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An Evaluation of the Use of
Calorimetry for Shipper-Receiver
Measurements of Plutonium

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ABSTRACT

The purpose of this report is to evaluate the relative merit of using calorimetry for shipper-receiver (S-R) exchanges of Pu. In particular, this evaluation concentrates on the accountability and the diversion detection aspects of the use of calorimetry. Three different modes of use were considered: (1) calorimetry alone, that is, S-R exchanges based on power (watts) measurements; (2) calorimetry plus chemical assay, similar to the present weight plus chemical assay system, and (3) calorimetry plus gamma-ray spectrometry, a totally nondestructive Pu assay method.

The relative merit of both applications was judged using the present methods as a base case. Some of the factors considered were random and systematic errors, timeliness, costs (both operating and capital) and reliability.

EXECUTIVE SUMMARY

Reason for Study

Rapid and reliable shipper-receiver (S-R) measurements are critical to providing acceptable safeguards for handling plutonium. Such measurements are necessary for diversion detection which is both timely and sensitive. Errors in these measurements are often the dominant errors in the limit of error of material unaccounted for (LEMUF) in throughput dominated plants. S-R differences are also valuable indicators of undetected biases which may exist in either the shipper or the receiver's plant.

Despite the importance of such measurements significant S-R differences in shipments of PuO_2 still exist today. In an evaluation of many shipments between various contractors at the Hanford site, Stewart and Wirfs¹ estimated an average intersite bias of 0.29%, even though the pooled precision of the Pu analysis was only 0.1%.

The major causes of these biases have long been known. In 1965² they were enumerated by researchers at the AEC's Rocky Flats installation. The primary causes cited were variations in moisture content, incomplete dissolution of analytical samples, incomplete transfer of contents, sampling and analytical errors.

Of these by far the most insidious is moisture variations since the bulk measurements, Pu assay and sampling are all affected by this variable. For example, water absorption of as much as 3% was observed for finely powdered PuO_2 . Incompletely calcined material was observed to gain as much as 5% of the original weight due to moisture pickup.

This evaluation was begun because calorimetry seemed capable of resolving most of these problems. First the power measurement is not affected by the moisture content. Second, the power measurement is performed on the sealed container thus eliminating transfer errors. Third, the watts/g of Pu can be determined by two independent methods, one by direct comparison against chemistry or based on an isotopic measurement. Thus analytical errors can be detected and minimized.

In addition the ability to make precise bulk measurements on the sealed containers provides a highly sensitive method for rapid diversion detection.

Scope of Study

Three different modes of using calorimetry measurements to improve shipper-receiver measurements of plutonium were evaluated: (1) calorimetry alone (a watts exchange); (2) calorimetry plus chemical analyses; and (3) calorimetry plus gamma-ray spectrometry of solids to provide a totally nondestructive measurement.

The evaluation was carried out in three steps. First, measurement reliabilities were estimated for all measurements. Next, using these estimates the effect of the three different modes of application on diversion detection and S-R differences were evaluated.

Measurement Reliability

Random and systematic errors were estimated for all related measurements from a variety of available sources. The measurements evaluated included calorimetry, Pu assay, mass spectrometry, alpha spectrometry and gamma-ray spectrometry. For each technique a range of typical errors was estimated

as well as an average value. The average random and systematic errors were used as a basis for comparison between present shipper-receiver methods and those evaluated in this report.

Diversion Detection

Diversion detection sensitivities were estimated for single containers as well as for a typical shipment of 40 cannisters containing a total of 100 kg PuO₂. As a result of this study it was found that calorimetric power measurements of plutonium provide the most sensitive method presently available for detection of diversion. Assuming average calorimeter performance levels, diversions of 0.1% are detectable at the 95% confidence level within 24 hours of receipt of a typical shipment of 40 cannisters containing a total of 100 kg of PuO₂.

Comparable figures for weight plus chemical assay were estimated to be 0.24% in 48 hours. This estimate assumes that all 40 containers would be weighed, opened and sampled in the first 40 hours after receipt of the shipment. The calorimetry estimate assumes that the 40 cannisters be removed from the ten drums.

Gross neutron counting of the drums as received would reduce the time required to one hour but the diversion sensitivity would be only about 6% of the total shipment.

Effect on Shipper-Receiver Accountability

As a result of this study it was determined that for homogeneous material, calorimetry combined with chemical analysis will provide a method comparable to weight plus chemical assay in terms of measurement accuracy and reliability. In addition the use of calorimetry can minimize the problems

of moisture absorption by oxides or oxidation of metals. For example, Stewart and Wirfs observed an average S-R bias of 0.61% on the bulk measurements of plutonium oxide between five different facilities located in the Hanford, Washington area. By contrast it is estimated that when calorimetry is used for the bulk measurement the S-R agreement on a typical shipment will be less than 0.11%, 95% of the time, using average calorimeter performance figures.

It was also determined that calorimetry combined with gamma-ray spectrometry can provide an effective method for achieving better S-R agreement on scrap sent to a recovery site. Using average performance figures shipper-receiver differences are expected to be less than 1%, 95% of the time. The totally nondestructive nature of the measurement makes it especially attractive for scrap since it is often stored for months prior to recovery.

The use of calorimetry can also provide an early indication of potential S-R differences. Since the calorimetry measurements are made on sealed containers differences in the bulk measurements can be detected prior to opening the containers. Thus these differences can be resolved by third party measurements or other means.

1.0 BACKGROUND

The calorimetric assay of plutonium is a two step process similar to the use of weight and chemical assay for Pu assay. The first step, analogous to the weight measurement, is a power measurement of the heat emitted by the bulk sample due to radioactive decay. The second step is to determine the effective specific power, which is the conversion factor from watts to grams of Pu analogous to the g-Pu/g-sample factor determined by chemical analysis.

Calorimetric assay offers several distinct advantages over chemical analysis and other nondestructive assay techniques: 1) the conversion factor remains the same as long as the isotopic composition is not changed, thus the same factor is applicable to all Pu bearing materials from a particular batch of PuO₂ including PuO₂, mixed oxides, scrap, etc. 2) The attribute measured (heat) is directly related to Pu content. 3) The power measurement is matrix independent since it is unaffected by variable self-attenuation of gamma and neutron radiation in the sample matrix. 4) Calorimetry is highly accurate and precise. 5) Calorimetric assay is directly traceable to the national measurement system.

Some important limitations of the method are: 1) the calorimeter cannot distinguish between heat produced by radioactive decay and other sources such as chemical reactions, and 2) when applied to chemically inhomogeneous materials very accurate isotopic measurements are required (see Computational Method below).

Recommended methods for calibrating calorimeters and determining the effective specific powers are detailed in ANSI N15.22-1975

"Calibration Techniques for the Calorimetric Assay of Plutonium Bearing Solids Applied to Nuclear Materials Control"³.

ANSI N15.22-1975 defines two methods for determining the effective specific power. The first, known as the empirical method, involves a microcalorimetry measurement and the chemical assay of a small aliquot of material. P_{eff} is defined as

$$P_{eff} = \frac{W_i}{Pu_i} \quad [1]$$

where W_i = measured thermal power of the aliquot (watts)

Pu_i = total plutonium content of the aliquot.

Note: An isotopic measurement is also required in the empirical method to determine the average atomic weight of the plutonium and to make corrections for nuclear decay. For example, P_{eff} typically increases 0.01%/day due to the ingrowth of Am-241 from the beta decay of Pu-241.

