different times.

Measurement tanks should be calibrated periodically to maintain control over bias. Because the tank must be empty and clean and recalibration may take several days, calibrations are usually practical only during plant shutdowns. Some other techniques are available to check volume measurements between calibrations:

(1) transferring known volumes of liquid from a "volume prover" or weigh tank to the measurement tank,

(2) making comparisons of in-plant volume measurements of liquid transferred from one calibrated tank to another, and

(3) measuring the dilution factor for a constituent of the tank solution (for instance, by use of the tracer addition method).

These techniques will have somewhat limited sensitivity for detecting bias because of the large variability of the measurements, but they can serve as checks for serious errors in calibration.[4]

The calibration of instruments associated with volume measurement should be checked periodically. Differential pressure instruments can be checked by parallel measurements with portable precision manometers. Density instruments can be monitored by comparison with analytical laboratory measurements. In addition, the instruments should be inspected and tested on a routine maintenance schedule, with adjustment or repair as necessary. Control charts for bias and random error should be maintained on each measurement instrument.

C. Sampling

Sampling of liquids and solids is discussed briefly in Chap. XI. References 12 and 13 offer excellent detailed discussions of sampling problems and errors. Some of the common sources of error in sampling are heterogeneity of the material, changes in composition of samples, contamination or dilution in sampling equipment, suspended solids or multiple liquid phases, and segregation among powder fractions because of particle size or density differences. Improper design or malfunction of sampling and mixing equipment as well as failure to follow prescribed procedures are additional sources of error.

Sampling error can be controlled by continual monitoring and by establishing accurate sampling procedures. The performance of operators should also be monitored to ensure that procedures are followed. Those that provide representative samples (that is, procedures that have no significant sampling bias) are usually developed by experimental testing. The Nuclear Regulatory Commission (NRC) regulations[14] specify

> In order to assure that potential sources of sampling error are identified and that samples are representative, process and engineering tests shall be performed using well characterized materials to establish or to verify the applicability of existing procedures for mixing and for sampling special nuclear materials and for maintaining sample integrity during transport and storage. The program shall assure that such procedures are maintained and followed, and that sampling is included in the procedures for estimating biases, limits for systematic errors, and random error variances.

Sampling procedures should be tested periodically for bias using one of the following methods:

(1) comparing the measurement data from samples taken by the method under test with data from samples taken by an independent sampling procedure known to be substantially unbiased;

(2) determining the effect of variations in a mixing and sampling procedure on sample composition, including such effects as mixing time, mixing and sampling technique, time delay before analysis, and ambient conditions--a mixing and sampling procedure having a negligible bias is designed on the basis of the test results; and

(3) testing the sampling equipment and process using known synthetic mixtures, which is commonly done in pilot plant studies to aid in the design of a sampling system and sampling procedures.

The random error of sampling should also be monitored to ensure that process changes have not affected the degree of homogeneity of the material and to obtain current information for estimating the sampling standard deviation. Independent replicate samples may be analyzed to estimate the combined random error of sampling and analysis. Subtraction of the random error of the analysis will give the random sampling error. To achieve a valid estimate of the sampling error, all sources of error that may affect routine sampling should be included when the replicate samples are obtained. The samples should be taken as independently as possible, but with identical procedures.

D. Chemical Measurements

Laboratory analysis of nuclear materials may involve many measurement steps and manipulations that have the potential of introducing errors in the measurement. Determining individual sources of analytical error and controlling them is often more complex and demands greater effort than does sampling or bulk measurements. The errors inherent in individual measurement methods are detailed in Refs. 15-20.

A generic listing of sources of error encountered in chemical analyses might include

(1) instrument variability, both within the normal limits of reproducibility and as caused by environmental factors,

(2) contamination of equipment and reagents,

(3) calibration or standardization errors,

(4) changes in composition between sampling and analysis,

(5) incomplete dissolution of samples,

(6) the presence of interfering constituents in samples,

(7) the presence of the polymeric form of plutonium in solution samples being analyzed for plutonium,

(8) performance differences between operators and between instruments,

(9) operator variability in making critical measurements and determining endpoints of titrations,

(10) errors in subdividing (and subsampling) samples received for analysis, and

(11) errors in weighing analytical sample aliquots and measuring volumes of aliquots and reagents.

This list is no doubt incomplete. For measurement control, it is usually sufficient to monitor the overall effects of all sources of error on the measurement results without attempting to distinguish between the sources. However, individual sources of error must be known when it is necessary to diagnose and correct loss-of-control situations.[4]

The bias and precision of analyses can be monitored and controlled by calibrations, standardizations, method testing, and independent replicate measurements. The actions involved are analyses of reference materials, duplicate analyses of samples or items, method tests for the sources and magnitude of potential biases, and comparative analyses of process materials by independent methods.

To ensure continuous monitoring of bias, the analyses of reference materials/standards should be distributed throughout the time that the analytical method is used. The frequency of measurements of reference materials must be sufficient to obtain a precise estimate of bias and its standard deviation for each materials balance period. Reference materials used for monitoring bias should simulate process samples as closely as possible in form and composition. Efforts should be made to perform analyses of reference materials and routine samples in an identical manner, including any preparatory steps normally carried out on routine samples.

The random error standard deviation of an analytical method is determined by evaluation of data from independent replicate analyses of samples. The usual procedure is to perform duplicate analyses routinely on some fraction of the samples received. These duplicate analyses should be made independently, including replication of all normal procedural steps. The data obtained from analyses of reference materials and working standards are sometimes used to calculate the random error variance of the method. However, these results may indicate better precision than is actually obtained from process samples because the standards data may not include the effects of variations in composition and because the standards may not be carried through all the analytical steps.

Process samples may also be measured by two different methods and the bias of one method calculated with respect to the other, which is accepted as the standard method or is known to have negligible bias. The means of a number of measurements by each method may not agree within their respective standard deviations for several reasons:[3]

(1) matrix effects in one or each method may not be fully compensated by the calibration procedure used;

(2) systematic errors (biases) may not be fully compensated or unsuspected ones may exist;

(3) the more precisely one can make a measurement, the smaller the detectable difference; and

(4) the standard deviation of one method, or both, is underestimated.

Errors in isotopic analysis by mass spectrometry are not considered here. Discussions are in Refs. 4, 15-22.

E. Nondestructive Assay

Nondestructive assay (NDA) methods are subject to sources of error not common to other measurement methods. The NDA methods are affected by errors caused by extraneous radionuclides in the material, variations in the background radiation, and attenuation of the radiation being measured. Attenuation may be due to the SNM itself, the matrix, or the container. For discussions of this topic, see Refs. 15, 23-26.

Sources of measurement error in NDA may be divided into three categories:[4]

(1) Measurement-to-Measurement Variations. Replicate measurements of the same item are affected by

- random variations in the counting rate;
- changes in background;
- instrument instabilities and temperature and power fluctuations;
- nonuniform item positioning with respect to detector and, if applicable, to the excitation source (a geometry effect); and
- nonuniform distribution of SNM or matrix material within a container (geometry and attenuation effects).

(2) Item-to-Item Variations. Material variability can cause a difference in the response from items of the same SNM content because of differences in

- SNM radionuclide composition (isotopics and daughter nuclides);
- distribution and density of SNM in containers;
- amount, distribution, and density of extraneous materials in the containers; and
- container geometry and composition.

(3) Calibration Error. This type of error is due to uncertainty in the SNM content of the reference materials and uncertainty in the measurements performed on the reference materials.

Bias due to material variability (differences between reference materials and unknowns or item-to-item error) occurs because calibration standards that simulate every unknown in every respect usually cannot be prepared. For each NDA application, efforts are made to fabricate reference materials that have the expected average characteristics of the unknowns. Errors caused by material variability are generally small for pure feed or product materials, provided they are homogeneous in chemical and isotopic composition. Other materials, such as scrap and waste, may vary so widely in composition from item to item that evaluating bias presents a more difficult problem.

It is sometimes possible to minimize sources of bias by

(1) designing the instrument to be insensitive to the perturbing effect,
(2) controlling the operating conditions or environment of the system,
(3) segregating items to be assayed into categories having similar properties and calibrating for each category separately, and
(4) using a different NDA technique, one insensitive to the perturbing effect.

Obviously, eliminating the source of item-to-item bias is preferable, but if this is not possible, correction factors may be applied.

The NDA measurement bias and precision should be monitored by the following actions:

(1) the routine measurement of working reference materials with known SNM contents, similar physical and chemical forms for the reference materials and for the process sample items, known distributions of interfering constituents and other material characteristics of typical sample items, and working reference materials with these characteristics at the mean values of the distributions;
(2) the independent replicate measurements of process items to estimate random error of analysis; and

(3) a periodic comparative analysis of items by an accepted reference measurement method (either chemical analysis or another NDA method, if the other method is known to be free of bias) to estimate bias.

VI. CONTROL CHARTS

The sequences of results from the analysis of reference materials, ranges of replicate measurements, or estimates of error should be monitored to detect any shifts in error levels. Control charts are convenient devices for observation of such sequential data. Control charts were already discussed in Part One of Chap. IV. When a shift or trend is suspected, a physical explanation is sought. If there is no physical explanation, statistical tests should be applied to the data. Reference 27 and many textbooks on statistics discuss such tests.

The philosophy of the use of control charts is based on the premise that measurements may be systematized to provide a process simulating a manufacturing process in many respects. As a result of quality assurance procedures, a system may be debugged and attain a state of statistical control of its data output. The accuracy of the system for typical test samples can be evaluated and thus can be assigned to all similar measurement data generated by the system.[3]

A control chart is simply a graphical way to interpret test data. In its simplest form, a selected reference material is measured periodically, and the results are plotted sequentially (or time ordered) on a graph. When limits for acceptable values are defined, the measurement system is assumed to be in control (variability is stable and due to chance alone) as long as results stay within these limits. A second useful form of a control chart is one in which the standard deviation or range of a series of measurements is plotted in a similar manner. The residence of the values within expected limits is accepted as evidence that the precision of measurement remains in control. Changes in the trend of sequential data can often be detected more readily by a so-called cusum chart, in which the cumulative differences from a target value are plotted sequentially. Examples of several types of control charts can be found in the illustrations used for the oral presentation of measurement control and quality assurance. (See also the detailed discussions of control charting procedures in Ref. 28.) The use of cusum techniques for data analysis and quality control is described in Ref. 29.

The NRC regulations[14] prescribe

> The licensee shall evaluate with appropriate statistical methods all program data and information, and relevant process data used to establish bias corrections and their associated uncertainties, random error variances, limits for systematic error, and other parameters pertaining to special nuclear materials control and accounting measurements, and to control measurement performance pursuant to paragraph 70.58(f). He shall establish and maintain a statistical control system, including control charts and formal statistical procedures, designed to monitor the quality of each type of program measurement.

To summarize this chapter: an effective quality assurance program for measurements results in data that meet the needs of production, materials control and accounting, and the regulatory authorities.

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CHAPTER VIII

FUNDAMENTAL DATA ANALYSES FOR MEASUREMENT CONTROL*

by

K. Campbell, G. L. Barlich, B. Fazal, and R. B. Strittmatter

I. INTRODUCTION

An important aspect of a complete measurement control program is the analysis of data from periodic control measurements of known standards. A set of measurement control data analyses was selected to provide the desired detection sensitivity and still be easy to interpret. These criteria allow the analysts responsible for maintaining measurement quality to make local and timely review of control data. The analyses consist of control charts for bias and precision and statistical tests used as analytic supplements to the control charts. The charts allow visual inspection of data and enable alert reviewers to spot problems possibly before they are detected by statistical tests. The statistical tests are used for automating the detection of departures from the controlled state or from the underlying assumptions, such as normality.

The algorithms described here are

- control charts for bias,
- control charts for precision,
- sequential tests for shifts in the mean, and
- tests for randomness and normality.

A detailed review of the statistical algorithms is presented in Sec. II.

Page's sequential test, used to automate the detection of changes in bias, can signal a single observation deviating greatly from the mean or a sequence of observations deviating slightly from the mean. This test can

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be described as a cumulative sum (cusum) of the past observations, with a restart mechanism that prevents a recent problem from being obscured by a long history of satisfactory behavior.

Control charts and other statistical tests are based on the assumption that measurements from the control program are approximately normally distributed. Failure of normality can affect the false-alarm rate of the tests and decrease their usefulness for detecting real problems. The recommended test for normality is the Shapiro-Wilk test, applied to predetermined sample sizes.

Although randomness is not precisely defined, features exist that are not considered random, such as extreme observations, slow upward or downward drifts, and cycles with a definite period. Detection of such nonrandom behavior alerts the analyst to look for factors affecting the measurements that could be controlled. The test based on the von Neumann ratio is sensitive to many types of nonrandom fluctuations.

The Los Alamos Safeguards Systems Group implemented the described algorithms in a measurement control code for personal computers. The code, Measurement Control Charts and Tests (MCCAT), is being evaluated at the Oak Ridge Y-12 facility for highly enriched uranium scrap recovery.

II. BASIC ALGORITHMS

This section describes standard control charts and algorithms in the context of what we call the "standard case," namely, daily control measurements of a known, constant standard where the variance of the measurement process is also assumed known. This section contains the basic information needed by any user of the MCCAT software. Sections III and IV contain information probably needed only by individuals responsible for setting up and maintaining the system.

A. Introduction and Terminology

The algorithms described are designed for use with data collected as part of an ongoing measurement control program. Typically, one control measurement of a prescribed standard is made each day or after a fixed number of measurements on a given instrument. Archived with the result of this control measurement may be the certified value of the standard, a computed (that is, propagated) measurement error, and other relevant information, numerical or alphanumeric. Possible modifications of this scenario, including repeated measurements of the same standard or the use of two standards (to check different ranges of the instrument), do not significantly affect the procedures described here.

A sequence of control measurements made as above is referred to here as (a realization of) the "measurement process." Individual measurements (also called observations) typically cluster around an average value (or mean value) with a spread reflecting uncontrollable factors, such as a counting error in the measurement of radioactive material, small variations in atmospheric conditions and temperature, or slight differences in the procedures used by different operators. Generally, the distribution of observations about their mean value is adequately described by a Gaussian, or normal, probability distribution. It is also assumed that the result of one measurement does not in any way affect the result of another (that is, the observations are independent).

The objective of examining the archived sequence of control measurements is to determine whether the instrument (and the associated procedures and operators) continues to function at an acceptable level of precision and accuracy. If so, we say that the measurement process is "in control." Specifically, given a sequence of control measurements, we assume that the process continues in control as long as the average value and standard deviation of the observations do not deviate significantly (in a statistical sense) from their historical values. (Adjustments for a decaying radioactive standard or a predictably deteriorating precision are considered in Sec. III.) The algorithms described below are designed (1) to produce graphical displays that provide visual indications of deviation from the historical norms and (2) to provide timely, automatic indicators of such deviations, based on statistical tests of the null hypothesis that the measurement process is, in fact, in control.

B. The Standard Case: Known Mean and Standard Deviation

In the standard case, the measurement process is considered to be in control if the observations are independently normally distributed with known mean and standard deviation. Verification of normality and independence are the subjects of Secs. IV.C and IV.D, and these properties are assumed in all other sections. Here we are dealing with the problem of detecting deviations in the measurement process from the known mean value (that is, detecting bias) and also with changes in the historically determined standard deviation that provides a measure of the significance of differences between the actual observations and the known mean value.

The mean value is assumed to be known with high precision (without error for practical purposes). This is the situation, for example, when a certified standard is used (such as a National Bureau of Standards calibrated weight), when a supplementary measurement of the standard has been made by another more accurate method (for example, chemical analysis), or when a careful measurement of a secondary standard has been made after the instrument has been calibrated using primary standards.

The standard deviation of the process, on the other hand, can be determined only by analysis of historical data or of data from a designed experiment. These data are collected under circumstances that accurately reflect all of the sources of random error affecting routine accountability measurements, for example, using several operators and continuing over a reasonably extended period of time. The determination of the historical standard deviation is discussed in Secs. IV.A and IV.B.

This historical standard deviation must be carefully distinguished from specification limits claimed by the manufacturer of the instrument or required by the user. If the latter are significantly smaller than the historical limits, a problem may require investigation, but it is separate from the measurement control program. The limits that are relevant for measurement control are the historical, empirical ones. As long as the standard deviation of the observations is not significantly different from its historical value (and no bias is apparent), the measurement process is considered to be in (statistical) control, even if the precision or accuracy of the measurements fails to meet administrative requirements.

Controlling (or at least correcting for) bias in special nuclear material (SNM) measurements is clearly important: consistent bias in a series of accountability measurements leads quickly to the appearance of inventory differences where none actually exist (or may possibly conceal a true difference). The importance of controlling the standard deviation may be less obvious. However, comparison of observed differences with a standard deviation that is, in fact, smaller than the process is capable of maintaining may lead incorrectly to the conclusion that inventory differences exist, and comparison of the observations with a standard deviation that is too large will mask bias. Changes in either direction are possible as a result of changes in procedure or personnel; change may also become apparent if the historical variance estimate was based on too few or nonrepresentative data.

C. Shewhart Control Charts

Let μ be the known mean and σ^2 the known variance of the measurement process when it is in control. Let x_t denote the control measurement of the standard made at time t. We will consider the standardized measurement

$$z_t = \frac{(x_t - \mu)}{\sigma} \quad . \tag{1}$$

Under the standard assumptions discussed in Sec. II.B, the z_t are independent realizations of a normal random variable with mean zero and unit variance. In particular, about 1 observation in 400 is expected to exceed 3 in absolute value.

A Shewhart control chart is a plot of the standardized measurements z_t vs time t and includes horizontal lines at zero (the mean value of the standardized measurement) and, generally, at plus and minus three units (the control limits). A standardized observation that falls outside these control limits indicates bias, and some action such as recalibration of the instrument or at least review of recent measurement control data is required.

A similar chart can be used to examine group means. The standardized measurements are divided sequentially into groups of five, and the mean of each group is calculated. This value is plotted on a chart with mean 0 and control limits at $\pm 3/\sqrt{5}$ and $\pm 2/\sqrt{5}$.

Shewhart charts are familiar to most people and are easy to interpret. A series of measurements (up to 81 observations in the MCCAT code) plotted in this way reveal abnormalities that have crept into the measurement process, which are not immediately detectable out of their historical context. However, the statistical tests implicit in the choice of control and warning limits are less than optimal, especially for the detection of small shifts in the mean value (although numerous ad hoc solutions to this problem have been developed).[1] Section II.D describes a two-sided Page's test that, as a modification of a sequential probability ratio test, is known to have some optimal properties in terms of the length of time (number of observations) required to detect shifts in the mean.

A Shewhart control chart can also be developed for control of the standard deviation of the measurement process. This chart is based on the sample standard deviation of a sequence of individual observations of length r = 5. Specifically, the statistic

$$(r - 1)\, s_t^2 = \sum_{i=t-r+1}^{t} (z_i - \bar{z})^2 = \frac{\sum_{i=t-r+1}^{t} (x_i - \bar{x})^2}{\sigma^2} \qquad (2)$$

(where $\bar{z}$ is the average of the r standardized observations z_i, $i = t - r + 1, \ldots, t$, and similarly $\bar{x}$ is the average of the r observations x_i) has a chi-square distribution with r − 1 degrees of freedom, and upper and lower control limits for the sample standard deviations s_t, computed after r observations, are constructed using the tabled percentiles of this distribution. Specifically, the mean value of s_t, defined by Eq. (2), is c_r, given in Table I for r between 2 and 12. Upper and lower action limits may be set at j_r^+ and j_r^-, and optional warning limits may be set at v_r^+ and v_r^-.

TABLE I

MEAN VALUE, ACTION LIMITS, AND WARNING LIMITS FOR THE SAMPLE STANDARD DEVIATION OF r STANDARDIZED OBSERVATIONS

Number of Grouped Observations r	Mean Value of s_t c_r	Lower Action Limit j_r^-	Upper Action Limit j_r^+	Lower Warning Limit v_r^-	Upper Warning Limit v_r^+
2	0.798	0.00	3.29	0.03	2.24
3	0.886	0.03	2.63	0.16	1.92
4	0.921	0.09	2.34	0.27	1.77
5	0.940	0.15	2.15	0.35	1.67
6	0.952	0.21	2.03	0.41	1.60
7	0.959	0.25	1.93	0.45	1.55
8	0.965	0.29	1.86	0.49	1.51
9	0.969	0.35	1.81	0.52	1.48
10	0.973	0.36	1.76	0.55	1.45
11	0.975	0.38	1.72	0.57	1.43
12	0.978	0.41	1.69	0.59	1.41

D. Sequential Test for Bias

Page's test is based on a statistic closely related to the cumulative sum of the past observations.[2] It has been described as a cusum test with a restart mechanism to prevent recent problems from being obscured by a long history of satisfactory instrument behavior. It can be alarmed by a single observation deviating from the mean by a large amount [$(h + k)\sigma$ in terms of the notation given below], by a short sequence of observations deviating from the mean by a smaller amount, or by a longer sequence of observations deviating by an even smaller amount. Thus, a single test encompasses many of the modifications proposed by Roberts[1] as alternatives to the simple test implied by a Shewhart chart with control limits at $m \pm 3\sigma$.

A two-sided Page's test for deviations in the mean of the measurement process takes the following form:

1. Select a reference value k (typically about 0.5) and a decision value h (typically in the range of 4 to 5).

2. Initialize the Page statistics: $m(0) = 0$ and $M(0) = 0$.

3. For t = 1, 2, 3, ..., compute

$$m(t) = \max \{0, m(t-1) + z_t - k\}$$

and

$$M(t) = \max \{0, M(t-1) - z_t - k\} \tag{3}$$

(max {x, y} denotes the larger of the two numbers x and y).

4. Declare the measurement process out of control at time t if either m(t) or M(t) exceeds h.

Typically h and k are chosen so that it will take about 10 or 12 observations to detect a shift of magnitude 1 in the mean of the standardized measurements z_t (that is, a shift of 1 standard deviation in the mean of the raw observations x_t), while allowing an average run length of the process in control (that is, the average time until a false alarm) to be approximately 300 to 400 observations.[3]

The interesting region of the (h,k) parameter space is indicated in Fig. 1. The two heavy curves bound a region in which the average run length of the process in control exceeds 300 observations, and the average number of observations until detection of a shift of 1σ is less than 12 observations. Values of (h,k) chosen from the right-hand side of this region lead to tests that have longer run lengths when the process is in control, but that also take longer, on the average, to detect a shift in the mean. Shaded regions indicate where (a) the average run length of the controlled process exceeds 400 observations and (b) the average time until detection of a shift of 0.9σ is less than 12 observations. From the latter, we see that it is not possible to improve on the time to detection of even marginally smaller shifts without driving the average run length of the controlled process to unacceptably small values. Note also that even with an average run length of 400 observations for the process in control, a significant number of runs will be shorter, because the distribution of run lengths is approximately exponential; almost 1 run in

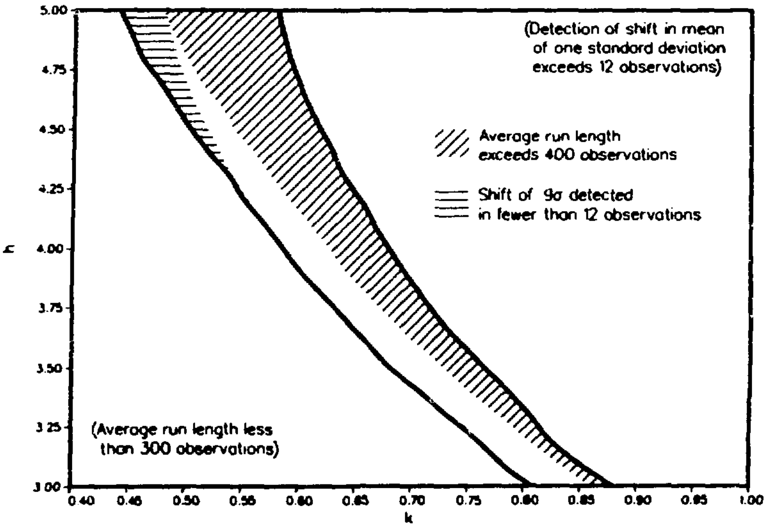
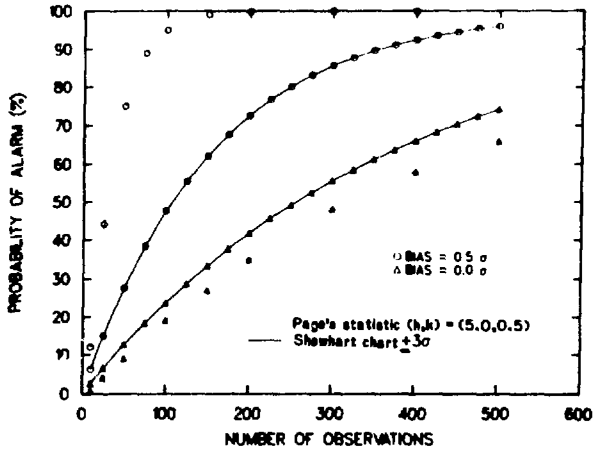


Fig. 1.
Usable region of (h,k) parameter space for two-sided Page test.

5 has fewer than 100 observations. The probability of at least one alarm occurring as a function of run length is shown in Fig. 2 for (h,k) = (5.0,0.5) and Fig. 3 for (h,k) = (7.5,0.5).

The Page statistics m(t) and M(t) may be plotted against t on a single chart with control limits at h and -h. Small changes in bias are reportedly easier to spot on such charts than on standard Shewhart control charts.

Fig. 2.
The probability of at least one alarm occurring based on the Page statistic with (h,k) = (5.0,0.5) for standardized measurement biases of 0.0 and 0.5 and the probability of at least one alarm occurring based on the Shewhart chart with control limits at ±3σ.



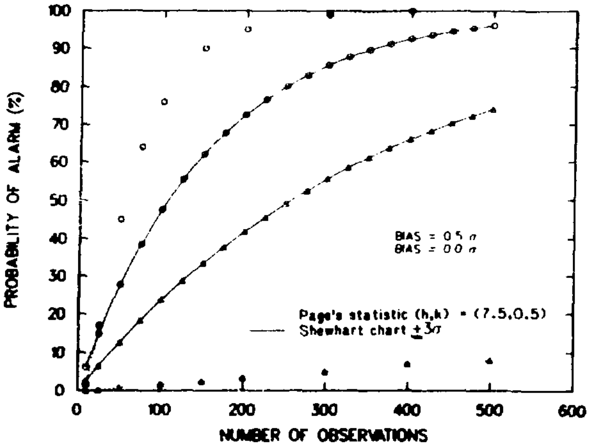


Fig. 3.
The probability of at least one alarm occurring based on the Page statistic with (h,k) = (7.5,0.5) for standardized measurement biases of 0.0 and 0.5 and the probability of at least one alarm occurring based on the Shewhart chart with control limits at ±3σ.

III. MODIFICATIONS FOR NONSTANDARD CASES

The modifications for nonstandard cases consist of replacing the known constant mean μ and/or known constant standard deviation σ, used to standardize the observations in Eq. (1), by functions of t. Specifically, we consider the cases where the mean at time t is a nonconstant but known function of t, μ_t, where the standard deviation at time t is a nonconstant known or estimated function of t, σ_t, and where repeated measurements are made (more than one measurement of the same standard each time a control measurement is scheduled).

A. Modification for Changing (Decaying) Standard Value

When the standard contains a radioactive element with a relatively short half-life, noticeable changes in the mean value μ of the measurement process may occur over the usable life of the standard. These changes are easily accommodated if they are not too significant, because the half-life of the element, as well as the initial quantity of material present, is assumed to be known precisely. Hence, the mean value μ_t of the measurement x_t at time t is computed and used to standardize the observation as described in Sec. II.C. Significant decay, however, may also affect the standard deviation σ, one component of which is a counting error (proportional to the square root of μ_t in a simple Poisson model of the measurement process, but frequently a more complicated function of the counting statistics that takes into account background and internal radioactive sources). One way to compensate for this effect is to increase the counting time used in making the control measurement. Otherwise, a model for the standard deviation, $\sigma = \sigma_t$, in Eq. (1) must be constructed and used as discussed in Sec. III.B.

B. Modification for Deteriorating Measurement Precision

For nondestructive assay (NDA) instruments with short-lived sources or when the standard itself is decaying, as mentioned in Sec. III.A, one component of the variance may change over time, although the other component (the part due to factors, such as varying atmospheric conditions and sample placement) remains constant if the measurement process is in control. For this case, we need a model for the changing component or some measurement of the changing component. The constant part is estimated using historical data in a manner similar to that used for the standard case (see Sec. IV.B). The time-dependent standard deviation $\sigma = \sigma_t$ needed for standardization of the observation [Eq. (1)] is then computed as the square root of the sum of the computed variance, τ_t^2, and the constant component, η^2:

$$\sigma_t = \eta^2 + \tau_t^2 \quad . \tag{4}$$

C. Modifications When Repeated Measurements Are Made

Multiple daily measurements of the same standard (if, for example, two control measurements are always made at a time) could be treated as independent observations. It is probably more instructive, however, to redefine the control measurement x_t as the average of these measurements, with the same mean μ as the original measurement process but with a standard deviation that is smaller by the square root of n, the number of replicates. Shifts that can be detected by Page's test using the resulting standardized observations, for example, are similarly smaller by a factor of the square root of n, with the same parameters as before. (For example, with 3 daily measurements, we can expect to detect a shift of approximately 0.6σ in 12 days while maintaining an average run length of 400 days for the controlled process.)

IV. MAINTENANCE INFORMATION

The information in this section is not required by the casual user of the measurement control program software but is needed by individuals with responsibility for setting up and maintaining the system. It includes (1) methods for estimating the historical standard deviation needed for standardizing the observations and (2) auxiliary tests of the assumptions underlying the control charts and sequential tests (namely, normality and independence of the observations).

A. Estimation of Historical Standard Deviation: Standard Case

We assume that the mean value μ is known precisely, whether as the result of independent assay or of careful measurement following calibration (in the case of a secondary standard). The value of the standard deviation σ, however, is obtained only by observing the process itself over a reasonable length of time (30-60 days, if possible). It depends both on controllable factors, such as standard procedures and the skill of the operator, and on relatively uncontrollable factors, such as air pressure and the inherently random nature of count data. Only some of these factors are captured in the propagated error reported by the software associated with the NDA instrument.

Therefore, to estimate σ we require an initial set of observations, which are obtained during a trial period or, if necessary, during the early phase of actual operation. To the extent possible, these data are collected using procedures, operators, and environments typical of actual accountability measurements. [Re-estimation of σ may be indicated later, in which case the recent history of the measurement process is used. However, once computed, σ, or η in the case of the modification described by Eq. (4), is assumed known and constant unless one of the standard tests or control charts indicates that it has been incorrectly estimated or has changed since originally computed.]

Thus, suppose we have a history of N measurements of the standard. Because these historical data may have some long-term problems (for example, a slow trend or recalibration in the middle of the series), we obtain an estimate of σ by segmenting the data into small, more nearly homogeneous subgroups (for example, by weeks); σ^2 is then estimated by the within-group variance of the historical data, rather than by the overall variance. If the historical data contain some extremely divergent observations (outliers) for which an assignable cause can be determined, these observations are deleted before performing the computations below, as they can strongly influence the estimate of σ^2. Testing the historical data for normality is also worthwhile (see Sec. IV.C).

Specifically, then, let the (edited or transformed, if necessary) historical observations be denoted by x_{ijk}, where $k = 1,\ldots,K$ for K calibration periods, $j = 1,\ldots,J_k$ for J_k subgroups within the k^{th} calibration period, and $i = 1,\ldots,I_{jk}$ for the individual measurements in the $(j,k)^{th}$ subgroup. Form the within-group means

$$\bar{x}_{\bullet jk} = \frac{1}{I_{jk}} \sum_{i=1}^{I_{jk}} x_{ijk} \quad . \tag{5}$$

Then compute

$$s^2 = \sum_{k=1}^{K} \sum_{j=1}^{J_k} \sum_{i=1}^{I_{jk}} (x_{ijk} - \bar{x}_{\bullet jk})^2 \quad . \tag{6}$$

Then σ^2 is estimated by

$$\hat{\sigma}^2 = \frac{s^2}{N - M} \quad , \tag{7}$$

where M is the total number of subgroups, that is,

$$M = \sum_{k=1}^{K} J_k \quad , \tag{8}$$

and N is the total number of observations.

With the data grouped into short intervals, the procedure described in Eqs. (5) through (8) is also suitable for the first nonstandard case considered in Sec. III, namely, a slowly changing mean value μ_t, unless σ changes significantly over the span of the historical data.

B. Estimation of Historical Standard Deviation: Changing with Time

Substantial complications are presented by NDA instruments with short-lived sources resulting in measurements of significantly decreasing precision during the periods between replacement. Similar problems occur when a rapidly decaying standard causes large changes in the counting statistics associated with its measurement. We assume that the data available for computation of the historical standard deviation cover a period sufficiently long to reflect such changes and possibly cover at least one replacement of the source (or standard). The standard deviation σ_t to be used in Eq. (1) is computed as the square root of the sum of two variances: first, a component τ_t associated with the observation at time t and estimated by the software package of the instrument, and second, a constant component η^2 to be estimated from the historical data (given the τ_t's associated with these data).

We assume that the mean value of the measurement process is approximately constant (or only slowly changing) during the period covered by the historical data. (For an instrument with a secondary foil standard, the "known" mean value may, in fact, change when the instrument is recalibrated using primary standards.)

Specifically, let the historical measurements be denoted by x_{ijk} as before, over K calibration periods, with J_k groups in the k^{th} calibration period (grouped observations obviously should not include replacement of the transmission source) and I_{jk} measurements in the $(j,k)^{th}$ group. Assume that the computed error (that is, the variable component of the measurement variance) is approximately constant in the $(j,k)^{th}$ group, and denote it by τ_{jk}. [In practice, τ_{jk} is computed as the average of the computed variances of the measurements in the $(j,k)^{th}$ group.] Compute the within-group means as in Eq. (5). Then η^2 is estimated by the solving the equation

$$\sum_{k=1}^{K} \sum_{j=1}^{J_k} \sum_{i=1}^{I_{jk}} \frac{(x_{ijk} - \bar{x}_{\bullet jk})^2}{\eta^2 + \tau_{jk}^2} = N - M \tag{9}$$

numerically. [If τ_{min}^2 and τ_{max}^2 are the smallest and largest values of τ_{jk}^2 in the historical data, and if s^2 is defined by Eq. (6), then the solution to Eq. (9) lies in the range

$$\left(\frac{s^2}{N - M} - \tau_{max}^2, \frac{s^2}{N - M} - \tau_{min}^2\right) ,$$

and a reasonable starting value for solving Eq. (9) numerically is

$$\frac{s^2}{N - M} - \frac{1}{M} \sum_{k=1}^{K} \sum_{j=1}^{J_k} \tau_{jk}^2 \quad .]$$

For a future measurement at time t, the expected value of the measurement is μ_t, the measured value of the standard obtained immediately after the last calibration (or computed in the case of a decaying radioactive standard), and the standard deviation will be σ_t,

$$\sigma_t^2 = \eta^2 + \tau_t^2 \quad , \tag{10}$$

where τ_t^2 is the computed variance returned with that measurement.

