A report submitted to the
United Kingdom Atomic Energy Authority
Safeguards R & D Project
December 1982

SRDP-R100

THE USE OF CALORIMETRY FOR PLUTONIUM ASSAY

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Safeguards R & D Project
AERE Harwell
December 1982
EXECUTIVE SUMMARY

Calorimetry is a technique for measuring the thermal power of heat-producing substances. The technique may be applied to the measurement of plutonium-bearing materials which evolve heat as a result of alpha and beta particle decay. A calorimetric measurement of the thermal power of a plutonium sample, combined with a knowledge or measurement of the plutonium isotopic mass ratios of the sample provides a convenient and accurate, non-destructive measure of the total plutonium mass of the sample.

The present report provides a description and an assessment of the calorimetry technique applied to the assay of plutonium-bearing materials. In Section 1, calorimetry methods are described in general and examples are provided of different types of calorimeters. Recent work in the area of "in reactor" absorbed dose microcalorimetry at Imperial College is described.

Section 2 contains a detailed technical description of calorimetry as it applies to plutonium measurements. Types and characteristics of plutonium calorimeters are considered, as well as calibration and operating procedures. The instrumentation used with plutonium calorimeters is described and the use of computer control for calorimeter automation is discussed. The analysis of calorimetry measurement errors is also considered.

Section 3 consists of a critical review and assessment of plutonium calorimetry literature since 1970. Both fuel element and plutonium-bearing material calorimeters are considered. The different types of plutonium calorimeters are evaluated and their relative merits are discussed. A combined calorimeter and gamma-ray measurement assay system is considered.

Finally, in Section 4, the design principles of plutonium assay calorimeters are considered. An automatic, computer-based calorimeter control system is proposed in conjunction with a general plutonium assay calorimeter design.
# THE USE OF CALORIMETRY FOR PLUTONIUM MEASUREMENT

## EXECUTIVE SUMMARY

## TABLE OF CONTENTS

## LIST OF TABLES

## LIST OF FIGURES

## 1. THE CALORIMETRY TECHNIQUE

### 1.1 Calorimeter Types

### 1.2 Calorimeter Operating Modes

#### 1.2.1 Adiabatic mode

#### 1.2.2 Steady state (heat flow) and isothermal mode

#### 1.2.3 Kinetic or pseudo-adiabatic mode

### 1.3 Applications of Calorimetry

#### 1.3.1 General calorimetry

#### 1.3.2 Radiation beam calorimetry

#### 1.3.3 Reactor radiation absorbed dose calorimetry

## 2. CALORIMETRY FOR PLUTONIUM ASSAY

### 2.1 Plutonium Decay

### 2.2 Characteristics of Plutonium Calorimeters

#### 2.2.1 Determination of effective specific power

#### 2.2.2 Plutonium calorimeter types

#### 2.2.3 General characteristics

### 2.3 Calorimeter Operation and Calibration Procedures

#### 2.3.1 Operating procedures

#### 2.3.2 Calibration procedures

#### 2.3.3 Typical measurement sequence
2.4 Instrumentation and Data Analysis
   2.4.1 Temperature measurement
   2.4.2 Temperature control
   2.4.3 Computer control and data analysis

2.5 Measurement Precision and Error Analysis
   2.5.1 Sources of error
   2.5.2 Error analysis
   2.5.3 Measurement precision and detection limits

2.6 Calorimetry and Other Plutonium Measurement Techniques

3. CRITICAL REVIEW AND ASSESSMENT OF THE LITERATURE OF PLUTONIUM ASSAY AND FUEL ELEMENT CALORIMETRY
   3.1 Calorimetric Assay of Plutonium-Bearing Materials
   3.2 Fuel Element Calorimetry
   3.3 Summary and Assessment of the Calorimetric Techniques for Plutonium Measurement

4. DESIGN OF A PLUTONIUM ASSAY CALORIMETER
   4.1 General Design Considerations
   4.2 Proposal for a Fast Response Plutonium Calorimeter

FIGURES

REFERENCES
LIST OF TABLES

Table 1  Nuclear Constants for Radionuclides in Plutonium-Bearing Solids.  16
Table 2  Isotopic Ratios and Components of Heat Output for American Plutonium Samples.  17
Table 3  Isotopic Ratios and Components of Heat Output for British Plutonium Samples.  19
Table 4  Typical Temperature Equilibrium Times.  29
Table 5  Typical Errors Associated With Plutonium Calorimetry.  37

