

**AN ANALYSIS OF THE SYSTEMATIC COMPONENTS OF CALORIMETRY
UNCERTAINTY**

Morag K. Smith, David S. Bracken, Clifford R. Rudy, and Peter A. Santi
Los Alamos National Laboratory
Los Alamos, NM 87545

*Presented at the
Institute of Nuclear Material Management
46th Annual Meeting
Phoenix, Arizona
July 10-14, 2005*



Chris J. Lindberg

An Analysis of the Systematic Components of Calorimetry Uncertainty

Morag K. Smith, David Bracken, Cliff Rudy, and Peter Santi
N-1, Safeguards Science and Technology Group
Los Alamos National Laboratory
Los Alamos, NM 87545

Abstract

There is a long-standing qualitative observation that the components of the measurement uncertainty in a calorimeter measurement of special nuclear materials are dominated by the random components with the systematic components treated as negligible. The small to zero biases seen in calorimeter measurements are attributed to the very small contribution of systematic effects. An effort to quantify the systematic contributors has been made to verify the correctness of the qualitative understanding. Possible systematic contributors to the uncertainty have been identified, the magnitude of the individual variations assessed, and the size of the effect of each individual variation on the final uncertainty in the measured item power output evaluated. This paper will discuss and summarize the results of each of these steps.

Introduction

Calorimetry is an important element of the DOE's Material Control and Accountability efforts. It is currently used at most DOE facilities as the most precise nondestructive assay (NDA) method for evaluating the mass of plutonium (Pu). Applications of calorimetry continue to be developed and include extending the range of calorimetry to low-power items such as highly enriched uranium (HEU) and constructing calorimeters for large items such as 55-gallon drums. While the high degree of precision and the low bias have been experimentally verified over decades of measurements, there has actually been little direct work on the sources of systematic uncertainties.

Underlying the very good performance of calorimetry is the small magnitude of the uncertainties associated with the measurement such that in a complete evaluation of the mass of nuclear material, the uncertainties associated with the isotopics measurement dominate the final uncertainty. There is a long-standing qualitative observation that the components of the measurement uncertainty in a single calorimeter measurement of special nuclear materials are dominated by the random components with the systematic components treated as negligible. The small to zero biases seen in calorimeter measurements are attributed to the very small contribution of systematic effects. This paper attempts in a quantitative way to document whether or not the assumption that systematic uncertainties may be neglected is correct.

In the course of looking at the variability in replicate measurements, questions have been raised about systematic uncertainties or biases in calorimeter measurements. Some work has been done to evaluate these and historically they have been treated as small components of the overall calorimeter uncertainty and therefore small components of the inventory uncertainty. We have carried out a more detailed evaluation of these systematic uncertainties and have considered their overall role in the analysis of calorimeter measurements. In a high-throughput facility processing large quantities of SNM, systematic error is the largest component of the inventory uncertainty.

Definitions

Precision – the closeness of agreement between independent test results obtained under stipulated conditions. Precision depends on random errors and does not relate to the accepted reference value. [AS177]

Bias – the difference between the expectation of the test results and an accepted reference value. Bias is the total systematic error as contrasted to random error. [AS177]

Random error of result – a component of the error which in the course of a number of test results for the same characteristic, varies in an unpredictable way. [AS456]

Systematic error of result – a component of the error, which in the course of a number of test results for the same characteristic, remains constant or varies in a predictable way. [AS456]

One of the difficulties in the analysis presented here is to differentiate between random and systematic errors. In the course of evaluating a wide range of factors that affect the total uncertainty of a measurement, it is easy to find both appearing. For example, the measurement reported by a digital multimeter may have both random and systematic errors. Where useful information about random errors is encountered, it is included with the specific systematic error information, but it will not be discussed further. A more complicated situation arises with variations that may occur in a random way over the whole set of calorimeter measurements, but may have a well defined pattern in a specific situation. It is expected that a set of constant current sources will have small differences in the true output current so random selection of a current source will lead to a random shift in the measured voltage. However, once a particular current source is selected, its intrinsic offset from the nominal current will be fixed for the calorimeter system of which it is part.