C. Normality and Outliers

The control charts of Sec. II and other tests are all based on the assumption that measurements obtained from the measurement control program are approximately normally distributed. Failure of normality can affect both the false-alarm rate of the tests and their ability to detect real problems in the process. Therefore we recommend occasionally running a test of normality. Verification of normality of the historical data before estimating the standard deviation to be used in future control charts and tests is particularly important. If serious deviations from normality are discovered (and if these deviations cannot be ascribed to the presence of a few outliers), we may wish to consider the application of some normalizing transformation to our measurements. For example, distributions with long tails on the right may be made more symmetric by a logarithmic or square root transformation.

The most powerful test of normality found in the literature is the Shapiro-Wilk test.[4] Application of this test requires a table of coefficients that are different for each sample size and a table of critical values. For practical purposes, we set standard sample sizes n and stored the required coefficients $a_{n,i}$, $i = 1,2,\ldots n/2$, for these sample sizes. Coefficients for samples of size $n = 20, 30, 40$, and 50 are tabulated in Table II. Critical values c_n for significance levels (false-alarm rates) of 0.05 and 0.01 are tabulated in Table III. The statistic W for a sample of n observations from the measurement control process is computed as follows:

1. Order the n observations from smallest to largest. Label the ordered observations $x_1,\ldots,x_n$. (We assume n is even.)
2. Compute

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

where $\bar{x}$ is the usual sample mean,

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

TABLE II

COEFFICIENTS $a_{n,i}$ FOR SHAPIRO-WILK STATISTIC W[a]

Coefficient i	Number of Observations (n) 20	30	40	50
1	0.4734	0.4254	0.3964	0.3751
2	0.3211	0.2944	0.2737	0.2574
3	0.2565	0.2487	0.2368	0.2260
4	0.2085	0.2148	0.2098	0.2032
5	0.1686	0.1870	0.1878	0.1847
6	0.1334	0.1630	0.1691	0.1691
7	0.1013	0.1415	0.1526	0.1554
8	0.0711	0.1219	0.1376	0.1430
9	0.0422	0.1036	0.1237	0.1317
10	0.0140	0.0862	0.1108	0.1212
11		0.0697	0.0986	0.1113
12		0.0537	0.0870	0.1020
13		0.0381	0.0759	0.0932
14		0.0227	0.0651	0.0846
15		0.0076	0.0546	0.0764
16			0.0444	0.0685
17			0.0343	0.0608
18			0.0244	0.0532
19			0.0146	0.0459
20			0.0049	0.0386
21				0.0314
22				0.0244
23				0.0174
24				0.0104
25				0.0035

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[a] From Ref. 4, pp. 603-604.

TABLE III

CRITICAL VALUES FOR SHAPIRO-WILK TEST[a]

Level	Number of Observations (n) 20	30	40	50
0.01	0.868	0.900	0.919	0.930
0.05	0.905	0.927	0.940	0.947

---

[a] From Ref. 4, p. 605.

3. Compute

$$b = \sum_{i=1}^{n/2} a_{n,i} \ (x_{n-i+1} - x_i) \quad ,$$

where the coefficients $a_{n,i}$ are obtained from Table II.

4. Compute $W = b^2/S^2$ and compare the result to the critical value with the desired significance level in Table III. If W is smaller than the given critical value, the data appear to depart significantly from normality and should be examined further to determine if the problem is very light tails, heavy tails, skewness, or perhaps just a small number of outliers for which an assignable cause can be determined.

The storage requirements of this test preclude its routine use for samples of arbitrary size. If, perhaps, 38 historical observations are available, we use the most recent 30.

A common form of nonnormality is a "contaminated normal" distribution, that is, data that are fundamentally normally distributed but that include occasional outliers. When such observations are detected, and when the reason for the change can be determined, these observations should be deleted from the data.

The most effective way to detect such outliers, given an adequate historical record, is by means of the control chart; points lying outside the action limits are considered outliers. In general, outlier tests look for observations that are substantially removed from the bulk of the data; for example, the tests described by Grubbs[5] are based on the statistic

$$T_{extreme} = \frac{x_{extreme} - \bar{x}}{s} \quad ,$$

where $x_{extreme}$ is the observation in the set farthest removed from the sample mean $\bar{x}$ and s is the sample standard deviation. ($T_{extreme}$ is called the "extreme studentized residual.") Occasionally it may be useful to have a test for outliers that uses only the observations of the current week. For detecting a single outlier in samples of size three to eight, the absolute value of $T_{extreme}$ above can be compared to the critical values in Table IV, with $x_{extreme}$ being considered an outlier if the critical value is exceeded. This test is not part of MCCAT but may be useful in setting up the system parameters from historical data. Generalizations for the detection of two or more outliers are considered by Rosner.[6]

TABLE IV

CRITICAL VALUES FOR ABSOLUTE VALUE OF $T_{extreme}$[a]

Number of Observations n	Level 0.01	Level 0.05
3	1.15	1.15
4	1.49	1.46
5	1.75	1.67
6	1.94	1.82
7	2.10	1.94
8	2.22	2.03

---

[a] From Ref. 5, p. 4.

D. Other Tests of Randomness

The statement that there is no "assignable cause" contributing to the variability in the measurement control data is equivalent to asserting that the remaining variability is random--the result of uncontrollable factors that vary from day to day or from measurement to measurement. Although randomness is not precisely defined, we have some intuitive opinions of features that we do not consider random, such as extreme observations (four or more standard deviations removed from the mean) or a slow upward drift in the observations. Visible cycles, possibly with weekly or other natural periods, or correlations between measurements and other factors, such as the operator, would alert us to look for potentially controllable factors affecting the measurements.

A test included in MCCAT that is quite sensitive to many types of nonrandom fluctuations is based on the von Neumann ratio (the ratio of the mean square successive difference to the variance, or equivalently, the serial correlation coefficient).[7,8] This test statistic is computed as follows:

1. Let $x_1,\ldots,x_n$ be the n observations in the order in which they were made.

2. Compute

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

   where $\bar{x}$ is the usual sample mean.

3. Compute

$$\delta^2 = \sum_{i=1}^{n-1} (x_{i+1} - x_i)^2 .$$

4. Compare the value of the ratio $T = \delta^2/S^2$ with the critical values in Table V. Generally, in measurement control programs, the alternative to no correlation of interest between measurements is the possibility of positive correlation between successive measurements, and so we perform a one-sided test. Positive correlation tends to reduce the value of T, and thus we reject the hypothesis of no correlation if T is smaller than the value indicated in Table V.

TABLE V

LOWER PROBABILITY POINTS FOR VON NEUMANN RATIO[a]

Number of Observations n	Level 0.01	Level 0.05
5	0.538	0.820
6	0.561	0.890
7	0.614	0.936
8	0.665	0.982
9	0.709	1.025
10	0.752	1.062
11	0.791	1.096
12	0.828	1.128
13	0.862	1.156
14	0.893	1.182
15	0.922	1.205
16	0.949	1.227
17	0.974	1.247
18	0.998	1.266
19	1.020	1.283
20	1.041	1.300
21	1.060	1.315
22	1.078	1.329
23	1.096	1.342
24	1.112	1.355
25	1.128	1.367

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[a] From Ref. 7, p. 287 and Ref. 8, p. 446.

5. For samples of size $n > 25$, compute

$$Z = \left(\frac{n^2 - 1}{n - 2}\right)^{1/2} \left(\frac{T}{2} - 1\right) ,$$

and compare Z with the percentiles of a standard normal. Z is small in the positively correlated case. Thus, the hypothesis of no correlation is rejected at the 5% level if $Z < -1.645$ or at the 1% level if $Z < -2.326$. A two-sided test for either positive or negative correlation between successive measurements rejects the null hypothesis at the 5% level if $|Z| > 1.96$ or at the 1% level if $|Z| > 3.09$.

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CHAPTER IX

DETERMINATION OF DETECTION SENSITIVITIES OF NUCLEAR MATERIALS ACCOUNTING SYSTEMS

by

D. Stirpe

I. INTRODUCTION

An important element in safeguarding nuclear facilities against the loss of special nuclear materials (SNM) is accounting for this material through the periodic measurement of all input and output transfers and inventories. These measured values can be substituted into the materials balance equation

MB = sum of input transfers + sum of beginning inventories

- sum of output transfers - sum of ending inventories ,

and the value of MB calculated (MB is sometimes also called the inventory difference, ID). If the MB equation includes all material crossing the materials balance area (MBA) boundary, either as input transfers or output transfers, over the accounting period and all material residing within the MBA boundary at the beginning and end of the accounting period, then measurements of all this material will give a value of MB in the neighborhood of zero. We say "in the neighborhood of zero" because measurement instruments have errors, and repeated calculations of the value of MB, based on measurements made for daily or weekly materials balance closings, for instance, will result in somewhat different values. If there is no diversion of SNM and we have calculated a large number of MB values, the average (or expected) value of the distribution of the MBs will be very nearly zero. However, it is the value of sigma, a measure of the width of this distribution of MB values, that determines the sensitivity (in kilograms or grams of SNM, for example) of a materials accounting system to the diversion of SNM. Hence, aside from some comments regarding the types of terms often found in MB equations, measurement error models, and variance expressions for the different error models, the major portion of this discussion concerns itself with the calculation of sigma (σ), the measure of the width of the distribution of MB values.

In Sec. II, we present a few examples of the types of transfer and inventory terms that appear in MB equations. Measurement error models and their associated variance expressions are discussed in Sec. III. Using several different assumptions regarding MBA structure, we calculate values of the variance of MB (and values of σ, the square root of this variance) for a simplified version of a mixed uranium-plutonium oxide (MOX) fuel fabrication line in Sec. IV. In Sec. V, we calculate the detection sensitivity for each of the values of σ. A few suggestions for effective materials accounting are given in Sec. VI.

II. TERMS OF A MATERIALS BALANCE EQUATION

Determination of the detection sensitivity of a materials accounting system requires

(1) writing the MB equation for an MBA (which may include the entire facility or some subdivision of the entire facility),

(2) obtaining a relation for the variance of the MB equation by propagation of the instrument errors for those measured quantities that appear in the MB equation,

(3) substituting measured values and their error standard deviations (SDs) into this variance relation and calculating the variance of the materials balance, and

(4) calculating the detection sensitivity for a specified detection probability by using σ, the square root of the variance of the MB.

In carrying out Step (1) for, perhaps, a processing or fuel fabrication facility, we would soon notice that transfer or inventory terms of the MB equation can be reduced to a few general types. The type of term encountered is determined exclusively by the facility operating and measurement procedures. For example, assume that operating procedures call for using several cans of MOX powder per accounting period as input to a fuel fabrication line. Measurement procedures require that a sample be taken from each can to determine the plutonium concentration and, in addition, to determine the net mass of each can. For this particular transfer stream, the form of the MB term will be

$$T1 = \sum_{i=1}^{N} C_i (BX - LX)_i \quad . \tag{1}$$

In this equation, N is the number of cans of MOX powder transferred during the accounting period, the C_i's are the N measured values of the SNM concentration for the N cans [in kilograms of plutonium per kilogram (kg Pu/kg) of oxide powder, for instance], and the differences, $(BX - LX)_i$, represent the N net masses of the N cans in kilograms (BX is the gross mass of a can and LX is the tare mass). If, instead of transferring bulk powder, one were transferring SNM solution from several columns, then the C_i's might be expressed as kg Pu/liter and the differences, $(BX - LX)_i$, in liters. In either case, the form of Eq. (1) implies that for each measurement of C, there are corresponding measurements of BX and LX. In an MB equation, there may be several input or output transfer streams that have the form of Eq. (1), although the values of the measured quantities, C, BX, and LX, may be very different for the different streams.

A second type of transfer term that occasionally occurs in materials balance equations is of the form

$$T2 = \sum_{i=1}^{NC} C_i \sum_{j=1}^{NX} (BX - LX)_{ij} \quad . \tag{2}$$

This form of MB term shows explicitly that there are NX measurements of BX and LX per C measurement and NC measurements of C during the accounting period. A term like Eq. (2) is necessary for dealing with material from a blender, for instance, where a single concentration measurement is made of a blended sample, but the blended material is subsequently apportioned among several bottles, the individual masses of which are measured. It is assumed that this procedure is repeated NC times during the accounting period. Obviously, if NX = 1, T2 reduces to the form T1.

Beginning and ending inventory differences must also be included in MB equations, and these can have different forms. A type of inventory difference that sometimes appears has the form

$$\text{beginning inventory} - \text{ending inventory} = IO - F{*}IO \quad , \tag{3}$$

where IO is the initial inventory of SNM and F is the ratio of final to initial inventories. If F = 1, then the beginning and ending inventories are nominally the same, although they represent different measurements made on different material.

Another type of inventory difference that occurs in MB equations is given, in its most general form, by

$$\text{beginning inventory} - \text{ending inventory} =$$

$$\sum_{i=1}^{NC1} C_i \sum_{j=1}^{NX1} (BX - LX)_{ij} - \sum_{k=1}^{NC2} C'_k \sum_{l=1}^{NX2} (BX' - LX')_{kl} \quad . \tag{4}$$

Such a form of inventory difference might be necessary for boats of material loaded into a calciner, for instance, where the SNM concentration of material in each boat is not measured but the mass of each boat is. One concentration measurement may be assigned to several boats of material. A similar form is also used for a number of columns holding SNM solution. Equation (4) is most often used with NX1 = NX2 = 1 but, of course, not exclusively. If the pairs of values {NC1,NX1} = {NC2,NX2}, the initial and final inventories are equal, otherwise they are not.

As stated earlier, an MB equation may contain one or more MB terms of the type discussed above. To carry out Step (2), listed at the beginning of this section, the variance of each term that appears in the MB equation must be derived, along with the covariance between MB terms if such covariances exist. Covariances between MB terms will exist if different materials, as represented by different MB terms, are measured on the same instrument. In the next section, we briefly discuss measurement errors, measurement models, and variance equations.

III. MEASUREMENT ERRORS AND ERROR MODELS

Errors associated with measurement instruments can be divided into two broad classes, those that are random and those that are correlated. Random errors are due to the lack of repeatability of the measurement instrument (for whatever reason). Correlated errors are due to the calibration procedure or errors in the calibration standard used to calibrate the instrument. The same correlated error persists through a series of measurements made with an instrument until a new calibration of the instrument is performed, in which case a new correlated error is associated with the measurement instrument until another calibration is performed.

Measurement instruments are often described as having an associated additive or multiplicative error model. Scales to measure mass, for instance, are often characterized by an additive error model, with a measurement result that can be written as $x = X + \varepsilon + \eta$, where x is the observed value of the mass, X is the true (but unknown) value of the mass, ε is the random error of the scale, and η is the correlated error of the scale. The variance of x in this case is

$$\mathrm{var}(x) = \sigma_x^2 = \sigma_\varepsilon^2 + \sigma_\eta^2 \quad ,$$

where σ_ε^2 and σ_η^2 are the variances (square of the standard deviations, SDs, where the SDs are in kilograms, possibly) of the random and correlated error components, respectively. For a series of measurements on N items, all having nominally the same observed value of x, the variance of all N measurements can be derived by a Taylor expansion (which we do not discuss here). The result is

$$\mathrm{var(sum\ of\ N\ similar\ items)} = N\sigma_\varepsilon^2 + N^2\sigma_\eta^2 \quad .$$

Many measurement instruments/procedures are characterized by a multiplicative error model, where the measurement result is given by $c = C(1 + \varepsilon + \eta)$. Now, the variance of c is

$$\mathrm{var}(c) = C^2(\sigma_\varepsilon^2 + \sigma_\eta^2) \quad ,$$

and, for a series of measurements on N similar items,

$$\mathrm{var}(\text{sum of N similar items}) = C^2(N\sigma_\varepsilon^2 + N^2\sigma_\eta^2) \quad .$$

Because C is unknown, the observed value, c, is substituted for C in the last two equations. In the variance expression for the total variance of the sum of N measured items assuming an additive error model, the SDs are expressed in absolute units, such as grams, kilograms, or liters; in the last two variance expressions, the error SDs are expressed in relative terms--that is, in a percentage or a fraction. To be useful in variance calculations, a fraction, like 0.005 (kg Pu/kg MOX, for instance) is needed.

Materials balance equations often have several input/output transfer terms of the type given by T1 and T2, and, in addition, measurements of C or X for some of these terms may be made using the same measurement instruments/procedures. For instance, if there are two input transfers given by

$$t1 = \sum_{i=1}^{N1} x_i \qquad \text{and} \qquad t2 = \sum_{j=1}^{N2} y_j \quad ,$$

and these two transfers share the same measurement instrument, there are correlations between these measurements that must be included in the total MB variance. If the instrument is described by a multiplicative error model, the covariance equation is

$$\mathrm{cov}(t1,t2) = N1{*}N2{*}x{*}y{*}\sigma_\eta^2 \quad .$$

If t1 and t2 represented an input transfer and an output transfer, respectively, the covariance equation would have a minus sign on the right-hand side. If t1 and t2 were both input transfers or both output transfers, the covariance between them would be positive.

To illustrate how these simple equations are used in variance calculations, let us assume a form of input transfer term given by T1 [Eq. (1), Sec. II] and our wish to determine both the X and C variance contributions. Further, we assume that these N items are nominally identical, so that the N C_i measurements all have very nearly the same value, C, and the N $(BX - LX)_i$ measurements have very nearly the same value, (BX - LX). Also, we assume that the X measurements can be described by an additive error model and the C measurements can be described by a multiplicative error model (which is actually the case if we are dealing with mass and concentration measurements for cans of bulk powder).

Because we have assumed that these N items are nominally the same in concentration and net mass, we can write T1 in two equivalent forms;

$$T1 = C \sum_{i=1}^{N} (BX - LX)_i \quad , \tag{5}$$

where we treat C as a constant in this equation, and

$$T1 = (BX - LX) \sum_{i=1}^{N} C_i \quad , \tag{6}$$

where we treat BX - LX as a constant in Eq. (6). We use the first form of T1, Eq. (5), to calculate the X variance contribution and the second form of T1, Eq. (6), to calculate the C variance contribution. In general, the variance of a constant (A) times a measured value (Z) is given by

$$\mathrm{var}(AZ) = A^2 \mathrm{var}(Z) \quad , \tag{7}$$

and we can use this relation to obtain our two variance contributions. Using Eqs. (5) and (7), where the constant A = C, we write the X variance contribution of T1 as

$$\mathrm{var}(T1)_x = C^2 \mathrm{var}[\Sigma(BX - LX)_i] \quad ,$$

and the sum over i goes from 1 to N. The measured values, BX and LX, are given by

$$BX = BXT + \varepsilon_{x1} + \eta_x$$

and

$$LX = LXT + \varepsilon_{x2} + \eta_x \quad ,$$

where BXT and LXT are the true, but unknown, values of BX and LX, and the two random errors in the X measurements are different, but the two correlated errors in the X measurements are the same because the two measurements were made on the same scale. Hence, the difference,

$$BX - LX = BXT - LXT + \varepsilon_{x1} - \varepsilon_{x2} \quad .$$

The quantity, BXT - LXT, is a constant and has a variance of zero. The variance of only one difference, BX - LX, is then $2\sigma^2_{\varepsilon x}$ (where we have assumed that $\sigma^2_{\varepsilon x1} = \sigma^2_{\varepsilon x2} = \sigma^2_{\varepsilon x}$), and we have N such differences. Therefore, we can write

$$\mathrm{var}(T1)_x = 2NC^2\sigma^2_{\varepsilon x} \qquad (8)$$

as the X contribution to the variance of T1.

To obtain the C variance contribution to T1, we use Eqs. (6) and (7), where the constant A = BX - LX, and write

$$\mathrm{var}(T1)_c = (BX - LX)^2 \mathrm{var}(\Sigma C_i) \quad ,$$

where the sum over i goes from 1 to N. Using the relation, discussed earlier in this section, for the var(sum of N similar items) for a multiplicative error model, we obtain

$$\mathrm{var}(T1)_c = [C(BX - LX)]^2 (N\sigma_{\varepsilon c}^2 + N^2\sigma_{\eta c}^2) \tag{9}$$

for the C variance contribution to T1. Substituting the values for N, BX, LX, C, and the appropriate error SDs for the X and C measurements into Eqs. (8) and (9) allows us to obtain values for both contributions to the variance of T1. These contributions are added to obtain the total variance of T1 from measurement errors in the C and X measurement instruments. A procedure similar to the one just described must be carried out for each term in an MB equation, and the individual variance (and covariance) results must be summed to determine the total variance of MB.

IV. AN EXAMPLE PROBLEM IN MATERIALS ACCOUNTING

With the preliminary comments of Secs. II and III behind us, we can turn our attention to an example problem concerning the design of a materials accounting system for a MOX fuel fabrication line. Although not entirely realistic because the example chosen has been greatly simplified, the example illustrates many aspects that require consideration in designing a materials accounting system for a real problem. We describe the process in general terms, define the MBA boundaries, write the materials balance equations for plutonium (the SNM of interest here), and calculate the variances of the MBs (and sigma, the square root of the variance) using different assumptions regarding measurement procedures to determine the effects of the different assumptions on our accounting system.

Primary input to our simplified MOX fuel fabrication line consists of cans of 1:1 mixed uranium-plutonium oxide (50% PuO_2 or 44.1% Pu). This material is blended with MOX (5.98% PuO_2) from a waste recovery processing area and sufficient natural-enrichment UO_2 to produce a MOX that has 17.6% plutonium. After approximately a dozen additional process steps, such as milling, binder addition, pellet pressing, calcining, the pellets are grouped into pellet stacks (the primary output of this process line). We divide this line into two MBAs, as shown in Figs. 1 and 2, where we also specify flows and inventories. Note that the blender alone is in MBA-1, and the remaining process equipment is in MBA-2. For simplicity, we retain only one inventory in each MBA (the original problem had a total of 28 inventories).

Drawing flow diagrams for each MBA, as in Figs. 1 and 2, is useful and is highly recommended when starting a problem in materials accounting. Materials balance equations can be easily written when referring to such diagrams. However, the equations of Secs. II and III show that much more detailed information is needed to calculate the variance of the MB. For each transfer and inventory term, we need the number of measurements made during the accounting period (N), the gross mass (BX), the tare mass (LX), the SNM concentration (C), and the various error SDs associated with the different measurements. Before beginning a problem in the design of a materials accounting system, this information should be collected in a table for each MBA, as we show in Table I for MBA-1.

TABLE I

DATA FOR MBA-1

					1σ			
Term No.	N (No.)	C (frc)	BX (kg)	LX (kg)	Rand. C (%)	Corr. C (%)	Rand. X (kg)	Corr. X (kg)
1	150	0.441	2.25	0.25	0.60	0.35	0.0004	0.0008
2	30	0.053	2.65	0.25	5	2	--	--
3	60	0.176	13.0	0.50	0.60	0.35	0.005	0.009
4	2	0.176	13.0	0.50	3	1	--	--

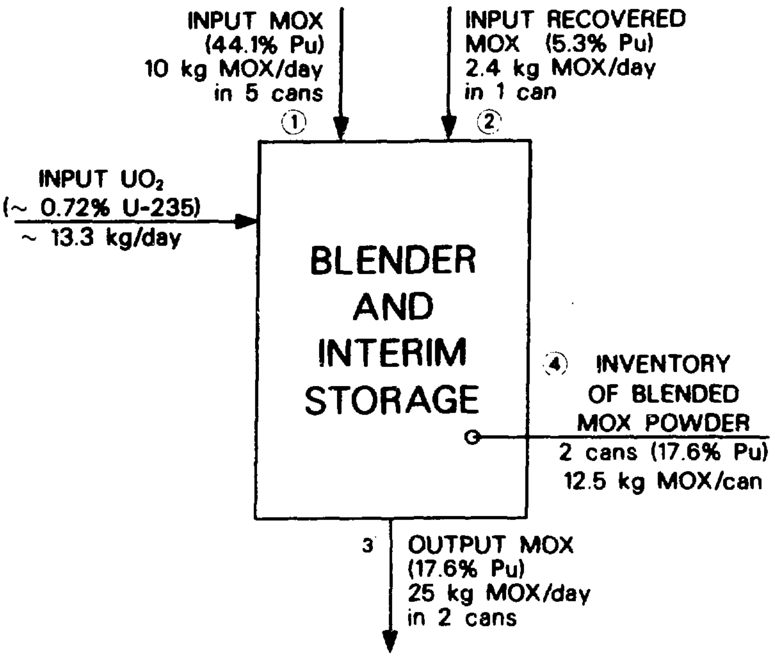


Fig. 1.
Flow diagram of MBA-1.

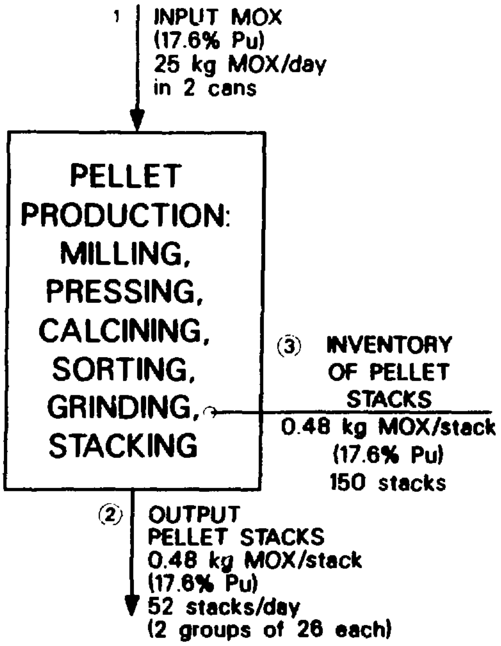


Fig. 2.
Flow diagram of MBA-2.

A. Variance Calculation for MBA-1

From Fig. 1, one can see that MBA-1 has two input transfer streams (designated Nos. 1 and 2), one output transfer stream (designated No. 3), and an inventory (designated No. 4). The input UO_2 stream does not contain plutonium and need not be considered in our MB equation. From the general MB equation in Sec. I, it is clear that the MB equation for this MBA must contain two (positive) input transfer terms, one (negative) output transfer term, a (positive) beginning inventory term, and a (negative) ending inventory term. The forms of these terms, in the sense of the forms discussed in Sec. II, are decided by facility operating/measurement procedures. We decide that, for transfer streams 1 and 3, the concentration and net mass of each can of MOX is measured. Hence, the form T1, Eq. (1), can be used for both these transfer streams. Because different scales are used to measure the net masses of the cans from streams 1 and 3, there are no mass error correlations between these two streams. Normally, samples from these cans are sent to the same laboratory for concentration measurements (by destructive electrochemical analysis). If the same instrument measures the concentration of samples from both streams, a correlation exists between these measurements that must be considered. We assume that if different instruments are used, no correlations exist. We calculate the variance of MB for both cases.

The material in stream No. 3 (Fig. 1) is similar to the material in the inventory, No. 4. Both materials are blended MOX powder. However, at the times we wish to close the materials balance (each 30 days), we decide to measure the plutonium content of the blended powder held in cans as inventory by using nondestructive assay (NDA) methods. There is good reason for this decision. Although, in our simple problem, we have specified only two cans of blended MOX powder in inventory, in a real facility there may be 20 or more cans held in inventory. Under such conditions, it becomes important that the plutonium content of this material be measured quickly. Hence, NDA instruments are often used for large inventories.

The form of the MB term for stream No. 2 can be taken as the type T1, Eq. (1), where the error in measuring the plutonium content is all in the concentration measurement (in NDA measurements, the mass of the container is not measured). The form of the inventory difference (No. 4) can be assumed as given by Eq. (4), where NX1 = NX2 = 1 and NC1 = NC2 = N.

The MB equation then can be written as

$$MB = \left[\sum_{i=1}^{N} C_i(BX - LX)_i\right]_{No.\ 1} + \left[\sum_{i=1}^{N} C_i(BX - LX)_i\right]_{No.\ 2} - \left[\sum_{i=1}^{N} C_i(BX - LX)_i\right]_{No.\ 3}$$

$$+ \left[\sum_{i=1}^{N} C_i(BX - LX)_i - \sum_{i=1}^{N} C_i'(BX' - LX')_i\right]_{No.\ 4} \quad .$$

The subscripts No. 1, No. 2, etc., refer to the Term Nos. in Table I for MBA-1, and it is understood that the values of N, C, BX, LX, and the measurement error SDs for the different Term Nos. are to be substituted into the expression for the variance of MB, term by term, to calculate the variance of MB.

The expression for the variance of MB is the sum of the variances and covariances of the right-hand side (RHS) of this equation. The variance of Term No. 1 is given by the sum of the RHSs of Eqs. (8) and (9), or

$$2NC^2\sigma_{\varepsilon x}^2 + [C(BX - LX)]^2(N\sigma_{\varepsilon c}^2 + N^2\sigma_{\eta c}^2) \quad .$$

The variance of Term No. 3 is similar. If the concentration measurements of the material in these two streams are correlated, the total covariance term is given by

$$-2[NC(BX - LX)]_1[NC(BX - LX)]_3\sigma_{\eta c}^2 \quad .$$

The leading 2 is needed because we have a covariance between Terms 1 and 3 and between Terms 3 and 1. Note that this covariance is negative. We will see the effects of this correlation shortly.

The variance of Term No. 2, the recovered MOX input, is given by the RHS of Eq. (9), for NDA instruments are usually described by a multiplicative error model. The variance of Term No. 4 is also only in the C measurement and is obtained by summing the C variance of the first part, the C variance of the second part, and twice the C covariance between them. The result is

$$2[C(BX - LX)]^2 N\sigma_{\varepsilon c}^2 \quad .$$

The total variance of MB is then

$$\begin{aligned} \mathrm{var}(MB) = {} & \{2NC^2\sigma_{\varepsilon x}^2 + [C(BX - LX)]^2(N\sigma_{\varepsilon c}^2 + N^2\sigma_{\eta c}^2)\}_{\mathrm{No.}\ 1} \\ & + \{[C(BX - LX)]^2(N\sigma_{\varepsilon c}^2 + N^2\sigma_{\eta c}^2)\}_{\mathrm{No.}\ 2} \\ & + \{2NC^2\sigma_{\varepsilon x}^2 + [C(BX - LX)]^2(N\sigma_{\varepsilon c}^2 + N^2\sigma_{\eta c}^2)\}_{\mathrm{No.}\ 3} \\ & + \{2[C(BX - LX)]^2 N\sigma_{\varepsilon c}^2\}_{\mathrm{No.}\ 4} \\ & - 2[NC(BX - LX)]_1 [NC(BX - LX)]_3 \sigma_{\eta c}^2 \quad . \end{aligned}$$

With this variance equation, we can now carry out Step (3) of Sec. II; that is, we can substitute measured values from Table I and obtain the variance of MB.

Although one can perform this calculation using a simple desk calculator, we have developed an interactive, menu-driven computer program called PROFF (for PROcessing and Fuel Facilities) that expedites this procedure considerably. The PROFF program asks a few preliminary questions of the user to establish the form of each transfer term [Eq. (1) or (2)] in the MB equation and each inventory term [Eq. (3) or (4)]. It also asks whether the X measurements are described by a multiplicative or additive error model. All C measurements, PROFF assumes, are described by a multiplicative error model. Further, PROFF asks which, if any, transfer terms have a covariance because of shared measurement instruments. Then it presents the user with a menu for each term of the MB equation; this menu is to be completed with values of N, C, BX, LX, and the error SDs, as given in Table I. After all the menus are complete, PROFF branches to the appropriate variance (or covariance) equation for each term (or terms), performs the individual variance and covariance calculations, sums these to give the total variance, and takes the square root of the total variance to give the sigma of the MB. More detail regarding PROFF can be found in the instruction manual (LA-CC-86-34, available from the National Energy Software Library, Argonne, Illinois). The variances for the individual terms of MBA-1, as obtained using PROFF, are given in Table II.

TABLE II

VARIANCE AND COVARIANCE RESULTS FOR MBA-1

Term No.		Variance/Covariance (kg^2 Pu)
1		0.2186
2		0.0070
3		0.2240
4		0.0174
Cov(1,3)		-0.4278
	Sum	0.0392

The square root of this sum, mentioned above, is $\sigma = 0.1980$ kg of plutonium for the sigma of MBA-1. If we had assumed that the plutonium concentration of material from Term No. 1 was measured on a different instrument from that of material from Term No. 3, the covariance entry in Table II, Cov(1,3), would be zero. In that case, the variance of MBA-1 would be $\sigma = 0.4670$ kg^2 Pu, or $\sigma = 0.6834$ kg of plutonium, which is considerably larger than 0.1980 kg. Obviously then, if one can arrange for measurements of input and output transfers using the same instrument, the total variance (and sigma) for an MBA can be reduced. We shall see shortly how these values of sigma are used to obtain detection sensitivities. First, we perform a similar variance calculation for MBA-2.

B. Variance Calculation for MBA-2

From Fig. 2, it is clear that MBA-2 has one input transfer stream (No. 1, blended MOX powder from MBA-1), one output transfer stream (No. 2, 52 pellet stacks per day), and a beginning and ending inventory of 150 pellet stacks (No. 3). We assume that no measurement correlations exist between the input and output transfers and, at materials accounting times, the plutonium content of the pellet stacks held as inventory is measured by NDA methods. We also assume that for each 26 pellet stacks, a few pellets are sent for laboratory analysis. Hence, one concentration measurement is applied to 26 pellet stacks, where the mass of each stack is measured. The materials balance equation can then be written as

$$\mathrm{MB} = \left[\sum_{i=1}^{N} C_i(\mathrm{BX} - \mathrm{LX})_i\right]_{\mathrm{No.}\ 1} + \left[\sum_{i=1}^{\mathrm{NC}} C_i \sum_{j=1}^{\mathrm{NX}} (\mathrm{BX} - \mathrm{LX})_{ij}\right]_{\mathrm{No.}\ 2}$$

$$+ \left[\sum_{i=1}^{N} C_i(\mathrm{BX} - \mathrm{LX})_i - \sum_{i=1}^{N} C_i'(\mathrm{BX}' - \mathrm{LX}')_i\right]_{\mathrm{No.}\ 3} .$$

Note that the output transfer, Term No. 2, has the form T2, given by Eq. (2), Sec. II. We did not derive the variance of a term of this type in Sec. III, but we include it in the equation below, which is the variance of MB for MBA-2.

$$\mathrm{var(MB)} = \{2\mathrm{NC}^2\sigma_{\varepsilon X}^2 + [C(\mathrm{BX} - \mathrm{LX})]^2(N\sigma_{\varepsilon c}^2 + N^2\sigma_{\eta c}^2)\}_{\mathrm{No.}\ 1}$$

$$+ \{2\mathrm{NCNX}(C\sigma_{\varepsilon X})^2 + [\mathrm{NX}C(\mathrm{BX} - \mathrm{LX})]^2[\mathrm{NC}\sigma_{\varepsilon c}^2 + (\mathrm{NC}\sigma_{\eta c})^2]\}_{\mathrm{No.}\ 2}$$

$$+ \{2[C(\mathrm{BX} - \mathrm{LX}]^2 N\sigma_{\varepsilon c}^2\}_{\mathrm{No.}\ 3} .$$

To carry out the calculation for the variance of MB, we use the data in Table III.