For the second general method, known as the computational method, the relative abundances of all heat producing isotopes are measured, and P_{eff} is defined as:

$$P_{eff} = \sum_{j=1}^{j=6} R_j P_j \quad [2]$$

where R_j = mass abundance of the i th isotope relative to total Pu

P_j = specific power of the i th isotope (watts/g)

$i = 1, 2, 3, 4, 5$ and 6 for Pu-238, -239, -240, -241, -242, and Am-241, respectively.

The specific power of the individual isotope is directly related to fundamental nuclear constants by the following equation:

$$P_i = \frac{2119.3 Q}{T_{1/2} A} \quad [3]$$

where Q = total disintegration energy (MeV) of alpha-particle emitters, or the average energy (MeV) of beta particles

$T_{1/2}$ = half-life (years) of the isotope

A = gram atomic weight of the isotope.

The matrix independence of the method arises from the fact that most of the decay energy (>99.99%) is associated with the alpha particles and recoil of the parent nucleus and is all absorbed as heat in the sample. Less than 0.01% of the decay energy escapes undetected as neutrons and gamma-rays³.

2.0 ASSOCIATED MEASUREMENT RELIABILITIES

2.1 Estimation of Random and Systematic Errors

In estimating the random error of a measurement great care was taken to estimate the random error of the measurement rather than instrument reproducibility. Instrument reproducibility is defined as the precision of repetitive measurement on a limited number of known or unknown materials. The estimate of the random error of a measurement, on the other hand, is based on a sufficient period of time and variety of samples to include all sources of variability found in normal plant operation. Wherever possible, a range of expected errors, from highest to lowest, is given so that the reader can judge for himself the expected error in his own operation.

In addition, an average error was determined by averaging the variances as follows:

$$S(\text{ave}) = \sqrt{\frac{\sum_{i=1}^n S_i^2}{N}} \quad [4]$$

where $S(\text{ave})$ = average random error

S_i = random error of laboratory i

N = number of laboratories.

Systematic error is defined as those nonrandom errors of unknown sign and magnitude which have not been detected. Estimation of systematic error is in reality an attempt to determine the maximum value any unknown error can assume without detection.

If one assumes that his standards have the same sources of error as the unknowns, systematic errors can be estimated by a method recommended by Jaech⁴. First, a series of standards are run to determine measurement bias. Bias corrections are made and the systematic error variance, S_S^2 , is estimated as follows:

$$S_S^2 = S_{B/n}^2 + S_0^2 \quad [5]$$

where S_B^2 = error variance of the bias determination based on n measurements on standards

S_0^2 = systematic error variance of the standard used.

The assumption that the same type of errors exist for the measurement of both standards and unknowns is not always valid, however. Thus when equation 5 is used one must always test this vital

assumption. The most practical method is to review bias between different methods and different laboratories. For example, in the Safeguards Analytical Laboratory Exchange (SALE) all the participants use Pu assay methods calibrated against NBS standards. Yet some of the laboratories are persistently biased from the exchange mean. While it is not always possible to tell who is "right" these biases are a clear indication that undetected biases exist.

For the purposes of this report the estimates using equation 5 will be used unless clearly invalidated by observed biases.

For the sake of consistency all errors are relative errors in percent unless stated otherwise. When the term precision is used it means one relative standard deviation. While the terms, random and systematic errors, refer to the estimated limits of error at the 95% confidence level.

2.2 Calorimetry

2.2.1 Standards

Two different standards are available for calibration of the calorimeter power measurements. The first, electrical calibration, has a systematic error of approximately 0.02% (95% confidence level). This is based on the fact that electromotive force (EMF) measurements can generally be certified to $\pm 0.01\%$ (95% confidence level). Since the power measurement (watts) involves multiplying two EMF measurements together (heater voltage x heater current) the systematic error of the electrical standards is estimated to be 0.02%.

Plutonium-238 fueled heat standards are also available for calorimeter calibration. These standards prepared by Mound* also have a stated uncertainty of 0.02% (95% confidence level). In addition, a cooperative program is now underway with the National Bureau of Standards (NBS) to certify these heat standards as NBS standard reference materials. In general, ANSI N15.22-1975 recommends the use of heat standards over electrical standards, since the heat standards can be more readily used to test for heat distribution errors** and are less operator dependent.

2.2.2 Calorimetry of Bulk Materials

Two limited simulations of a shipper-receiver exchange were done with precision of 0.03%. One at this laboratory⁵ involved two 1-kg samples of PuO₂ and the other at General Electric's Vallecitos Nuclear Center⁶ involved a single container of PuO₂. In both experiments the containers were run repeatedly in a single instrument over a period of 60 days.

A more extensive simulation of shipper-receiver measurements on PuO₂ involving four samples and four laboratories was undertaken as part of the Metal Exchange Program***. In this experiment four samples containing about 600-g PuO₂ each were prepared from a single, well-blended lot of material. One sample was then distributed to each laboratory and calorimetry measurements were performed once a month for at least six months. The samples were then interchanged and run again at one-month intervals for at least six months. The results are shown in Table 1.

*Operated for the U. S. Department of Energy by Monsanto Research Corporation under U. S. Government Contract No. EY-76-C-04-0053.

**ANSI N15.22-1975 defines heat distribution error as "the error arising from the spatial distribution of the heat source within the calorimeter chamber".

***A program involving DOE contractors established to assure the reliability of a variety of plutonium measurements.

Table 1
METAL EXCHANGE SHIPPER-RECEIVER EXPERIMENT

	Watts/Gram of Sample*			
	<u>1975 Mean</u> <u>(Std Dev)</u>	<u>1976 Mean</u> <u>(Std Dev)</u>	<u>Diff Within Labs</u> <u>1975-1976</u> <u>(Std Error of Diff)</u>	<u>Diff Between Labs</u> <u>Shipper-Receiver</u> <u>(Std Error of Diff)</u>
Lab 1	2.03746 (<u>+</u> .00158)	2.03622 (<u>+</u> .00172)	0.00124 (<u>+</u> .00092)	-0.00305 (<u>+</u> .00138)
Lab 2	2.03317 (<u>+</u> .00291)	2.03834 (<u>+</u> .00236)	-0.00517 (<u>+</u> .00153)	-0.00088 (<u>+</u> .00113)
Lab 3	2.03775 (<u>+</u> .00028)	2.03778 (<u>+</u> .00064)	-0.00003 (<u>+</u> .00028)	-0.00193 (<u>+</u> .00050)
Lab 4	2.03585 (<u>+</u> .00113)	2.03806 (<u>+</u> .00022)	-0.00221 (<u>+</u> .00044)	-0.00031 (<u>+</u> .00016)
All Labs	2.03617 (<u>+</u> .00243)	2.03760 (<u>+</u> .00194)	-0.00143 (0.00063)	
All Data		2.03689 (<u>+</u> .00220)		

*All values decay corrected to 1/1/76

Thus over six month periods the precision of the four laboratories varied from a low of 0.01% to a high of 0.14% with an average of 0.07%. Translated to the 95% confidence level the random errors ranged from 0.03% to 0.37% with an average value of 0.17% (Table 2).

Using these estimates of random error and equation 5 systematic errors were estimated. For these four laboratories the estimated systematic error (95% confidence level) ranged from 0.023% to 0.14% with an average of 0.07% (assuming $n = 6$). In this case the observed laboratory to laboratory biases were reasonably consistent with the previously estimated systematic errors. Two of the laboratories had statistically significant year to year differences. The largest of these was 0.25%, apparently due to a lack of measurement control during the first year of the experiment.