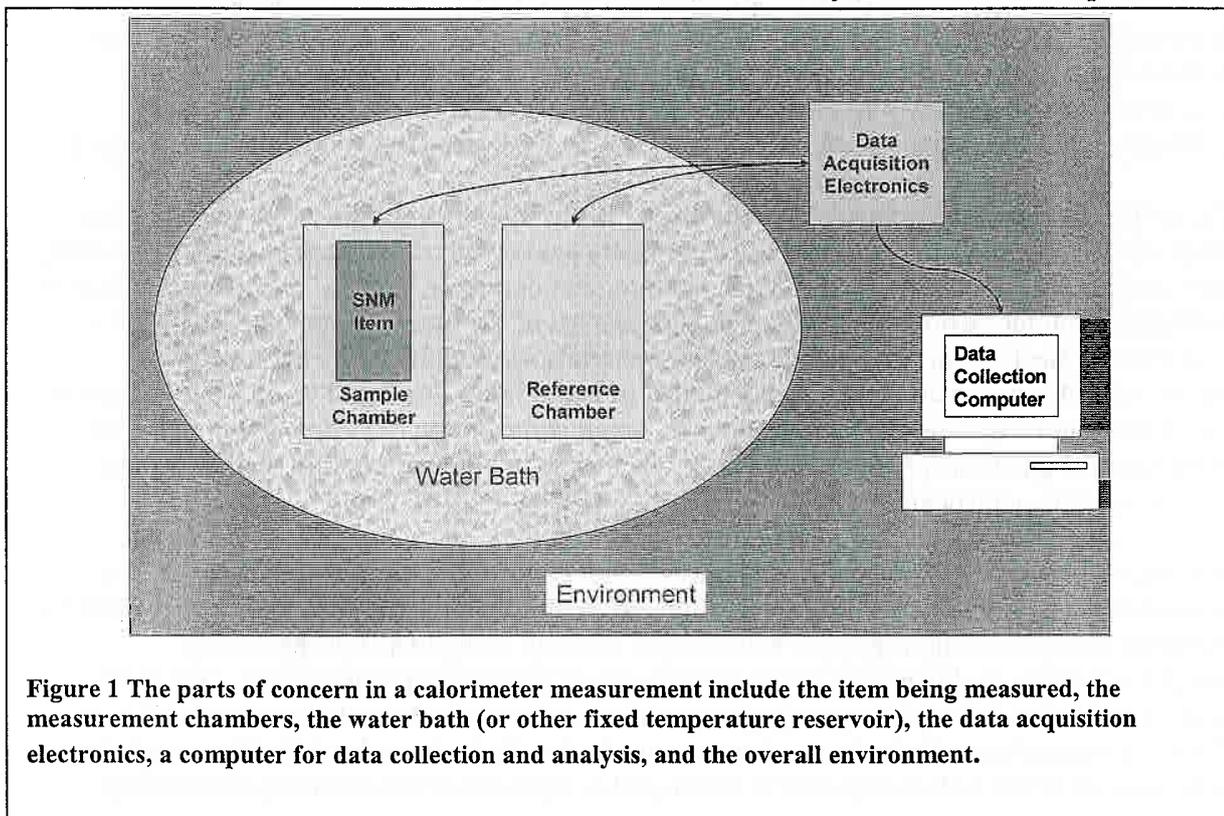


Figure 1 The parts of concern in a calorimeter measurement include the item being measured, the measurement chambers, the water bath (or other fixed temperature reservoir), the data acquisition electronics, a computer for data collection and analysis, and the overall environment.

Random Uncertainties

While the focus of this paper is the systematic uncertainties in calorimetry, it is useful to examine the random run-to-run variation to help determine how large a systematic uncertainty must be before it plays a significant role in the calorimeter measurement. Measurements were taken with an electrical heat standard on a passive and a servo calorimeter examining the run-to-run variation. These variations are on the order of 0.002 Watts for the passive calorimeter and 0.003 Watts for the servo calorimeter. This gives us a level at which other uncertainties may be ignored. Other uncertainties that affect the result at the 0.0002 Watt (one-tenth of the run-to-run) level will not play a significant role. In other terms, 0.0002 Watts corresponds to $4e-6$ V in terms of the bridge potential uncertainty typically for the Wheatstone bridge calorimeters studied. For each calorimeter, there are several data sets all of which have consistent results.