TABLE III

DATA FOR MBA-2

Term No.	N (No.)	C (frc)	BX (kg)	LX (kg)	1σ Rand. C (%)	Corr. C (%)	Rand. X (kg)	Corr. X (kg)
1	60	0.176	13.0	0.50	0.60	0.35	0.005	0.009
2	60 (NX=26)	0.176	0.73	0.25	0.75	0.40	0.0004	0.0008
3	150	0.176	0.73	0.25	10	1	--	--

Note that for Term No. 2, there are NC = 60 concentration measurements during the accounting period and, for each concentration measurement, there are NX = 26 mass measurements (that is, 26 pellet stacks). To carry out the calculation, we enter PROFF again and complete the data menus. The results are shown in Table IV.

The square root of this sum is σ = 0.7346 kg of plutonium for the sigma of MBA-2. Before we calculate the detection sensitivity for this value of sigma, we want to perform one additional variance calculation, and we do this in the next section.

TABLE IV

VARIANCE RESULTS FOR MBA-2

Term No.	Variance/Covariance (kg^2 Pu)
1	0.2240
2	0.2942
3	0.0214
Sum	0.5396

C. Variance of MBA-1 and MBA-2 Combined

Combining MBAs-1 and -2 into a single MBA results in the flow diagram shown in Fig. 3; this combined MBA we call MBA-C. One can see that this combined MBA has two input transfers, one output transfer, and two inventories, for a total of five strata of items. The transfers internal to MBA-C, the output MOX from MBA-1 and the input MOX to MBA-2, are omitted in the flow diagram of MBA-C. The two MBAs separately required measurements on seven different strata of items. From the viewpoint of the facility operator, combining the two MBAs into one has a distinct advantage; fewer measurements are necessary. From the viewpoint of materials accounting, however, there is a distinct disadvantage. The combined MBA includes more process equipment, so the ability of the materials accounting system to localize possible loss of SNM is reduced to some degree.

The value of the variance of MBA-C can be easily calculated from results already obtained. First, we suppress all variance and covariance values of those transfers of MBA-1 and MBA-2 that become internal transfers in MBA-C. In Table II, these are the variance of Term No. 3 and the

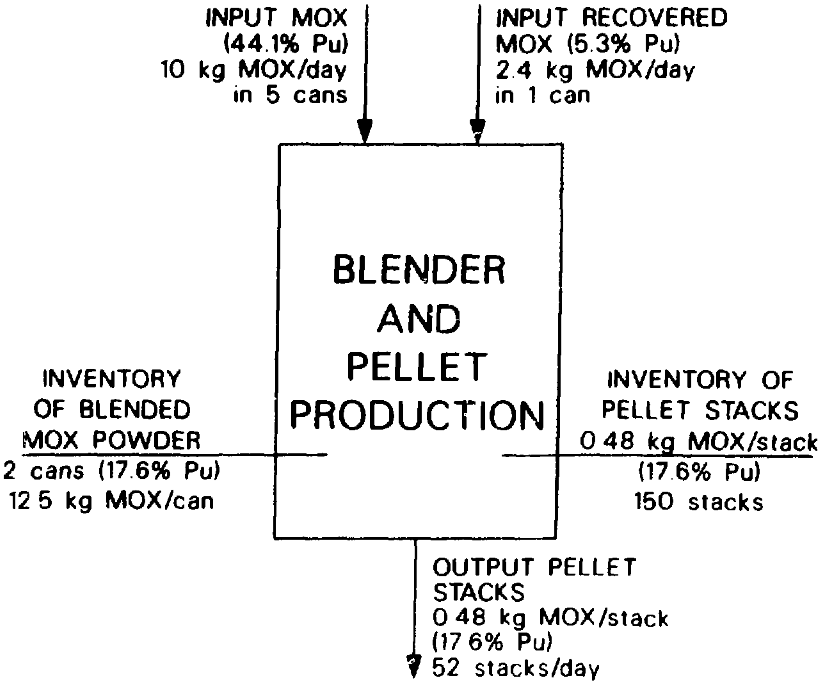


Fig. 3.
Flow diagram of MBA-C.

value of cov(1,3); in Table IV, we suppress the variance value of Term No.1. Then we sum the remaining variance contributions. These include Terms 1, 2, and 4 from Table II and Terms 2 and 3 from Table IV. Then, for the combined MBA, MBA-C, the variance of MB is 0.5586 kg^2 Pu or $\sigma = 0.7474$ kg of plutonium.

The values of sigma for the different MBAs are presented in Table V for comparison. If the concentration measurements of transfer streams 1 and 3 of MBA-1 were not correlated (line 2 of Table V), then the sigma value of the combined MBA is not very much greater than those of MBAs-1 and -2. In this particular case, combining MBAs-1 and -2 into MBA-C would have the advantage of saving the number of measurements to be made while not increasing the sigma or reducing the degree of localization significantly. If the concentration measurements of transfer streams 1 and 3 of MBA-1 were correlated, it would probably be best to keep the two MBAs separate. General conclusions regarding the advantages of combining MBAs cannot be drawn. Each case must be examined in detail and the quantitative results weighed against other possible priorities (such as cost of measurements, the degree of localization that must be preserved, and whether detection sensitivities are sufficiently low for those MBAs that contain SNM in a form particularly attractive to a diverter).

TABLE V

VALUES OF SIGMA FOR THE DIFFERENT MBAs

MBA	σ (kg Pu)
1 (with corr. 1,3)	0.1980
1 (w/o corr. 1,3)	0.6834
2	0.7346
C	0.7474

V. DETECTION SENSITIVITY OF MATERIALS ACCOUNTING SYSTEMS

We are now in a position to proceed with Step (4) of Sec. II. We have made several references to the "detection sensitivity" and the fact that it is related to the sigma, the standard deviation of the materials balance, MB. In this section, we quantify this concept and indicate what role the sigma plays. To do this, we introduce new terminology: detection probability (DP), false-alarm probability (FAP), and alarm level (AL). These terms must be specified whenever the "effectiveness" or "detection sensitivity" (DS) of a materials accounting system is stated. The treatment we give below is applicable to short-term (or abrupt) material loss, which refers to a loss, within one materials balance period, of a relatively large amount of material.

We begin with the definitions of DP, DS, and FAP.

- DP is the probability of detecting a loss of a given magnitude with an alarm level established at a value, AL.
- The DS of the materials accounting system is the magnitude of a loss that can be detected with probability, DP.
- The FAP is the probability that the test statistic of interest (for example, the materials balance) will exceed the AL when no loss has occurred. The FAP, in other words, is the probability that a loss will be indicated when none has occurred.

Figure 4 illustrates the relationship of DP, FAP, AL, and DS. We assume that the materials balance (MB) is a random variable, distributed normally with the variance σ^2. The left-hand probability distribution curve represents the distribution of the MB in the case of no material loss. The area under this curve for values of MB $\geq$ AL is the FAP. The AL is set at a value nσ, where n is chosen to give the desired (or tolerable) false-alarm rate. The right-hand curve corresponds to the MB distribution in the case of loss of material of magnitude Nσ, the DS. The area under this curve for values of MB $\geq$ AL is the DP.

We assume that the MOX fuel pellet line under discussion can tolerate a FAP of 5%; then FAP = 0.05. This value of FAP specifies that AL = nσ = 1.65σ. If we assume that we wish the DP to be 95%, the DP = 0.95. This value of DP requires that DS = Nσ = 3.30σ.

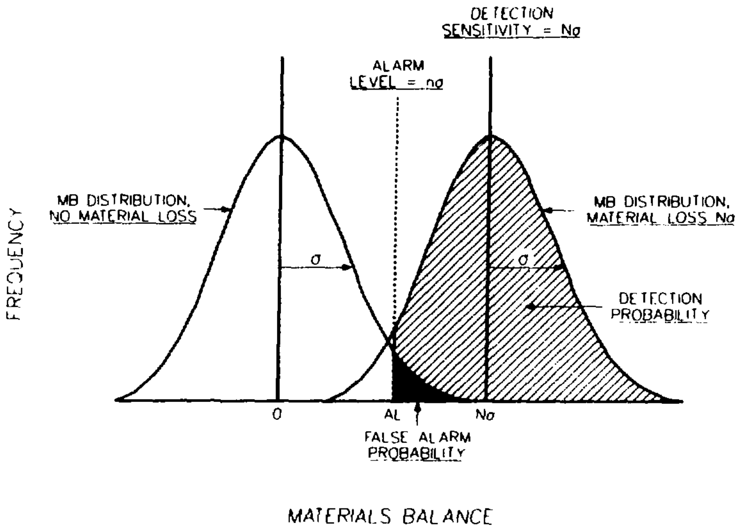


Fig. 4. Relationship of DP, FAP, AL, and DS.

Under these assumptions, the alarm levels and detection sensitivities for the various sigmas listed in Table V are shown in Table VI.

As can be seen, it is only for MBA-1, with correlations between transfer streams 1 and 3, that the DS is less than 1% of plutonium throughput (which is 132 kg for a 30-day accounting period). For the other MBAs, the DSs are closer to about 2% of throughput. These detection sensitivities can be improved (decreased) only by decreasing the instrument measurement standard deviations, which explains why using the best instruments available for measurement is so important.

TABLE VI

DETECTION SENSITIVITIES AT 95% DP AND 5% FAP

MBA	σ (kg)	AL (kg)	DS (kg)	Throughput (%)
1 (with corr.)	0.1980	0.33	0.66	0.5
1 (w/o corr.)	0.6834	1.13	2.26	1.7
2	0.7346	1.21	2.42	1.8
C	0.7474	1.23	2.46	1.9

VI. ADDITIONAL SUGGESTIONS

Some general comments to provide additional guidance in the design of improved materials accounting systems appear below:

- Correlations between input transfers (or between output transfers) are to be avoided; however, correlations between input and output transfers are desirable.
- Processes having small in-process inventories and holdup are preferred.
- Operating procedures should include frequent calibration of instruments to reduce correlations in the accounting data.
- Materials accounting areas can sometimes be restructured to improve the sensitivity of the safeguards system by eliminating the variance contributions of intermediate transfers.
- Changes in process equipment and procedures can often improve the sensitivity of the safeguards system by permitting better measurements on well-characterized material.

ABOUT THE AUTHOR

Dante Stirpe received his Ph.D. from the University of Missouri in physics and began working at Los Alamos National Laboratory in 1962. He joined the Safeguards Systems Group in 1978. His interests include systems analysis and error propagation, and he is the primary author of a course in error propagation techniques for safeguards being developed for the Department of Energy Safeguards Technology Training Program.

CHAPTER X

MATERIALS CONTROL AND ACCOUNTING IN A PLUTONIUM PROCESSING FACILITY

by

J. W. Barnes, A. L. Baker, and T. G. Marr

I. INTRODUCTION

We discuss materials control and accounting (MC&A) as practiced in currently operating plutonium processing facilities, illustrate the application of system analysis techniques presented in this course, and describe some problems typically encountered in implementation of an effective MC&A system. We draw upon our experience of reviewing MC&A systems in operating plants and assisting in the implementation of MC&A systems.

II. BACKGROUND

Prior sections of the course text outline the basics of MC&A in a modern plant that implements the latest in measurement technology and MC&A techniques. Many existing facilities have MC&A systems that are quite different than the up-to-date systems described. Such plants frequently have fewer measurements than are desirable and lack the full scope of MC&A technology. Lack of adequate funds to allow modernization of older facilities requires that we live with what exists.

The MC&A systems in older plants are typically characterized by

- materials balance closure at periods of 30 days to 360 days,
- samples being sent to remote analytical laboratories--with a week or more to obtain results, and
- manual record keeping although some computer data processing may be used.

These older materials accounting systems are by-products from the time these plants were constructed. Modern materials accounting systems of the type described in this book are seen in the special nuclear material

(SNM) processing plants presently under construction. Modern materials accounting systems are characterized by

- near-real-time (~24 h) materials balance closure on process units or individual process batches,
- on-line or at-line analyses with rapid return (<1 h) of results to the process control and MC&A systems, and
- computerized data analysis and instrumentation with attendant rapid data processing and automated control.

III. THE EXAMPLE PROCESS

For the purposes of this discussion, we examine a typical SNM process commonly used in DOE facilities. The process, shown as Fig. 1, converts plutonium nitrate in aqueous solution to plutonium metal. This process includes three major processing steps:

- feed purification and concentration by ion exchange,
- plutonium conversion to a solid by fluoride precipitation, and
- conversion of the precipitate to plutonium metal by roasting and calcium reduction.

The process shown in Fig. 1 is simplified from what would be encountered in a real facility; however, the description is adequate for our purposes. The real facility might contain 50 or more processing steps (for example, various chemical additions, handlings, and transfers) and over 100 process vessels for intermediate processing steps.

The example process converts 10 batches of nitrate solution, each containing 10 kg of plutonium, into metal product. The primary output consists of 80 plutonium buttons weighing approximately 1.1 kg each. Other outputs are

- ion-exchange column effluent,
- filtrate from the precipitate filtration-step,
- sweepings from the process line, and
- scrap from the calcium reduction step.

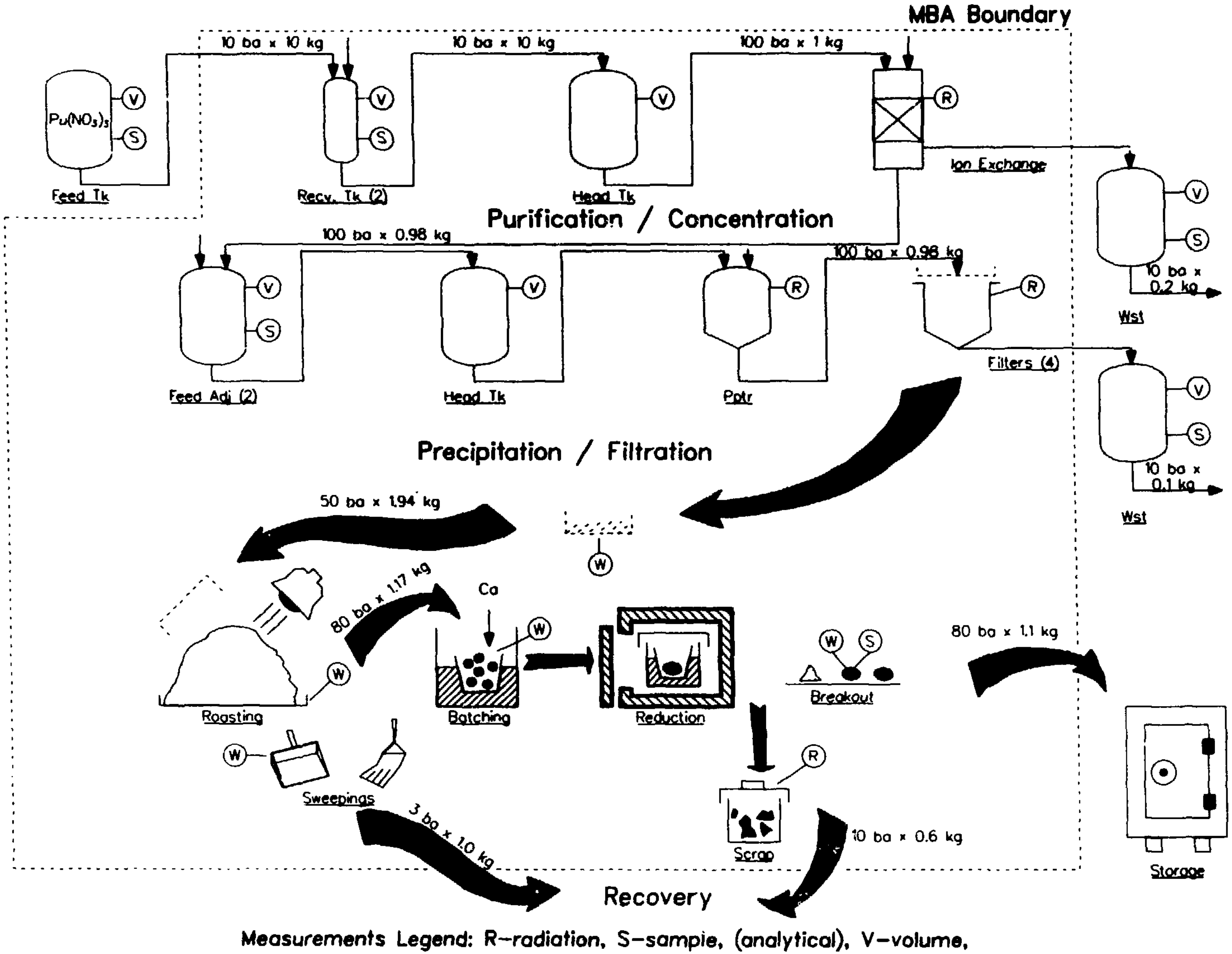


Fig. 1.
The example process—plutonium nitrate to metal conversion.

Each feed batch is sampled and analyzed to obtain plutonium concentration. The volume transferred is determined by measuring the feed tank volume before and after transfer. Receipt of material in the materials balance area (MBA) is verified by comparison with the volume received. Chemicals are added to the feed batch to prepare the material for subsequent processing. A sample of the received material is also taken and analyzed to confirm that the proper material was received. In the example process, two receipt tanks provide surge capacity and allow time for chemical addition, mixing, sampling, and verification of material composition prior to transfer to the ion-exchange system.

The prepared batch is transferred to a head tank that feeds the ion-exchange column. The solution is passed through the ion-exchange column until approximately 1 kg of plutonium is loaded onto the ion-exchange resin. Impurities pass through the column and into the ion-exchange waste tank. The plutonium, free of impurities, is then eluted from the ion-exchange column by the use of suitable chemicals and accumulated in a precipitator feed adjustment tank. A small amount of plutonium also passes through the ion-exchange column to the ion-exchange waste tank. Ion-exchange waste from 10 ion-exchange cycles is accumulated, the volume measured, and samples taken and analyzed. The waste is then transferred from the MBA for recovery of residual plutonium.

Two precipitator feed adjustment tanks provide surge capacity for ion-exchange eluent accumulation, chemical adjustment, and analysis. The concentrated, purified plutonium is adjusted by addition of appropriate chemicals and transferred to a precipitator head tank that feeds the precipitator. This purified plutonium solution and solution containing fluoride ion are continuously metered to the precipitator where solid plutonium fluoride is formed. The solution containing suspended plutonium fluoride is passed through filter boats to recover the precipitate. Filtrate, which passes through the filters, is collected in a filtrate tank where it is sampled and analyzed for plutonium content. After its volume is measured, the filtrate is transferred from the MBA for recovery of SNM values.

The wet precipitate is dried, weighed, and accumulated in surge storage. The dry material is roasted to produce a mixed plutonium oxyfluoride and weighed into a crucible with a charge of calcium metal. The crucible is placed in a sand bed in a closed vessel, which is placed in a furnace heated to 700°F. At this temperature, the calcium metal reacts with the plutonium oxyfluoride to yield plutonium metal, calcium fluoride, and calcium oxide. The container is removed from the furnace, cooled, opened, and the product plutonium metal button is removed. The button is cleaned and weighed, and a small sample is taken for determination of impurities. The product buttons are labeled and transferred from the MBA to storage. The waste sand, slag, and crucible material from four buttons are collected in a container, assayed for SNM content, and transferred from the MBA to SNM recovery.

The drying, roasting, and reduction operations require handling of fine dry powders. Some amount of these powders is lost to the glove box interior through spillage. This spillage, routinely recovered by sweeping the glove boxes and equipment, is collected in containers, removed from the boxes, weighed, and transferred from the MBA to recovery.

The greatly simplified process description above is adequate for the discussion that follows and illustrates the points we offer about a real MC&A system and some of the inherent problems of such a system.

IV. ACCOUNTABILITY MEASUREMENTS

Measurements should be made to determine SNM content of all streams entering and leaving the MBA and of all SNM inventories within the MBA if accurate materials accounting is sought. In some cases (spillage, holdup in transfer piping and complex geometry vessels, etc.), measurements may be impossible or, at best, quality measurements may be impractical. In these cases, it may be necessary to use estimators of unmeasured inventory (holdup) if all terms in the material equation are to be addressed.

Data on errors associated with each measurement or inventory estimate must also be available for error propagation and determination of limit-of-error inventory difference (LEID). Tables I and II show the measurement values and errors associated with inventory and transfer determinations respectively for the example process. These errors are typical of those we have observed in operating facilities. Such error terms may differ by an order of magnitude or more between facilities, depending primarily upon the instrumentation used and the care taken to maintain and operate it.

TABLE I

EXAMPLE PROCESS
INVENTORY MEASUREMENTS AND ERRORS

Description	No.	Quantity	Percent Error		Concentration	Percent Error	
			Random	System		Random	System
Feed Recvr.	2	2000 L	3.0	2.0	0.005 kg/L	4.0	1.0
IX Head Tk.	1	2500 L	5.0	3.0	0.004 kg/L	4.0	1.0
IX Column	1	1.00 kg	5.0	25.0			
Feed Ad. Tk	2	400 L	5.0	3.0	0.025 kg/L	2.0	0.5
Prcp.Hd. Tk.	1	500 L	5.0	3.0	0.020 kg/L	2.0	0.5
Precipitator	1	2.00 kg	25.0	10.0			
Filters	4	1.25 kg	0.5	1.0	0.800 kg/kg	20.0	5.0
Roasters	2	2.22 kg	0.3	0.7	0.901 kg/kg	15.0	5.0
Batching	2	2.61 kg	0.3	0.7	0.901 kg/kg	15.0	5.0
Reduction	2	2.61 kg	0.3	0.7	0.901 kg/kg	15.0	5.0
Breakout	1	2.35 kg	0.1	0.05	0.998 kg/kg	0.1	0.1
Sweepings	2	2.00 kg	0.4	0.8	0.500 kg/kg	50.0	
Scrap	3	0.90 kg	0.6	1.2	0.667 kg/kg	25.0	5.0

TABLE II

EXAMPLE PROCESS
TRANSFER MEASUREMENTS AND ERRORS

Description	No.	Quantity	Percent Error		Concentration	Percent Error	
			Random	System		Random	System
Feed	10	2000 L	0.5	0.3	0.005 kg/L	0.4	0.1
IX Waste	10	-2500 L	10.0	4.0	0.0001 kg/L	5.0	1.0
Filtrate	10	-500 L	10.0	4.0	0.0002 kg/L	5.0	1.0
Sweepings	3	-2.00 kg	0.4	0.8	0.500 kg/kg	50.0	
Scrap	10	-0.90 kg	0.6	1.2	0.667 kg/kg	25.0	5.0
Product	80	-1.10 kg	1.0	0.05	0.999 kg/kg	0.01	0.01

The two very large measurement errors on purities for sweepings and scrap, indicated in Tables I and II, result from lack of a concentration measurement on individual batches of material. Sampling errors (that is, difficulty of obtaining representative or homogeneous samples) may further increase uncertainty. The value for sweepings is based upon historical data from samples taken at infrequent intervals. In an ideal system, each material batch would be measured in an appropriate NDA device. Large errors associated with the ion-exchange column, precipitator, and scrap are the result of measurement problems associated with system geometry and matrix composition. Filters containing SNM have large errors because of variations in chemical composition and moisture content. These variations make precise measurements difficult.

V. MATERIALS BALANCE EQUATION

It is shown elsewhere in this manual that closure of a materials balance about a materials balance area typically involves evaluation of the equation

$$MB = I_B - I_E + T_I - T_O ,$$

where

MB = materials balance,

I_B = beginning inventory,

I_E = ending inventory,

T_I = input transfers, and

T_O = output transfers.

Each of the inventory and transfer terms has one or more (usually many) components associated with it. For approximation purposes, each component is assumed to have the following form:

$$t_j = \sum_{i=1}^{m} (n_i * q_i * c_i) ,$$

where

t_j = j^{th} term in the materials balance equation,

m = number of components in the j^{th} MB term,

n_i = number of items in the i^{th} component,

q_i = quantity of the i^{th} component, and

c_i = concentration of SNM in the i^{th} component.

The steady-state assumptions we made for our example process are evident in two areas: the first, the assumption that beginning and ending inventories for each process unit are equal and, the second, the assumption that each item in the i^{th} component has the same value. (For example, each feed input of the nitrate solution has the same quantity and concentration of SNM.) Specialized and/or well-controlled processes tend to be well approximated by the above assumptions. A large number of components (for example, inventory items) will tend to "average-out" to some nominal value. In addition, measurement noise can swamp item differences.

For approximation purposes, we assume a lack of correlation (independence) could occur in two cases. The first case is between the methods used in estimating q_i and c_i values. The assumption of independence between such methods is usually justified. The second case is between components, that is, between methods used in estimating q_i and q_j and/or c_i and c_j. This second assumption could lead to an estimate of the total MB variance that is significantly different from the "true" variance under certain conditions. Such a condition, for example, would occur if the same method were used in estimating the concentration of SNM in the filters and roasters shown in Table I. If the systematic errors associated with the common methods were relatively large, this effect would be especially significant. This can be shown in the propagation of error in a materials balance term, t_j.

(1) Under the independence assumption,

$$\mathrm{var}\ (t_j) = \sum_{i=1}^{m} \sigma_i^2 \quad ,$$

where equals variance of the i^{th} component. In other words, the variance of a sum of random variables is the sum of the variances when the random variables are independent.

(2) When independence is not assumed,

$$\text{var}\ (t_j) = \sum_{i=n}^{m} \sigma_i^2 + 2 \sum_{j,i} \text{(covariance between components j and i, where } j < i).$$

The last sum extends over each of the n pairs of correlated components, where n is the number of combinations taken two at a time. For example, if the same instrument were used to measure the q_i for six different components, there would be 15 terms in the covariance summation. If this same instrument were used for 12 different components, there would be 66 terms in the covariance summation.

VI. VARIANCE CALCULATIONS

Results of an error propagation exercise using the data from Tables I and II are summarized in Table III. Only those components of the materials balance equation that are known and defined in Tables I and II are included in the error propagation. In a real system, there generally are unknown terms in the materials balance equation or unknown measurement errors. If these unknown terms and errors are not included in the error propagation, the calculated variance is less than the "real" system variance. However, if the major terms and errors are included, the results are adequate for analysis of the system. In many cases, the system can be characterized by a very limited set of terms.

Table III gives the variance for individual inventories and transfers in the example process. The uncertainty in the materials balance closure is 2.849 kg at one standard deviation. The LEID is twice this value, or 5.70 kg. Review of these data shows that the inventory variances are the major contributors to uncertainty in the material balance closure. No single inventory term dominates the total inventory variance. To effect a significant reduction in total inventory variance would require that improvements be made in many of the measurement systems. Investment of capital to improve these measurements may not be cost effective.

TABLE III

EXAMPLE PROCESS
ERROR PROPAGATION RESULTS

INVENTORY VARIANCE

Description	No.	Inventory (kg)	Variance (kg)
Feed Receiver	2	20.000	1.0000
IX Head Tank	1	10.000	0.8200
IX Column	1	1.000	0.0050
Feed Adjust. Tk.	2	20.000	1.1600
Precip. Head Tk.	1	10.000	0.5800
Precipitator	1	2.000	0.5000
Filters	4	4.000	0.3202
Roasters	2	4.000	0.3602
Batching	2	4.703	0.4979
Reduction	2	4.703	0.4979
Breakout	1	2.345	0.0000
Sweepings	2	2.000	1.0001
Scrap	3	1.801	0.1352
Inventory Total		86.552	6.8765

TRANSFER VARIANCE

Description	No.	Transfer (kg)	Variance (kg)
Feed	10	100.000	0.1410
IX Waste	10	-2.000	0.0118
Filtrate	10	-1.000	0.0029
Sweepings	3	-3.000	0.7506
Scrap	10	-6.003	0.3206
Product	80	-87.912	0.0117
Transfer Total		0.085	1.2386

Total MBA Variance = 8.1152 kg^2

Total MBA Standard Deviation = 2.849 kg

Although improvements in the inventory measurements may not appear warranted, an alternate cost-effective strategy should be considered. Draining of vessels containing solutions and cleanout of solids-handling vessels at inventory time will, in effect, reduce the magnitude of these terms in the materials balance equation to zero. This may be impractical, especially if daily balances are attempted. However, for longer inventory periods (for example, monthly), cleanout and flushdown will greatly reduce uncertainty.

The evaluation of inventory terms assumes steady-state operation; that is, inventories at the start and end of the balance period are the same for each process unit. In a dynamic simulation where these inventories vary, the variance of each process unit is higher and wider ranging. Dynamic simulations of the example process typically show standard deviations that range from those given in Table III to about 0.2 kg higher. If vessels are emptied at balance closure, lower variances may be obtained for those vessels.

Three transfers provide significant contributions to the total transfer variance: the large input feed stream and the two solid waste outputs (sweepings and scrap) that have small flows relative to the feed. The sweepings and scrap transfers contribute more to the total transfer variance than does the feed; therefore, improved measurements of sweepings and scrap could affect a significant reduction in the transfer variance. Although the measurement errors on ion-exchange waste and filtrate are larger than for the feed, the variance contribution of these terms is relatively low because small quantities are transferred. Improving these measurements produces no significant benefit.

VII. THROUGHPUT EFFECTS

Figure 2 shows the effect of throughput on uncertainty in the materials balance closure for the example process. The uncertainty is relatively constant at approximately 2.8 kg for throughputs below 200 kg per inventory period. At throughputs above 150 kg, the transfer terms become important and begin to dominate above a throughput of 500 kg. The slope of the total uncertainty vs throughput plot is determined by the relative contribution of the random and systematic errors.

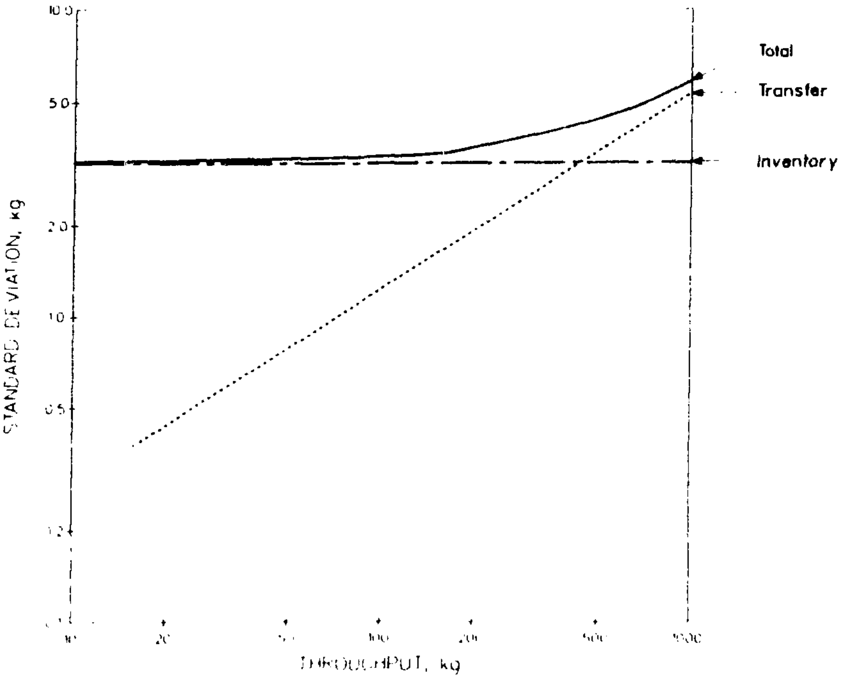


Fig. 2.
Materials balance uncertainty vs throughput.

The contributions of inventory and transfer components are also shown in Fig. 2. In a nonsteady-state plant, the curves are not as smoothly shaped as with the example case (inventories will vary, transfers are not continuous, and operations are discrete occurrences at variable intervals). Figure 2 plots the standard deviation for a steady-state system. In dynamic simulations of similar systems, we typically see variations of 10 to 20% about the steady-state centerline. Real plants may have much larger variations because of unmeasured inventory (holdup) changes and because all sources of measurement error are not known.

The contribution of individual transfers to total transfer uncertainty as a function of system throughput is shown in Fig. 3. Sweepings, scrap, and feed transfers are all significant contributors to transfer variance. Other transfers are not significant contributors to the total system uncertainty. Note that individual plots do not have the same slope, thereby reflecting the differences in the random and systematic error components.

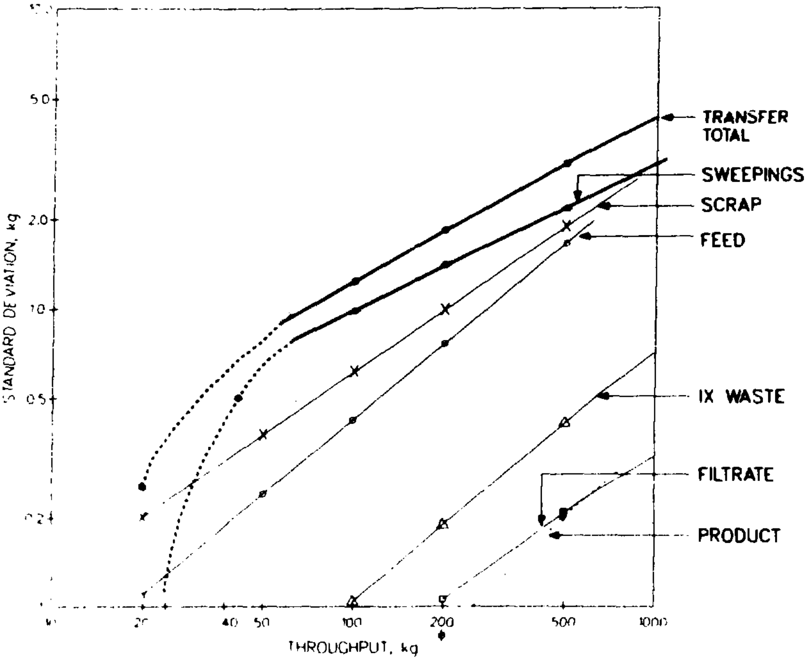


Fig. 3.
Materials balance uncertainty for material transfers.

Three primary conclusions can be drawn from a study of the above exercise:

(1) materials balance uncertainty increases as the time between balance closures (throughput) increases;

(2) transfer measurements become the primary source of uncertainty with long closure periods; and

(3) short balance periods do not necessarily reduce materials balance uncertainty; that is, inventory terms may dominate the material balance equation.

Shorter balance periods can actually lead to increased inventory differences as system cleanout may be impractical, resulting in a larger (often controlling) contribution of holdup.

A knowledge of system sensitivities and weaknesses is essential to materials accounting. Thorough analysis and understanding of the system are required to assure that the most information is obtained from the least amount of data. Such analysis also helps optimize the materials accounting system and assures maximum return on capital and manpower expenditures.

VIII. UNMEASURED INVENTORY (HOLDUP)

The magnitude of inventory difference upon materials balance closure is frequently driven by "unmeasured inventory" (holdup) and not by inaccuracies in measurements. Spillage in glove boxes, deposits in pipes and vessels, holdup in equipment, etc., frequently control inventory difference and associated LEID.