Several comments are in order here. 1) This data was judged to be a reasonably valid indication of the normal range of performance since two of the laboratories, Atlantic Richfield Hanford Company* and Rocky Flats, are basically production environments, and two of the laboratories, Mound and Lawrence Livermore Laboratory, are basically research and development type facilities. In addition the data with largest variability probably represents a credible upper bounds since the samples were submitted as unknowns to the production personnel and were not run in the same instrument each time. Thus this data contains an additional error variance due to calorimeter to calorimeter differences not present in the data from the other three laboratories. 2) The results are relevant to license conditions

*Now operated by Rockwell International.

Table 2
RELATIVE CALORIMETER PERFORMANCE
AT 95% CONFIDENCE LEVEL

	<u>Random Error (%)</u>	<u>Systematic Error (%)</u>	<u>Bias (%) Yr to Yr</u>	<u>Bias (%) on Sample Exchange (Lab to Lab)</u>
Lab 1 - 1975	0.20	0.084	0.06	-0.15
1976	0.22	0.092		(2 to 1)
Lab 2 - 1975	0.3 ⁷ 5	0.14	-0.25*	-0.04
1976	0.29	0.12		(1 to 2)
Lab 3 - 1975	0.035	0.025	0.00	-0.09
1976	0.078	0.038		(4 to 3)
Lab 4 - 1975	0.14	0.060	-0.11*	-0.02
1976	0.028	0.023		(3 to 4)

*Bias greater than combined systematic errors

$$\text{Bias} > \left[S_S^2(1975) + S_S^2(1976) \right]^{1/2}$$

since a measurement assurance program (MAP) was set up and operating at all four of the laboratories (a requirement of 10 CFR Part 70). The MAP's employed were relatively simple ones involving running heat standards periodically, typically once a week to once a month. 3) These analyses assume no error variance due to inhomogeneity of the oxide used.

2.2.3 Calorimetry of Analytical Samples

Microcalorimeters with sample chambers 2.7 cm in diameter by 7.0 cm tall have been used for approximately 20 years at Mound. These instruments can easily hold 5 CC of PuO_2 inside a (double containment) metal capsule. In research environments precision of 2-5 μW over several years of operation have been demonstrated. Precisions of production type instruments range from 10 to 30 μW with an average of 20 μW .

The expected precision of the microcalorimetric measurement will vary with the sample size of the P_{eff} of the Pu being determined. P_{eff} values typically vary from 2.3 to 23 mW/g of Pu due to isotopic composition. Thus, the expected precisions under a variety of conditions are given in Table 3.

2.2.4 Time Requirements

The transient response of a heat flow calorimeter can be defined by a general equation of the form:

$$S = \sum S_e(1 - e^{-t/RC}) \quad [6]$$

where S = calorimeter signal at time t

TABLE 3
 EXPECTED PRECISION OF MICROCALORIMETER MEASUREMENTS
 AS A FUNCTION OF Pu BURNUP AND SAMPLE SIZE

Burnup (1000 MWD/t)	Peff (mW/g)	Precision ^A (RSD)		Sample Size to Achieve 0.1% RSD (g-Pu)	
		Research	Production ^C	Research ^B	Production ^C
Low	2.3	0.25%	1.0%	2.2	8.7
8-10	3.0	0.19%	0.76%	1.7	6.7
16-18	4.3	0.13%	0.52%	1.2	4.7
25-27	9.3	0.06%	0.24%	0.5	2.2
38-40	22.1	0.03%	0.10%	0.2	0.9
>50	8.7	0.06%	0.23%	0.6	2.3

^A Assuming sample size of one gram PuO₂

^B Precision = 5 μ W

^C Precision = 20 μ W

ΣS_e = calorimeter signal at equilibrium ($t = \infty$)

R = thermal resistance

C = heat capacity,

and the summation is carried out over all R's and C's present.

As a result the time to reach equilibrium increases with the quantity and thermal resistance of the material being assayed and its container. At the same time the calorimeter sensitivity can be increased by increasing the calorimeter's thermal resistance. Thus a tradeoff must be made between the speed and sensitivity of the instrument. For example, containers used for the metal exchange experiments described earlier (section 2.2.2) were typical shipping containers with the oxide packed inside a "tuna fish" can which is then packed inside a No. 404 tin can. This type of loose packing causes a slow calorimeter response due to the additional thermal resistance between the sample and the calorimeter. The ideal packaging arrangement is close-fitting, right cylinders with minimum tolerance between the two cylinders (if multiple packaging is required) and between the calorimeter walls and outer cylinder diameter. The ridges at the top and bottom of standard tin cans make them less than ideal in achieving good thermal contact with the calorimeter. Due to the poor packaging and high precision, some of the calorimeters used in the metal exchange experiments took as much as 12 to 13 hours to come to equilibrium.

The effect of several different approaches to reducing the assay time are shown in Table 4. For example, improving the packaging by using a single, close-fitting container reduced the time required to reach equilibrium by 40%.

TABLE 4

METHODS OF REDUCING CALORIMETER MEASUREMENT TIME OF BULK SAMPLES

Time (hours) to reach desired equilibrium for 1-kg of PuO₂

Case	0.01% Equilibrium	0.1% Equilibrium	1.0% Equilibrium	Comments
1	13.1	10.2	8.1	Poorly packaged sample in calorimeter without servo-control ⁵
2	8.0	6.1	4.7	Calorimeter servo-controlled ⁵
3	3.0	1.6	0.8	Servo-control plus pre-equilibration ⁵
4	8.0	6.3	5.2	Same as case 1 except improved packaging ⁵
5		5.0		Case 1 plus prediction of equilibrium ⁷
6		1.0		Improved packaging plus servo-control plus pre-equilibration ⁸
7		0.75		Ideal packaging ⁹

An alternate approach is the use of a servo-control loop to maintain the calorimeter chamber at a constant temperature. The advantage of this approach is that the calorimeter is always at equilibrium and only the sample need come to thermal equilibrium. An additional reduction of time can be gained by pre-equilibrating the sample. That is, store the sample in a constant temperature environment at the same temperature as the sample chamber. A note of caution here, the total assay time for a single sample will be at least as long since it will take just as long to come to equilibrium in the pre-equilibration chamber as in the calorimeter. The advantage is that the number of samples which can be run through the calorimeter in a given period of time can be increased by a factor of 4 to 6 times.

An automated plutonium assay system (APAS)⁸, has been developed at Mound which incorporates automation, pre-equilibration and improved packaging. Although all the results are not complete, initial evaluation indicates the throughput rate for 1-kg PuO₂ samples to be 1 hour/calorimeter. The material is singly contained inside a 1-liter vessel approximately 7.0 cm in diameter.

Still another alternative is prediction of equilibrium. That is, measure the calorimeter response at equal time intervals and predict the calorimeter's equilibrium value assuming an exponential response similar to equation 6. For a calorimeter system without a servo-controller this technique has been demonstrated to reduce the time per assay by 50% or more⁷.

In addition Mound is developing a new servo-controller which will use digital techniques. This will make it possible to combine servo-control and prediction of equilibrium. Completion is expected late in 1978.

The last case shown is an example of the strong interdependence between geometry and speed of calorimetric assay. In this case a 1-kg sample in a long thin single container 3.2 cm (1.25 in.) diameter by 89 cm (35 in.) long reached 0.1% equilibrium in only 45 minutes. This was without the use of servo-control, pre-equilibration or prediction of equilibrium.

A similar situation applies to the time/assay for analytical samples (Table 5). The present Mound analytical calorimeter vial is 2.7 cm diameter by 7.0 cm long. To reach 0.1% equilibrium required approximately 100 minutes.

The assay time can be reduced if a smaller diameter sample is used. For example, using a 1.2 cm diameter sample, a Mound calorimeter system automatically loads a sample and records its calorimeter response once every 38 minutes¹⁰.