Systematic Uncertainties

A very simplified schematic of a calorimeter is provided in Figure 1. The basic object of a calorimeter is to measure the power output from an item of special nuclear material. This is typically done by measuring the temperature at a well defined location in a sample chamber containing the item being measured. At equilibrium that temperature relative to the temperature within a reference chamber is proportional to the power output by the item. Both the sample and reference chambers are contained within a water bath which is maintained at a constant temperature and provides a buffer between the chambers and the external environment. The data acquisition electronics provide any necessary power or excitation current to the chambers and measure the response passing the data along to the data collection computer. The computer records the data and applies the known calibration to provide the power output from the item. There are a wide range of variables that potentially affect the performance of a calorimeter. The schematic provides a useful way to divide these variables into broad categories which are discussed below.

Systematic Uncertainties – Environmental

When one begins examining calorimeter data, the most obvious source of factors affecting the response of the calorimeter is the “weather” by which is meant the room temperature, external heat loads, drafts etc. Two variables are of particular interest: room temperature and water bath temperature. Room temperature affects the water bath temperature, but may also directly feed into the other parts of the calorimeter so will be treated as an independent variable. Many of the other external effects such as external heat loads and drafts are transmitted to the sensitive parts of the calorimeter via the water bath. Previous examinations of the temperature distribution in the water bath suggests that it is actually very uniform so we have assumed that the effect of variations in the water bath temperature will capture the potential affect of an external change that feeds into the system via the water bath.

- Water bath - Absolute temperature - Because the properties of each part of the calorimeter affect the thermal transport properties and variations in these properties may effect the overall response, it is possible that changes in the absolute temperature of the water bath may effect the measured response. The absolute temperature is primarily determined by the water bath control system settings. Based on examining calorimeter water bath data, for small changes in the bath temperature, there is a shift of about -0.8 V per degree. This corresponds to $2.4e-4$ V over a typical shift of $3e-4$ degrees Celsius overall. For a calorimeter sensitivity of 10000 microvolt/Watt, this leads to a shift of 0.024 Watts.

- Water bath - Stability - The water bath for a calorimeter serves to isolate the response from the environment such that changes in the calorimeter response are purely driven by changes in the item power. The extent to which this is true is a function of the overall stability of the water bath. This stability is defined as how well the water bath temperature is maintained at some fixed value. An ongoing measurement of the bath temperature is standard in calorimetry. By examining the calorimeter response as a function of the stability (noise level) of the bath temperature, the magnitude of the affect on the calorimeter response may be estimated. Based on our current data, for realistic variations in the bath temperature as estimated by the standard deviation, there is little or no effect on the baseline response.
- Water bath - Uniformity - Since perfect stability is not achievable, in some calorimeter designs a reference chamber is provided so that overall changes in the water bath temperature can be subtracted out by comparing the sample chamber to the reference chamber. The value of such a comparison is strongly dependent on the degree to which the water bath temperature is uniform. Previously work has evaluated the uniformity of the water bath and found no measurable variation. Any spatial variation in the water bath was less than 0.0002°C, the resolution of the thermistors used. [LA-UR-03-4022]
- Facility Power Stability - Another environmental aspect to be considered is the facility power stability. There are two aspects to consider: overall power reliability and how clean the power is. Overall power reliability primarily affects the uncertainty of the calorimeter response by affecting the ability to maintain a constant bath temperature. Periodic power outages will lead to drifts in the bath temperature while the power is out and some time between power restoration and the return of the bath temperature to its set point. This will affect a current measurement in a manner similar to that discussed above when the set point is not maintained. It may also be a factor when changes in the baseline are considered. Baseline changes may be driven by changes in the water bath. The magnitude of such a change would then need to be included when the baseline uncertainty is included as discussed below. Noisy facility power will be discussed later under the discussion of calorimeter electronics.
- Room Temperature and Constant Current Source - Another room temperature based effect is a swing in room temperature driving a swing in the output of the constant current source. For room temperature variations on the order of a degree Celsius, the variations in the constant current source response are at the level of the noise in the constant current source. For changes of 5 degrees Celsius or more, the constant current source will change by 2e-6 A or 0.02% which will directly translate into a shift of 0.02% in the bridge potential.