Figure 4 shows three cases in which spillage (loss to holdup) is assumed constant at 1.0% of system input. In the top case, the process and equipment are thoroughly cleaned at the end of each 100-kg campaign. In the second scenario, the process line is cleaned at irregular intervals

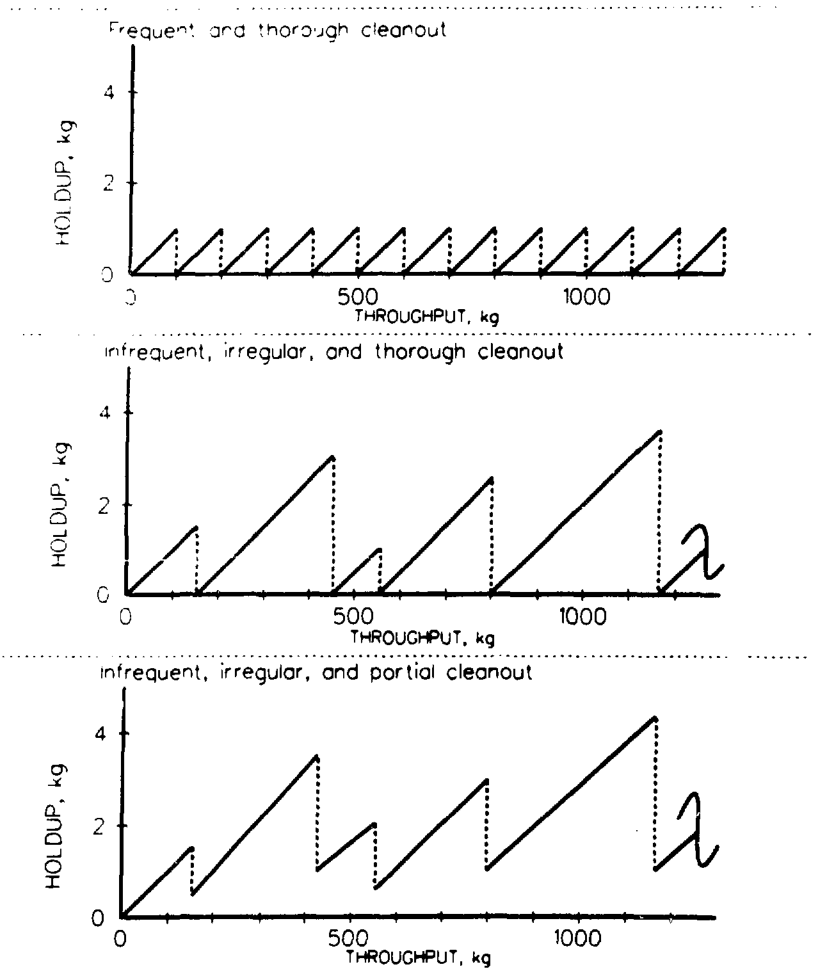
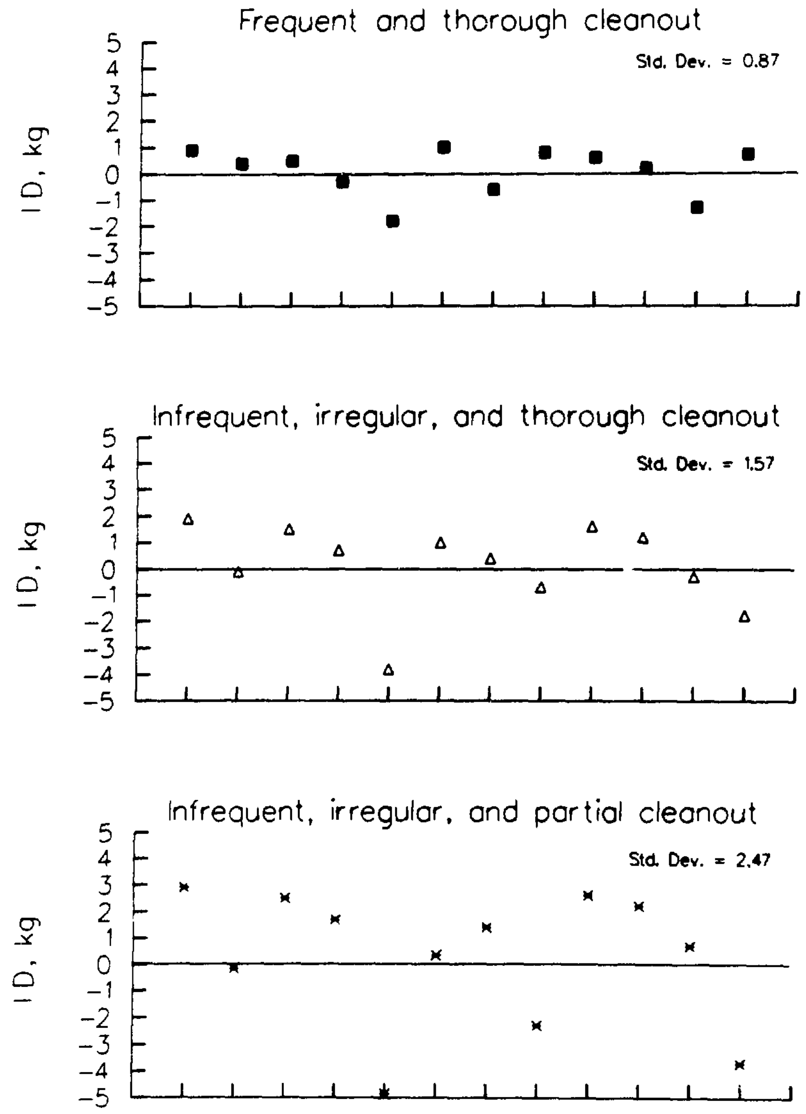


Fig. 4.
Process holdup in the example process.

of from 100 kg to 350 kg throughput. In the last case, the same irregular cleanout intervals are assumed; however, only 70% of the system holdup is recovered during cleanout.

The impact of holdup on inventory difference (ID) for the three cases is shown on Fig. 5. The IDs for a process with a 1.0-kg standard deviation on measured inventories are plotted for a series of 12 balance closures at intervals of 100-kg throughput. The top case has no holdup in the process. The observed IDs result from measurement errors only as the system is thoroughly cleaned before balance closures.



Frequent and thorough cleanout

Std. Dev. = 0.87

Infrequent, irregular, and thorough cleanout

Std. Dev. = 1.57

Infrequent, irregular, and partial cleanout

Std. Dev. = 2.47

Fig. 5.
Inventory differences with process holdup.

The top plot shows an ID behavior that follows the error propagation results. Approximately two thirds of the IDs fall within one standard deviation, and approximately one third lie in the one-to-two standard deviation range. In the bottom two cases, the holdup (unmeasured inventory) appears as apparent abnormalities. There is now much more "noise" in the data. The data spread does not behave as statistics tell us it should, and there is an apparent bias in the data (or material is being lost from the process).

In many of the older process plants, we find that process holdup (unmeasured inventory) is the major source of materials accounting problems. Operations that handle finely divided solids (powder) are especially troublesome. Losses to holdup may amount to several percent of throughput, and individual equipment pieces (blenders, calciners, hydrofluorinators, etc.) may have holdups of 10 kg or more.

Thorough cleanout (or cleanout to a consistent residual level) is essential for "good" materials accounting. Because cleanout operations can reduce production and lead to increased (or reduced) radiation exposure to personnel, materials accounting and operating concerns can be in conflict.

To realize the goal of effective materials accounting, we must appreciate the importance of holdup and other elusive factors and include these factors in materials balances. Using holdup measurements (however crude) and holdup estimators based upon historical cleanout data, or both, is vital if we are to overcome the holdup problem.

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CHAPTER XI

SURVEY OF CHEMICAL AND BULK MEASUREMENT METHODS

by

R. G. Gutmacher and D. D. Jackson

I. INTRODUCTION

Determination of the quantity of uranium and plutonium in nuclear materials generally requires two types of measurements: a bulk measurement, such as weight or volume, and a concentration measurement. Concentration is determined by a variety of destructive and nondestructive techniques. This chapter surveys bulk and chemical measurement methods used for either conventional or near-real-time materials accounting as well as for process control in nuclear facilities, with emphasis on fuel fabrication, conversion, and reprocessing. Nondestructive methods of analysis that rely on a nuclear signature are discussed in Chap. III.

The sequence of measurements usually involves three steps. First, the mass or volume and density of the material are determined. Next, samples representative of the material are obtained and analyzed, and, finally, the total quantity of uranium or plutonium is computed from the mass or volume and the analysis results.

II. MASS, VOLUME, DENSITY, AND FLOW MEASUREMENTS

The mass of solids and gases is generally determined by weighing. Solution measurements include mass, volume, and density determinations and, in some cases, flow measurements integrated over time.

A. Mass Measurement

A wide variety of weighing devices is available. Some commonly used devices include pan balances, beam balances, hydraulic load cells, and mechanical load cells. Selection of the weighing device depends on the application. Load cells have application where high capacity is required, where weights of highly radioactive materials are determined, or where the environmental conditions are harsh. Pan and beam balances are generally selected where small quantities are measured and where environmental conditions are controlled (that is, in a noncorrosive atmosphere). All of these devices require frequent calibration. For accurate work, the measured weights require correction for buoyancy.

B. Volume and Density Measurement

The volume of solution in a tank is measured by weight methods or by measuring liquid level and density of the solution. The use of load cells on a tank has the potential for the most accurate measurement of the amount of solution. However, in practice it is difficult to isolate the tank effectively from the remainder of the process, and vibrations transmitted through connecting pipes impair measurement accuracy.[1] Accordingly, methods now rely on measurements of liquid level and density.

The liquid level and density of solutions in process and storage tanks are most commonly measured with a pneumatic bubbler system, also called dip-tube manometers or pneumercators. The pressure differences between ends of purged dip tubes are measured with precision equipment. Three pressure probes are required: one extends near to the bottom of the vessel, the second ends at a known elevation above the lower probe, and the third terminates in the vapor space of the tank (see Fig. 1). The dip tubes are connected to differential pressure transmitters and are purged continuously to prevent the entry of process solution and vapors into the tubes. Rotameters are adjusted to give equal flow of dry air or nitrogen in each probe.

The differential pressure between either of the two lower probes and the vapor space probe is proportional to the liquid level, whereas the differential pressure between the two lower probes is proportional to the solution density. For differential pressure measurements, an electromanometer or a precision pressure transducer with digital output is used. Direct computer-compatible output is obtained from these instruments. Given values for the liquid level and density, one calculates the solution volume from an experimentally determined relationship between liquid level and volume for each tank.

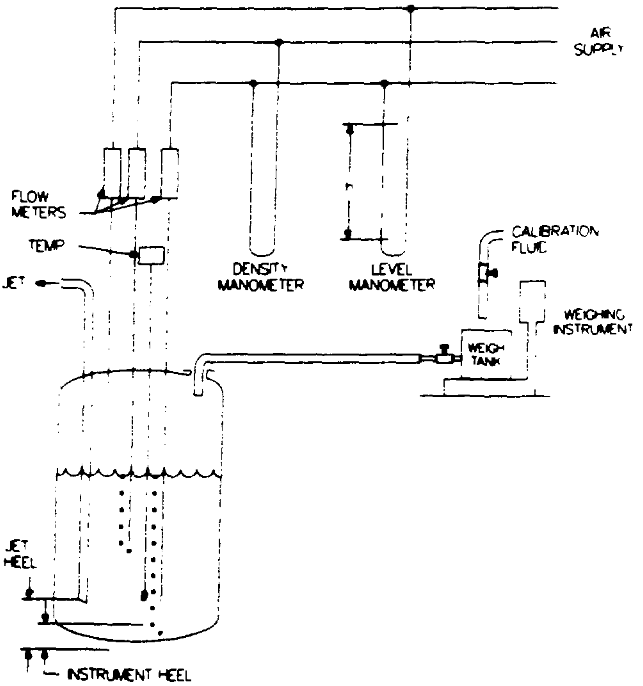

**Fig. 1.
Schematic of instrumentation with a pneumatic bubbler system.**

Tests of high-precision electromanometers at the Allied General Nuclear Services plant suggest that relative accuracies of 0.1% in level measurement and 0.2% in density measurement can be achieved.[2] The Paroscientific "Digiquartz" transducer and the Ruska Corporation model DDR-6000 transducer were compared in a calibration exercise at Tokai, Japan. A precision piston gauge was the pressure source. Uncertainties of <1 mm of water were found for both transducers.[3] The Paroscientific transducer uses a quartz crystal resonator whose frequency of oscillation is changed by the applied pressure difference. The Ruska instrument is a precision electromanometer that uses a hollow helix quartz Bourdon tube as the pressure sensor. Experiments were generally made with water or non-radioactive nitrate solutions. If these transducers are used in a highly radioactive environment, special hardening is required.

Although good results were achieved with pneumatic bubbler systems, problems are associated with them. Because the dip tubes contact the solutions, salt crystallization gradually plugs the tubes or probe. Variations or imbalances in bubbler air flow affect measurement accuracy, and bubbling of air through the solution changes its concentration. Leaks or restrictions in pressure sensing lines cause other problems.[4]

Other types of level detectors were tested. For these, the density of the solution need not be known, a distinct advantage. The problem of finding suitable detectors is compounded by the variety of tanks found in nuclear materials processing plants. Obviously, more than one type of detector is needed to meet different applications.

The time domain reflectometer (TDR) consists of a coaxial probe suspended from the top of the tank. Liquid level is inferred from the time delay after an electrical pulse is initiated in the probe until the reflected electrical signal is received from the impedance mismatch at the liquid surface. The TDR systems were installed in tanks at the Itrec and Eurex plants in Italy. Laboratory tests of the technique gave an accuracy of ±0.2 cm in the measurement of liquid level.[5] The accumulation of solids in the tank does not affect the TDR technique, and an air supply is not needed.

An ultrasonic level probe that can also detect the aqueous-organic interface in solvent-extraction contactors was developed at Harwell, in the United Kingdom.[5] Trials showed that the position of an interface or the liquid level was measured with a precision of 0.3 cm over levels of 15-500 cm.

A pulsed sonic liquid-level indicator, the Bartex Aquatrak, was extensively studied[6] at the Rocky Flats Plant and the Savannah River Plant. A calibration accuracy of 0.025% of measurement with a resolution of 0.3 cm throughout a 762-cm (25-ft) range was verified. One of the Aquatrak systems was recently recalibrated after continuous operation for approximately 1 year. The difference between the original calibration data and the recalibration data was negligible.

Conductivity probes have been found unsuitable. Malfunctioning regularly, they collected a coating of solids that prevented them from contacting the liquid, they dissolved in the solution, or they shorted out.[7]

Large tanks filled with Raschig rings and horizontal pencil tanks present special problems. Raschig rings break and settle in the tank with time, so that the volume they occupy changes. The liquid level in the tank is usually determined with a sight glass. Horizontal pencil tanks are only 15 cm in diameter and often have precipitate on the bottom. There is at present no satisfactory technique for measuring the volume of liquid in such tanks.

Density measurements also were used to estimate uranium or plutonium concentrations in process tanks for process and criticality control. Empirical relationships between the uranium or plutonium concentration and the density, temperature, and hydrogen ion concentration were developed.[8-10] Density measurements on flowing streams are useful for process control and near-real-time materials accounting for continuous processes. Such measurements, used in conjunction with flow measurements, require a knowledge of the solution acidity. A prototype in-line free acid monitor was developed at Oak Ridge.[11]

On-line density instruments that use a vibrating U-tube or a vibrating vane are commercially available. These instruments have not been tested under the conditions encountered in nuclear processing plants.

An on-line instrument that relates transmission time of an ultrasonic signal to the concentration of uranium and plutonium in solution was developed in the United Kingdom. Under ideal conditions, the relative standard deviation on solutions containing 60 g U + Pu/L was ~1%. The instrument is calibrated and standardized during operation against material that is sampled and analyzed chemically.[5] Acoustic measurements are also useful and deserve investigation.

Density measurements are nonspecific and require complementary information from other measurement techniques for accountability purposes. On-line density measurements have two advantages: they can be continuous and their results are immediately available.

C. Flow Measurement

Flow measurement instruments in nuclear materials processing plants are used primarily for process control where high precision is not a requirement. Monitoring process streams is held to a minimum, and only those instruments essential for plant operation generally are provided. Such instruments were not designed for use in accountability systems.

Near-real-time materials accountability requires measurements or estimates of the in-process inventory of major process vessels and columns. For continuous processes, such as solvent extraction where volume measurements and sampling are not possible, the requirement is met by flow measurements and on-line concentration (or density) measurements on streams entering and leaving the vessels and columns. Flow and on-line concentration measurements are also valuable in batch processes where the volume of solution in a tank is difficult to measure and the solution is difficult to homogenize.

Flow rates are generally low. Some streams, such as the output from the plutonium concentrator in a reprocessing plant, have flow rates below 10 L/h. In other streams, flow rates of 400 L/h (1.7 gpm) must be measured with a precision of 1% and an accuracy of 0.5%.

Flowmeters with no moving parts are preferred. It is often desirable that the flowmeter neither contacts the process fluid nor intrudes into the process piping. The ideal flowmeter would have the above properties and be totally unaffected by viscosity, density, pressure, temperature, air bubbles, or suspended solids. The meter's calibration would be unaffected by material buildup in the flow sensor. Furthermore, the ideal flowmeter, accurate to better than 0.5% of rate at low flow rates, would be easy to calibrate and maintain remotely.

Flowmeters used in radioactive environments include differential pressure devices (orifice plates and weir meters), positive displacement flowmeters, electromagnetic flowmeters, and electronic rotameters. Thermal, gyroscopic deflection (coriolis effect),[12] and ultrasonic[13] flowmeters offer promise of approaching the properties of the ideal flowmeter and deserve evaluation in a corrosive, radioactive environment.

III. SAMPLING PROBLEMS AND TECHNIQUES

The purpose of a sampling program is to obtain material for characterization that represents the bulk material in analysis; no analytical method can provide accuracy or precision better than that associated with obtaining an increment that is truly representative of the total population. In addition to the normal operations of selecting, splitting, and compositing the material, sampling also encompasses ancillary operations, such as grinding, evaporating, drying, and screening. For on-line or in-line measurements, sampling may be as simple an operation as installing the measuring device directly in the process line or into a bypass line that samples a fraction of the process stream.

Samples are solids, powders, or liquids (and occasionally gases). Samples derived from reprocessing operations may be associated with fission product activity of thousands of curies per kilogram. Each type of material presents its unique sampling problems. This section reviews some of the basics of sampling; more detailed descriptions are found in Ref. 14, pp. 25-56, and Ref. 15.

A. Sampling of Liquids

Liquids in process materials normally are sampled using an air-lift sampling system. Such a system is designed to permit extensive recirculation of solutions through the sample lines and the sample bottle. Vessel sparging, mixing time, and sample-circulation time are considered in establishing proper sampling procedures for replicate analyses. Any solids are dissolved after sampling and are included in the total analysis. For highly radioactive samples, the possibility of bubble formation is considered in volume measurements, and temperature corrections are applied.

Certain sources of sampling error for solutions are likely: (1) concentration or dilution of the sample by the air-lift system, (2) incomplete mixing of the solution in the tank, (3) contamination of the sample in the sample lines, and (4) sample heterogeneity caused by suspended solids. Where analytical precision better than 0.5% is required, all sampling is by weight rather than by volume. Remote volume samplers seldom provide routine precision better than 0.5%, and even normal volumetric measurements are no better than 0.2% routinely.

A sampling apparatus capable of providing pipetting accuracy of 0.1% under hot-cell conditions was described.[16] All steps, including pipet rinsing, are remote, and the Teflon piston surface does not touch the solution being pipetted.

B. Sampling of Powders

Sampling of process powders to obtain a representative sample generally is more difficult than sampling liquids. Sample heterogeneity is a function not only of such factors as mixing but also of particle size and proximity to the surface. Sampling plans of proper design assure representative samples. Flowing streams generally are easier to sample than are bulk containers. Powder samples are obtained using dippers, scoops, core samplers, powder thief probes, or rifflers.

Samples are further subdivided using a splitting or riffling technique. Alternatively, the total sample is dissolved and suitable aliquots are removed for analysis.

C. Problems Associated with Sampling

A homogeneous sample does not necessarily assure a representative sample. Care must be exercised that the sample form or composition is not altered after sampling. In the case of liquids, evaporation or radiolytic decomposition of the solution is a concern if subsamples are obtained subsequently. Dilution of plutonium nitrate solutions with water leads to formation of plutonium polymers that could precipitate or adsorb on container surfaces.[17] Therefore, plutonium-nitrate solutions are diluted with some concentration of nitric acid rather than with water.

Powders of UO_3 and PuO_2 are hygroscopic and gain weight rapidly, particularly in humid atmospheres. Powders of UO_2 change mass through air oxidation as well as by moisture adsorption.

IV. MEASUREMENT UNCERTAINTIES

Although measurement statistics are not discussed here, it is necessary to introduce the concept of measurements relative to true values.

For any analytical or physical measurement, one is never absolutely certain that the measured value represents the true value of the measured parameter. Two basic types of errors contribute to this uncertainty.

First, if we perform multiple analyses of the same material, we cannot exactly duplicate the sample either in quantity or quality (sampling error) or perform the measurement in exactly the same manner (measurement error). These errors are commonly referred to as random error of sampling and random error of measurement. The combination of these two errors, the random error of the analysis, is a measure of how precisely we can reproduce the same value for the measurement, or the precision of the analysis.

Secondly, after we perform the analyses and obtain the best estimate of the quantity we are measuring, we cannot be sure that the measured value equals the true value. Contributing factors to this uncertainty result from uncertainties (biases) in reference materials used in calibrating instruments or procedures or unknown biases in the instruments or procedures. These errors, referred to as systematic errors, are a measure of how accurately we can reproduce the true value, or the accuracy of the analysis.

V. ELEMENTAL METHODS OF ANALYSIS

A. Gravimetric Methods

Gravimetric methods involve separating a compound of the element to be determined and igniting it to a constant-weight stoichiometric compound. The technique is applicable only to relatively pure materials; impurities are determined by spectrographic or other procedures, and the final weight is corrected by difference. When clean separations from impurities are obtained, precisions better than 0.1% often are realized.

1. Uranium. Gravimetric methods are used for the determination of uranium in pure product streams, such as uranyl nitrate, U_3O_8, or UO_2, and UF_6. Nitrates are evaporated to dryness; UF_6 is hydrolyzed and evaporated to dryness. Ignition is at 850-900°C to U_3O_8, and the final weighing provides a relative standard deviation (RSD) of 0.02 to 0.5% (Ref. 14, pp. 70-74). Ignition at temperatures >946°C leads to formation of UO_2; temperatures <800°C yield slow decomposition reactions.[18] Presence of NO_3^-, F^-, Cl^-, or SO_4^{2-} does not interfere, but the presence of PO_4^{3-} leads to formation of uranyl pyrophosphate rather than U_3O_8.[19]

2. Plutonium. Of the plutonium precipitates, only PuO_2 is reported to form a compound suitable for gravimetric analysis (Ref. 20, pp. 297-298). Even with PuO_2, the stoichiometry of the compound depends on initial composition and ignition temperatures, and, even when the compound is heated to 1200°C, the final composition is variable. In addition, PuO_2 is hygroscopic, with the amount and rate of water adsorption dependent upon the ignition temperature. The suitability of gravimetry for determination of plutonium is questionable.

B. Spectrophotometric Methods

Spectrophotometric methods rely on the principle that a compound or complex in solution will absorb light of a specific wavelength in a quantity proportional to the concentration of the measured species. Generally, the concentration-absorbance function is a simple proportional relationship expressed by Beer's law, but variations may result at high concentrations or when other competing reactions occur. The RSD attainable by direct spectrophotometric methods usually is 0.5% or more and is seldom better than 0.2%. However, it can be improved to 0.05% with differential techniques that compare the absorbance of the unknown to a reference that is known precisely.

Specificity in spectrophotometry is a complex function of factors, such as sharpness of absorption bands, specificity of reagents, other elements or compounds present, and the quality of the monochromators. Specificity often is improved by using preliminary separations, masking agents, and pH control. Because of the nonspecificity of reagents for uranium and plutonium in the presence of each other and because of the nuclear reaction products (americium, neptunium, and fission products), time-consuming separations often are involved. These additional separations may limit the precision in major element analysis. For these reasons, spectrophotometric methods, of limited use for measuring uranium and plutonium in fuel-cycle materials, are usually restricted to process-control applications and analysis of waste streams.

The sensitivity of many spectrophotometric reagents to high radiation levels necessitates several supplemental separations during analysis of dissolver or waste-stream solution, even in the absence of elemental interference.

1. Uranium. Spectrophotometric methods for determining uranium in reprocessing streams generally are limited to measurement of trace concentrations of uranium in waste streams and possibly in the final product plutonium. Reagents of interest are listed in Table I (Refs. 21-39).

The method for determination of uranium with 2-(2-pyridylazo)-5-diethylaminophenol (PADAP) was modified specifically for determining uranium in reprocessing-plant waste streams[25] and in plutonium nitrate and

TABLE I

SPECTROPHOTOMETRIC METHODS FOR DETERMINATION OF URANIUM AND PLUTONIUM

Element	Compound	Concentration Range or Amount/Sample	RSD (%)	Interference; Comment[a]	Ref. No.
U	Uranyl nitrate	10-300 g/L	1-5	Temperature-sensitive	21,22
U	Dibenzoylmethane	30-750 μg	1.7	Ce, Th, W, Fe(III), Cr(IV); Pu at Pu/U = 2	14,[b]23
U	Peroxide	1-25 mg		Cr, Cu, Fe, Mn, Ni	14,[c]24
U	PADAP	1-100 μg	5	As^{5+}, Cr^{3+}, V^{5+}, PO_4^{3-}, SiO_4^{2-}, Pu, Pd; Pu removed by extraction	25,26
U	PAR	1-100 μg	1	R.E.s, TH(IV), Pu(IV)?	27
U	5-Me-2-PAN	10-80 μg	?	F^-; extraction removes most interfering cations	28
U	Bromo-PADAP	0.5-100 μg	2	Cr^{3+}, V^{5+}, PO_4^{3-}	29
U	Tetrapropylammonia	0.12-14 mg	0.3-10	Ce, Th	14,[d]30-33
U	Arsenazo-III	1-50 μg	1-10	Th, Pu, R.E.s, others	34,35
Pu	Tetrapropylammonia	1-30 mg	0.2-2	Cr^{6+}, Th	32,36
Pu	Pu(III) nitrate	12-18 g/L	0.05	Differential spectrometry	37,38
Pu	Arsenazo-I	5-100 μg	2-6	U, Zr, others	39

[a] R.E. = rare earth.

[b] Ref. 14, pp. 337-343.

[c] Ref. 14, pp. 222-225.

[d] Ref. 14, pp. 343-353.

oxide products.[26] The method for determination of uranium as the tetrapropylammonium complex was automated for determining uranium and plutonium simultaneously in scrap materials.[32]

The uranyl-nitrate method[21,22] used for in-line process control is sensitive to variations in nitric acid concentration and temperature and lacks the precision required for safeguards applications. Browning of the optics is a serious problem in process streams containing fission products. However, by measuring absorbance at two wavelengths with an on-stream detector, analysts adapted the method to measure uranium concentration in-line with a precision of 3% (see Ref. 40). Instruments that use fiber optics for light transmission and narrow-band interference filters for wavelength isolation have been described.[41-43] Only the process flow cell and the fiber optics are exposed to radioactivity.

2. Plutonium. Most chromogenic reagents that react with plutonium also yield intensely colored species with uranium and many fission products; therefore, if plutonium is determined in reprocessing samples, a separation is required. For low plutonium concentrations, methods such as x-ray fluorescence, alpha, or gamma spectrometry are preferred.

The tetrapropylammonium method[36] is of interest because uranium and plutonium are determined sequentially in the same sample. The method is automated.[32] A more sensitive method for determination of plutonium with chlorophosphonazo III in n-pentanol was developed especially for use with an automated spectrophotometer. The relative standard deviation was 1.5% for the range of 2.5-17.5 μg Pu (see Ref. 33).

The differential spectrophotometric method of determining plutonium[37] is used for plutonium-nitrate product with precision and accuracy equivalent to that obtainable by the best electrometric methods for the analysis of scrap material.[38]

A rapid off-line spectrophotometric method was described for determining plutonium in dissolver and other reprocessing samples.[44] Plutonium is oxidized to the hexavalent state using silver peroxide (AgO); neodymium is added as an internal standard; and plutonium and neodymium absorbances are measured in the near infrared region. Fission-product activity to 500 Ci/L and uranium concentration to 400 g/L do not interfere for determining 1-5 g/L of plutonium. Precision of better than 1.5% (1σ) and accuracy of 0.5% are claimed for an analysis time of 1 h.

C. Electrometric Titration Methods

Both uranium and plutonium can be determined with high precision and accuracy by the use of titrations involving oxidation-reduction reactions. Electrometric methods are classified by the technique used to detect the titration end point, such as potentiometric, amperometric, or coulometric. All these methods provide RSDs of better than 0.1%. To attain the highest precision, weight burets are used in all critical volume measurements.

Potentiometric titrations are based on measurement of the change in potential of the system as a component is removed by oxidation or reduction. Because the change in potential is the critical measurement, the accuracy of potentiometric titrations is limited by the sharpness of the potential break at the equivalence point. Relative standard deviations of 0.02 to 0.5% are attainable; therefore, the method is used for measurement of final product, such as U_3O_8, UF_6, PuO_2, or $Pu(NO_3)_4$.

Amperometric titrations involve measurement of the change in current between two electrodes maintained at a constant potential as titrant is added. The precision of amperometric titrations is limited by the accuracy of the inflection point measurement in the current-titration curve; hence, the potential is selected so that the limiting current for reactant, titrant, or product can be measured, depending on which produces the sharpest end point.[45]

Controlled-potential and constant-current coulometry are well-established methods for determining uranium and plutonium in solutions. Both methods are based on the principle that the weight of a substance oxidized or reduced at an electrode is proportional to the quantity of electric charge passed through the electrode.[45] In controlled-potential coulometry, the potential of the electrode is maintained at a constant value relative to a reference electrode to minimize the number of reactions that can occur. Interference from reactions occurring at lower potentials is eliminated by performing a preliminary coulometric titration at a selected potential so that those reactions occur before measurements are started. Reactions requiring higher potentials cannot occur. Both uranium and plutonium are titrated in the same sample without separation by performing successive titrations at different potentials. In constant-current coulometry, an electrogenerated reagent reacts with the substance to be determined.

Coulometric methods can provide RSDs of 0.1% without chemical standards. Generally, smaller samples are required than for potentiometric or amperometric measurements. Coulometric methods have gained increased popularity in recent years, but the determination of plutonium is subject to the following considerations (Ref. 46).

- The method is applicable to the determination of plutonium in nitrate product solutions and in dissolver solutions following an anion-exchange separation of fission products.
- The titration is performed in $1\underline{N}$ $HClO_4$, $1\underline{N}$ HNO_3, $1\underline{N}$ H_2SO_4, or $1\underline{N}$ HCl electrolytes. However, any Pu^{6+}, if present, is only partially reduced to Pu^{3+} in HNO_3, HCl, or $HClO_4$; therefore, $1\underline{N}$ H_2SO_4 is preferred if the sample is believed to contain appreciable Pu^{6+}. Titration in $1\underline{N}$ H_2SO_4 is performed in an oxygen-free atmosphere.

- If iron is present, it is titrated quantitatively in H_2SO_4 and a correction is applied. Iron does not interfere in 1N $HClO_4$ if the plutonium-iron ratio is >50.
- If 1N HNO_3 is used as electrolyte, sulfamic acid is added to reduce nitrites.
- Polymeric plutonium does not titrate in any case and must be destroyed. Fluorides, used to destroy polymeric plutonium, and organics interfere in all media and are removed.
- Although electrical calibration is used, for optimum accuracy, the instrument is calibrated using NBS-SRM-949, and a correction for isotopic composition of the sample is applied.
- Replacement of the platinum electrodes with gold results in a lower and more reproducible background and an approximately fivefold improvement in precision.[47]
- Coulometers are subject to serious interference from nearby rf generators, such as induction heaters.

1. Uranium. The electrometric methods for determining uranium rely on the reaction $U^{4+} - U^{6+}$ after quantitative reduction of the uranium to the tetravalent state (Ref. 1, pp. 74-83 and 86-88; Refs. 48-51). Differences between methods result from the reductants and oxidants used. Reducing agents used to obtain U^{4+} include zinc amalgam, the Jones reductor, Ti^{3+}, the lead reductor, Fe^{2+} in phosphoric acid, and electrical reduction. The Jones reductor generates a mixture of U^{3+} and U^{4+}, and the trivalent uranium is air oxidized to the tetravalent state before titration. Reduction with an excess of ferrous ion in concentrated phosphoric acid is followed by titration with dichromate, performed in the presence of Pu^{4+} without interference. Some of the standard electrometric techniques for determination of uranium are summarized in Table II. Of these methods for determining uranium, the Davies-Gray method[48-49] is the most versatile and is automated for rapid analysis of process samples (Ref. 14, pp. 77-83 and 86-88; Refs. 49-52).

TABLE II

ELECTROMETRIC METHODS FOR DETERMINING URANIUM

Reductant	Oxidant	End Point	Interference	RSD[a] (%)	Sample Size	Ref. No.
Zn amalgam	$K_2Cr_2O_7$	Colorimetric	None	0.62	200-300 mg	14, pp. 74-77
Fe^{2+} H_3PO_4	$K_2Cr_2O_7$	Potentiometric	Ag, Hg	0.07	200-300 mg	48,49
Electrolytic	Excess $K_2Cr_2O_7$ back-titrated with Fe^{2+}	Potentiometric	Cr, Fe, Mo, Ti, V	0.02	1-10 g	14, pp. 77-83
Electrolytic	Electrolytic	Coulometric	Fe, Hg, Ag, V	0.06-0.44	2-20 mg	14, pp. 86-88; 50
Pb reductor	Ce^{4+}	Potentiometric	Mo	0.03	0.5-1 g	51

[a] Generally, the optimum obtainable for fuel process or product samples.

2. Plutonium. For the electrometric determination of plutonium, the plutonium is oxidized quantitatively to Pu^{6+}, then titrated to Pu^{4+}. This couple is preferred if uranium or iron is present. Oxidants for the first step include AgO and $HClO_4$. If AgO is used, the excess is destroyed by gentle heating. The oxidizing power of $HClO_4$ is countered by diluting the sample after the plutonium is oxidized. Errors are introduced into the plutonium measurement if conditions for the dilution are not followed properly. The reduction to Pu^{4+}, usually carried out with Fe^{2+}, is performed directly or, by using a potentiometric end point, is sharpened by adding a measured excess of Fe^{2+}, the excess being titrated with Ce^{4+}. Methods involving the Pu^{4+}-Pu^{6+} couple are summarized in Table III (Refs. 53-60).

TABLE III

ELECTROMETRIC METHODS FOR PLUTONIUM DETERMINATION USING THE Pu(VI)-Pu(IV) COUPLE

Reductant	Oxidant	End Point	Interference	RSD[a] (%)	Sample Size (mg)	Ref. No.
Fe^{2+}	AgO	Amperometric	Ce, Cr, V, Mn Ru, Au, Rh, Pt Pb, Am, Np	0.03	10-20	53,54[b] 55-57
Excess Fe^{2+} Ce^{4+}	AgO	Potentiometric	Ce, Cr, V, Mn	0.1-0.19	4	14, pp.261-268
Excess Fe^{2+} $K_2Cr_2O_7$	AgO	Potentiometric	Cr, Ce, Mn, V, Ru	0.17	20-80	58
Excess Fe^{2+} Ce^{4+}	$HClO_4$	Potentiometric	Cr, Au, Mn, Pt,	0.03	200-250	59[c]
Electrically generated Fe^{2+}	$KMnO_4$	Coulometric	Ag, Hg, Ru, Pd, Os, Ce, Au, Sn, (U)	1	0.003-10	60
Electrical	Electrical	Coulometric		0.1	1-10	46

[a] Generally, the optimum obtainable for fuel process or product sample.