Argonne National Laboratory (ANL) has built several calorimeters for even smaller rods (1 cm diameter). One of these (36 in. long) can provide a measurement precise to about 0.2% in 15-20 minutes¹¹. In addition, ANL¹² is now in the process of adapting this design for use as an analytical calorimeter with a design goal of 0.1% RSD on 10 mW samples. This instrument is expected to be delivered in September 1977 to New Brunswick Laboratory for evaluation.

TABLE 5

TIME REQUIREMENTS FOR ANALYTICAL CALORIMETERS

Case	Time to reach 0.1% equilibrium (min.)	Sample diameter (cm)	Comments
1	100	2.7	Mound calorimeter vial ⁸
2	38	1.0	Mound quality control ⁸ (includes pre-equilibration)
3	15-20	1.0	ANL rod calorimeter (includes servo-control and pre- equilibration) ¹¹
4	<60	5.0	TRONAC "battery" calorimeter includes pre-equilibration ¹³
5	60-80	1.6	Calvet calorimeter ¹⁴

The last two entries are commercially available calorimeters developed for other applications. While they have not been tested with radioactive materials, both have sufficient sensitivity to be useful as analytical calorimeters for samples in the 1- to 5-g range. Prior to use they will require testing and calibration according to procedures in ANSI N15.22-1975.

2.2.5 Commercial Availability

At the present time there are no commercial suppliers of heat flow calorimeters with instruments suitable for plutonium oxide shipments. All the instruments used in the experiments described earlier (section 2.2.2) were custom built in DOE laboratories. Descriptions of several of these instruments may be found in references 2 and 5*. Typical requirements are a good machine shop with precision wire winding capabilities and a competent electronics technician. Circuit diagrams for servo-controllers can be found in references 4 and 11.

At a 1973 Symposium on the Calorimetric Assay of Plutonium¹⁰, four commercial firms** expressed an interest in supplying such equipment.

At this time (September 1977) none of these companies have an off-

*Drawings for this Mound instrument are available from National Technical Information Service, Springfield, Virginia, 22161, by referencing Mound Laboratory Technical Report MLM-1798.

**The firms and their representatives at that time were: TRONAC, Inc., Orem, Utah, R. Hart, representative; Monsanto Research Corporation (Dayton, Ohio), B. Taylor, representative; Sandia, Inc., Philadelphia, Pennsylvania, P. Sadtler, representative; Babcock & Wilcox, Lynchburg, Virginia, S. Nattsas, representative.

the-shelf model for bulk samples and none were willing to make any definite commitments without specific customer requirements as to quantity, size and expected accuracy. Interested parties are advised to contact the individual companies with their specific needs.

One of these companies, TRONAC, Inc., and a French firm, Setaram American distributor: Marche Instruments, Inc., Waco, Texas) have off-the-shelf microcalorimeters which are potentially useful as analytical calorimeters for small samples. Approximate costs of these two instruments were \$20,000 and \$40,000, respectively.

2.3 P_{eff} by the Computational Method

2.3.1 Random Errors Using Alpha and Mass Spectrometry

When P_{eff} is determined by the computational method, the random error is defined by ANSI N15.22-1975 as follows:

$$S(P_{eff}) = \sqrt{\sum_{i=1}^6 F_i \left(\frac{S(R_i)}{R_i} \right)^2} \quad [7]$$

where $F_i = \frac{R_i P_i}{P_{eff}}$ heat fraction due to the i th isotope

$\frac{S(R_i)}{R_i}$ = relative error of the mass abundance measurement of the i th isotope.

The amount of heat from each isotope varies widely with isotopic composition. For example, Pu-238 in low burnup plutonium contributes about 2.5% of the heat and in saturated LWR recycle contributes 85% of the heat. Thus, the precision of P_{eff} varies considerably with isotopic composition. A range of typical isotopic compositions from

the Reilly-Evans report¹⁵ on measurement reliabilities is given in Table 6. Reilly and Evans have also estimated the precision of P_{eff} for three different cases; high and low precision mass spectroscopy and high resolution gamma-ray spectroscopy of solutions.

To test the validity of the Reilly-Evans estimates, actual isotopic data from a variety of sources was used to calculate $S(P_{eff})$ and thus to provide an independent assessment of random errors. In general it was found that these estimates were in line with Reilly-Evans estimates for high precision mass spectroscopy and in several cases were significantly better. As a general rule it was also found that the primary source of random error in the computational method is in the Pu-238 measurement.

The data for mass spectroscopy and alpha spectrometry are summarized in Figure 1. Lines A and B are Reilly-Evans estimates of random error based on high and low precision mass spectroscopy. Points C, D and E represent the range and mean of three different isotopic compositions from the metals exchange program. Four or five laboratories participated in each exchange and all used mass spectroscopy for the measurements. In every case at least 90% of the variance of the P_{eff} measurement was due to the variance of the Pu-238 measurement. The laboratories with the most precise Pu-238 measurements were also the laboratories with the most precise P_{eff} determination and vice versa.

Points F represent the use of high resolution mass spectroscopy in a carefully controlled experiment to test the limits of the P_{eff} determination. This "calibration alternatives"¹⁶ experiment involved

TABLE 6

TYPICAL PLUTONIUM ISOTOPIC COMPOSITIONS

<u>Burnup (1000 MWD/t)</u>	<u>Description</u>	<u>Isotopic Abundance (%)</u>				
		<u>^{238}Pu</u>	<u>^{239}Pu</u>	<u>^{240}Pu</u>	<u>^{241}Pu</u>	<u>^{242}Pu</u>
Low	Low burnup plutonium	0.01	93.6	5.9	0.38	0.015
8-10	FFTF feed	0.08	86.1	11.7	1.89	0.21
16-18	-----	0.25	75.7	18.5	4.5	1.1
25-27	Spent LWR	1.1	61.6	20.9	12.6	3.8
38-40	Saturated LWR recycle	3.3	41.1	27.6	17.6	10.4
--	Spent LMFBR	0.94	59.9	27.0	7.5	4.7

FIGURE 1

RANDOM ERROR OF P_{eff} DETERMINATION BY THE COMPUTATIONAL METHOD
USING MASS SPECTROSCOPY OR MASS SPECTROSCOPY + ALPHA SPECTROSCOPY

FIGURE 1

Random error of P_{eff} determination by the computational method using mass spectroscopy or mass spectroscopy and alpha spectrometry.

Mass spectroscopy alone

- A Reilly-Evans¹⁵ estimates for high resolution mass spectroscopy
- B Reilly-Evans¹⁵ estimates for low resolution mass spectroscopy
- C Metal exchange data on NBS #948, March 1975 to May 1976, mean and range (four laboratories reporting)
- D Metal exchange data on NBS #946, September 1975 to June 1976, mean and range (five laboratories reporting)
- E Metal exchange data on UK-131, December 1975 to March 1977, mean and range (five laboratories reporting)
- F Reference 16

Mass spectroscopy plus alpha spectrometry

- G Reference 16
- H Reference 17

mass spectroscopy, alpha pulse height analysis, and chemical analysis at New Brunswick Laboratory and at Mound, as well as high resolution gamma-ray spectroscopy measurements at Lawrence Livermore Laboratory, E. I. duPont's Savannah River Plant and Mound. At the time of this writing, 11 of 18 P_{eff} determinations had been completed. The remaining data is expected to be available by the end of CY-1977. Again the random error in point F was dominated by the variance of the Pu-238 measurement.