Systematic Uncertainties – Calorimeter Hardware

- Heat distribution error. - The simple model of a calorimeter assumes an item with the power generating material evenly or at least centrally located. The correct operation of a calorimeter is based on similar central placement of the item in the sample chamber. Then, it is a reasonable assumption that the power is exiting the calorimeter through the central heat sensing portion. For example, the middle region of the nickel windings in a Wheatstone bridge calorimeter. Any deviation from such a symmetric placement of the heat generating material is a deviation from the expected heat distribution. Heat distribution effects have been observed at the 0.1% level. However, this effect is highly calorimeter dependent as some calorimeters show no measurable effect. [RU01]

- Weight effect (strain on Ni windings) – The typical Wheatstone bridge calorimeter uses thin nickel wire windings. These windings not only respond to changes in temperature, but respond to mechanical strains as well. One such mechanical strain is loading excessive weight into the calorimeter. Measurements on a typical calorimeter show that a baseline shift of 40microvolts is possible when loads of 0 kg and 7 kg are compared. If the calorimeter sensitivity is 10000microvolts/Watt, this shift corresponds to 0.004 W. This effect appears to be approximately linear. It can be eliminated by measuring the baseline with a weight similar to that of the item being measured. [RU01]
- Moving sample in and out. - The process of moving an item and the containing cal can creates both a thermal and mechanical perturbation of the calorimeter. While it manifests as a random uncertainty, it should be considered as a significant effect. Using the electrical heat standard, it was possible to take data at different powers without removing the cal can. The data collected showed that the variation drops to 0.0003 (about 1/10 of the run-to-run). This strongly supports the run-to-run variation being primarily driven by the mechanical and thermal perturbations of the calorimeter from loading and unloading.

Systematic Uncertainties – Calorimeter Electronics

- Digital multimeters (DMM) precision and bias – Digital multimeters are the basic measurement tool used by a calorimeter. The bridge potential is measured by a DMM and the constant current source and temperature monitoring thermistors are monitored with DMMS. In servo-mode, the control of the supplied power is based on monitored voltages and currents. For the measurement on which the passive power assessment is made, the DMM uncertainty is negligible. The other measurements in passive mode are for monitoring purposes so do not enter into the systematic uncertainty unless they disguise a problem. With respect to servo measurements, the potential affect is larger as the current is part of the measurement.
- Lead lengths – evaluated in noise testing – no significant effect. [SM03]
- Signal shielding – evaluated in noise testing – no significant effect. [SM03]

Systematic Uncertainties – Item Properties

One of calorimetry's major claims is its immunity to the properties of the material being measured or the way it is packaged. The heat (or power) from the nuclear material will always get out eventually. There are, however, some assumptions that have been made to allow this claim to be made about the sources of the power output and the effect of the packaging. We have examined some of these assumptions.

- Escaping Radiation - When considering the power output from SNM, the primary source is the energy lost by the alpha particles emitted in the alpha decay of the SNM. Of course, the alpha decay process is accompanied by gamma radiation and the SNM will also be undergoing fission events which will be accompanied by neutron radiation. While the alpha particles and fission fragments are expected to be completely stopped in the item itself, the gamma and neutron radiation may be expected to completely escape the calorimeter. Detailed information about just how much energy may be lost due to these effects may be found in the Application Guide. [BA02] An evaluation of the potential energy loss at a range of plutonium isotopics shows a range from 0.01% to 0.14% of the total item energy may be lost. This would lead to a power measurement hence item mass measurement lower than expected. It should be noted that the potential loss is dominated by the ²⁴¹Am content

where the low energy gammas are the primary mode. Therefore a lower missing power is expected if the item has a low Am241 content or is packaged such that the material or container is highly self-attenuating.

- Chemical Reactions - Another assumption is that all of the power generation is from nuclear events. Since a calorimeter cannot differentiate between sources of energy, chemical, biological, or radiolysis reactions will count the same as nuclear decay events. The possibility of a chemical or biological driver for the calorimeter power measurement has largely been discarded due to the time constants associated with such events. Radiolysis, being driven by the ongoing alpha decay, will have a similar lifetime to the item so should be considered. If an item contains sufficient water, a series of reactions of the alpha particles with the water could lead to a bias of 2.9% low of the energy output of the nuclear material as measured by the calorimeter. [RU05]
- Matrix - Matrix effects refer to changes in the heat transport properties of an item depending on the chemical form of the special nuclear material and the non-nuclear material with which it is mixed. The use of different materials for source packaging is included in the evaluation of matrix effects. An additional packaging variable is the shape of the packaging which affects the internal convection and conduction of heat from the item to the calorimeter walls. Measurements have been carried out using the same source and several different matrix materials and configurations. There did not appear to be significant variations among the results. Any variability is of the order of the run-to-run variation. If there is a matrix or packaging effect, it is of the order of <0.2%.