[b] See also Ref. 14, pp. 254-261.

[c] See also Ref. 14, pp. 274-285.

Alternatively, plutonium is determined by quantitative reduction to Pu^{3+} and subsequent titration to Pu^{4+} (Ref. 14, pp. 268-299 and 385-388; Refs. 55, 57, 61-65). Common reducing agents are liquid zinc amalgam, the Jones reductor, the lead reductor, Ti^{3+}, Cr^{2+}, and electrical methods. The liquid-zinc-amalgam method suffers in that an extra transfer is required to remove the amalgam before titration. Small amounts of titratable material are leached from the Jones reductor. Fewer elements are reduced with $TiCl_3$ than with the Jones or lead reductors; therefore, there may be fewer potential interferences.[62] However, Ti^{3+} is readily destroyed by contact with air.

The oxidation titration to Pu^{4+} usually is performed electrolytically or with Ce^{4+} or $K_2Cr_2O_7$. Dichromate has the advantage of being available as a primary standard and is more stable than Ce^{4+} over extended storage periods. Uranium and iron interfere with methods involving the Pu^{3+}-Pu^{4+} couple. An exception is the controlled-potential coulometric technique in the presence of uranium, and with this method, the two elements are measured successively in the same sample.[55] A measurement technique for plutonium that incorporates a concurrent correction for iron or neptunium has been described.[56] For the controlled-potential coulometric determination of plutonium in dissolver solutions, zirconium is removed completely to prevent fouling of the electrode through adsorption of hydrous zirconia.[46] Methods involving the electrometric determination of plutonium using the Pu^{3+}-Pu^{4+} couple are summarized in Table IV.

D. Fluorometry

The fluorometric determination of low concentrations of uranium is based on the principle that uranium fluoresces when excited by ultraviolet light; the method is not applicable for determining plutonium. The fluorescent spectrum for uranium consists of four bands in the visible region, with the most intense band at 554.6 nm. If 365-nm excitation from a high-intensity mercury lamp is used, few other elements will interfere by fluorescence.

TABLE IV

ELECTROMETRIC METHODS FOR PLUTONIUM DETERMINATION USING THE Pu(III)-Pu(IV) COUPLE

Reductant	Oxidant	End Point	Interference	RSD[a] (%)	Sample Size (mg)	Ref. No.
Zn amalgam	Ce^{4+}	Potentiometric	Fe, Mo, Ti, W	0.02-0.02	600	14, pp. 274-285
Zn amalgam	$K_2Cr_2O_7$	Potentiometric	Cr, Fe, Mo, Ti, U, V, W	0.03	250-400	61[d]
Pb or Jones reductor	Ce^{4+}	Spectrophotometric	Fe, Ga, Mo, Tl, U, W, V, Cr, NO_3^-	0.07	500	14, pp. 268-274
Ti^{3+}	Ce^{4+}	Potentiometric	Cu, Fe, U, W NO_3^-	0.1	25	62[e]
Cr^{2+}	Ce^{4+}	Potentiometric	Fe, U, Cu, W	0.4	20-50	57
Electrical	Electrical	Controlled potential coulometric	Dependent on electrolyte	0.04[b] 0.63[c]	1-10	47,63-65[f]

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[a] Generally, the optimum obtainable for fuel process or product sample.

[b] For nitrates.

[c] For dissolver solutions.

[d] See also Ref. 14, pp. 285-292.

[e] See also Ref. 14, pp. 293-299.

[f] See also Ref. 14, pp. 385-388.

Samples generally are evaporated and fused in a carbonate flux containing 10% NaF (Ref. 66) or a NaF flux, sometimes containing LiF (Ref. 67) or some carbonate. Carbonate fluxes, which are preferred for ease of handling the fusion mass, provide better analytical precision. Fluoride fluxes provide better uranium sensitivity but are more sensitive to variations in flux temperature and cooling conditions.

Although few elements or compounds interfere with the method by overlapping fluorescent spectra, a number of elements interfere through quenching or enhancement. Quenching results from absorption of the incident light, absorption of the fluorescent light, interference with the energy transfer paths at phosphor centers, or precipitation of uranium.[68]

Most of the transition elements interfere by quenching to some degree. With a flux of 98% NaF-2% LiF, serious quenching is observed in the presence of small amounts of cadmium, chromium, cobalt, copper, iron, magnesium, manganese, nickel, lead, platinum, silicon, thorium, and zinc. Many of the interferences are removed by a combination of precipitation and solvent extraction of the uranium into methyl isobutyl ketone containing tetrapropylammonium nitrate (Ref. 14, pp. 398-403) or into ethyl acetate (Ref. 14, pp. 232-237). Alternatively, quenching interference is minimized by measuring the fluorescence from a fused button of the sample and a similar button containing a known added amount of uranium (spiking).

Fluorometry evolved as the standard method for determining small amounts (1-100 ng) of uranium. High-throughput, off-line measurements of uranium in waste streams are made by processing samples in the analytical laboratory. The RSD for measuring uranium in simulated reprocessing plant waste streams is reported to be 13% (Ref. 69). In addition, an automated fluorometer capable of processing sixteen samples per 1.5 h was designed and tested at ORNL;[70] sensitivity is 0.2 µg/L and precision is 6% at the 10-µg/L level.

In the early 1980s, a laser fluorometric method was described that is simpler, more sensitive, and more rapid than the pellet fusion method.[71,72] The method is direct, requiring no separations, extractions, or fusions. The commercially available laser fluorometer employs a pulsed nitrogen laser that emits at 337 nm. The uranium sample is added to a proprietary buffered pyrophosphate reagent, which causes the uranium to emit a green luminescence when exposed to the laser light. A green filter between the sample cell and the photomultiplier tube removes the blue fluorescence from organics. Longer wavelengths are still transmitted, however. The instrument has electronic gating circuitry that waits for other fluorescence from organics to decay before the longer-lived uranium phosphorescence is measured. A standard addition technique overcomes the sample matrix effects.

E. X-Ray Fluorescence

X-ray fluorescence techniques have been applied to the analysis of actinide solutions for over 25 yr. Such techniques are sensitive, accurate, and capable of measuring microgram quantities of material to relative accuracies of about 1%. Typical analysis times are short (0.5 h or less). Currently, x-ray fluorescence is used primarily to measure solutions from the reprocessing of spent fuels, but the technique was applied to solutions at all stages of the fuel cycle.

The fundamentals of x-ray fluorescence analysis are reviewed in detail in the literature.[73-76] The analyst has considerable latitude in selecting a technique, including choices of x-ray line, excitation source, and detector.

For uranium and plutonium measurements, lines in the K, L, or M series are used; the more intense lines in these series are summarized in Table A-III of Ref. 77. Two considerations in line choice for x-ray fluorescence measurement are line intensity above background and interferences from adjacent lines. The most common choice is one or more of the L lines, which provide good intensities in an air path for solution or solid analyses, with any type of excitation or detection system.

The predominant excitation source is the x-ray generator. Using radioisotopes is becoming more common because the solid-state detectors to measure the lower-intensity x rays now are readily available. Both wavelength- and energy-dispersive detection systems are used to measure uranium and plutonium in solution. Wavelength dispersion offers high resolution but at low efficiencies. Energy dispersion is generally more efficient but has poorer resolution at energies >20 keV. At energies >20-25 keV, a Si(Li) energy-dispersive spectrometer provides better resolution as well as efficiency. Energy dispersion using Ge(Li) or intrinsic germanium detectors is required for measuring actinide K-series x rays.

Although x-ray fluorescence measurements of nuclear material solutions are prominent in the literature, current safeguards applications are limited by the competition from other less complex and less matrix-dependent methods. To reduce the matrix sensitivity, samples are often evaporated as thin films. That technique reduces the scattered background compared to the sample signal, thus increasing sensitivity and reducing counting times.[78] Measurements of thin films are linear with the concentration of nuclear material over a small range, above which saturation effects become important.

Several systems were developed to assay highly radioactive spent-fuel solutions. One of these systems[79-81] uses the $L\alpha_1$ x rays measured with a wavelength-dispersive spectrometer to assay solutions having uranium-plutonium ratios of 50:1 to 300:1 with accuracies of ~1% (1σ) in 2-5 min. Solutions having activities of <1 Ci/mL are handled routinely by evaporating small samples onto a filter paper. Samples having low beta-gamma activities are analyzed directly in solution after addition of an internal standard. The fission products cause no serious line interference. An automatic sample-preparation system is being developed to allow on-line analysis.

Uranium and plutonium solutions that have beta-gamma activities to 1 Ci/L were measured directly through a Plexiglas window.[82] An automatic sampler removes solutions from the sample line and yttrium is added to serve as an internal standard. Solution transfers are made by pneumatic tube. A minicomputer performs data reduction, and overall precision and accuracy of better than 1% are claimed for the technique.

In another system,[83] dissolver solutions containing uranium and plutonium at ratios up to 400:1 and uranium concentrations of ~50 g/L are measured with an x-ray tube in combination with a Si(Li) detector. Preliminary tests indicate that accuracies of 1-2% are possible with 10-min analysis times. However, accuracies of only 3% were obtained because of problems in sample preparation.

A proposed wavelength-dispersive system may be able to measure uranium and plutonium concentrations in irradiated samples to a precision of better than 1% (Ref. 84). The instrument is adaptable to off-line analysis of dissolver-type samples (as slurries or solution) with an analysis time of 4-8 h. For samples of lower activity, analysis time is significantly shorter.

A system, developed for automatic sampling and sample preparation of dissolver solutions from the reprocessing of thorium-uranium fuels,[78] could apply to uranium-plutonium fuels. For solutions emitting up to 2000 Ci/L, samples containing 1.0 mL of solution are automatically aliquoted and mixed with an internal standard. The aliquots are evaporated onto filter paper, which is transferred to a shielded x-ray spectrograph. All operations are performed remotely under computer control.

The introduction of stable x-ray generators[85] that operate to 200 KeV and the use of ^{57}Co gamma-ray sources[86,87] have increased interest in K x-ray fluorescence analysis of uranium and plutonium. X-ray generators provide a significant improvement in peak-to-background intensity compared with radioactive sources such as ^{57}Co. The primary advantage of K x rays lies in the use of normal process materials, such as stainless steel for cells; thus, in-line analysis is possible. The method is proposed for sample analysis at any step of reprocessing, from dissolver solutions to final product. Tests of an online monitor for uranium concentrations in process streams showed that 300-s data collection times were sufficient to measure concentrations of 20-150 g/L with less than 2% error.[88] Energy-dispersive K x-ray fluorescence and ^{57}Co sources were used.

The high sample throughput for analytical laboratories at large reprocessing plants dictates automated analytical methods, such as x-ray fluorescence, to provide timely, accurate information for both process control and safeguards.

F. X-Ray Absorption Edge Densitometry

X-ray absorption edge densitometry is an element-specific analytical method that can be applied in-line, at-line, or off-line to meet many process measurement needs. In this technique, the transmitted intensity through the sample is measured for two x rays or gamma rays (selected above and below an absorption edge for the element determined). For determining uranium and plutonium, both L_{III} and K absorption edges can be used. The L_{III} edge is useful for uranium and plutonium concentrations below ~100 g/L. The K edge, which allows greater versatility in selecting cell materials and cell thickness, thus is applicable over a wider concentration range in process-type cells. With proper selection of cell path length and absorption edge, the method is applicable to concentrations in the range 1-500 g/L.

Instruments using K and L_{III} edges were developed at the Los Alamos National Laboratory for determining uranium and plutonium in a variety of process samples.[89] A radioactive ^{169}Yb source is used for routinely determining uranium in the 100-400 g/L range. The precision is better than 0.5%. For the determination of plutonium, a radioactive ^{75}Se-^{57}Co source is employed. Field tests at Tokai-mura, Japan, demonstrated a precision of 0.3% for concentrations of 150-300 g/L (Refs. 90 and 91). A K-edge instrument designed by Lawrence Livermore National Laboratory and evaluated at Allied General Nuclear Services gave a precision of 0.5% for the design concentration of 150-300 g/L (Refs. 92-94). An on-line K-edge densitometer designed for lower concentrations, typically 30 g/L, is being evaluated at the Savannah River Plant. Solution is circulated from process tanks through a 7-cm path-length cell. Well-characterized control samples having concentrations in the range 25-40 g/L were analyzed with a precision of 0.3% (Ref. 95).

An L_{III} edge instrument using an x-ray generator as a source to permit simultaneous determinations of uranium and plutonium was designed at Los Alamos for the Savannah River Laboratory.[96] Precision of 0.25% was reported at the optimum concentration of 50 g/L.

A versatile densitometer for K- or L-edge analysis using x-ray tube excitation was designed and evaluated at Karlsruhe.[97] Proposed applications include determination of uranium in accountability tank solutions and both uranium and plutonium in intermediate-process and final-product solutions. The x-ray tube excitation approach to absorption edge densitometry also is being developed in the United Kingdom.[98]

K-edge densitometry, which has a limited dynamic range, is unable to provide precise plutonium assay in the presence of a large excess of uranium [for instance, plutonium in light-water reactor (LWR) dissolver accountability solutions, where the ratio of uranium to plutonium concentration is 100:1]. An instrument that allows simultaneous K x-ray fluorescence measurements and K-edge densitometry may provide the solution to this problem.[99]

G. Alpha-Spectrometric Methods

Quantitative alpha-particle spectrometry is based on measurement of the alpha-radiation intensity of the sample. The alpha particles are ejected with discrete energies; for the uranium, neptunium, plutonium, and americium isotopes found in the nuclear fuel cycle, these energies are 4 to 5.5 MeV. Alpha-particle energies are rapidly degraded by interactions with bound electrons, and complete attenuation is effected by ~5 cm of air. Absorption by water and self-absorption by the sample are even more rapid, and normal quantitative alpha spectrometry is limited to analysis of thin, dry films. The method was applied to determination of plutonium in dissolver solutions following solvent-extraction separation of the plutonium (Ref. 100; Ref. 14, pp. 392-398). The RSD for dissolver samples is 3-5% (1σ). The method also is used for determining plutonium in process waste and uranium product streams.[101]

Detectors used for alpha spectrometry include standard radiation instruments, such as proportional counters, scintillation detectors, and solid-state devices. Special techniques were developed for alpha-counting of Purex process streams, where the detector must be in direct contact with the alpha-radiation sources.[102-106] Performance requirements are severe. The detector operates in a flowing-liquid environment that is often of high acidity; it must resist corrosion and abrasion; it should discriminate alpha signals in the presence of high beta-gamma fluxes from fission products; and it should be insoluble in organics. Originally, ZnS(Ag) scintillation detectors were used, but were too fragile and difficult to fabricate. Organic scintillators generally cannot withstand the liquid environments. A cerium-activated Vycor glass detector was developed[103] that operates for months in a Purex process stream. The stopping distance for 5-MeV alpha particles in Vycor glass is estimated at 25 µm, whereas beta particles of energies >0.5 MeV have penetration thicknesses in excess of 900 µm (Ref. 105). Thus, by reducing the cerium-activated layer to the alpha-particle penetration thickness, alpha particles are stopped in the active layer while most of the high-energy betas pass through undetected. A further decrease in beta interference is attained by using thin sample cells[107] and electronic pulse-shaping circuitry.[108]

The instruments can measure plutonium solutions in concentrations between 10^{-4} and 1 g/L in the presence of beta-gamma fields up to 10^{8} dis/min-mL (see Ref. 109). Deviations from linearity at low plutonium concentrations ($<10^{-3}$ g/L) are caused by plating on the detector window and at high plutonium concentrations (>0.1 g/L) are caused by pulse pile up. Interference results from large variations in sample density that cause self-attenuation problems and from the presence of other alpha emitters, such as neptunium, americium, or uranium. Calibration is performed empirically for each stream by chemical analysis. Modification of the electronics system was reported for concentrations of 0.1 to 30 g/L (see Ref. 110).

In-line alpha counters using a scintillation (ZnS) probe (and a rotating drum to present the sample to the probe) were developed in France for routine use in reprocessing plants.[111] The relative standard deviation is 3.2% for the aqueous phase and 4.6% for the solvent phase in the first cycle extraction and partition banks. An improved version of this alpha monitor was compared at Karlsruhe with an instrument that uses cerium-activated Vycor glass.[112] The drum cell of the improved monitor is less sensitive and more likely to fail because of its moving parts, but it can be used with concentrations of 1-10 mg Pu/L. The cerium-activated instrument can be used for concentrations below 1 mg Pu/L, but the detector surface is easily contaminated.

Diamond detectors were investigated in the Soviet Union as in-line alpha monitors, but data for process operation in the presence of high beta-gamma fluxes are not available.[113]

H. Mass-Spectrometric Methods

In most nuclear fuel-cycle facilities, thermal-ionization mass spectrometry is used to determine the amount of each isotope of uranium and plutonium and, subsequently, to determine the effective atomic weights used in calculating the total uranium and plutonium from the chemical analysis of accountability-tank samples. Isotope-dilution mass spectrometry is used for high-precision/high-accuracy measurement of the plutonium and uranium concentrations in tanks.

The instrumentation for mass spectrometry is complex and expensive, consisting basically of a source, which is either a single or triple filament; a mass spectrometer; a detector, which is either a Faraday cup or an electron multiplier; and associated control and readout electronics.[114,115] Much of the instrumentation is computer controlled.[116] Single-filament ion sources require precarburization to provide high metal ion yields, and triple filaments are preferred. The mass spectrometer should have an abundance sensitivity of 100 000 or better and a resolution, expressed as $M/\Delta M$, of 400 or greater, where ΔM is the peak width at 5% of the height above background. The Faraday cup detector provides better measurement accuracy; the electron multiplier, better sensitivity.

The methods require elaborate sample preparation (Ref. 14, pp. 353-368; Refs. 117-119). A typical mass-spectrometric procedure involves (1) dissolving and diluting the sample with HNO_3; (2) for isotope-dilution mass spectrometry, spiking part of the diluted sample with accurately known amounts of ^{233}U and ^{242}Pu or ^{244}Pu; (3) oxidizing plutonium to the hexavalent state; (4) sequentially separating the fission products, plutonium, and uranium by an anion-exchange procedure or by solvent extraction; and (5) transferring aliquots of the separated uranium and plutonium fractions to separate mass spectrometer filaments.

Because small amounts of uranium (<100 μg) and plutonium (generally <1 μg) are analyzed, meticulous sample preparation and filament loading are required to avoid contamination by environmental uranium. Determination of ^{238}Pu is particularly sensitive to the presence of ^{238}U, and for ^{238}Pu concentrations <0.7%, alpha spectrometry is preferred. For the measurement of ^{241}Pu, ^{241}Am is completely separated. For the isotope-dilution mass-spectrometric determination of plutonium, both spiked and unspiked samples are analyzed to correct for ^{242}Pu in the sample, if ^{242}Pu is added as the spike.

Chemical errors may arise also from the presence of high concentrations of alkali elements. Potassium, in particular, interferes with the measurement of ^{234}U and ^{236}U because of overlapping K_6 polymers. Filaments are checked to ensure freedom from organics. If organics are detected at ion currents greater than background, the analyses are suspect.

In thermal ionization sources, the light isotopes are evaporated and ionized preferentially, relative to the heavier isotopes of an element.[115] This temperature-dependent effect is a function of the mass, sample size, and time. It is referred to as the filament bias and is measured for the instrument every 6 months and controlled as accurately as possible between samples and standards in a series. Temperature is controlled by direct pyrometer measurement or by adjusting to a constant signal intensity of a filament ion. Double spiking with ^{233}U and ^{236}U was proposed to increase the accuracy of uranium isotopic measurements.[120-121] This technique cancels almost completely the effects of mass fractionation during the analysis.

The abundances of major isotopes are determined with RSDs of 0.01 to 0.02% (see Ref. 122). The precisions obtained for well-characterized material (a solution of a standard reference material) are significantly better than for process and product solutions, particularly at isotopic concentrations >1%. Studies show that improvements in precision and accuracy are obtained if proper care is taken to minimize instrumental and operating errors. In an interlaboratory exchange program, an overall RSD of 0.1% was obtained in measuring total plutonium in four samples having different isotopic compositions.[123] Consequently, an RSD of 0.1 to 0.2% is attainable for measuring total plutonium in fuel-cycle samples with meticulous separation chemistry and instrument operation.

High gamma-radiation levels limit the mass-spectrometric analysis of dissolver solutions to extremely small samples or to samples purified previously in shielded facilities. Microsamples of uranium and plutonium are adsorbed on ion-exchange resin beads for subsequent analysis.[124] The analytical precision is better than 1% (RSD). Alternatively, the mass spectrometer is modified for analysis of radioactive samples by enclosing the sparking chamber and the initial stage of the flight tube with 10 cm (4 in.) of lead shielding.[125] Samples emitting up to 100 R/h of gamma activity are analyzed in this fashion.

Mass spectrometry currently provides the most accurate isotopic analysis, even in the presence of fission products. The isotope-dilution method provides overall accuracy of 0.3-1% for the measurement of total uranium and plutonium concentrations in dissolver solutions. However, improvements in sampling and analysis techniques improve accuracy to better than 0.3%. The control of sample preparation is crucial to accuracy, particularly for nanogram amounts of uranium or plutonium.

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CHAPTER XII

A DOE VIEW OF SAFEGUARDS

by

Glenn A. Hammond*

I. INTRODUCTION

In presenting this course, lecturers emphasized the techniques, methods, and systems for designing and implementing a conventional and near-real-time accounting system for safeguarding nuclear materials. Establishing an accurate and timely materials accounting subsystem is essential for a strong and effective overall national safeguards and security system. This chapter presents the departmental perspective of April 1988 as well as new developments for materials control and accounting in integrated safeguards systems.

This presentation is divided into six segments:

(1) a brief review of the mission of safeguards and security,
(2) the integrated safeguards and security approach,
(3) the basic principles and rationale for materials control,
(4) the basic principles and rationale of materials accounting,
(5) the enhancement of assurance and overall credibility, and
(6) the directions and prospects for safeguards.

II. MISSION AND OBJECTIVES: PROTECT AGAINST THE THREAT

The primary objective is to maintain an integrated safeguards and security system of carefully selected elements or subsystems that provide effective protection against a wide range of threats. This system must be cost effective and minimize its impact on facility operation.

Threat assessment includes analyzing historical data and current information. Adversaries, these days, tend to be well trained, well

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financed, and well organized. The potential threat from them is increasingly multinational, as terrorist groups in various countries provide arms, financing, training, and other support. In addition to the criminal/terrorist external threat, knowledgeable employees, if disgruntled, can pose internal threats that present very complex problems for safeguards systems.

Because adversary characteristics and capabilities change in time, flexibility is a necessary feature of the safeguards system. Flexibility is achieved by utilizing a variety of equipment and subsystems. When selected for a specific facility, they will detect and deter adversary attempts; in the unlikely event that sensitive materials are sought, these subsystems will assess and respond in sufficient time to neutralize the threat.

III. INTEGRATED SAFEGUARDS AND SECURITY APPROACH: DEFENSE-IN-DEPTH

The concept of "defense-in-depth" is employed at DOE facilities through the use of an integrated safeguards system with graded levels of intensity depending on target attractiveness and/or sensitivity of a particular facility. The integrated system now in use consists of three basic subsystems that emphasize

- strong physical protection equipment and procedures to provide multiple obstacles between the target and a would-be thief or saboteur and response forces, such as on-site security personnel and off-site law enforcement assistance;
- reliable and rapid materials control to assign responsibility and maintain vigilance over the material, to govern internal movement, location and utilization, and to monitor the status of process flows and inventories; and
- accurate and timely materials accounting to determine quantities of material in flows and inventories, to provide information for determining the intensity of physical protection required, and to maintain records and provide reports that account for material and perform data analysis.

Basic to any effective system of safeguards are programs of personnel reliability and independent field and headquarters surveys and inspections to assure that effective procedures are being practiced.

The following discussions focus primarily on materials control and materials accounting. The terms materials control and accountability, often used interchangeably to describe the collective meaning of these activities, have been considered a single entity for many years. With the present emphasis on insider threats, the fundamentally different functions of the two subsystems are being recognized. To emphasize these differences, the Department has characterized and defined materials control and materials accounting separately. Typically, complex problems and issues require isolating the exact functional areas for study, development, and ultimate improvement. The Office of Safeguards and Security is proposing numerous steps to emphasize the functional distinctions between materials control and accounting so that they become more effective and compatible elements of integrated safeguards systems throughout the complex.

IV. THE MATERIALS CONTROL SUBSYSTEM

The major objectives of the materials control subsystem are to

(1) govern internal movement of nuclear materials and monitor status of material flows and inventories for early warning and effective localization of attempted diversion;

(2) provide assurance that contents of containers and data are not altered, that data entered into the accounting system are valid and unfalsified; and

(3) provide back-up documentation that no theft or diversion has occurred and support an audit trail relating nuclear material to specifically identified locations and authorized individuals.

At DOE facilities, several materials control techniques are integrated to meet these objectives. These techniques include containment technology, nuclear materials detection and surveillance, confirmatory and semiquantitative measurements, process operations monitoring, signal analyses, and assessment systems.

A. Containment and Custodianship

Containment refers to buildings, vaults, shipping containers, processing tanks, etc., which in some way physically restrict or control the movement of nuclear materials. Containment measures are used by plant operators for many reasons, such as process operations, transfer, and safety. In general, containment measures are not provided specifically for safeguards purposes, but their existence in a facility often simplifies the application of safeguards. The use of containment in safeguards is intended to limit removal to authorized materials only. There are basically two forms of containment. The first is intended to prevent removal of items, such as containers, from the controlled area. This measure is implemented by ensuring that every item leaving the area is indeed part of an authorized transfer. The custodian of the area, informed of the transfer, authorizes it. The second form of containment involves using bottles and canisters and applying seals or tamper-indicating devices to monitor integrity of the container.

In-plant equipment, such as instrumentation to monitor nuclear material stored in vaults, should be coupled with the physical protection system. Automated data-processing equipment that provides essentially continuous control and monitoring at the same time helps reduce personnel exposure to radiation.

B. Nuclear Materials Detection and Surveillance

Nuclear materials detection and surveillance instruments and devices indicate that either no nuclear material has left a certain location or that it has left only via legitimate routes. In their role of verifying independently the effectiveness of containment, surveillance instruments thus indicate whether containment of nuclear material in a location was constant or interrupted during a certain period.

The DOE requires a search for special nuclear material (SNM) each time an individual departs a material-access area and certain protected areas. Radiation monitoring offers a convenient and effective means of searching personnel for SNM because all forms of SNM are radioactive. Two types of monitors are used: manually operated, hand-held monitors that a guard must sweep over an individual's body or within a vehicle and automatic SNM portal monitors that monitor personnel walking or vehicles passing through a portal formed by gamma-ray detectors. Other techniques, such as detection of metal shielding and explosives, are being integrated with the personnel and vehicular portals.

C. Confirmatory and Semiquantitative Measurements

Because the current threat includes an "insider," consideration must be given to safeguards against concealment methods, such as

- diversion hidden by nuclear material measurement uncertainties and
- diversion hidden by falsification of data, such as understating input, overstating output, or misstating current inventory.

Concealment may be of particular concern in areas where measurements are difficult. Therefore, additional materials controls are required, and new techniques are being developed to provide vigilance over the material and monitor status (continuity of knowledge). Nondestructive assay, for example, can monitor the "fingerprints" of transfers between material balance areas (MBAs) where quantitative values cannot be determined in a few days.

Confirmatory and semiquantitative measurements are being developed and used to test whether an attribute or characteristic of the SNM exists in the range consistent with the expected quantity. Such information provides an approximate measurement or verification of sufficient accuracy to validate a previous attribute without the degree of accuracy required for the longer-term high-quality balance accounting. Current techniques involve nondestructive methods that verify the neutron or gamma-ray count or that suggest the internal radioactive heat generation is of the right order.

D. Process and Operations Monitoring

Advanced techniques and instrumentation are being developed and selectively applied to DOE facilities that process bulk quantities of nuclear materials. These techniques involve computers and multiple in-plant sensors that allow remote monitoring of tank levels, stream flows, solution concentrations, and valve positions to detect the "signature" of a diversion attempt. Material monitoring determines whether the quantities of nuclear material in bulk form are approximately consistent with the amounts indicated by the facility records, liquid levels of storage tanks, or gross weights of storage containers. Another form of bulk material monitoring uses process parameters, especially product yields, to detect possible material losses.

V. THE MATERIALS ACCOUNTING SUBSYSTEM

The major objectives of the materials accounting subsystem are to provide

(1) timely characterization and measurement of the material to evaluate the intensity of protection needed and to determine what, where, and how much material is being protected;

(2) frequent testing for credible assessment that the protection and control subsystems are working properly and are not circumvented; and

(3) if necessary, effective means and information for investigation and recovery.

The guiding principle for meeting the objectives is the sensitivity and reliability of gauging the true status of material balances involving material flows, transfers, inventories, and process holdup. The integrity of material transfers and of material on hand is dependent upon accuracy--of the measurements and of the supporting record system.

Measurements and measurement control programs are vital to the materials accounting subsystems. Material balance accounting is drawn around a plant and several major portions of the plant processes by periodically adding all measured receipts to the initial (or beginning) measured inventory, subtracting all measured removals, and comparing the resulting quantity ("book inventory") with the ending measured "physical inventory." Measurements that establish the quantities of nuclear material in each custodial area and in an entire facility create a principal safeguards subsystem and contribute control in localizing losses and in generating and assessing safeguard alarms. Of course, appropriate checks and balances are required to detect mistakes or anomalies; a strict measurement control program ensures the accurate calibration of the measurement systems as well as the reliability and reproducibility of the measurements.

High-quality measurement control programs permit monitoring

(1) relative accuracy between input and output measurements--the limiting factor being the uncertainties in fundamental constants, that is, the relative biases between reference materials and methods used for measurement;

(2) precision and relative accuracy of physical inventory measurements;

(3) recalibration schedules or redundant methods at key measurement points to reduce systematic errors; and

(4) for near-real-time accounting, the precision of in-process inventory measurements or estimates.

Improved materials accounting, better measurement techniques, and measurement control programs are necessary to help address "insider" concerns and to provide site-specific material balances that are well characterized, documented in terms of measurement capability, and validated with standards and certified reference materials.

Chemical, spectrometric, and nondestructive assay methods and related control programs rely on the availability of suitable standards that are traceable to a national system of standard reference materials. For many years, the National Bureau of Standards (NBS) distributed standard reference materials. In recent years, restricted budgets and facilities to handle SNM have limited that distribution. The DOE has elected to continue a program of certification of reference materials at the DOE New Brunswick Laboratory (NBL). The NBL activities include development, certification, and distribution of reference materials for calibration and standardization of nuclear material measurements, with priority given to related materials at DOE facilities that may reduce measurement uncertainties of highly strategic nuclear materials. The NBL also evaluates measurement programs and reference sources for DOE field office calibration checks that monitor and validate operator and instrument performance.

The guiding principle for materials control is to provide ongoing cognizance or "continuity of knowledge" of the status of all materials. The guiding principle for materials accounting is to provide "completeness of knowledge" by establishing fully measured material balances within predetermined limits.

VI. INDEPENDENT SUBSTANTIATION: ENHANCEMENT OF ASSURANCE AND OVERALL CREDIBILITY

Although trustworthiness, personnel reliability programs, and delegation of responsibilities are important elements of "defense-in-depth," periodic independent verification by the cognizant DOE office is required to enhance assurance and overall credibility of the safeguards system. Independent field office surveillance, monitoring, and inspection help ensure integrity of measurements with participation in measurement control programs and with review of measurement procedures. The integrity of the operator and the instrument is enhanced with inspector-controlled calibration devices. Materials control and accounting subsystems should permit an inspector to monitor the performance of an operator relative to the site-specific capability. The design of these subsystems must permit verification that facility materials accounting data are complete and unfalsified and that the material receipt or removal is through a material-access area or other material-controlling boundary of the physical protection system, especially where irreducible measurement uncertainties or operational constraints preclude timely or accurate measurements.

VII. SUMMARY: DIRECTIONS AND PROSPECTS

Materials control and materials accounting are vital to effective safeguards systems. The primary vehicle for improvements in protection against sophisticated and subtle insider threats within the DOE complex is material control. The desired level of protection sought by the Department calls for high-quality information to be generated and examined for diversion or theft possibilities, timely decisions, and, especially, the integration of material control into a responsive and integrated safeguards system.

In addition to a direct detection role, material control is also expected to help validate the procedures and data supplied to the material accounting system.

The implementation of safeguards systems with these features requires the use of internally generated information on process control, health and safety, and relevant physical protection. The key feature of such an expanded detection network is that many of these data already exist at operation facilities, yet few are employed effectively for safeguards.

The directions for nuclear material accounting improvements and upgrades within the Department are ultimately driven by the desire for quality and credibility. The advantage for the Department with respect to material accounting is that the system is already in place; that is, MBAs exist, transfers and inventories are measured routinely, and inventory differences are computed. In nuclear material accounting, we are concerned with how well the system is working and the technical possibilities for improvement. To address these concerns, the major material accounting improvements for the Department tend toward the following objectives:

- understanding the causes of inventory differences on an MBA-by-MBA basis,
- developing demonstrable programs for the systematic reduction of inventory-difference control limits to the point of diminishing returns, and
- expanded measurement control concepts and programs for all terms appearing in the manufacturing and processing material balances.

Improvements at various nuclear facilities, DOE-sponsored research and development, and emerging new techniques are providing greater measurement accuracy, versatility, and timeliness. State-of-the-art conventional measurement methods, newly developed technology, in-plant instrumentation, innovative data-analysis techniques supported by computer and data base management technology are becoming available. The challenge continues for a systematic approach to the development and application of integrated, appropriately graded, and cost-effective safeguards and security throughout the DOE complex.

ABOUT THE AUTHOR

Glenn A. Hammond is Director, Division of Safeguards, Office of Safeguards and Security (Defense Programs), at the Department of Energy. He has served over 30 years in various technical positions at both field and headquarter offices in nuclear materials production, quality assurance, and management and in safeguards and security programs involving policy, procedures, standards, and R&D for both domestic and international safeguards.

CHAPTER XIII

MATERIALS ACCOUNTING AT LOS ALAMOS NATIONAL LABORATORY

by

B. H. Erkkila and N. J. Roberts

I. INTRODUCTION

This presentation gives an overview of the accounting system used at the Los Alamos National Laboratory by the Los Alamos Nuclear Material Accounting and Safeguards System (MASS). This system processes accounting data in real time for bulk materials, discrete items, and material undergoing dynamic processing. The MASS draws heavily upon our experience with DYMAC, a system developed by the safeguards research and development (R&D) groups at Los Alamos. From its inception at the Los Alamos Plutonium Facility (PF) in 1979, the DYMAC system demonstrated that the concepts of near-real-time accountability were both practical and achievable. When funding for the DYMAC program was cancelled by the Department of Energy/Office of Safeguards and Security (DOE/OSS) in 1980, the DYMAC system was transferred to the Nuclear Materials Department, now part of the Operational Security/Safeguards Division. The system was initially scoped to handle approximately 1000 transactions each month and eventually as many as 5000 monthly. We currently process 20 000 per month from all Laboratory users.