Points G and H represent the use of alpha spectrometry for the Pu-238 determination combined with high resolution mass spectrometry. These points were significantly better than Reilly-Evans estimate for high resolution mass spectroscopy, especially for high burnup plutonium. The major difference is that Reilly-Evans estimated that when Pu-238 concentration exceeded 0.7%, the mass spectrometry measurements were more precise than the alpha spectrometry measurements. This was not found to be true, in fact, precisions of 0.1% were achieved by alpha spectrometry of 1.1% Pu-238 concentrations.

Based on points G and H the random error under optimum conditions was estimated to be 0.15%. The average random error based on twice the average of C, D and E, was estimated to be 0.6%. The upper end of the range of C, D and E was used to estimate maximum random errors of 1.0%. The maximum errors are somewhat less than those estimated by Reilly-Evans, but it was felt that a reasonable measurement assurance program (a requirement of 10 CFR part 70) would maintain equivalent measurement control. An additional factor which should improve the situation is the availability of better isotopic standards, covering a wider range of isotopic compositions with more precise and accurate values.

In those cases where no americium analyses were available (C, D and E) the power fraction of americium was assumed to be less than 4% (equivalent to about one years ingrowth) and with relative standard deviations of 1 and 5% for the high and low resolution extremes.

2.3.2 Random Errors Using Gamma-Ray Spectrometry

The determination of P_{eff} using isotopic values determined by gamma-ray spectrometry has several unique advantages: 1) the method measures all isotopes which are significant heat producers, including Am-241; 2) when applied to liquids sample preparation is minimized and even in-line measurements are possible¹⁸; and 3) when applied to solids it provides a totally nondestructive assay.

The major limitation of the technique is that Pu-242 has no useful characteristic gamma-rays and thus cannot be measured directly. This does not affect the precision of the P_{eff} determination, however, since Pu-242 has a very low specific activity and contributes no significant amounts of heat (<0.01%). The effect on the systematic error will be discussed in the next session.

For recent reviews on the subject see references 15, 17 and 19-25. In general, it can be said that the method is best understood as applied to dilute solutions and becomes increasingly more complex as one progresses to higher Z materials. As a result liquids and solids will be discussed separately.

Liquids

Recently, Gunnink¹⁹, using a computer simulation has estimated the expected precisions of the individual atomic ratios under optimum

conditions. Using these estimates Reilly-Evans estimated (line A in Figure 2) the expected precision of the P_{eff} determination.

Points B are based on actual measurements of low burnup Pu at the E. I. duPont Savannah River Plant²⁴. Points C are from the "calibration alternatives" experiment described earlier in this section¹⁶. Points D are from tests made at the Allied-General Nuclear Services Plant¹⁸.

The average relative standard deviation of these measured values was 0.19%, with a range from 0.06% to 0.33%. This technique shows great promise since all the measured values are better than expected from Gunnink's estimates. The average random error is estimated to be 0.4% with a range of 0.12% to 0.8% (twice the highest estimated relative standard deviation).

Solids

Gunnink has also simulated gamma-ray isotopic measurements on solids. Line A in Figure 3 was calculated using Gunnink's estimates of attainable precision for atom ratios in solid materials. The simulation assumed a 1-hour count of a 1-kg sample of PuO_2 . The detector was a 1-cm³ intrinsic germanium crystal with a resolution of 550 eV at 122 KeV.

These predictions are very encouraging but a great deal of development effort will be required before these predictions are applicable. Among other things the simulation study showed that the gamma-ray spectrometer system must be very stable. For example, a 1% change in peak position or width can cause a 1% shift in the determination of some of the isotopes.

FIGURE 2
RANDOM ERROR OF P_{eff} DETERMINED BY THE COMPUTATIONAL METHOD
USING HIGH RESOLUTION GAMMA-RAY SPECTROMETRY OF LIQUIDS

FIGURE 2

Random error of P_{eff} determined by the computational method using high resolution gamma-ray spectrometry of liquids.

- A Estimate based on Gunnink's ⁹~~18~~ simulation study
- B Reference 24
- C Reference 18
- D Reference 18

FIGURE 3
RANDOM ERROR P_{eff} DETERMINED BY GAMMA-RAY SPECTROMETRY OF SOLIDS

FIGURE 3

Random error of P_{eff} determined by gamma-ray spectrometry of solids

- A Calculation based on Gunnink simulation study¹⁹
- B Private communication, R. Hamilton, Atlantic Richfield Hanford Company, April 1977
- C Reference 17
- D Reference 26 plus private communication with J. F. Lemming, Mound, October 1977. Upper value = 4,000 sec count, lower value = 10,000 sec count
- E Reference 21 - upper value = 2 hr count, lower value = 10 hr count
- F Reference 16
- G Private communication, J. F. Lemming, Mound, October 1977

Points B in Figure 3 are from a series of product type materials at the Atlantic Richfield Hanford Company²⁸. A simple straight line background determination as described by Zimmer²⁹ was used. Isotopic ratios were calculated using a modification of a method described by Parker and Reilly³⁰. The modification consisted of making corrections to the 160.35 keV peak of Pu-240 for the 161.45 keV peak of Pu-239 and the 161.60 keV peak of Am-241. In addition ARHCO did not observe a bias in the Pu-238 measurements and thus no bias corrections were made.

The precisions were based on five measurements performed randomly over a period of two to four weeks. Counting times were 10,000 seconds for low density (ash) materials and 20,000 seconds for high density materials.

In general the precisions of the P_{eff} determinations are two to four times greater than those predicted by Gunnink's simulation study. This is not too surprising, however, since the data represents a wide range isotopic compositions. Am, for example, was as high as 2% in one of the older samples (~ 9 years). In addition, Gunnink's simulation assumed a much more complex spectrum fitting routine than the one used.

Points C and D represent work^{17,25} done at this laboratory and are generally comparable with the ARHCO data. The upper values of D represent 4,000 sec counts and the lower values represent 10,000 sec counts. In general, the longer counting times improved the precision of the measurement by a factor of two or more.

Points E by Gunnink²¹, represent a 7,200 sec count (upper value) and a 36,000 sec count (lower value). Again the longer counting times significantly reduced the overall precision of the measurement.

Points F and G are from the calibration alternatives experiment described earlier. Point F represents 8,000 sec counts and was done at Argonne National Laboratory by Bellinger¹⁶. Points G represent 14,400 sec counts at Mound by Lemming.

Assuming a minimum of a 10,000 sec count the average random error (95% confidence level) of P_{eff} is estimated to be about 1.5% with a range of 0.25% to 3.0%. Hopefully, future developments in this field will push the precision toward the lower extremes. Perhaps most important at this time is the testing of Gunnink's more sophisticated peak analysis program on a wider variety of isotopic compositions and material forms, especially since it has already been demonstrated to work very well on high concentration Pu solutions¹⁸ and low burnup solids (Points E, Figure 3).

2.3.3 Systematic Errors of the Computational Methods

ANSI N15.22-1975 defines the systematic error in P_{eff} determined by the computational method to be:

$$S(P_{eff}) = \left(\sum_{n=1}^6 \left(F_i \frac{S(P_i)}{P_i} \right)^2 \right)^{1/2}$$

where $S(P_i)/P_i$ = relative uncertainty of the specific power, P_i , of the i th isotope. Recommended values are given by ANSI N15.22-1975.

Any errors in P_i will cancel in the S-R exchange since both shipper and receiver are expected to use the same values for P_i . However, these errors will contribute to both the shipper and receiver plant limit of error on material unaccounted for (LEMUF). These errors have been estimated for the typical isotopic compositions given in Table 6 and are shown in Figure 4 as points A. These errors are generally small and range from 0.1% to 0.2%. In addition a half-life evaluation sponsored by DOE's Division of Safeguards and Security, is now underway to reduce these errors to less than 0.1%³¹.