Systematic Uncertainties – Data Analysis

- Equilibrium
 - False equilibrium – The approach to equilibrium is a combination of exponential terms. If the right set of rising and falling long time constant exponentials are present, the sum can, to the resolution of the detection algorithm, appear to be flat even though waiting will reveal that true equilibrium has not been reached. This has been seen in measurements when a low power item is measured right after a high power item.
 - Time to equilibrium – In order to evaluate time to equilibrium as it affects the equilibrium detected, we can look at the response as a function of time to equilibrium for the same source in different matrix materials. Looking at data from the HEU calorimeter, a dependence of $-2e-9$ V/sec is seen and a range of equilibrium times up to 80000 seconds. Given 35.6 W/V, this corresponds to a possible bias of 0.006 W.
 - Prediction of equilibrium - Various prediction algorithms have been proposed for calorimeters. Because prediction is based on using calorimeter data before equilibrium is reached, it is a strong candidate for creating a bias in the measurement results. Based on our results, a variation of 0.001 to 0.01 W for Wheatstone bridge calorimeters varying from calorimeter to calorimeter may be seen if a prediction algorithm is used. If the calorimeter is tending to approach equilibrium from the same direction, this variation will tend to be either consistently high or consistently low. [INMM 2000]
- Calibration – Part of the setup procedure for a passive mode calorimeter is the determination of the calibration which defines the relationship between the measured change in the bridge potential and the power output of the item measured. The relationship is given by:

$$BP_{std} - BP_{0avg} = S_0 W_{std} + kW_{std}^2$$

where BP_{std} is the measured assay bridge potential, BP_{0std} is the baseline bridge potential which would ideally be the average of the bridge potential before and after the assay bridge potential, W_{std} is the power of the standard item measured, S_0 is the estimated sensitivity for zero power, and

k is the slope of the varying sensitivity over the power range. A least-squares-fit of a series of measurements of known heat standards is done to determine the values of S_0 and k .

There are several ways systematic uncertainties can be introduced through the calibration. As can be seen from the expressions above, the magnitude of the potential bias cannot be specified in general, but is a function of exactly how a calibration is carried out.

- Limited number of terms used – The expression given assumes the dependence of the bridge potential on the item power goes as a second order polynomial.
- All measurement uncertainties – As there is an uncertainty associated with each bridge potential measurement, there will be an uncertainty associated with the calculated values of k and S_0 .
- Precision and bias in standards – If there is a significant difference in the declared power of a standard and the actual power, the calculated values of k and S_0 will contain a bias.
- Limited range of standards – In general, a calibration is considered good only in the range bracketed by the power output of the standards measured. However, it is possible that items will be presented for measurement with powers larger or smaller than the available heat standards. Since the calibration is dominated by a linear term at higher power values, the affect of extrapolation is likely to be small if the calibration is used above the highest power of the heat standards. The affect at the low end of the calibration will be larger relative to the item power.
- Limited number of standards – Any facility will only have a finite number of standards that can be used to calibrate a calorimeter. The more standards that are available, the more likely it will be that problems with using a 2nd order polynomial will be identified.
- Drift in calorimeter response – It is possible for the response of a calorimeter to change over time particularly if it has been moved or significant changes have been made to the system. Even undisturbed though, a drift in response may occur. The magnitude of such a drift is most easily evaluated by periodically remeasuring the original calibration heat standards. If the measured powers cease to agree with the declared powers within the measurement uncertainty, the calorimeter must be recalibrated.
- Baseline stability – In the ideal case, the calorimeter response when no item is being measured is zero. This is rarely if ever true so the practice is to intersperse baseline measurements which establish the zero-power response with assay measurements and subtract the baseline from the assay response. Data taken over a period over several months shows a typical variability in the baseline corresponding to 0.001 to 0.004 Watts. The typically variability is on the order of the run-to-run variation discussed above and is probably itself due to run-to-run variations. However, it is also clear that while there are random fluctuations, there are also larger scale drifts in the baseline. This drift can

correspond to changes of 0.01 Watts in the response. This would appear as a systematic bias if the baseline measurements are being done too infrequently.