The Los Alamos Safeguards System (LASS) began in the 1950s and was based primarily on an "80-column" card system developed by the Plutonium Metallurgy Group at Los Alamos. The system served the Laboratory well for many years and still strongly influences our concepts of operational nuclear materials accounting. The LASS was the basis for the data supplied to the DYMAC operations. The PF/LASS, in operation at the Los Alamos Plutonium Facility from 1982-1984, was an operational version of the experimental DYMAC system. Today, the MASS is a logical extension of PF/LASS and uses remote terminals, call-in service, and a modified batch entry mode for data input. The most significant difference between PF/LASS and MASS is the external capabilities of MASS.

II. DEFINITIONS

The following list includes widely accepted definitions as well as those we apply at the Laboratory.

(1) *Accountability* is the combination of management, control, and accounting that provides assurance that resources are available and guards against their misuse by timely analysis and reporting of data to Laboratory management, users, and program sponsors. (Note: The terms accountability and accounting as used here are not interchangeable.)

(2) *Nuclear materials management* provides the assurance that necessary nuclear material is available for Laboratory programs, that proper levels of inventory are maintained, and that material no longer needed is used in other programs, by other contractors, or is discarded or recovered properly.

(3) *Control* stems from knowledge of the *physical* status and location of all nuclear material in inventory at all times. Knowing where the material is and in what form is vital to a good accountability system. At the Laboratory, we have stringent controls on the movement of nuclear materials between sites and between material balance areas (MBAs) within a site. Our group is responsible for the on-site movement of all special nuclear material. We are now responsible for the central storage of uranium; when our new central storage facility is completed, the long-term and intermediate storage of all nuclear materials at the Laboratory will be our responsibility. The Technical Support Section of the Material Control and Accountability Group (OS-2) also is responsible for providing measurement consultation to users; implementing and monitoring the Laboratory-wide measurement control program; performing inventory measurement confirmations; and maintaining the operation, upkeep, and calibration of all portal and vehicle radiation monitors.

(4) Accounting is the book record of the status, location, and amount of all nuclear materials in inventory at all times. It is the responsibility of Group OS-2 to provide the official Laboratory records for quantity, form, and location of all nuclear materials. The computer operations, maintenance, and development work are performed by the support section of another group in the OS Division, one dedicated to this purpose.

(5) MASS, the Nuclear Material Accounting and Safeguards System of Los Alamos, refers to the entire system, not to any isolated component; MASS includes the central computers, instruments, measurement control program, etc.

III. NUCLEAR MATERIAL STORAGE

At the present time, the Laboratory has several working vaults for nuclear material. The central storage of nuclear materials is now limited to a uranium storage facility and a portion of the vault at the Plutonium Processing Facility (PF-4). In 1989, a new Nuclear Materials Storage Facility (NMSF) will come on-line for the intermediate and long-term storage of nuclear material.

IV. COMPUTER SYSTEM

The updated computer hardware configuration for MASS is listed below.

Production System	Training and Development
4 tandem TXP CPUs,	2 tandem EXT CPUs,
4-megabyte memory each	4-megabyte memory each
1 gigabyte disc storage	0.5 gigabyte disc storage
1600/6250 BPI tape drive	800/1600 BPI tape drive
96 communication ports	17 communication ports

Print Station -- no change

All applications programs use FORTRAN, and program modules are written to be self-documenting. The transactions programs rely on the concept that a limited number of operations can be performed; all operations are some form or combination of the following basic transaction types.

(1) Modify is the transaction used to change administrative and/or process-related data in the inventory record (but is not used to change any accountability data).

(2) Split is the transaction used to record the splitting of one lot into two or more lots in the processing environment, the disassembly of parts, or some similar action.

(3) Combine is the transaction used to record the combination of two or more lots into a single lot in the processing environment, the assembly of two or more parts, or some similar action. It is the opposite of the split transaction.

(4) Move is the transaction used to move an item within its present location or from one MBA to another within the same material access area (MAA). If the user of this transaction (for movements between MBAs) does not have access to both MBAs, a special move, called send/receive, is required.

Use of the system is limited by several levels of security. These levels provide a high degree of assurance that users are adequately trained and qualify for the system privileges. This security is assured with password-controlled system sign on through the system software and a valid-user record that grants privileges. Users are limited to the on-line production programs.

One of the strengths of the MASS is its versatile report system. Eight reports are available to users, on-line, at their CRTs. In most cases, a local print-out can be obtained. The on-line reports available are

- Inventory by account
- Inventory by account/material type
- Inventory by process/status
- Inventory by location
- Item status

- Items in transit
- Transaction look up
- Activity of an item

In addition to on-line reports, many off-line reports are also available. These are listed below.

Select Data By

Account, material type (MT), process/status, project location, special designator, item description, COEI, measurement code, lot identification

Sort, Subtotal, and Print By

Account - MT - lot identification
Location - shelf - MT - account - lot identification
Project - MT - process/status - lot identification
Special designator - MT - account - lot identification
Process/status - MT - lot identification
Account - MT - item description

Sort In Any Manner and Print Without Totals

Graphics and Trace Functions

Plot activity for any item in the inventory file, both current and historical

Trace activity of any item and all of its products or predecessors both forward and backward in time

The MASS primary computer system has a significant hardware upgrade. The software conversion was completed in early 1988; the switchover to the new system, in March 1988. The immediate advantage in the upgrade is central-processing-unit speed, increased memory and storage, faster and more compact input/output, and system hardware compatibility with other safeguards and security systems at Los Alamos.

V. MEASUREMENT CONTROL PROGRAM

The plutonium and uranium processing groups at the Laboratory perform a wide range of measurements, using both nondestructive analysis (NDA) and conventional analytical techniques. Various matrices of nuclear material, especially plutonium and uranium, are processed and analyzed by the Laboratory. The instruments performing NDA measurements all operate under the MASS measurement control program. In addition, the Laboratory participates in several sample exchange programs to assure that measurements are performed at an accuracy and precision level commensurate with their intrinsic and strategic value. The measurement control program now used stems from the program developed under DYMAC and extended and refined using PF/LASS. Further changes and expansion will follow the MASS upgrades.

The NDA instruments covered by the measurement control program in MASS are listed in Table I. Most radiation-sensing instruments now used were developed for specific applications by the safeguards R&D groups at Los Alamos or are modifications, refinements, or extensions of the R&D designs. The primary exceptions to this are the calorimeters developed by Mound Laboratories.

TABLE I

INSTRUMENTS UNDER MASS MEASUREMENT CONTROL

No.	Instrument
2	Segmented gamma scanner (SGS)
12	Thermal neutron counter (TNC)
6	Solution assay instrument (SAI)
96	Scale and balance
10	Calorimeter
3	Gamma isotopic analyzer
1	Uranium solution assay system (USAS)
1	Random driver
3	Vehicle monitor
10	Personnel portal monitor
144	

Where measurement instruments are used for accountability, a program must assure everyone using the data that the measurements are accurate, precise, and timely. Timeliness is satisfied through in-line instrumentation where practical and where consistent with availability and resources. To ensure data accuracy, the data input to the computer must be correct and the data presented to the user, meaningful and easily understood.

Unfortunately, we cannot use on-line instrumentation now because of the limited number of communication ports on our computer hardware. We therefore rely on administrative procedure and a "friendly" software system to achieve the maximum accuracy. A well-engineered system with design specifications mutually agreed to by the process, instrumentation, and accountability representatives can opportunely offer the needed assurances.

The current measurement control program has proven both effective and workable. While a "pure statistician" may have considerable problems with the program, it is useful within the limits of its design. The basic philosophy of the program requires regular accuracy and precision checks for each instrument. The data for the measurement control program are gathered either by the technical staff of Group OS-2 or by operations personnel. The accuracy and precision checks are associated with appropriate action and warning limits. When a particular check reveals an instrument that exceeds the warning limit, that instrument is rechecked, and, if it fails a second time or if it exceeded the action limit on either check, the instrument is removed from service until the reasons for failure are determined and corrected.

The basis for the accuracy checks is essentially the same for all instruments and consists of a "t-test" on the data. The test used is

$$t = \frac{\bar{m} - m_0}{s}\sqrt{N} \quad ,$$

where

$\bar{m}$ = average value observed for N trials,

m_0 = value of the standard,

s = standard deviation for the N trails equals 0.15, and

$s/\sqrt{N}$ = unbiased estimate of the standard deviation.

For balances used at the Plutonium Facility, the accuracy check is performed at zero, half, and full scale using calibrated weights, and the "t-test." For these calculations, the value of 0.15, which is used for the population standard deviation, is based on a historical estimate of the population variance and is shown to be empirically valid. An effort was made to determine the individual uncertainties for the balances; however, incorporating the uncertainties into the program awaits restructure of the new and upgraded MASS computer system.

The accuracy check for the gamma and neutron instruments is very similar, except the value for the standard deviation is based on the propagation of the Poisson counting statistics and other identified random errors from a well-characterized standard. No attempt is made to include corrections based on systematic errors.

The action and warning limits for the accuracy checks are 2.58 and 1.96, respectively.

The precision check for scales and balances requires five readings at both the midrange and upper limits of the scales and balances and then subjects the data to an "F-test." Because this technique has serious limitations, using a series of accuracy checks to perform the precision checks will constitute an early change in the MASS measurement control program. The "F-test" used is

$$F = \frac{s^2}{\sigma^2} ,$$

where

s = the standard deviation of N measurements and

σ = the estimated population standard deviation (0.08).

As is the case for the accuracy check, the value 0.08 is based on a historical estimate and is shown to be empirically valid. A true value for each instrument is determined and entered into the new MASS measurement control program. The action and warning limits for this test are 3.32 and 2.37, respectively.

The precision test for the NDA instruments other than scales and balances is based on the results of 15 consecutive measurements. As is the case for the scales and balances, the use of a series of accuracy checks may prove more reasonable, especially when coupled with internal consistency checks of the software of the instrument. The present program uses two basic checks, one for precision and another for randomness of the results. These are the reduced chi-square and the eta tests. The mathematical expressions for these tests are

$$\chi_R^2 = \frac{s_m^2}{\sigma_m^2} \quad \text{and}$$

$$\eta = \frac{\delta^2}{s_m^2} \quad ,$$

where

s_m^2 = the variance of m measurements (~15),

$$\sigma_m^2 = \frac{\sum_{i=1}^{m} s_i^2}{m} \quad \text{and}$$

$$\delta^2 = \frac{\sum_{i=1}^{n-1} (x_{i+1} - x_i)^2}{n - 1} = \text{mean square successive difference} \quad .$$

The action and warning limits for these tests are given in Table II.

Because the 15 measurements normally used for these tests are taken consecutively over a short time, one cannot, from a single data set, use the chi-square test to identify trends or systematic errors. The eta test does detect the lack of randomness in the data observed from the 15 data points. The eta test, for example, is useful in determining that hardware items, such as shutters and other mechanical devices, are not operating

ACTION AND WARNING LIMITS

Limit	Test Reduced Chi-Square	 Eta
Action		
Upper	2.24	3.08
Lower	0.29	0.92
Warning		
Upper	1.87	2.79
Lower	0.40	1.21

correctly. If the value of eta differs significantly from two, it indicates a trend in the data. Values much less than two tend to show a long-term trend; values much larger than two, oscillations or short-term trends.

Although this system may be lacking in rigor, it is proven useful in detecting instruments needing recalibration or maintenance. A measurement control program is only as effective as its procedural controls and the diligence of the operational personnel to look for, recognize, and correct deficiencies.

We suggest that when you anticipate purchasing any equipment for accountability measurements you very seriously consider measurement control. To the maximum extent possible, the equipment should incorporate an integral measurement control program that is both functional and auditable. You can assure yourself that equipment meets this requirement by buying proven products. Familiarize yourself with ANSI Standards in the N-15 series. Your equipment should comply with these and other standards where practical.

VI. INVENTORY DIFFERENCES

The evaluation of inventory differences is a tedious, time consuming, but necessary, function of any nuclear material accountability system. The timely reporting of significant inventory differences (IDs) is often hindered by too much examination of insignificant IDs. The real problem is determining which IDs are significant. For instance, is a 50-g ID significant? It depends on the process and circumstances. An interesting parallel is in fire protection; your local fire department would be much more efficient if it responded only to <u>real</u> alarms, not <u>false alarms</u>. Although this is true, all fire alarms must trigger response and investigation before decisions can center on which are real and which are false.

At Los Alamos, we have a schedule for ID reporting, evaluation, and approval. All IDs receive at least five levels of review before their significance is decided. These review levels are

(1) evaluation by the line supervisor or lead technician,

(2) review by the nuclear materials officer (NMO) and/or the custodian, with approval of the line management,

(3) review by the Group OS-2 Technical Support Section,

(4) joint review and agreement by the NMO, line management, and Group OS-2, and

(5) review by the Special Nuclear Material ID Review Board.

Following this review, the explanations for significant IDs are submitted to the DOE/AL-NSB. For some IDs, this review process is a few days, but for others, it encompasses several weeks. The duration depends on the complexity of the factors leading to the ID.

Several MASS tools, developed to aid in this evaluation, are listed below. When a large discrepancy exists in the material balance, it is entered into the MASS as material in process (MIP). Any MIP unresolved by the last day of the month becomes an ID and is evaluated and reported according to DOE requirements and Laboratory policy. Yearly we declare about 2 000 instances of MIP, which reduce to about 50-75 IDs per month. Security restraints prevent our giving specific examples, but generic examples are provided.

<u>Inventory-Difference Evaluation Tools</u>

- Daily listing of all MIP transactions
- On-line listing of MIP history
- Off-line listing of MIP history
- Off-line plots of MIP history
- Process flow charts

VII. CURRENT PROGRAMS AND FUTURE PLANS

Our intention is to use the versatile features of the MASS to develop better and faster ways of analyzing the MASS data to improve overall safeguards and accountability at the Los Alamos National Laboratory. We will concentrate our efforts on several areas. Some short term concerns are to

(1) improve techniques for nuclear material inventories, including automated inventory of storage areas and confirmation measurements for inventory, both static and dynamic;

(2) improve and automate techniques for categorizing and identifying inventory differences;

(3) develop a methodology for establishing dynamic action and warning limits for processing environments;

(4) use more modeling and simulation studies in development of accountability plans and instrumentation for new programs and processes;

(5) monitor progress in the development of automated storage and retrieval systems for vault storage applications;

(6) develop a nuclear materials measurement facility in conjunction with the new central storage facility; and

(7) study the feasibility of real-time ID evaluations.

ABOUT THE AUTHORS

Bruce Erkkila joined the Los Alamos National Laboratory in 1963 after receiving a B.S. and an M.S. in physics. He has spent the last ten years working on a variety of safeguards problems in instrumentation, material storage, and operations. He is currently the group leader of the Material Control and Accountability Group, which is responsible for safeguards issues at Los Alamos.

N. J. Roberts was the group leader of the Material Control and Accountability Group that developed the Los Alamos Material Accounting and Safeguards System (MASS) and continues to maintain and oversee its use. Most recently he served as the Los Alamos Safeguards Assurance Officer with oversight of safeguards at the entire facility.

CHAPTER XIV

INTERNATIONAL SAFEGUARDS

by

E. A. Hakkila, C. R. Hatcher, and J. L. Sapir

I. BASIS FOR INTERNATIONAL SAFEGUARDS

International safeguards for nuclear facilities are applied under one of two international agreements. For States signatory to the Nuclear Non-Proliferation Treaty (NPT), safeguards are applied under INFCIRC/153 (corrected[1]); for those States that have not signed the NPT, safeguards are applied under INFCIRC/66 (Rev. 2).[2] These documents and the IAEA Statute[3] are the only legal basis for application of international safeguards by the International Atomic Energy Agency (IAEA). The United States is a NPT signatory and INFCIRC/153 safeguards apply.

Document INFCIRC/153 specifies that "...the objective of safeguards is the timely detection of diversion of significant quantities of nuclear material and deterrence of such diversion ... ." (#28) Both documents specify that material accounting will be used to keep track of nuclear material; INFCIRC/153 specifies "... the use of material accounting as a safeguards measure of fundamental importance, with containment and surveillance as important complementary measures." (#29)

Although, as noted, INFCIRC/153 requires "timely detection" of "significant quantities," neither is defined in the document. In 1980, the IAEA issued "The IAEA Safeguards Glossary,"[4] attempting to more quantitatively define its detection goals. The goals are defined (Paragraph 107) in terms of significant quantities, detection times, and detection probability. The significant quantities defined in Paragraph 107 are shown in Table I.

Detection time, defined in terms of the estimated time required to convert the nuclear material to the metallic components of a nuclear device (Paragraph 87), is shown in Table II. Detection probability is normally set at 90-95%, with an associated false-alarm probability of 5% or less (Paragraph 91).

TABLE I

SIGNIFICANT QUANTITIES

Use	Material	Significant Quantity	Safeguards Apply
Direct	Pu[a]	8 kg	Total element
	U-233	8 kg	Total isotope
	U[U-235≥20%]	25 kg	U-235 contained
	--Plus rules for mixtures where appropriate		
Indirect	U[U-235<20%][b]	75 kg	U-235 contained
	Thorium	20 t	Total element
	--Plus rules for mixtures where appropriate		

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[a] For plutonium (Pu) containing less than 80% Pu-238.

[b] Including natural and depleted uranium.

TABLE II

ESTIMATED MATERIAL CONVERSION TIMES TO FINISHED PLUTONIUM (Pu) OR URANIUM (U) METAL COMPONENTS

Beginning Material Form	Approximate Conversion Time
Pu, HEU, or U-233 metal	Days (7-10)
PuO_2, $Pu(NO_3)_4$, or other pure Pu compounds; HEU or U-233 oxide or other pure compounds; MOX or other nonirradiated pure mixtures containing Pu, U[(U-233 + U-235)≥20%]; Pu, HEU and/or U-233 in scrap or other miscellaneous impure compounds	Weeks (1-3)[a]
Pu, HEU, or U-233 in irradiated fuel[b]	Months (1-3)
U containing <20% U-235 and U-233; Th	1 year

---

[a] This range is not determined by any single factor, but the pure Pu and U compounds will tend to be at the lower end of the range, the mixtures and scrap at the higher end.

[b] Criteria for establishing the irradiation to which this classification refers are under review.

Note that "The IAEA Safeguards Glossary" has no legal basis as far as member States are concerned. However, it is used by the IAEA in inspection planning, and many inspections, particularly at item-handling facilities, are planned to meet the significant quantity, detection time, and detection probability goals of the Glossary.

For larger bulk-handling facilities, the IAEA considers that possibly detection time and significant quantity be considered in terms of facility throughput.

Two other important documents in the IAEA information series are "IAEA Safeguards--Guidelines for States' Systems of Accounting for and Control of Nuclear Materials,"[5] and "IAEA Safeguards--An Introduction."[6] The former provides guidance for establishing a State's system of accounting so that it can interact smoothly with the IAEA. The requirements at the State level, as well as the facility level, are reviewed. Elements included are the information system, the materials accounting and control system including the materials balance area (MBA) structure, and inspections.

The latter, the introductory document, reviews evolution of IAEA safeguards, safeguards objectives, approaches, and the organization of IAEA safeguards. Again, these documents have no legal basis but provide excellent information for establishing an effective and efficient safeguards system.

II. BASIS FOR APPLYING INTERNATIONAL SAFEGUARDS IN U.S. FACILITIES

The requirements for nuclear materials accounting at the State level are somewhat different than at the international level. The State is concerned with accounting for nuclear material transfers within the State and with meeting international bilateral and IAEA treaty commitments.

In the U.S., regulations guiding the application of nuclear materials accounting for commercial facilities under Nuclear Regulatory Commission (NRC) authority derive from the Code of Federal Regulations[7] and from DOE Order 5633.3 for government-owned facilities.[8] The latter declares that "Safeguards is an integrated system of physical protection, accountability, and material control measures designed to deter, prevent, detect, and respond to unauthorized possession and use of special nuclear material."

The requirements for safeguards in nuclear materials accounting systems in U.S. commercial facilities are defined in the Code of Federal Regulations (see Ref. 7, Part 74). Both NRC and DOE require well-defined nuclear materials accounting systems.

In practice, the U.S. domestic safeguards places heavy emphasis on physical protection against theft of nuclear material and sabotage of nuclear facilities. However, the materials accounting system is the only quantitative indicator of locations and amounts of nuclear material. Reported material unaccounted for (MUF) and limit of error on MUF (LEMUF) data must be explainable to the appropriate national authorities, including Congress. Thus, the ultimate ability to resolve anomalies lies in the materials accounting and control system.

The requirements for application of IAEA safeguards at U.S. commercial facilities are defined in in the Code (see Ref. 7, Part 75). The section is written so that the facilities safeguards nuclear materials accounting system conforms to requirements of INFCIRC/153 in reporting requirements in the format and quality and quantity of information provided to the IAEA. No provision is made in the DOE orders for application of international safeguards at noncommercial facilities. However, the Gas Centrifuge Enrichment Plant (GCEP) at Portsmouth, Ohio, and the Secure Automated Fabrication Line (SAF-line) at Hanford were offered to the IAEA for international inspection prior to cancellation of these projects in 1986 and 1988. The Facility Attachment was being negotiated under the same requirements as in the Code, Part 75 (see Ref. 7). Other DOE facilities, such as the atomic vapor laser isotope enrichment plant and the spent-fuel storage facility, would likely be offered in similar arrangements.

III. APPLICATION OF INTERNATIONAL SAFEGUARDS AT THE FACILITY LEVEL

The major vehicle for defining the safeguards system at the facility level is the Facility Attachment. This is negotiated between the U.S.

government and the IAEA with facility participation. The Facility Attachment includes a description of the facility and a description of equipment and procedures either existing or proposed for nuclear materials accounting and control. It specifies the material balance area structure, key measurement points, and procedures for physical inventory taking.

Thus, the main activities of the IAEA at each safeguarded facility involve verification of all transfers into and out of the facility and verification of the in-process inventory. Note the key word verification. The IAEA does not establish its own materials accounting system at the facility but can only verify what exists in the facility. Thus, it is in the interest of the Agency to assure during Facility Attachment negotiation that the materials accounting system provides the best possible effectiveness and efficiency.

The Agency uses two basic tools in its verification activities--materials accounting and containment/surveillance.

Materials accounting verification can include checking operators' materials accounting records and reports, verifying measurements in the facility, and withdrawing samples for verification analysis at the IAEA analytical laboratory at Seibersdorf, Austria, or at one of the IAEA Network Laboratories.

Containment measures include taking advantage of natural physical boundaries in process buildings or in areas that can assure that nuclear material cannot be transported except through designated channels. Surveillance, which comprises measures to observe that nuclear material is not moved clandestinely, includes seals on individual items or item storage areas as well as cameras or TV monitors. Containment/surveillance assures the integrity of the materials accounting system.

IV. EXAMPLE OF APPLICATION OF INTERNATIONAL SAFEGUARDS AT A LOW-ENRICHED URANIUM (LEU) FUEL FABRICATION FACILITY

The following is an example of the application of international safeguards at a LEU fuel fabrication facility. (See details in Appendix of Chapter VI.)

A. MBA Structure and Key Measurement Points

The MBA structure at LEU fuel fabrication plants depends on the particular plant and associated Facility Attachment. Generally, there is a feed storage MBA (shipper/receiver differences are established) and at least one process MBA. If a conversion section is present, an additional process MBA may be included. There may also be a product storage MBA for maintaining item accountability on fuel assemblies awaiting shipment.

A key measurement point (KMP) is defined as "...a location where nuclear material appears in such a form that it may be measured to determine material flow or inventory. Key measurement points thus include but are not limited to the input and outputs (including measured discards) and storages in materials balance areas."[1] In some Facility Attachments, KMPs are defined in terms of material types rather than specific physical locations.[9] The KMPs for a model light-water reactor (LWR) fuel fabrication plant for the case of one shipper/receiver MBA and one process MBA are presented below.[10]

For determination of nuclear material flow

MBA-1 (Shipper/receiver difference area)

KMP1--Receipts of nuclear material into MBA-1

KMP2--Shipments of nuclear material from MBA-1 to off-site location

KMP3--Transfers from MBA-1 to MBA-2

MBA-2 (Process area)

KMP3--Receipts into MBA-2 from MBA-1

KMP4--Shipments of nuclear material from MBA-2 and all other decreases of the inventory of nuclear material at MBA-2 except measured discards

KMP5--Measured discards

For determination of physical inventory

MBA-1

KMPA--All the nuclear material kept on the basis of shippers' measurements

MBA-2

KMPB--Samples, misc, etc, which are not in KMPs C through J

KMPC--UF_6 cylinders

KMPD--UO_2 powder and green pellets

KMPE--UO_2 pellets and unscanned fuel rods

KMPF--Scanned fuel rods

KMPG--Fuel assemblies

KMPH--U_3O_8 powders

KMPI--Solid or sludge scrap and waste

KMPJ--Recoverable liquid

B. Inspection Activities

The IAEA generally performs 6-12 inspections per year at LEU fuel fabrication plants, including 1-2 physical inventory verifications (PIVs) to close the materials balance and 5-10 interim inspections to verify flow and audit records. These activities comprise 50-140 inspector man-days depending on the type of agreement and plant specifics.

1. Auditing Records and Reports. Facility records must be maintained to provide complete knowledge and documentation of all nuclear material inventory and flow for each MBA. As in the case of LWRs, the inspector audits these records for completeness and accuracy and compares them with source documents and reports submitted to the IAEA by the State. From these records, the inspector determines a book inventory for each MBA to compare with the stated (and later verified) physical inventory.

2. Auditing Operator's Measurement System. At bulk facilities, an additional activity is the verification of the operator's measurement system and associated errors. Calibration and measurement control procedures are reviewed along with the operator's derived estimates of random and systematic errors. In some cases, the inspector may observe the calibration and control measurements and even supply independent IAEA standards. Typical operator accountability measurements at a LEU fuel fabrication facility appear in Table III (Ref. 11).

TABLE III

PLANT ACCOUNTABILITY MEASUREMENTS

Item	Measurement Method
UF_6 in cylinders	Weighing, sampling, U and U-235 assay
Uranium powder in buckets	Weighing, sampling, U and U-235 assay
Pellets in boats and trays	Weighing, sampling, U and U-235 assay
Solid wastes in barrels and filters	Passive gamma, waste assay counter
Liquid waste in large basins	Volume, sampling, U and U-235 assay
Fuel rods	Pellet column weight, sampling, U and U-235 assay
Fuel bundles	Summation of rod values

3. Verifying Nuclear Material. Closing a materials balance requires verification of both nuclear material flow and inventory. Flow verifications are performed during the interim inspections; inventory verifications, during PIVs. Initial inspector verification activities involve counting, identifying, and tagging a large percentage of the items present (buckets, trays, rods, and assemblies). The purpose is to verify the presence of all of the inventory items stated by the operator and to establish the item population in preparation for implementing a random sampling plan.

The population is then stratified into material categories. Guidelines for stratification include material type, amount of material per item, and measurement errors associated with the planned verification technique. Based on a random sampling plan, a subset of the population is selected for further verification.

The Agency employs a two-level verification approach consisting of many less accurate (and therefore easily accomplished) measurements to detect large falsifications and fewer more accurate (but usually more costly, more intrusive, and less timely) measurements to detect small falsifications. In the first category, called the attribute test, measured observations are compared item-by-item with the operator's value and classified as either acceptable or defective. The second category, called the variables test, provides a measured, quantitative value and associated uncertainty for each item. The variables test is looking for small biases, less than the measurement sensitivity on individual items. An item-by-item comparison is not possible, but the results are statistically analyzed to find average operator-inspector differences. Examples of attribute and variable measurements performed by the IAEA at LEU fuel fabrication plants appear in Table IV.

4. **Containment and Surveillance Measures**. Seals are normally employed during a PIV to assure that all items are inventoried without duplication and to ensure the integrity of samples taken for analysis. If the operator can identify items not expected to be processed prior to the next PIV, these may be sealed to reduce the verification effort at the next PIV. Waste and scrap stored for extended periods at the facility fall into this category. Seals are also applied to shipments of final or intermediate products.

5. **Inspector's Conclusions**. The inspector's strategy is to carefully compare the operator's claims for amounts of material received, shipped, stored, or lost with his own observations. His evaluation includes the correctness and completeness of the accounting records, the consistency of the operating records, and the results of his verification measurements. Attribute measurements are evaluated on an item-by-item basis. Because the sampling plans are based on zero defects, any observed discrepancy is

TABLE IV

IAEA VERIFICATION MEASUREMENTS

Item	Attribute Measurements	Variable Measurements
UF_6 cylinders	Enrichment by NDA (high-resolution gamma ray plus cylinder wall thickness)	Observe operator weighing, sample for assay of uranium fraction by chemical analysis and ^{235}U enrichment by mass spectrometry
UO_2 powder UO_2 pellets	Enrichment by NDA (SAM-II,[a] dual channel NaI)	Weighing, sample for uranium fraction by chemical analysis and ^{235}U enrichment by mass spectrometry
Fuel rods	Homogeneity by use of operator's rod scanner, enrichment by NDA (dual channel NaI)	Observe operator weighings, total fissile by use of operator's rod scanner
Fuel assemblies	Enrichment of outer rods by NDA (dual channel NaI)	Coincidence neutron collar being tested

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[a] Stablized assay meter.

thoroughly investigated and resolved. Variables data are analyzed for any significant bias between the inspector's and operator's results. Finally, the inspector compares his calculated MUF with that of the operator and, considering the uncertainties in these values, concludes whether any diversion is indicated. These evaluations result in an Agency statement of acceptance or rejection of the operator's materials balance for the period in question.

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11. R. Schneider and E. Herz, "Implementation of International Safeguards--An Operator's Viewpoint," Fifth Intenational Conference on Nondestructive Evaluation in the Nuclear Industry, San Diego, California, May 1982.

ABOUT THE AUTHORS

Arnie Hakkila joined the Los Alamos National Laboratory in 1957 after receiving a Ph.D. in analytical chemistry from Ohio State University. A charter member of the Los Alamos Safeguards Systems Group in 1976, he has served the group as associate, deputy, and group leader. Since 1983, he has been involved exclusively in international safeguards and is currently the Los Alamos Program Coordinator.

Charlie Hatcher received a Ph.D. in physics from the University of Texas in 1958. Prior to joining the Safeguards Assay Group at Los Alamos in 1977, he worked at Lawrence Livermore National Laboratory and EG&G as a scientist and manager for the development of gamma-ray and neutron detectors. In 1979 and from 1984 to 1986, he served as a cost-free expert with the International Atomic Energy Agency in Vienna. He is currently researching the use of Californium ion chambers to study neutron detector characteristics and serving as chairman of the interdivisional Safeguards Implementation Project Team at Los Alamos.

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CHAPTER XV

WORKSHOP ON REAL-TIME MATERIALS ACCOUNTING SIMULATOR

by

R. R. Picard, G. L. Barlich, and J. F. Hafer

I. INTRODUCTION

The Real-Time Materials Accounting Simulator (RTMAS), developed as an educational tool, investigates the relationships of a diversion scenario applied to a simple process model and materials accounting evaluation procedures used to detect diversion.

The three components of the simulator, the process model, the measurement model, and the evaluation procedures, are described below.

Instructions for running the simulator on a microcomputer follow the component descriptions.

II. PROCESS MODEL

For pedagogic purposes, a simple process serves nearly as well as a more complicated one. A simple tank with a single input transfer and a single output transfer is used for the process in the simulator (Fig. 1). The materials balance equation for the tank during each balance period is

$$MB = T_{IN} + I_B - I_E - T_{OUT} \quad ,$$

where

T_{IN} is the input transfer,
T_{OUT} is the output transfer,
I_B is the beginning inventory, and
I_E is the ending inventory.

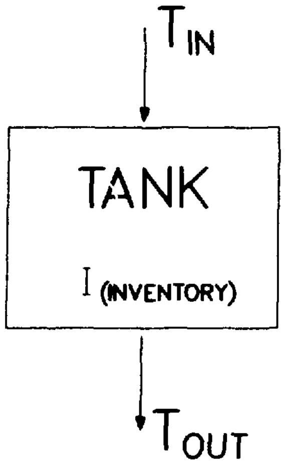

Fig. 1.
The process model, a simplified materials balance area.

$$MB = T_{IN} + I_B - I_E - T_{OUT}$$

The tank has an inventory of 100 kg of material at the start of the simulation. A transfer in and a transfer out of 10 kg is assumed for each balance period.

III. MEASUREMENT MODEL

The inventory and transfer terms in the materials balance equation given above are simulated by using random normal numbers generated within the computer program. Each inventory measurement has a standard deviation given by siginv. Each net transfer has standard deviations of sigeta for the so-called systematic component and sigeps for the so-called random component. Initial values in the program for the standard deviations are

siginv = 0.200 kg,
sigeta = 0.038 kg, and
sigeps = 0.100 kg.

The standard deviation of the materials balance is given by

$$SD = sqrt(2 \bullet siginv^2 + sigeta^2 + sigeps^2) \quad .$$

Using these values, the standard deviation of each materials balance is roughly 0.3 kg.

IV. EVALUATION PROCEDURES

As the simulator runs, a series of up to 50 materials balances is obtained. Each balance may or may not involve material diversion. If there were no measurement errors, the evaluation procedures would detect the loss of material without fail. With measurement errors, observed anomalies may be due to actual diversion, to measurement errors, or both. The following standard test procedures are evaluated to aid in diversion detection:

(1) chart for materials balance,
(2) chart for cumulative materials balance,
(3) chart for standard innovations, and
(4) chart for Page's test.

In each of the above charts, the observed results are plotted against the sequential materials balance number, which is a measure of time. Table I gives the diversion summary for a computer run with "no diversion" in each of the 50 materials balances. The charts for this "no diversion" case are shown in Figs. 2-5.