When systematic errors are calculated in this manner, errors in the actual isotopic measurements are not included as systematic errors. To test the size and effect of such errors, P_{eff} was calculated for three different isotopic compositions using the same metal exchange data used earlier to estimate random errors in determining P_{eff} . The interlaboratory precision, points B in Figure 4, was then used to estimate an average systematic error of P_{eff} . The interlaboratory biases were used as an indicator of the range of systematic errors which might occur. These biases were as much as 16 times larger than the errors due to uncertainties in the specific powers used.

One method for minimizing systematic errors when using the computational method is to calibrate it directly against the empirical method. This approach is very attractive because the bias determined includes corrections for biases in each of the individual isotopic measurements as well as any biases in the specific powers used.

FIGURE 4

SYSTEMATIC ERROR OF P_{eff} DETERMINED BY THE COMPUTATIONAL METHOD
USING ALPHA SPECTROMETRY AND/OR MASS SPECTROMETRY

FIGURE 4

Systematic error of P_{eff} determined by the computational method using alpha spectrometry and/or mass spectrometry.

- A Systematic error due to uncertainty in specific powers used¹⁵
- B Metal exchange data
- C Reference 16

Points C in Figure 4 give an example of such an approach. Here alpha spectrometry was used to determine the Pu-238 and Am-241 content and mass spectroscopy was used to determine the remaining Pu isotopes. The P_{eff} values were found to be from 0.1% to 0.2% higher than those determined by the empirical method and were consistent with the preliminary results of the half-life evaluation. In addition the variance in the bias correction (S_B^2/n) was only 0.03% (RSD). This uncertainty combined with the uncertainty of the Pu assay standards yields an overall systematic error of 0.12% (95% confidence limits).

Calibration of the computational method against the empirical method has several unique advantages and has been described previously³². It is especially attractive for gamma-ray spectrometry measurements since Pu-242 is not measured at all and some method is necessary to correct for Pu-242 content. Two alternatives are mass spectroscopy measurements to determine a "stream average" or to use isotopic correlation methods. Dragnev²², for example, has reported on the latter technique. All of these techniques require a relatively steady Pu-242 composition or knowledge of the particular reactor type in which the Pu was produced.

One other alternative is to determine the Pu-242 with a by-difference measurement using differential gamma-ray absorptimetry of solutions to determine total Pu and direct gamma-ray spectrometry to determine the amount of the other Pu isotopes present¹⁸. This is not a very accurate or precise method and is not applicable to solids.

2.3.4 Systematic Error of P_{eff} Using Gamma-Ray Spectrometry of Solids

Systematic errors for P_{eff} by gamma-ray spectrometry were estimated using equation 5 and the random and systematic errors estimated previously. For the optimum case, calibrating high precision gamma-ray measurements against good chemical measurements and assuming 10 bias determinations, the systematic error is 0.13%.

$$S_S^2 = 0.25^2/10 + 0.10^2$$

$$S_S = 0.13\%.$$

Likewise, for the average and upper extreme of the range

$$S_S^2(\text{ave}) = 1.5^2/10 + 0.21^2$$

$$S_S(\text{ave}) = 0.52\%$$

$$S_S^2(\text{upper}) = 3.0^2/10 + 0.35^2$$

$$S_S(\text{upper}) = 1.0\%.$$

Dragnev²⁴, using an "intrinsic self-calibration" of the gamma-ray spectra was able to achieve very good agreement between gamma-ray and mass spectrometry. P_{eff} determined by mass spectrometry agreed with P_{eff} determined by gamma-ray spectrometry of mixed oxide fuel rods within 0.04%. This is a somewhat fortuitous agreement since biases in Pu-240 and Am-241 were large enough to cause biases of 0.26% and 0.20% in P_{eff} . These biases had opposite signs however, and cancelled each other out.

Some typical biases from the ARHCO data presented earlier (Figure 3) between chemical recovery values and calorimetric assay using gamma-ray spectrometry of solids are given in Figure 5. The range of biases for 11 different determinations was -3.3% to +4.8% (Cal-Chem). The average bias was -0.8% with a standard deviation of 2.6%. When a simple linear regression was applied to the data a correlation

FIGURE 5

TYPICAL BIAS BETWEEN CHEMICAL RECOVERY AND CALORIMETRIC ASSAY
USING GAMMA-RAY SPECTROMETRY

was found between the Pu-239 content and the observed bias. The bias was found to be zero at 91% Pu-239 with a slope of 0.237%/ % Pu-239. The relative standard deviation about this line was 1.2% and the uncertainty of the bias correction was 0.4%.

Again it must be noted that these results cover a wide range isotopic composition and material types. With Dragnev's results on mixed oxides and Gunnink's success on a wide range of isotopic compositions and concentrations in mind it was decided the systematic errors estimated earlier in this section are reasonable.

2.4 P_{eff} by the Empirical Method

The random error in P_{eff} , $S(P_{eff})$, determined by the empirical approach arises from errors in the microcalorimetry and chemical analysis:

$$S^2(P_{eff}) = S^2(W) + S^2(Pu) \quad [7]$$

where $S^2(W)$ = random error variance of the wattage measurement

$S^2(Pu)$ = random error variance of the plutonium assay.

The errors associated with chemical analysis of plutonium have recently been reviewed by Reilly-Evans¹⁵. Their estimates based on exchange data from a variety of laboratories, are realistic and provide a reasonable assessment of the present state of the art. For PuO_2 their data is summarized in Table 7. Precisions for plutonium assay are estimated to average 0.2% and range from 0.04 to 0.86%. The systematic errors were estimated to range from 0.1% to 0.62% with an average of 0.17%. It was assumed eight standards

TABLE 7

RELIABILITY OF PLUTONIUM CONCENTRATION MEASUREMENTS OF PuO_2
IN INTERLABORATORY EXCHANGE PROGRAMS

Program	Method	Precision Intralaboratory (%)		Average Precision Interlaboratory (%)	Bias (%)	
		Average	Range		Average	Range
Umpire	Titration	0.09	-	0.48	-	-
SALE	Titration (Potentiometric)	0.25	-	0.23	0.20	-
SALE	All Methods	0.35	0.09-0.86	0.13	0.11	0.0-0.35
BNWL-1682	-	0.10	0.04-0.28	-	0.29	-
All programs	-	0.20	0.04-0.86	0.28	0.20	0.0-0.35
Optimum Conditions		0.04-0.05		0.06	-	-

determinations were made (1/week), with a random error of twice the precision. The uncertainty of the standards was assumed to be 0.1% (95% confidence level) from the NBS #949 series.

The estimated systematic error could be decreased by assuming a greater number of standards determinations. The magnitude of the biases however, indicated the higher estimate to be more reasonable. For example, in the Reilly-Evans study the average bias was about 0.2% and ranged from 0.0% to 0.35%. These biases seem a bit high since standards were used in all cases, but is consistent with Reilly-Evans' comment that "often there are one or two laboratories whose results exhibit good precision but lie 0.5% or more from the mean of the other laboratories".

Stewart and Wirfs observed a similar phenomena in their analysis of a large number of actual plutonium shipments at the Hanford site. Even though the pooled precision of the Pu analysis was 0.1%, the average intersite bias was 0.29%.

The fact that observed biases are often larger than expected is cause for concern. Apparently the analytical procedures are not being well controlled or some additional unidentified variables are present. The most likely undetected errors identified by Stewart and Wirfs were dissolution problems and moisture pickup or loss. Thus the systematic errors of the plutonium analysis were estimated to range from 0.1% (the uncertainty of the Pu assay standard) to 0.62% with an average of 0.20%.