- Uncertainty in specific power values – The point where the power measurement is translated into a mass measurement is the application of the specific power and the item isotopics. The specific power is the power emitted per mass of an isotope and the specific conversion value is the isotopic weighted average of the specific powers. There are known uncertainties in the specific powers that will affect the understanding of a given measurement. For tritium the 0.14% standard deviation translates directly into a 0.14% uncertainty on the reported mass. For plutonium items, the variation in the % standard deviation among the different isotopes will lead to different effects. For a range of isotopic combinations ranging from low to high burnups, uncertainties of 0.03% to 0.12% are found. This is a systematic uncertainty. It should be noted that the roots of this uncertainty are the same as the uncertainty discussed previously regarding the possible loss of energy through escaping gamma radiation. Direct measurements of the specific power will also depend on exactly how much radiation is lost. This means these two systematic uncertainties are correlated and should not simply be added together.

Unexamined Issues

There are still some possible sources of systematic uncertainty that we have not yet fully evaluated. It is suspected, but not yet demonstrated that these are small to negligible contributors. These possible sources are:

- Servo power stability
- Unstable or multiple ground lines
- Required degree of balancing of the bridge
- Vibration
- Mechanical shocks

Conclusions:

We have evaluated a number of potential contributors to the error in a calorimeter measurement which are summarized in the table below. While our initial focus was on the systematic error, the random error was also considered so that minimum level could be set for the consideration of uncertainty.

Most of the potential systematic uncertainties are small compared to the run-to-run variability which itself is small compared to the uncertainty in the typical gamma isotopics measurement. However, given very good isotopic values for a measured item the systematic uncertainty should be considered as part of the overall uncertainty.

Summary of Uncertainty Contributors

Error Type	Magnitude	Other considerations
Random		
Random run-to-run variability	0.002 Watts (passive)	
	0.003 Watts (servo)	
Systematic		
Absolute water bath temperature	0.024 Watts typical	2.4e-4 V/10000uV/W per 3e-4 deg C
Water bath temperature stability	negligible	
Water bath temperature uniformity	negligible	
Facility power stability	Situation dependent	Unstable facility power will cause problems with maintaining the water bath temperature at a fixed value.
Room temperature affect on constant current source	0.02% per 5 degrees C	
Heat distribution error	0.1%	For large variations in heat distribution. Very calorimeter dependent.
Weight effect	0.004 W	Very calorimeter dependent. Can be avoided by using similar weights for both baseline and assay measurements.
Digital multimeters precision and bias	negligible	
Lead lengths	negligible	
Signal shielding	negligible	
Unabsorbed radiation	0.01%-0.14%	Lower for lower Am241 content items. Packaging dependent
Chemical reactions	negligible	
Chemical reactions – radiolysis	Up to 2.9%	Dependent on composition of item particularly how wet it is.
Matrix effects	<0.2%	At the limit of detectability for current data
False equilibrium	Procedure dependent	Evaluate measurement procedure and review equilibrium detection
Time to equilibrium	0.006W	At the limit of detectability for current data
Prediction of equilibrium	0.001 W to 0.01 W	Calorimeter and algorithm dependent
Calibration	Process dependent	Evaluate for given calorimeter calibration process.
Baseline stability	0.01W	Can limit by doing frequent baseline measurements.
Specific power	0.03% to 0.12%	Dependent on the isotopics of the item measured.

References

- [AS177] Standard Practice for Use of the Terms Precision and Bias in ASTM Test Methods, ASTM E 177-04, ASTM International, West Conshohocken, PA, 2004.
- [AS456] Standard Terminology Relating to Quality and Statistics , ASTM E 456-02, ASTM International, West Conshohocken, PA, 2002.
- [BA02] D.S. Bracken et al., Application Guide to Safeguards Calorimetry, LA-13867-M, 2002.
- [RU01] Clifford Rudy, "Standards and Error Analysis," Calorimetric Assay Training Course, Los Alamos, NM, 2003.
- [RU05] Clifford Rudy, private communication, 2005.
- [SM03] M.K. Smith, "Sources of Calorimeter Noise," Proceedings of the Institute of Nuclear Materials Management 44th Annual meeting, Phoenix, AZ, July 14-17, 2003.

Acknowledgement

This work was sponsored by the DOE Office of Security, Office of Materials Inventory and Technology Development (SO-20.3).