TABLE I

DIVERSION SUMMARY FOR SCENARIO WITH "NO DIVERSION"

```
Bal   Div    Acc        Bal   Div    Acc        Bal   Div    Acc

  1   0.00   0.00        18   0.00   0.00        35   0.00   0.00
  2   0.00   0.00        19   0.00   0.00        36   0.00   0.00
  3   0.00   0.00        20   0.00   0.00        37   0.00   0.00
  4   0.00   0.00        21   0.00   0.00        38   0.00   0.00
  5   0.00   0.00        22   0.00   0.00        39   0.00   0.00
  6   0.00   0.00        23   0.00   0.00        40   0.00   0.00
  7   0.00   0.00        24   0.00   0.00        41   0.00   0.00
  8   0.00   0.00        25   0.00   0.00        42   0.00   0.00
  9   0.00   0.00        26   0.00   0.00        43   0.00   0.00
 10   0.00   0.00        27   0.00   0.00        44   0.00   0.00
 11   0.00   0.00        28   0.00   0.00        45   0.00   0.00
 12   0.00   0.00        29   0.00   0.00        46   0.00   0.00
 13   0.00   0.00        30   0.00   0.00        47   0.00   0.00
 14   0.00   0.00        31   0.00   0.00        48   0.00   0.00
 15   0.00   0.00        32   0.00   0.00        49   0.00   0.00
 16   0.00   0.00        33   0.00   0.00        50   0.00   0.00
 17   0.00   0.00        34   0.00   0.00        51   0.00   0.00

Balance number:  50   Press return to Exit:
```

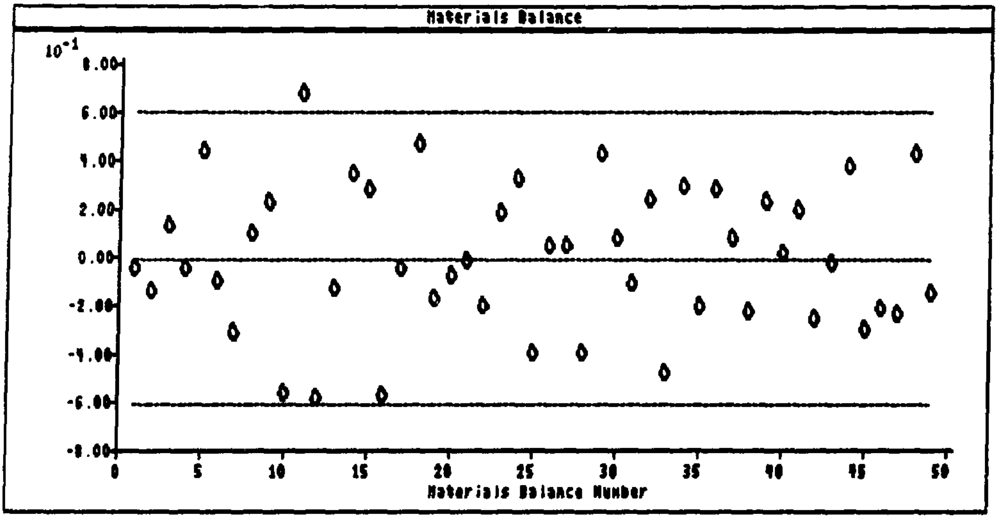

Fig. 2.
Materials balance chart for scenario with "no diversion."*

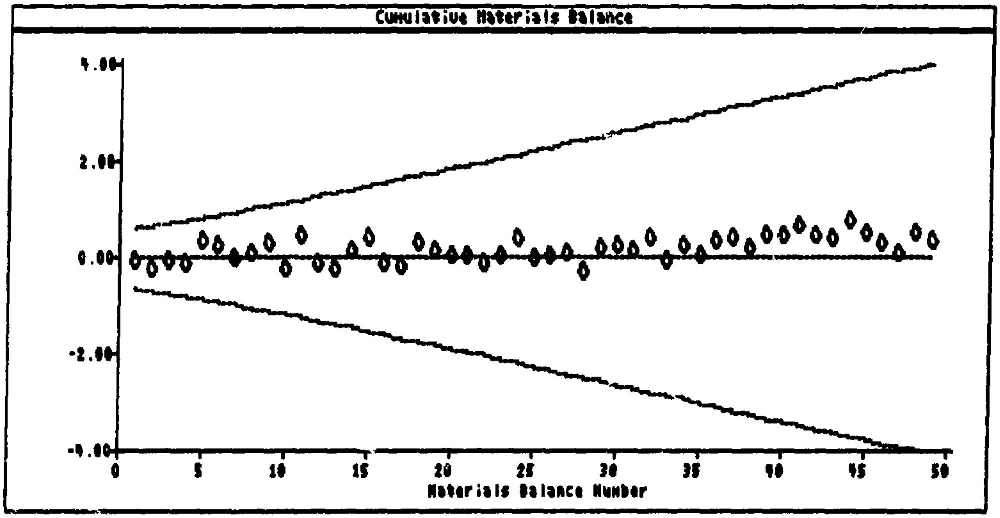

Fig. 3.
Cumulative materials balance chart for scenario with "no diversion."

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*Figures 2-17 are screen images.

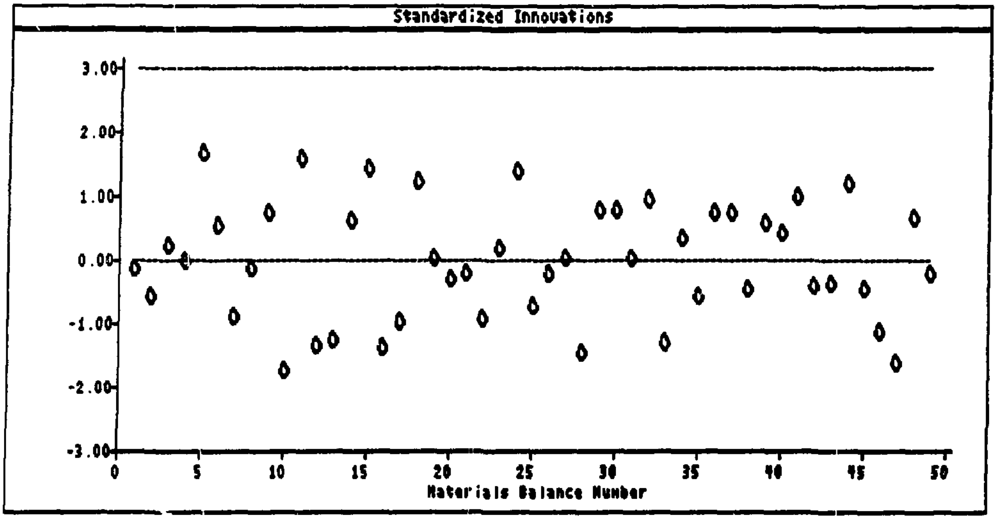

Fig. 4.
Standardized innovations chart for scenario with "no diversion."

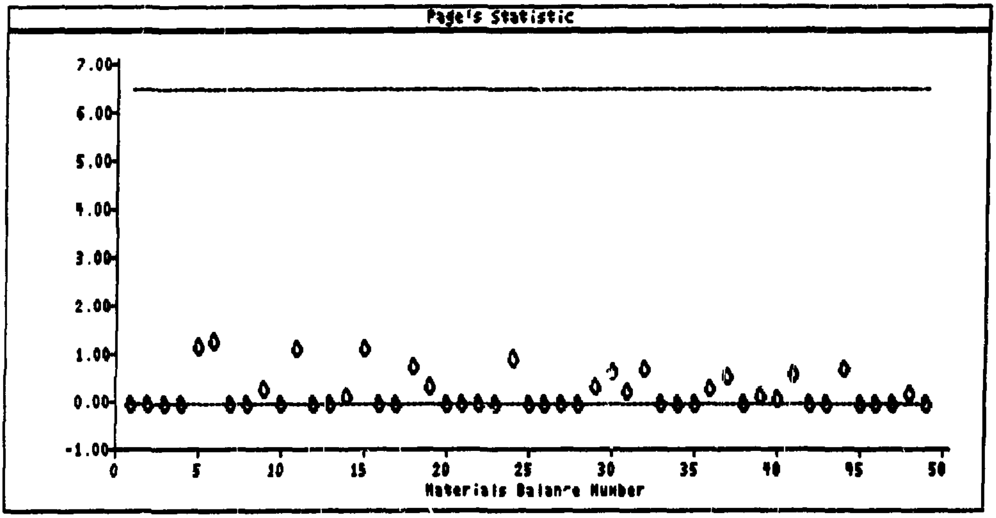

Fig. 5.
Page's chart for scenario with "no diversion."

In the first chart (Fig. 2), sequential materials balances are plotted. Because there is no diversion, these balances fluctuate around zero with a standard deviation equal to the balance deviation of 0.3 kg for the errors, as stated in Sec. III. To aid in interpretation, control limits of twice the balance standard deviation are also plotted as dashed lines to indicate the limit of error.

In the second chart (Fig. 3), cumulative materials balances--that is, the sum of the sequential balances from the first to the last--are plotted. Again, the control limit is plotted, and note that this quantity increases with balance number.

In the third chart (Fig. 4), the standardized innovations are plotted. Loosely speaking, an "innovation" is the difference between a materials balance and its prediction based on

(1) all previously observed materials balances,

(2) error propagation information, and

(3) an assumption of no diversion.

To (over)simplify, the standardized innovations should behave, in the absence of diversion, as "white noise" or a sequence of independent values with each having a mean of zero and standard deviation of one.

In the fourth chart (Fig. 5), the Page's statistic is plotted. The Page's statistic is a type of cusum, is always nonnegative, and should remain within the plotted control limit. The control limit is calibrated to a 1% false-alarm rate for a 50-balance monitoring period.

Chapter V (Statistical Decisions) contains additional discussion on Figs. 4 and 5, with references to relevant safeguards literature.

V. RTMAS EXECUTION

The simulator is executed by typing RTMAS followed by a RETURN.

The copyright disclosure is the first screen; press RETURN to continue.

Next, the Main Options Menu appears on the screen as follows:

```
                         OPTIONS

             0 - Exit
             1 - Recalibrate/Replace Instruments
             2 - Divert Material
             3 - Inspect Charts


             Enter option:
```

Option 0 will exit the simulation, returning the user to the computer's operating system.

Option 1 allows the user to recalibrate or replace the measurement instruments. If replacement is chosen, the user can specify new values of the error terms from those initialized, as stated in Sec. III. The instruments can be changed at the start of a computer run to simulate a different process tank, or they can be recalibrated or replaced during the run. Any changes are reflected in the control limits plotted on the evaluation charts.

Option 2 is used to divert material. The user, who is presented with a Diversion Summary screen giving the balance numbers, amount diverted during that balance period, and the cumulative amount of material diverted from the start through that balance period, requests an additional amount to divert for the current period. An incomplete example of this screen with diversion is given in Table II. The charts for this partial example are shown in Figs. 6-9.

TABLE II

DIVERSION SUMMARY FOR SCENARIO WITH "DIVERSION"

```
Bal   Div    Acc         Bal   Div   Acc         Bal   Div   Acc

  1   0.00   0.00
  2   0.10   0.10
  3   0.20   0.30
  4   0.30   0.60
  5   0.40   1.00
  6   0.30   1.30
  7   0.20   1.50
  8   0.10   1.60
  9   0.00   1.60
 10  -0.40   1.20

Balance number:  1    Enter amount to divert or press return to Exit:
```

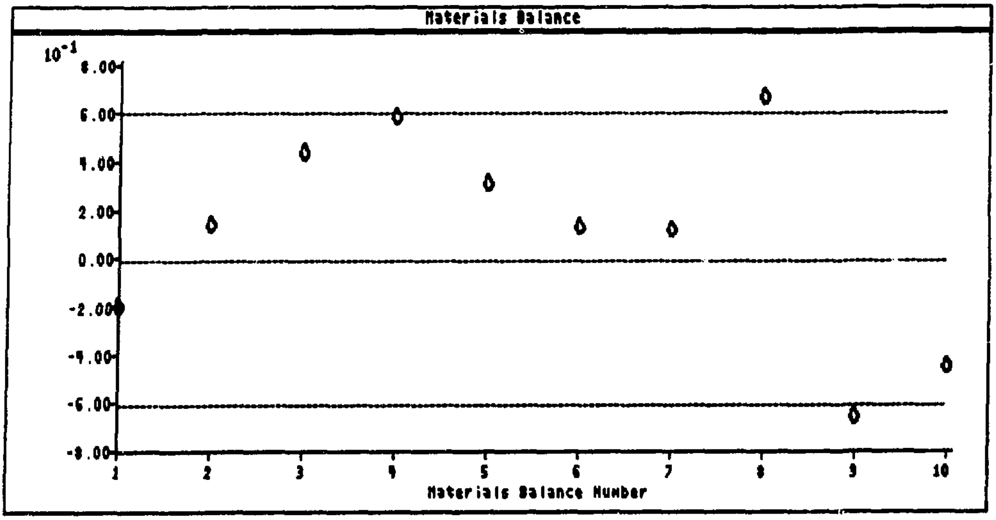

Fig. 6.
Materials balance chart for scenario with "diversion."

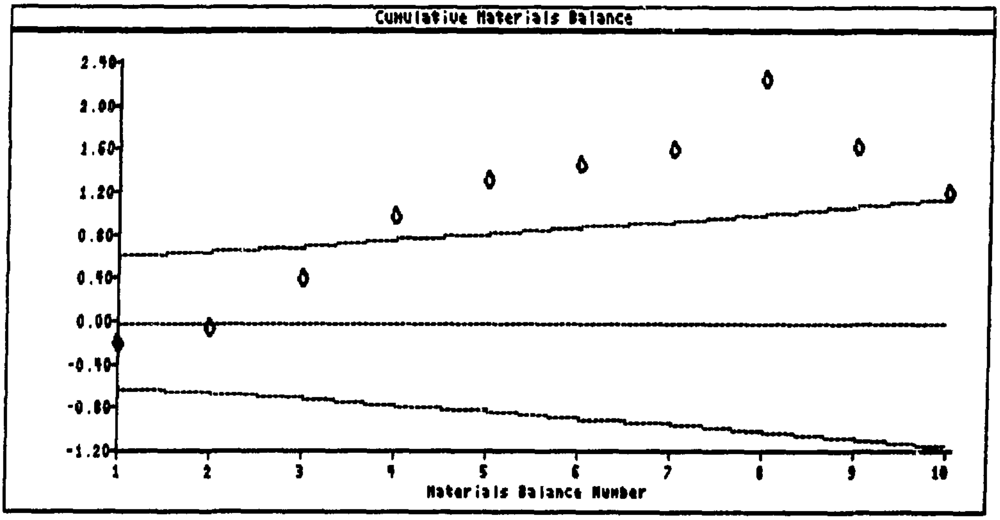

Fig. 7.
Cumulative materials balance chart for scenario with "diversion."

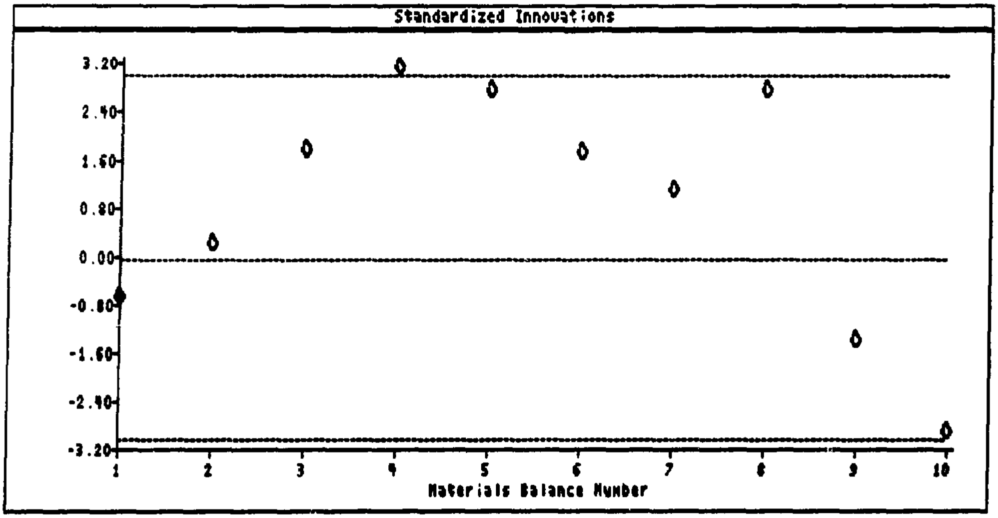

Fig. 8.
Standardized innovations chart for scenario with "diversion."

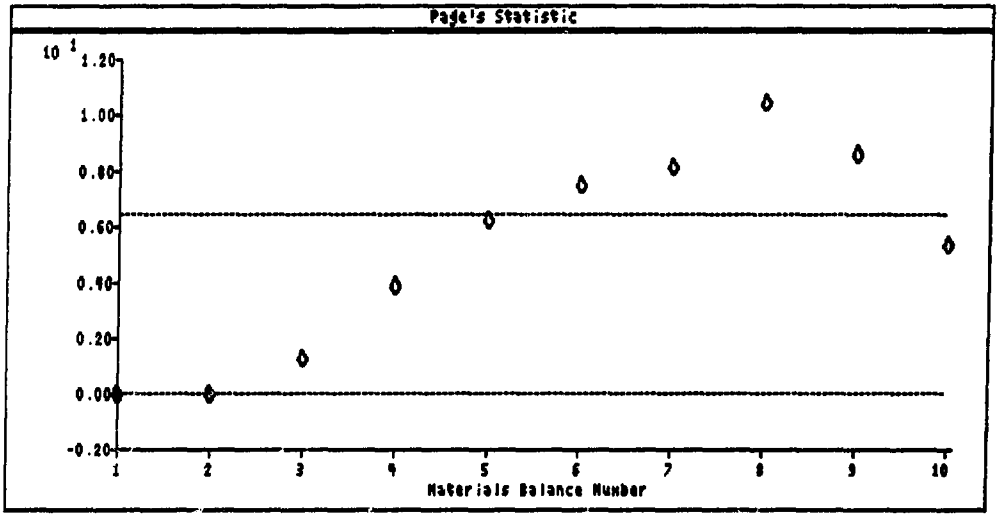

Fig. 9.
Page's chart for scenario with "diversion."

The units of the diversion are kilograms for the given process. Note that diversion can be negative--putting material into the process. The simulator will allow up to 50 balances. After any number of balances, the user can press return without entering a diversion amount, and the simulator will return to the Main Options Menu.

Option 3 is used to inspect the control charts produced by the evaluation procedures. When this option is chosen, the screen is cleared and the message "Please wait" is displayed at the bottom. While this message is on the screen, the program is calculating the evaluation procedure results. This may take only a few seconds if the results are requested after a few balance periods. If the results are being calculated for the full 50 balances, the delay to calculate the standardized innovations and the Page's statistics from the 50 x 50 covariance matrix may be up to a minute, depending on the computer being used. After this delay, a Chart-Choice Menu is presented to the user as follows:

```
                    CHART CHOICES

              0 - Exit to Main Menu

              1 - Materials Balance

              2 - Cumulative Materials Balance

              3 - Standardized Innovations

              4 - Page's Statistic


              Enter choice:
```

Choice 0 returns the user to the Main Menu so that more diversion can take place, or the user can exit the simulation.

Choices 1-4 produce the control charts described in Sec. IV.

After examining a chart, the user obtains a print of the chart by pressing the "p" key if the attached printer is Epson FX-80 or compatible. Pressing any other key returns the user to the Chart-Choice Menu directly without printing the chart.

VI. DIVERSION SCENARIOS

In addition to the examples given above, two diversion scenarios were run and are included here. A diversion scenario having "0.1 kg uniform diversion" of material removed during each of the 50 balances is shown in Table III, and the charts are shown in Figs. 10-13. A diversion scenario having "1.0 kg periodic diversion" of material removed every 10th balance is shown in Table IV, and the charts are shown in Figs. 14-17.

TABLE III

DIVERSION SUMMARY FOR SCENARIO WITH "0.1 kg UNIFORM DIVERSION"

Bal	Div	Acc	Bal	Div	Acc	Bal	Div	Acc
1	0.10	0.10	18	0.10	1.80	35	0.10	3.50
2	0.10	0.20	19	0.10	1.00	36	0.10	3.60
3	0.10	0.30	20	0.10	2.00	37	0.10	3.70
4	0.10	0.40	21	0.10	2.10	38	0.10	3.80
5	0.10	0.50	22	0.10	2.20	39	0.10	3.90
6	0.10	0.60	23	0.10	2.30	40	0.10	4.00
7	0.10	0.70	24	0.10	2.40	41	0.10	4.10
8	0.10	0.80	25	0.10	2.50	42	0.10	4.20
9	0.10	0.90	26	0.10	2.60	43	0.10	4.30
10	0.10	1.00	27	0.10	2.70	44	0.10	4.40
11	0.10	1.10	28	0.10	2.80	45	0.10	4.50
12	0.10	1.20	29	0.10	2.90	46	0.10	4.60
13	0.10	1.30	30	0.10	3.00	47	0.10	4.70
14	0.10	1.40	31	0.10	3.10	48	0.10	4.80
15	0.10	1.50	32	0.10	3.20	49	0.10	4.90
16	0.10	1.60	33	0.10	3.30	50	0.10	5.00
17	0.10	1.70	34	0.10	3.40			

Balance number: 50 Press return to Exit:

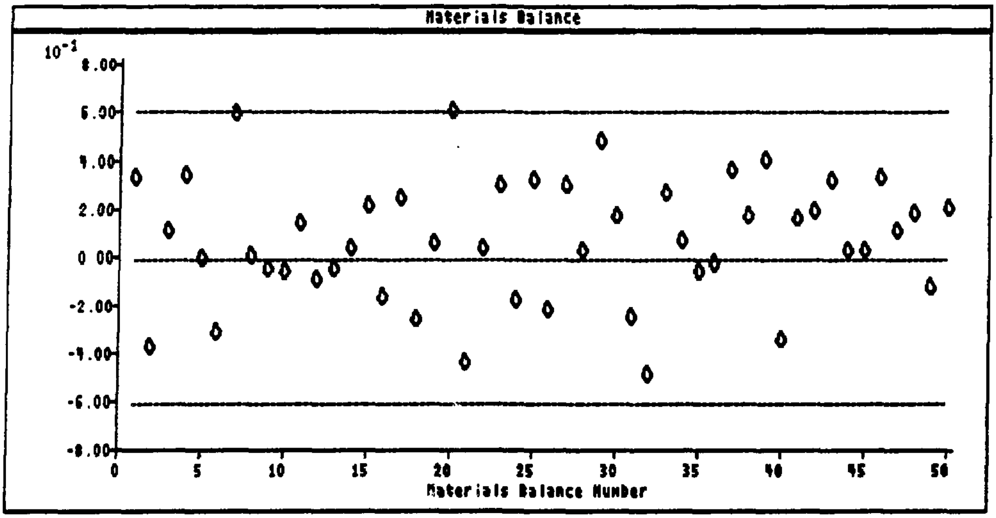

Fig. 10.
Materials balance chart for scenario with
"0.1 kg uniform diversion."

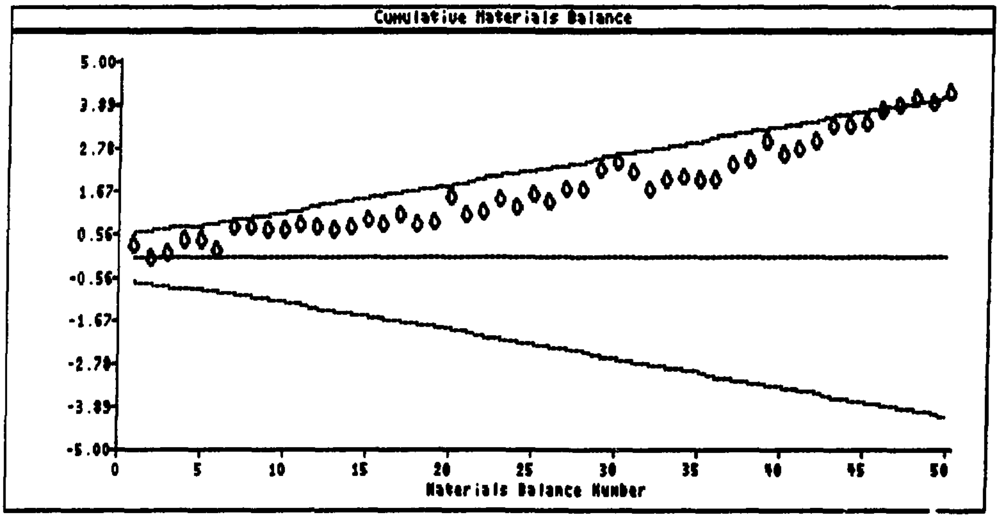

Fig. 11.
Cumulative materials balance chart for scenario with
"0.1 kg uniform diversion."

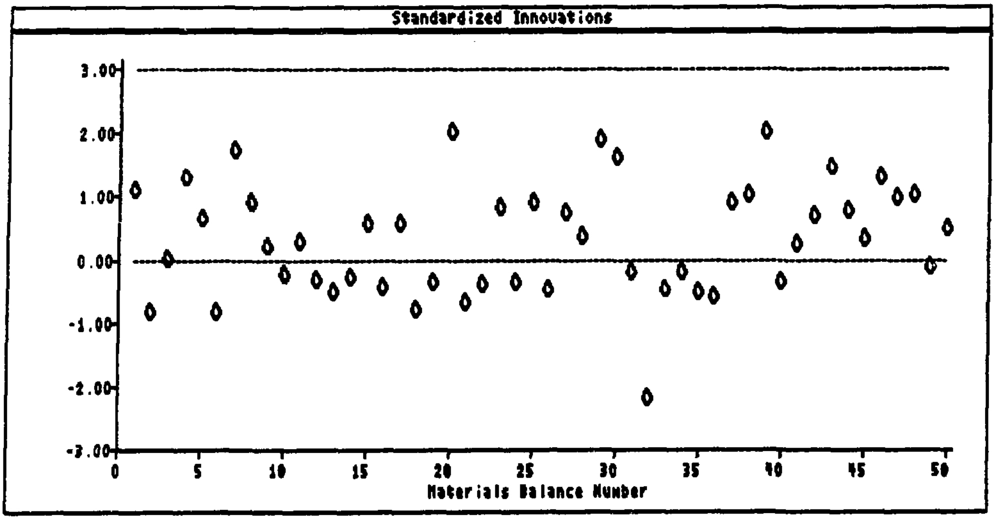

Fig. 12.
Standardized innovations chart for scenario with "0.1 kg uniform diversion."

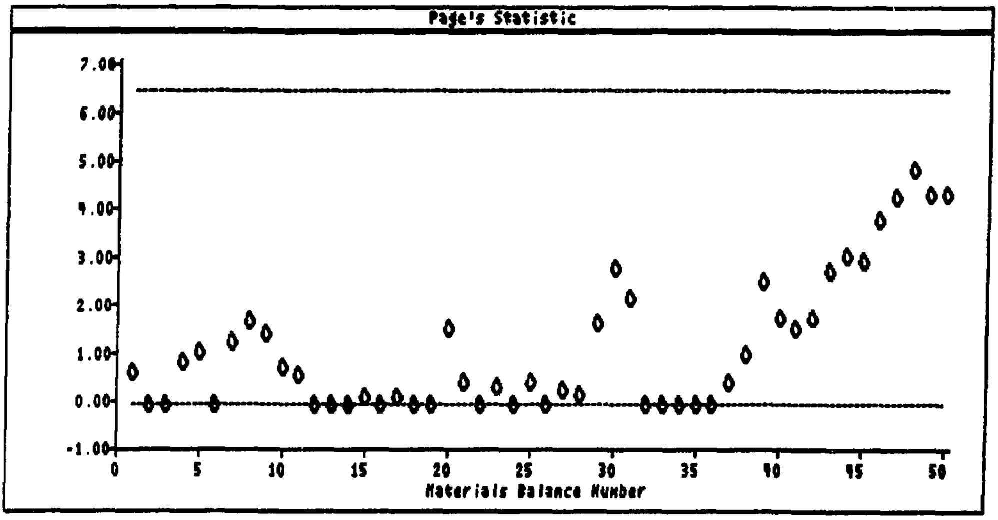

Fig. 13.
Page's chart for scenario with "0.1 kg uniform diversion."

TABLE IV

DIVERSION SUMMARY FOR SCENARIO WITH "1.0 kg PERIODIC DIVERSION"

```
    Bal   Div    Acc        Bal   Div    Acc        Bal   Div   Acc

 1 0.00  0.00    18        0.00  1.00    35        0.00  3.00
 2 0.00  0.00    19        0.00  1.00    36        0.00  3.00
 3 0.00  0.00    20        1.00  2.00    37        0.00  3.00
 4 0.00  0.00    21        0.00  2.00    38        0.00  3.00
 5 0.00  0.00    22        0.00  2.00    39        0.00  3.00
 6 0.00  0.00    23        0.00  2.00    40        1.00  4.00
 7 0.00  0.00    24        0.00  2.00    41        0.00  4.00
 8 0.00  0.00    25        0.00  2.00    42        0.00  4.00
 9 0.00  0.00    26        0.00  2.00    43        0.00  4.00
10 1.00  1.00    27        0.00  2.00    44        0.00  4.00
11 0.00  1.00    28        0.00  2.00    45        0.00  4.00
12 0.00  1.00    29        0.00  2.00    46        0.00  4.00
13 0.00  1.00    30        1.00  3.00    47        0.00  4.00
14 0.00  1.00    31        0.00  3.00    48        0.00  4.00
15 0.00  1.00    32        0.00  3.00    49        0.00  4.00
16 0.00  1.00    33        0.00  3.00    50        1.00  5.00
17 0.00  1.00    34        0.00  3.00

Balance number:  50   Press return to Exit:
```

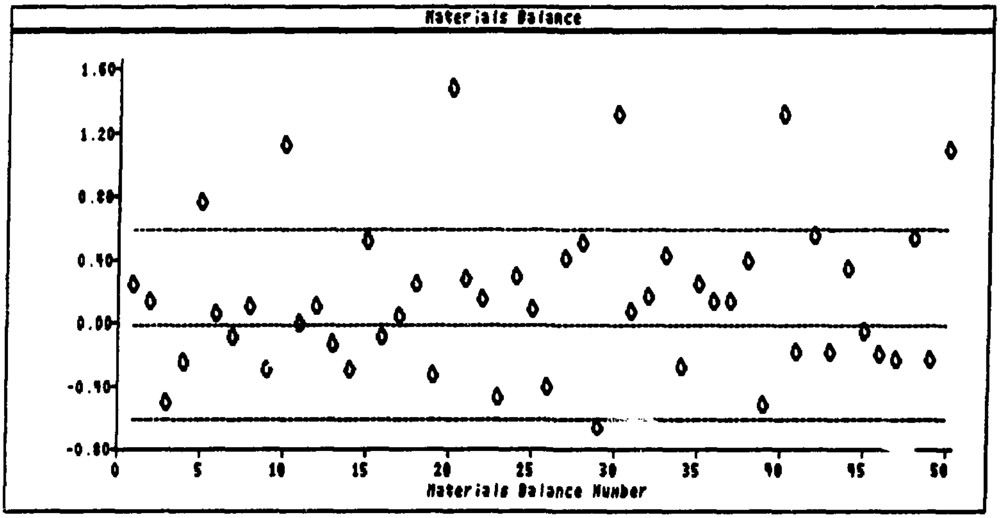

Fig. 14.
Materials balance chart for scenario with "1.0 kg periodic diversion."

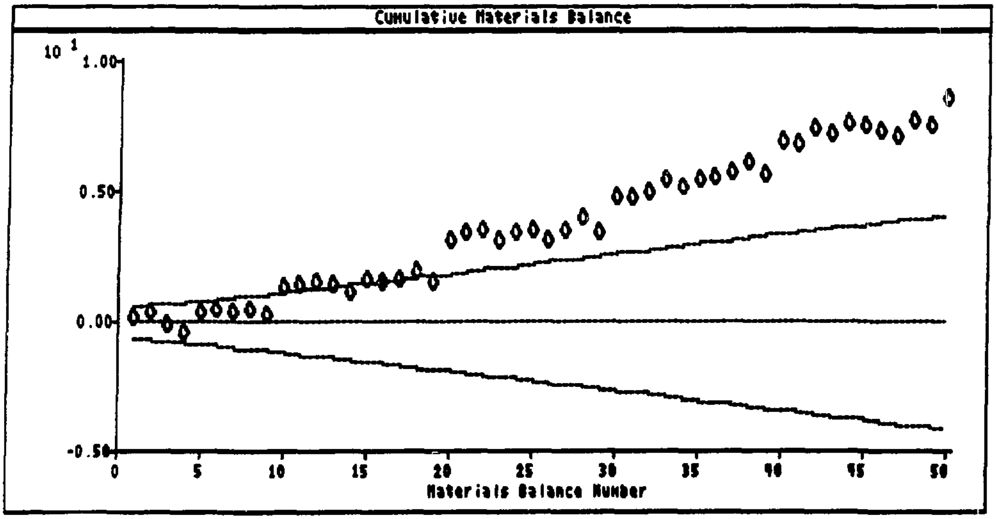

Fig. 15.
Cumulative materials balance chart for scenario with "1.0 kg periodic diversion."

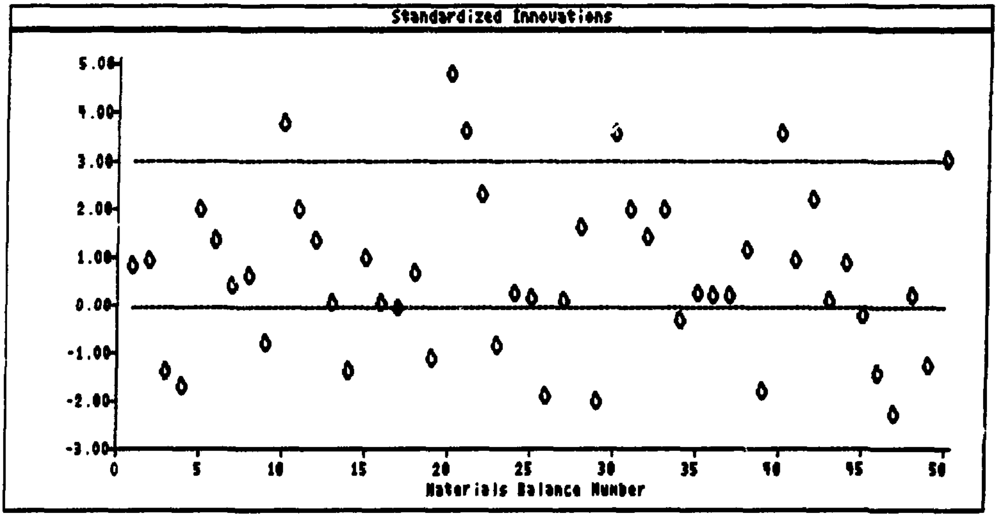

Fig. 16.
Standardized innovations chart for scenario with "1.0 kg periodic diversion."

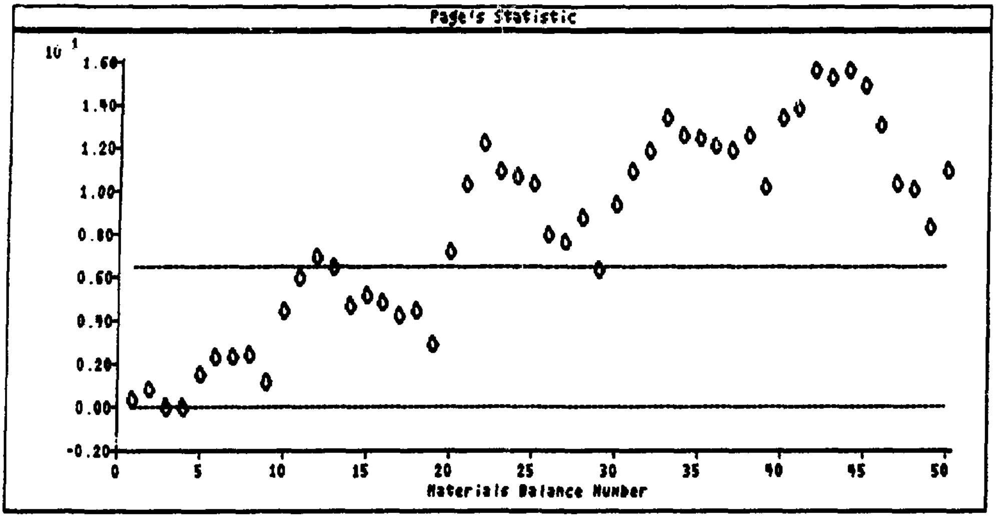

Fig. 17.
Page's chart for scenario with "1.0 kg periodic diversion."

ABOUT THE AUTHORS

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CHAPTER XVI

WORKSHOP ON MATERIALS CONTROL AND ACCOUNTING SYSTEM DESIGN

by

K. K. S. Pillay

I. INTRODUCTION

The purpose of this workshop is to reinforce, through participation in the design exercise, the concepts of nuclear materials control and accountability (MC&A) discussed during this course. Participants are given an opportunity to design the main features of a materials control and accounting system. The information presented during class sessions (and in other workshops) of this course may be used to develop an optimal system design. As safeguards measures, materials control and material accounting merge because both are essential components of an integrated safeguards system.