The overall estimated random and systematic errors in P_{eff} by the empirical method are summarized in Table 8.

TABLE 8

ESTIMATED ERRORS ASSOCIATED WITH THE DETERMINATION
OF P_{eff} BY THE EMPIRICAL METHOD

Case	Relative standard deviation, %		
	$S(W)^*$	$S(P_u)$	$S(P_{eff})$
<u>Random Errors</u>			
Average	0.56	0.40	0.68
Range-minimum	0.06	0.08	0.10
Range-maximum	1.0	1.7	2.0
<u>Systematic Errors</u>			
Average	0.07	0.20	0.21
Range-minimum	0.02	0.10	0.10
Range-maximum	0.14	0.62	0.64

*Assumed 2-gram sample size

$$S^2(P_{eff}) = S^2(W) + S^2(P_u)$$

2.5 Summary

The random and systematic errors estimated in this section are summarized in Table 9. In general this analysis indicates: 1) the random and systematic errors of calorimetric assay are generally comparable with those of chemical assay. 2) At this point in time the systematic error in both chemical and calorimetric assay is dominated by the uncertainty in Pu assay standards. This is an area where an immediate benefit can be gained from the present NBS program on improved standards. 3) For this application, Pu isotopic determinations by gamma-ray spectrometry are comparable to mass spectrometry in terms of accuracy and precision. Moreover, in terms of sample preparation, instrument cost and sample capacity it may have a definite advantage.

3.0 EVALUATION FOR ACCOUNTABILITY PURPOSES

The criteria used for evaluating the merits of calorimetry for S-R exchanges were: 1) how well the shipper and receiver would normally agree; 2) how reliable is the method, free from interferences, etc.; and 3) how do the costs of the various methods compare?

How well the shipper and receiver might normally be expected to agree on shipment of 40 containers was estimated by combining the random and systematic errors as follows:

$$S_R^2(\text{SRD}) = \frac{S^2(\text{S})}{40} + \frac{S^2(\text{R})}{40} + S_S^2(\text{S}) + S_S^2(\text{R})$$

where $S^2(\text{SRD})$ = total error variance of the S-R difference

$S^2(\text{S})$ = random error variance of shippers measurement

$S^2(\text{R})$ = random error variance of receivers measurement

TABLE 9 - SUMMARY: RELIABILITY OF CALORIMETRIC ASSAY FOR SHIPPER-RECEIVER
MEASUREMENTS ON PLUTONIUM

Case	Method	Random Error (%) (95% confidence level)		Systematic Error (%) (95% confidence level)	
		range	average	range	average
Base	Chemistry + weight	0.05-0.86	0.20	0.10-0.35	0.21
1	Calorimetry alone (watts exchange)	0.03-0.37	0.17	0.023-0.14	0.07
2	Calorimetry + P_{eff} (empirical)	0.07-1.1	0.33	0.10-0.40	0.22
3	Calorimetry + P_{eff} (computational) using alpha and/or mass spectrometry	0.15-1.1	0.62	0.11-0.61	0.31
4	Calorimetry + P_{eff} (computational) using gamma-ray spectrometry of liquids	0.12-1.1	0.43	0.11-0.58	0.27
5	Calorimetry + P_{eff} (computational) using gamma-ray spectrometry of solids	0.25-3.0	1.5	0.13-1.0	0.52

$S_S(S)$ = systematic error variance of shippers measurement

$S_S(R)$ = systematic error variance of receivers measurement.

Using the average random and systematic errors estimated earlier for chemical analysis $S(SRD)$ is estimated as follows:

$$S^2(SRD) = \frac{0.20^2}{40} + \frac{0.20^2}{40} + 0.21^2 + 0.21^2$$

$$S^2(SRD) = 0.0902$$

$$S(SRD) = 0.30\% \text{ of shipper or receiver value.}$$

For operating costs a figure of \$30,000/manyear or \$15/hr was used. For capital costs the calorimeters were estimated at \$50K each and the gamma-ray spectrometry system was estimated at \$50K each.

For the base case (weight plus chemistry) it was assumed that the analytical laboratory was equipped to perform a minimum of eight Pu assays per shift.

In terms of intersite agreement it appears that calorimetry plus chemistry is roughly equal to the base case. It must be remembered that the same values were used for the random and systematic errors of the chemical assay in both cases. Thus this comparison does not take into account that the largest source of variability in the chemical assay, moisture variations, can be essentially eliminated by the use of calorimetry. Case three (Table 10), calorimetry alone, gives an indication of the potential improvement if moisture problems are eliminated.

TABLE 10: SUMMARY: ACCOUNTABILITY ASPECTS OF USING CALORIMETRY
FOR SHIPPER-RECEIVER EXCHANGES

Case	Method	Average S-R Agreement	Interferences (Probability of Occurrence)	Incremental Costs			
				Capital		Operating ^A	
				Shipper	Receiver	Shipper	Receiver
Base	Weight plus chemistry	0.30%	Variation of moisture content (high)	-	-	-	-
1	Calorimetry plus chemistry	0.32%	Chemical reactions (low)	+\$100K	+\$100K	\$10	\$10
2	Calorimetry plus gamma-ray spectrometry	0.81%	Same as 2 plus other isotopes	+\$100K	+\$100K	\$10	\$10
3	Calorimetry alone (heat measurement only)	0.11%	Same as 2	+\$ 50K	+\$ 50K	\$ 5	\$ 5

^ACost/oxide container based on \$15/hr of hands-on time.

There are several alternative methods to solving the moisture problem. ASTM C 697-74 recommends that "all sampling and critical weighings are to be performed in an atmosphere with a dewpoint no greater than -23°C." In practice however, this has been very difficult to achieve and few if any laboratories have been able to do it on a consistent basis.

A second method now widely used in Europe³³ requires the receiver be present at the time the shipper makes his bulk measurements. The shipper first blends the oxide to be shipped. Analytical samples for both the shipper and receiver are then drawn and weighed from the blended material. The shippers bulk measurement is then made on the batch and observed by the receiver. It is important that the bulk sample and the analytical samples are all weighed at the same time so the moisture contents will be as similar as possible.

The shipper and receiver Pu contents are calculated as follows:

$$\text{For the shipper } C_S = D \times A_S \times \frac{B_S}{C_S}$$

$$\text{For the receiver } C_R = D \times A_R \times \frac{B_R}{C_R}$$

where C = Pu content (grams)

A = Pu assay (g Pu/g of sample)

$\frac{B}{C}$ = correction factor for moisture absorption based on shippers weight of aliquot, B, and ~~receivers~~ weight of aliquot at time of Pu assay, C.

D = shippers bulk measurement

and subscripts S and R refer to the shipper and receiver, respectively.

Using this approach an average shipper-receiver difference of +0.057% was achieved on 58 batches of oxide shipped to five different customers from the Windscale Works of British Nuclear Fuels, Ltd. (BNFL). The standard deviation of the differences was 0.14%.

Similar results were also achieved in the calibration alternatives experiment. As in the European case all samples for the two laboratories involved were drawn and weighed at the same time. The samples were then completely dissolved and analyzed based on the original sample weights. For the three isotopic compositions studied the intersite agreement was better than 0.02% for the average of six values.

The principal disadvantage to this approach is that shipper and receiver measurements are not independent. The received value is based on the shippers weights on the bulk samples and on the analytical aliquots applied to the receiver.