Materials control scrutinizes facility personnel in their access to, use of, and transfer of nuclear materials while monitoring the status of materials to prevent losses or to detect losses when they occur.

Materials accounting maintains knowledge of the quantities and locations of nuclear materials and provides for physical inventories and materials balances to verify the presence of materials or to detect losses after they occur.

II. WORKSHOP FORMAT

- The workshop begins with an introductory lecture complementing the information and data presented in this chapter.
- An overview of the example facility (a Plutonium Metal Button Production Plant) is part of the initial presentation. Figure 1 shows an abbreviated schematic of the process operations at the example facility. Additional details of the facility are given in the Appendix.

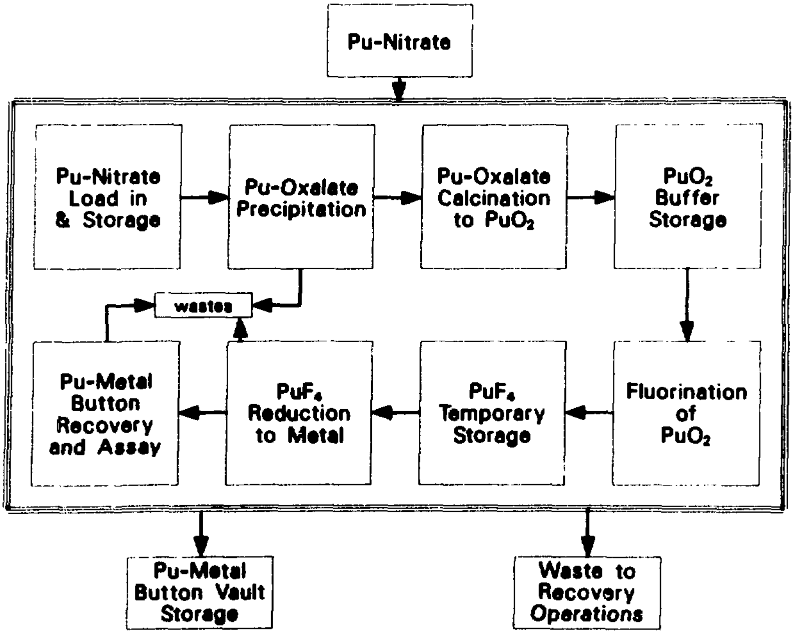


Fig. 1.
Process flow diagram for the example plant.

- Participants of this workshop are divided into two working groups; each group independently develops an outline of the key features it recommends for a MC&A system for the example facility.
- Several members of the course staff are available for consultation during the design exercise period.
- **A <u>rapporteur</u>, chosen by each group, presents its design to the entire class for open discussion.**
- Materials to prepare vugraphs are available.

During this exercise, the workshop participants are to identify and briefly describe features they would design into a MC&A system to facilitate the implementation of safeguards at the example facility described in detail in the Appendix of this chapter. Assume that the relevant regulatory agency will require

(a) conducting record audits,
(b) verifying receipts and shipments,
(c) reporting flows and inventories,
(d) verifying flow and inventory measurements, and
(e) closing material balances and estimating inventory differences (IDs) and the limit of error of inventory differences (LEIDs).

III. KEY ELEMENTS OF A MC&A SYSTEM

The primary objective of the MC&A system of an operator is to contribute to the timely detection of possible losses, unauthorized use, or removal of SNM. The MC&A system provides the basis for the application of national safeguards according to prevailing regulatory requirements. At the facility level, the functional and structural elements of a MC&A system are the following:

(1) Safeguards organization and management,
(2) Material access areas,
(3) Key measurement points,
(4) Nuclear materials measurements,
(5) Physical inventory,
(6) Materials balance closings,
(7) Internal controls,
*(8) Inspection and audits, and
*(9) Statistical analyses to determine SNM losses.

The workshop participants are to consider each of the first seven topics listed above in preparing and presenting a brief outline of features of the MC&A system they recommend for the example facility. Because of time limitations, the last two topics (marked with *) are included as Additional Work in Sec. V. Nondestructive assay techniques, variance propagation to determine LEIDs, real-time materials accounting simulation, and statistical approaches to measurement control and diversion detection are topics covered in other workshops included in this course.

To aid you in outline preparation of a materials control and accounting system, the first seven of the nine key elements listed above are briefly discussed below. The additional information in the Appendix may also help you with your discussions and decisions. Worksheets for outlining are available.

(NOTE: There may be more than one correct response to many of the questions you have to answer during this exercise. Use your best judgment, and be prepared to defend your response during discussions.)

IV. MC&A SYSTEM DESIGN TOPICS

A. Safeguards Organization and Management

The safeguards organization and management includes a structured approach to planning, coordination, and administration of nuclear material control and accounting activities with responsibility for distinct functions delegated to one individual or organization (see Tables Ia and Ib.)

- **Prepare an organizational chart, and show the structural and functional responsibilities of nuclear materials management at the example facility.**
- **Identify custodial, accounting, auditing, measuring, quality assurance, and security functions. (Note that some of these functions should be in different organizational components.)**

TABLE Ia

SAFEGUARDS ORGANIZATION AND MANAGEMENT

Topics to Consider	Details to Discuss
Organization chart[a]	Titles and functions (examine possible conflicts)
Procedures (safeguards manual)	Who develops and maintains the procedures manual?
Nuclear material custodian	Responsibilities and reporting channels
S/R[b] difference resolution	Actions required in case of suspected losses
Materials balance discrepancies	Who takes corrective actions?
Interface with regulators	Who? Why?
New and necessary functions	....

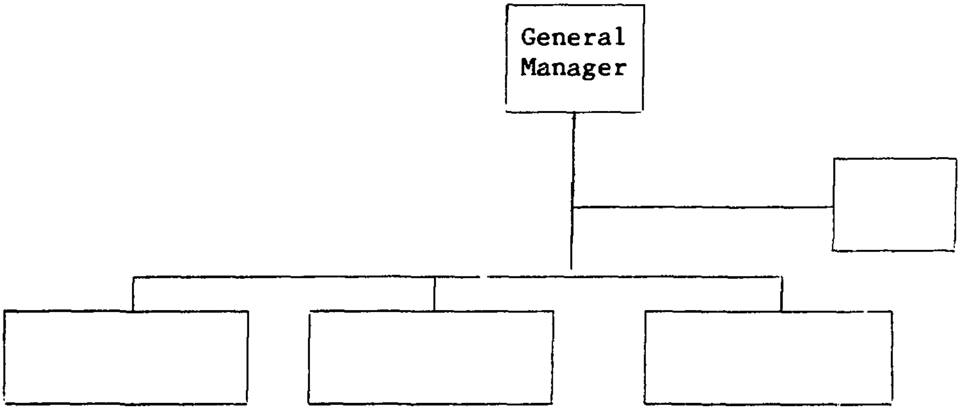
---

[a] Consult Table Ib.

[b] Shipper/receiver.

TABLE Ib

STRUCTURE AND FUNCTIONAL RESPONSIBILITIES OF NUCLEAR MATERIALS MANAGEMENT



- Policy
- Guidance[b]
- ......

- NM management[a]
- Safeguards accountability
- Integration[b]
- ....
- ....

- NM production
- Process eng.
- Manufacturing
- Quality assurance
- Analytical labs

- Technical support
- Central storage
- NM transfers
- Security
- NM custodian

---

[a] Nuclear material.

[b] You may consider other functional responsibilities.

B. Material Access Areas

For materials control and accounting purposes, a nuclear material production plant is divided into materials balance areas (MBAs) and item control areas (ICAs). A MBA is defined such that all movement of material into and out of the area and periodic inventories of materials within the area are measured and recorded. All transfers into and out of the MBAs are performed through key measurement points (KMPs). In an item control area (ICA), nuclear material is contained in identifiable items during its entire residence at this location. An item usually requires a tamper-indicating device (TID), and ICAs require a program of verifying the integrity of TIDs during transfers and inventories (see Table II).

TABLE II

MATERIAL ACCESS AREA

Topic to Consider	Detail to Discuss
MBA	Number, boundaries, logic of assignment
ICAs	Number, boundaries, logic of assignment
Material types	In process areas and in storage
Waste streams	Location at the time of MB closing
Acess controls	Administrative and other

- **Select the MBA structure that best represents the consensus of your group. Consider a single MBA for the entire facility; two parallel production lines and two MBAs; one production line and two MBAs; plutonium nitrate to PuO_2 (one MBA) and PuO_2 to plutonium (the other MBA); three MBAs (one each—feed, product, and process); or any other (describe).**
- **Show the boundaries of MBAs and ICAs on a copy of Fig. 1.**

C. Key Measurement Points

Key measurement points (KMPs) are strategic locations where nuclear material appears in a measurable form that allows determination of the material flow or inventory. The KMPs thus include input, output, and storage in MBAs. Table III shows the flow and inventories of nuclear materials during material balance periods.

- **Identify on a process flow diagram (a copy of Fig. 1) each KMP.**
- **Identify the types of measurements made at each KMP (for example, volume, weight, sampling, chemical analysis, or NDA).**

TABLE III

FLOW AND INVENTORY OF PLUTONIUM (Pu) DURING ONE MATERIAL BALANCE PERIOD

KMP	Item	Item No.	Total Pu (kg)
Input	Pu nitrate solution	200	360
Output	Pu button	100	200
	Liquid waste	20[b]	4
	Waste barrel	40	2
	Salt (can)	20	10
	Filters	10	2
Inventory[a]	Pu nitrate	50	90
	PuO_2	20[b]	20
	PuF_4	10	10
	Pu button	5	10
	Liquid waste	1	0.2
	Waste barrel	10	0.5
	Salt (can)	18	9.0
	Holdup	-	2.0

---

[a] These quantities present at both beginning and ending inventory.

[b] One thousand liters each.

D. Nuclear Materials Measurements

Nuclear materials accounting requires the establishment and maintenance of a measurement system to determine the quantities of nuclear material received, produced, shipped, stored or otherwise removed from inventory. An essential element of a good nuclear materials measurement system is a program to control the quality of those measurements. A measurement control strategy is necessary to determine and control random and systematic errors of all instruments and analytical methods used in materials accounting. Table IVa identifies various material types and lists measurement methods for materials accounting at the example facility.

- **List the types of materials present and specify the measurement method you would use at each KMP. Several independent measurement methods can adequately meet the needs of safeguards measurement. Facility-specific decisions are made depending on the local resources, laboratory facilities, and personnel. You may develop an alternative measurement scheme.**

TABLE IVa

MEASUREMENT METHODS

Material Type	Required Value	Measurement Method
Plutonium nitrate solution	Total plutonium	Potentiometric titration
	Plutonium isotopics	Mass spectrometry
	Volume	Sight gauge
	Weight	Electronic balance
Plutonium oxide	Weight	Electronic balance
	Isotopics	Gamma spectrometry/ mass spectrometry
	Plutonium content	Controlled-potential coulometry/neutron counting
Plutonium metal button	Weight	Electronic balance
	Plutonium content	Calorimetry/neutron counting
	Isotopics	Mass spectrometry
Liquid waste	Plutonium content	Titration
	Volume	Liquid-level method
Solid waste	Plutonium content	Passive neutron counting/ segmented gamma-ray scan

- **Consult Table IVb on measurement control and decide (a) the frequency of calibration and recertification of standards and (b) the data-analysis method for measurement control. Select elements that best represent the consensus of the group.**

TABLE IVb

ELEMENTS OF MEASUREMENT CONTROL PROGRAM

Topic to Consider	Possible Decision
Frequency of measuring	
Standard weights	One/day
Chemical standards	Once/analysis
Mass spectrometer	Never
NDA intruments	During equinox
Calorimetry	During winter months
Frequency of other activities	
Replicate analysis	....
Recalibration of instruments	....
Recertification of standards	....
Analysis for measurement control	Control charts for bias/ precision
	Sequential tests for shifts in the mean
	Other
Standards traceable to	
National measurement system	
National Institute of Standards and Technology	
Working secondary standards	
Production material standards	
Euratom (Geel, Belgium) standards	
Other	

E. Physical Inventory

Physical inventory is the bench mark of nuclear materials accounting and control. It is the sum of all the measured or derived estimates of batch quantities of SNM on hand at a given time within a MBA or an ICA obtained in accordance with established procedures. Table III provides average quantities of various forms of materials at materials balance closings.

- **Discuss topics relevant to physical inventory listed in Table V and develop a set of recommended procedures for taking a physical inventory. Also examine the Appendix and design a strategy for developing a physical inventory of the SNM in the plant and for physical inventory verification.**

TABLE V

PHYSICAL INVENTORY

Topic to Consider	Detail to Discuss
Approach	Cleanout inventory All material converted into measurable form
Strategy	A sampling plan Measure all material
Schedule	Once every month, other
Organization	Two-party team of accounting and custodial personnel
Source data	Book inventory of any prelisted item
Current measurement	Materials in measurable form
Prior measurement	Only tamper-safed item accepted on the basis of prior measurement
Residual holdup	Estimated by a predetermined model
Procedure	Written manual

F. Materials Balance Closings

Facility management conducts periodic material balance closings based on measurements to evaluate inventory differences (IDs). This requires taking a physical inventory and gathering records of receipts, inventory, disposal, and transfer of SNM. Material balances based on physical inventory and known uncertainties of measurements permits meaningful evaluation of undetected material losses. Table VI lists a typical 1-month materials balance for the example facility.

- **Consider the topics in Table VI and list the data required for materials balance closings at the example facility. Resolution of shipper/receiver difference, which is an important MC&A topic, requires participation of people outside the plant. For the purposes of this workshop, you may choose to assume that S/R differences are reconciled. Examples in Table VI are only suggestions. You may develop your own design and consider any additional relevant topics.**

TABLE VI

MATERIALS BALANCE CLOSING

Topic to Consider	Possible Decision
Accounting system	Double-entry computer-based bookkeeping
Account structure	Accounts based on Plant location MBAs & ICAs Material type
Source data	All transfers & inventories
Frequency of MB closing	Once a month
Bias adjustment	Separate account Hidden account
Account reconciliation	All accounts reconciled to Physical inventory Book inventory
Internal audit	Number, frequency, etc.
Record & report	Maintained for ... years

- **Write a materials balance equation and describe all the relevant terms of this equation.**

G. Internal Controls

Most activities of MC&A and management follow the policies and procedures of the facility. Implementation of these policies and procedures requires internal controls. In addition to materials accounting, the facility operator needs data on material flow through the facility to control criticality and materials and protect health and safety. It is possible to design internal controls that satisfy all these needs.

- **Discuss the topics listed in Table VII and list the internal control you recommend for the MC&A system, recognizing all the needs of the facility operator. The examples are suggestions only. Choose any design you think appropriate for your MC&A system, adding any suitable topics.**

TABLE VII

INTERNAL CONTROL

Topic to Consider	Possible Decision
Receiving procedure	Approved container with seal by designated custodian only
S/R comparison	Item verification within 24 h
Acceptance criterion	Individual item basis (with no anomaly)
Transfer condition	Plutonium metal button in sealed can transferred after verification by designated custodian only
Internal storage	Separate vault storage for plutonium-nitrate shipping container & plutonium metal button cans
Item identification	Unique bar-code identification
Tamper-safing	Tamper-indicating seals, bar-coded container, & computer logs
Scrap & waste control	By location, waste form, and measurement

V. ADDITIONAL WORK (Optional)

(NOTE: If time permits, the following topics may be discussed during the workshop design exercise after completing discussions on all other key elements of the MC&A system.)

- The design of a MC&A system should incorporate a system of inspection and audits to meet both facility safeguards requirements and regulatory requirements.
- Evaluating the diversion sensitivity of a MC&A system usually requires a quantitative assessment using
  (1) a propagation of measurement errors for inventories and transfers to estimate LEID for each MBA,
  (2) an estimation of the sigma of the ID for the measurement system for the plant material balance shown in Table A-I,
  (3) an analysis of the extent to which IDs can be localized, and
  (4) an estimate of the minimum and maximum time in which the loss of a discrete item can be detected.

APPENDIX

AN EXAMPLE PROCESS FOR DESIGNING A MATERIALS CONTROL AND ACCOUNTING SYSTEM

(Plutonium Metal Button Production)

I. INTRODUCTION

The objectives of this chapter are to describe in detail a facility that produces metallic plutonium and the safeguards requirements for this facility. This example facility is used during the workshop on materials control and accounting (MC&A) system design. Plants in the U.S. and in other countries use some or all of the aspects of the process described here to produce metallic plutonium. The physical plant layout of our example plutonium plant is shown in Fig. A-1, and the processes are described in Sec. III of this Appendix.

Designing a MC&A system requires the following:

(1) physical plant layout,

(2) data-gathering methods, and

(3) data-analysis methods to reach safeguards conclusions.

The layout of our plutonium plant and process lends itself to several options for MC&A purposes. The methods of gathering data for MC&A are topics of discussion in other chapters of this manual, as are aspects of the analyses required to reach safeguards conclusions.

II. PROCESS OUTLINE

The plutonium metal production facility (see Fig. A-1) described here uses plutonium nitrate [$Pu(NO_3)_4$] as the feed material brought to this location from a reprocessing plant. The plutonium metal production facility initially produces plutonium oxide (PuO_2) from plutonium nitrate by calcining an intermediate plutonium oxalate. This is followed by converting the PuO_2 into plutonium fluoride (PuF_4) by reaction with gaseous hydrogen fluoride in a vibrating tube fluorinator. The PuF_4 powder is then reduced to plutonium metal using a mixture of metallic calcium and a

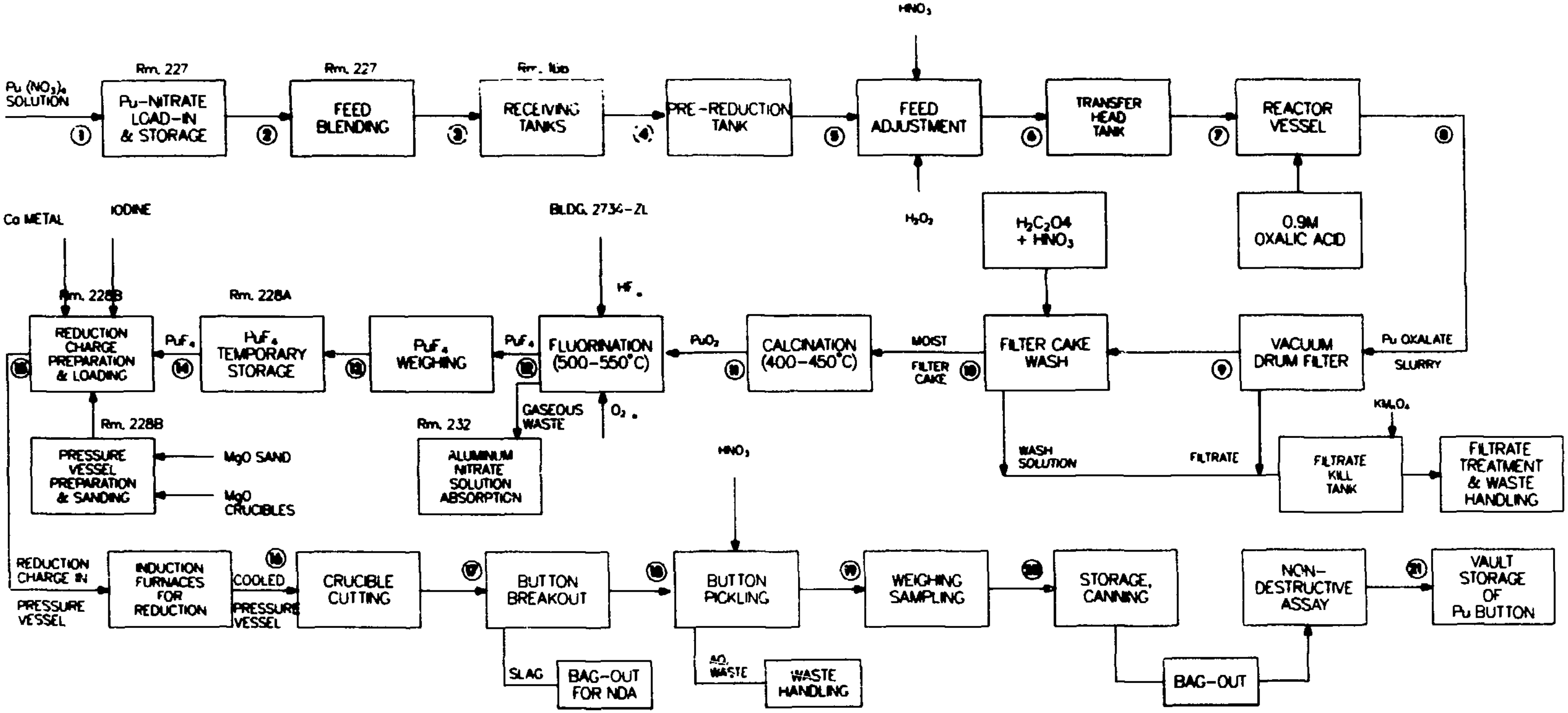


Fig. A-1.
Details of material flow within the example facility.

booster (elemental iodine). The plutonium metal buttons produced are pickled, sampled, weighed, and canned before shipment to a storage facility outside the plant. All operations take place in a continuous train of glove boxes.

III. PROCESS DETAILS

Details of some of the process steps relevant to understanding the operation of this facility and to designing a MC&A system for the facility operator (as in the workshop exercise) are briefly presented below.

A. Plutonium Nitrate Receiving

Plutonium nitrate is received in critically safe and tamper-indicating shipping containers. These are temporarily stored in special glove boxes in a secure area of the plant.

B. Feed Load-In

Plutonium nitrate solution from receiving/storage is loaded into receiver tanks. The outer containers of the plutonium nitrate bottles are grounded electrically and opened with nonsparking tools to prevent the ignition of radiolytic hydrogen. The contents of the bottle are vacuum transferred to a designated batch tank in a glove box. After the transfer, the containers are rinsed with a nitric acid solution, and the rinse solution is vacuum transferred to the batch tank.

C. Feed Blending

The contents of the batch tank are blended, and the solution is sampled for measuring plutonium content, acidity, and isotopics. This assay is used to control both process and criticality. Accountability measurements usually use a separate vial of solution, which has been previously analyzed by the shipper, and which accompanies the sealed container(s). The plutonium nitrate solution in the batch tank is vacuum transferred to a designated receiving tank after its acid content and plutonium concentration are adjusted. The plutonium nitrate solution is received in batches in the prereduction tank.

D. Oxalate Precipitation

The important chemical reactions that are relevant to precipitation of plutonium as oxalate are

$$PuO_2^{+2} + H_2O_2 + 2H^+ \rightarrow Pu^{+4} + O_2 + 2H_2O \qquad (A\text{-}1)$$

$$Pu(NO_3)_4 + H_2C_2O_4 \rightarrow Pu(C_2O_4)_2 + 4HNO_3 \qquad (A\text{-}2)$$

The first of these chemical reactions is used to reduce all Pu(VI) to Pu(IV). Before the valance adjustment, the acidity of the $Pu(NO_3)_4$ is adjusted so that the final concentration of the nitric acid in the reactor feed is about 6M. Following acidity adjustment, a predetermined quantity of approximately 15% hydrogen peroxide is added to the $Pu(NO_3)_4$ solution in the prereduction tank.

The feed-adjusted plutonium nitrate is then treated with a solution of oxalic acid, while agitated, to precipitate plutonium oxalate $[Pu(C_2O_4)_2 \cdot 6H_2O]$. This agitated mixture, in the form of a slurry, continuously overflows from the reactor vessel to a vacuum drum filter pan. The contents of this pan are subjected to a wig-wag agitator. The rotating drum picks up the plutonium oxalate precipitate in the form of a cake, which is washed with a solution of nitric and oxalic acids before it is scraped from the filter material with a doctor blade. The scraped plutonium oxalate is dropped into the chute of a screw calciner.

The filtrate from the vacuum drum filter and wash solution from the filter cake wash are transferred to a filtrate kill tank and treated with potassium permanganate to decompose the excess oxalic acid using the chemical reaction

$$2KMnO_4 + 5C_2H_2O_4 + 6HNO_3 \rightarrow 2KNO_3 + Mn(NO_3)_2 + 8H_2O + 10CO_2 \quad .$$

E. Plutonium Oxalate Calcination

The plutonium oxalate from the vacuum dry filter is dried and calcined in a screw calciner at a temperature of about 375°C. A measured air flow is allowed into the screw calciner to provide necessary oxygen for calcination. The overall calcination reaction is

$$Pu(C_2O_4)_2 \cdot 6H_2O + O_2 \rightarrow PuO_2 + 4CO_2 + 6H_2O \quad .$$

Cans of PuO_2 can be placed in buffer storage at this facility.

F. Fluorination

The next step of the process converts PuO_2 to PuF_4. The PuO_2 powder is allowed to drop through a rotary lock valve into a vibrating tube fluorinator located in a glove box. The temperature of the PuO_2 is maintained at 400°C and gaseous HF and O_2 are introduced simultaneously into the fluorinator tube at a controlled rate. The HF reacts with PuO_2 to form PuF_4 according to the reaction

$$PuO_2 + 4HF \rightarrow PuF_4 + 2H_2O \quad .$$

The PuF_4 is collected in polymethylmethacralate powder pans. These pans are weighed and placed in buffer storage in glove boxes in designated storage positions for criticality control.

G. Plutonium Tetrafluoride Reduction

The PuF_4 powder and any PuO_2 that was not fluorinated are reduced to metallic plutonium in a hermetically sealed pressure vessel placed inside an induction furnace. Metallic calcium is used as a reductant, and elemental iodine is used as a booster. A magnesia crucible acts as the reduction vessel. The crucible is placed inside a stainless steel pressure vessel, and the annular space is filled with dry magnesia sand. The reduction charge is prepared by mixing dry PuF_4 powder with calcium metal nodules and iodine booster in a mixer-dumper. The well-mixed reduction charge is loaded into the prepared magnesia crucible. The crucible is covered with a tantalum disk and secured in the pressure vessel. The pressure vessel is purged with argon gas before sealing. The sealed pressure vessel is heated slowly in an induction furnace. The charge is fired at about 750°C, and the temperature rapidly rises to about 2000°C. The PuF powder is reduced to molten plutonium and settles to the bottom of the crucible. The major high-temperature chemical reactions taking place within the pressure vessel relevant to plutonium metal production are

$$PuF_4 + 2Ca \rightarrow CaF_2 + Pu \quad ,$$

$$Ca + I_2 \rightarrow CaI_2 \quad , \text{ and}$$

$$PuO_2 + 2Ca \rightarrow 2CaO + Pu \quad .$$

These exothermic reactions lead to the rapid rise in temperature when the reaction is initiated. The iodine booster assists in increasing the heat of the reaction, in lowering the firing temperature of the reduction mixture, and in reducing the melting point of the slag.

H. Plutonium Metal Button Breakout

After reduction, the vent valve is opened, and the pressure vessel and its contents are allowed to cool. The cooled pressure vessel is opened, and the crucible is broken with a device having pneumatically actuated vibrating blades. The plutonium metal button is separated from the slag. The residual slag containing small quantities of plutonium is crushed, canned, and bagged out for recovery operations outside this plant.

I. Button Pickling, Sampling, and Storage

The plutonium metal button with surface contamination of residual slag materials is pickled (cleaned) in a dilute nitric acid solution, then rinsed with distilled water. The aqueous waste is transferred to a catch tank for further processing outside this facility. The plutonium metal button is weighed and sampled. Sampling consists of collecting small drill curls (1- to 2-g size) using a drill press in an argon environment. The drill curl is bagged out for analysis.

The clean plutonium metal buttons are temporarily stored before they are reweighed, individually canned, and sealed. The sealed cans are bagged out and placed in a second can. Tamper-indicating seals are applied to the outer can. The tamper-safe can containing the plutonium metal button is weighed before it is sent out of the facility to a storage vault.

J. Throughput and Inventories

This facility produces approximately 200 kg of plutonium metal buttons per month. The average material transfers and inventories of materials at various locations of this plant during monthly materials balance closings are shown in Table A-I. Between materials balance closings, the average inventory of plutonium at this location is about 300 kg.

K. Waste Handling

This facility produces a variety of solid and liquid wastes. The liquid wastes collected in catch tanks for temporary storage are periodically transferred via connecting pipe lines to a waste recovery facility. The catch tank contents are sampled for analysis both for materials accounting and safety.

Solid wastes in the form of slag from PuF_4 reduction are canned, assayed, and shipped to the waste recovery facility. Other forms of miscellaneous wastes are assayed for plutonium content and sent to burial or recovery operations, based on the discard level established by the facility.

IV. ELEMENTS OF SAFEGUARDS

Nuclear material safeguards is an integrated system of physical security and carefully designed administrative procedures. The administrative procedures necessarily include systems for accountability, detection, and materials control designed to deter, detect, and respond to unaccountable losses as well as unauthorized possession and/or misuse of nuclear materials. Basic concepts and a general overview of the materials accounting system are presented in Chap. I. No attempt is made here to review the aspects of MC&A so rigorously considered in other chapters. Some elementary, but important, aspects of MC&A applicable to the example process are briefly considered in the following paragraphs.

TABLE A-I

ONE-MONTH PLUTONIUM (Pu) MATERIALS BALANCE FOR THE MODEL PLANT[a]

KMP	Item	Item No.	Plutonium Concentration	Pu/Item (kg)	Total Pu (kg)
Input	Pu nitrate solution	200	300 g/L	1.8	360
Output	Pu button	100	99.9%	2.0	200
	Liquid waste	20[c]	200 ppm	0.2	4
	Waste barrel	40	-	0.05	2
	Salt (can)	20	-	0.5	10
	Filter	10	-	0.2	2
Inventory[b]	Pu nitrate	50	300 g/L	1.8	90
	PuO_2	20	88.2%	1.0	20
	PuF_4	10	75.9%	1.0	10
	Pu button	5	99.9%	2.0	10
	Liquid waste	1[c]	200 ppm	0.2	0.2
	Waste barrel	10	-	0.05	0.5
	Salt (can)	18	-	0.5	9.0
	Holdup	-	-	-	2.0

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[a] During materials balance closings, a planned shutdown of the plant can allow runout of materials in process and bring them to measurable form(s).

[b] These quantities present at both beginning and ending inventories.

[c] One thousand liters each.

A. Materials Accounting

Nuclear materials accounting is based on a system of measurements and reports that document the flow and disposition of special nuclear material (SNM). Inventory and transfer measurements and flow identification for process control and for materials accounting require a large number of measurements of varying quality. The actual number of measurement points for material flow and inventory measurements varies, depending on the facility, its process streams, and administrative controls.

Material balances can be drawn for this example process by suspending plant operations, cleaning the equipment, and measuring all the components of the in-process inventory. There are inherent limitations to this approach in sensitivity, timeliness, and localization of losses. The sensitivity is limited by measurement uncertainties that may conceal losses of significant quantities of material in large plants. The timeliness is limited by the frequency of physical inventories. The large size of the plant limits the ability to localize any losses. It is possible to improve the detection sensitivity and timeliness and to localize potential losses by implementing more timely materials accounting (or near-real-time materials accounting). This approach combines conventional analyses and measurements with on-line nondestructive assay (NDA) instrumentation to provide rapid and accurate assessment of the locations and amounts of nuclear material in a facility. Material balances may be drawn without suspending plant operations; in-process inventories are measured or otherwise estimated while the plant is operating, or balances may be drawn on small MBAs by timing closure when the equipment is empty.

To implement this approach, the plant is divided into several discrete accounting areas. Each accounting area includes one or more chemical or physical processes, chosen on the basis of process logic and the ability to draw a materials balance. By measuring all material flows and inventories in each area separately, quantities of material much smaller than the plant inventory are controlled on a timely basis; any discrepancies are localized to the portion of the process within the accounting area.

Near-real-time accounting is not a necessary approach for complying with the current regulatory requirements for plutonium facilities. However, it is a desirable approach for large-scale facilities handling plutonium and highly enriched uranium.

B. Materials Balance Areas and Item Control Areas

An important aspect of any MC&A system is the designation of material balance areas (MBAs) and item control areas (ICAs). Dividing the process areas and material storage areas into MBAs and ICAs is a necessary first step in designing a materials accounting strategy. Generally, MBAs have defined physical boundaries as each MBA represents a natural grouping of related processing and handling operations. The natural flow of materials between MBAs involves the transfer of discretely measurable quantities. There is no requirement that a facility be divided into any particular number of MBAs. However, the more MBAs, the better the localization of material loss, although the degree of improvement in overall sensitivity may be rather small and dependent on the quality of measurements. The MBAs are established in a manner that provides useful information, while retaining adequate internal control of SNM.

The ICAs are designated to provide maximum control over all materials not in an immediate processing status. Well-characterized and measured materials may be placed in containers (with tamper-indicating seals) and stored until they are needed for processing or are ready for transfer. Materials accounting of such items is easily achieved through seal verification and item counting and by using prior inventory values.

The example process described in this chapter lends itself to both single and multiple MBAs. Both MBAs and ICAs are modified in many ways, with selection depending on the plant layout and administrative convenience.

C. Difficult-to-Measure Quantities

It is often difficult to estimate some of the quantities necessary to calculate materials balances. These quantities include some waste inventories and a majority of the materials held up in equipment as hidden inventories. The waste streams of this facility are identified in Fig. A-1. Potential areas of holdup accumulation for the example process include oxalate precipitation vessel, vacuum drum filter, filtrate from oxalate precipitation, the screw calciner, the fluorinator, and slag from PuF_4 reduction. (A detailed examination of holdup problems in MC&A is presented in Chap. VI.) For a production facility that operates without large-scale process upsets, the quantities of SNM in poorly characterized wastes and holdup are generally low and are likely to remain fairly constant. Relatively large uncertainties in the estimations of these quantities, therefore, do not significantly impact the LEIDs.

D. Measurements and Mathematical Techniques

Chapters III and IX survey various measurement techniques appropriate for SNM measurements and describe their limitations. Choosing an appropriate measurement method for a particular measurement point requires knowledge of the material form and of measurement techniques and their limitations. Knowing the uncertainties of measurements is essential to quantitatively estimating the LEIDs.

Mathematical techniques that are necessary to propagate the errors of measurements and to detect significant losses of SNM on a timely basis are discussed in Chaps. IV, V, and IX.

E. Other Key Elements of Safeguards

Other key elements of a safeguards system for a SNM production facility include physical protection and additional administrative controls on operations. These topics are discussed in Chap. II.

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SUGGESTED ADDITIONAL READING

Developing extensive and specialized knowledge of nuclear material safeguards is a life-long process. The ideal curriculum should include instruction in nuclear fuel cycles, nuclear material measurements, mathematical methods, systems analysis, statistics, computer science, and the art of keeping up with the continually changing regulatory environment. In the absence of such a course of study, nuclear safeguards expertise must develop through continuous learning. Few books offer instructional materials for step-wise learning; however, a vast literature on safeguards-related topics exists. The following is a list, by no means comprehensive, of books and manuals generally available in libraries maintained by the DOE and the NRC as well as by their contractors. These publications are useful reading and reference material for the arts and sciences of nuclear material safeguards. Additional references specific to topics discussed in various chapters are cited throughout this manual.

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