Oxidation causes similar problems with the shipment of Pu metals. Sampling for chemical analysis is complicated by surface oxidation of the metal. Samples taken at the surface are lower in Pu content than the overall average for the metal ingots and vice versa for samples drawn from the core of the ingots. Accurate calorimeter measurements can be made, provided sealed containers are used so that no oxidation occurs during the calorimeter measurement.

The sampling method used by the Europeans for oxides will not solve this problem, since the metal cannot be homogenized as the oxide is by blending.

For inhomogeneous materials where sampling is difficult (i.e., scrap for recovery) calorimetry plus gamma-ray spectrometry shows most promise. Excellent intersite agreement can be achieved on power measurements and gamma-ray spectrometry can provide a measurement of the average isotopic compositions of material. In addition, this method is totally nondestructive and does not require opening of the container for receiver verification. This is a real advantage because scrap for recovery is often not processed for several months after receipt.

In summary the principal advantages to the use of calorimetry for S-R measurements of Pu materials are:

1. Calorimetry provides an excellent method for eliminating a primary problem with the present method, moisture pickup or loss in oxides or oxidation of metals between shipper and receiver.
2. For shipments of nonhomogeneous plutonium bearing materials, calorimetry plus gamma-ray spectrometry of solids provides an excellent totally nondestructive method^d for S-R measurements.
3. Precise power measurements on the sealed containers made possible an early identification of any S-R differences on the bulk measurements. Since these differences are identified prior to opening the container, resolution by a third party measurement is possible. This is an alternative not available with the present system.

4.0 EVALUATION FOR DIVERSION DETECTION PURPOSES

The two prime criteria for diversion detection are timeliness and sensitivity. That is, the best diversion detection system is the one which detects the loss of the smallest quantity of material in the least time.

For this evaluation the timeliness is determined by the elapsed time from receipt of material to detection of diversion.

The sensitivity of diversion detection was based on the average random and systematic errors determined earlier. For a single container the limit of diversion detection (95% confidence level) was estimated to be simply the random plus the systematic errors. For example, for chemical assay the detection limit of a single container (DLSC) was estimated as follows:

$$\begin{aligned} \text{DLSC} &= 0.20 + 0.21 \\ &= 0.41\%. \end{aligned}$$

For a shipment of 40 containers the random error is reduced by the 40. For example, for chemical assay the detection limit for a total shipment (DLTS) was estimated as follows:

$$\begin{aligned} \text{DLTS} &= \frac{0.20}{\sqrt{40}} + 0.21 \\ &= 0.24\%. \end{aligned}$$

The relative merits of the various cases are as follows.

4.1 Base Case

The present method of chemistry + weight was chosen as the reference case for the relative evaluation of various alternatives. The normal

procedure is as follows.

1. On receipt of the drums the seals and container identifications are checked.
2. The drums are then normally stored for periods of time varying from 0 to 14 days.
3. The drums when opened are monitored for alpha contamination and the seals on all containers are checked as they become exposed (about 2 hrs/drum).
4. The inner container is removed from the shipping drum and the gross weight is measured (1 hr).
5. Generally if this weight agrees with the shippers weight within 1-2% no potential diversion flag is raised.
6. The container is then passed into the glovebox, opened and the bulk powder is weighed and transferred (1-2 hrs). Again if the agreement is within 1-2% no flag is raised, especially if the receiver weights are larger than shippers (possible moisture pickup).
7. The product oxide is then sampled and analyzed for Pu content (8-24 hrs).

4.2 Calorimetry Alone

Calorimetry can only be effective after the container has been removed from the shipping drum. Thus steps 1 through 5 are the same as the base case. At step 6 a power measurement can be made. Assuming use of prediction of equilibrium, pre-equilibrium and servo-control of the calorimeter, the containers could be measured at a rate of 1/hr with the first sample requiring 4 hrs. For a typical shipment of 40 containers and only one calorimeter the

measurements would require 44 hrs. Assuming two calorimeters the time would be reduced to 24 hrs. The DLSC would be 0.24% and for the shipment the DLTS would be 0.10%.

4.3 Calorimetry Plus Chemical Assay

The time to complete the chemical assay would be essentially the same as the base case. The DLSC and the DLTS would be 0.55% and 0.27%, respectively.

4.4 Calorimetry Plus Gamma-Ray Spectrometry of Solids

In this case the time would be controlled by the time to make the gamma-ray measurement, about 3 hrs/sample or 120 hrs total. The DLSC and DLTS would be 2.0% and 0.75%, respectively.

4.5 Neutron Counting of the Drum

An alternative diversion detection measurement which has been previously suggested is to perform a gross or coincident neutron count on the as-received shipping containers. This has the advantage that the measurements are made immediately on receipt without the necessity of opening the drums.

Los Alamos Scientific Laboratory scientists have estimated the precision for a 3-min count to be 2 to 3% with an accuracy of better than 5%³⁴. Using the criteria set down earlier, the random and systematic errors are both estimated to be 5%. Thus, using neutron counting the DLSC is 10% and the DLTS is 6.2%. Including time to handle the drums it is estimated all 10 drums could be counted in 1 hr.

4.6 Summary of Diversion Detection Evaluation

The results are summarized in Table 11. In general, the best measurement for diversion detection depends on the diversion scenario which one is defending against and the type of material being shipped.

For example, by diversion path analysis or some other evaluation technique, an operator may determine the most likely method of diversion enroute is the theft of one or more containers from the shipping drum. In this case neutron counting provides sufficient sensitivity to detect such a loss and the timeliness is far better than any of the alternatives discussed.

On the other hand if it is decided that diversions of 6% or less from a single container are probable then calorimetry is a better method. The sensitivity is better and the time is comparable to the first bulk measurement by weighing. This method is most attractive to those plants in which the incoming shipments are immediately removed from the shipping containers and are stored separately in a vault, rather than using the shipping drums as storage containers.

The use of gamma-ray spectrometry seemingly has little to offer for diversion detection. The sensitivity is comparable to the combination of seal checks, alpha contamination checks and the bulk weight of the inner container. The timeliness is not nearly as good.

TABLE 11: SUMMARY: DIVERSION DETECTION ON A TYPICAL SHIPMENT
OF 40 2.5 kg CONTAINERS OF PuO₂ IN 10 DRUMS

Case	Method	Sensitivity of Detection (attribute measured)		Timeliness of Detection (hrs from receipt)	Incremental Costs	
		DLSC	DLTS		Capital \$K	Operating \$/oxide container
Base	Weight plus chemical assay	2% 0.41%	1% 0.24% (g-Pu)	20 48	- *	- -
1	Calorimetry only (1 cal)	0.24%	0.10% (heat)	48	\$ 50K	\$ 5
	(2 cal)	0.24%	0.10% (heat)	24	\$100K	\$ 5
2	Calorimetry plus chemical	0.55%	0.27% (g-Pu)	56	\$150K	\$10
3	Calorimetry plus gamma-ray spectrometry	2.0%	0.75% (g-Pu)	122	\$100K	\$10
4	Neutron count	10%	6.2% (N°)	4	\$ 50K	\$ 2

*Assumes analytical laboratory capable of assaying 8 containers/shift.

Thus, for diversion detection gamma-ray spectroscopy of homogeneous Pu bearing materials seems an expensive and redundant measurement. For inhomogeneous materials where the N emission rate is less predictable due to matrix variations the use of gamma-ray spectroscopy appears to be preferable.

In summary, using average values for random and systematic errors the present state of the art for diversion detection for a typical 100-kg shipment of PuO_2 is 6% in 4 hrs by neutron counting or 0.1% in 24 hrs by calorimetry.

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