LIST OF FIGURES

Figure 1  Example of a General Calorimeter.  56
Figure 2  Example of a Radiation Beam Calorimeter.  56
Figure 3  The Imperial College "In Reactor" Microcalorimeter.  57
Figure 4  Twin Thermoelectric Fuel Rod Calorimeter.  58
Figure 5  Mound Twin Resistance Bridge Plutonium Calorimeter.  58
Figure 6  Thermal and Heat Exchanger of the Mound Transportable Twin Resistance Bridge Plutonium Calorimeter.  59
Figure 7  ANL Dry Fast Response Fuel Rod Calorimeter.  60
Figure 8  Calorimeter Computer Control and Data Analysis System.  61
Figure 9  Proposed Single Isothermal Servo-Controlled Plutonium Assay Calorimeter.  62
1. **THE CALORIMETRY TECHNIQUE**

A calorimeter is an instrument which measures heat. There exists a wide variety of calorimeters of different types so the aim of the first part of this report is to describe calorimetry in general. The remaining parts of the report are specific to calorimetry for the measurement of plutonium.

Calorimetry is a long-standing, well-established technique and calorimeters have been employed in the measurement of a wide variety of heat-producing processes. Included among these are chemical reactions, radioactivity and biological processes. A number of general calorimetry references exist (Wh28, Sw46, Ro56). The specific category of radiometric calorimetry, of which plutonium calorimetry is a part, has been extensively reviewed by Gunn (Gu64, Gu70). The main types of calorimeters are considered in the next section.

1.1 **Calorimeter Types**

Although the choice is somewhat arbitrary, due to the great variation among calorimeters, one may identify three basic calorimeter types. A further distinction may be made between radiometric and non-radiometric calorimeters. Some calorimeters exist in both forms although the latter two types to be described are of the radiometric kind only. These distinctions will shortly be made clear.

Before describing calorimeter types it is essential to clarify some of the terminology currently in use. The most important part of the calorimeter and the part in which the heat is measured is known as the thermal element or thermel. The term thermel will be used throughout the present report. It is the component of the calorimeter in which either the heat-evolving material to be measured is placed, or the component of the device into which heat is deposited, for example by radiation. In other words, it
is either the vessel which holds the sample to be measured, or it is a fixed sample of a specific material into which heat is released. A calorimeter measurement is essentially a measurement of the change in temperature or heat evolution rate of the thermel. The thermel is usually insulated from its surroundings and it contains a temperature sensor.

The term general calorimeter will be used to describe the first and most common type of calorimeter. It is used to measure the heat evolved from substances which are placed entirely inside the thermel of the calorimeter. Examples of the use of this type of device include the measurement of heats of chemical reactions and half-life measurements of radioactive substances (Sw46). Both bomb calorimeters for measuring combustion processes, and the plutonium calorimeters described elsewhere in this report are of the general type.

The second type of calorimeter is the radiation beam calorimeter. It has been developed for the measurement of the energy deposited by a beam of radiation (Do74, Co80). Some calorimeters of this type measure the total beam energy, while others measure the local absorbed dose as seen by a small sample (the thermel) placed in the beam. The principal use of beam calorimeters is in the measurement of the energy deposited by beams from medical radiotherapy sources, especially $^{60}$Co sources. The basis of the operation of such calorimeters is the absorption of energy from the radiation beam where the absorbing sample of material (the thermel) acts as a form of target. The energy absorbed by the thermel causes its temperature to rise and this is measured. High measurement accuracy may be achieved because the calorimeter can be placed, as with general calorimeters, in a stable temperature-controlled environment.

The third type of calorimeter is what Gunn describes as the "in pile" or "in reactor" local absorbed dose calorimeter (Li65, Gu70, Ma81). These calorimeters measure the energy deposited, or the local absorbed dose, in a small
sample of material (the thermel) placed in a radiation field. The field may be generated by an external radiation source, or it may be the mixed radiations found in the core region of a nuclear reactor. Although "in pile" calorimeters may sometimes be used for beam measurements, they are designed to receive radiation from all directions and to operate in physically-restricted and thermally-unstable environments.

An important variation of calorimeters of the first two types is that they are sometimes designed with twin thermels. The measurement is made by comparing the thermel in which heat is released or deposited with the reference or dummy thermel. In this manner, some temperature drift errors in the calorimeter may be eliminated. Some plutonium calorimeters employ the principle of twin thermels.

1.2 Calorimeter Operating Modes

In all calorimeters heat is either deposited in a sample (by radiation), or evolved in the thermel or active volume of the device as a result of a heat-producing process such as a chemical reaction or radioactivity. The operation of calorimeters is determined by the processes through which this heat is transferred between the calorimeter thermel and its surrounding environment. In general, for a calorimeter with an external jacket, the equation for the heat transfer may be written as,

\[ \frac{dQ}{dt} = m \cdot C \frac{dT}{dt} = P - L(T - T_j) \]  

(1)

where \( Q \) = heat (Ws)
\( P \) = power input (W)
\( m \) = mass of the thermel (g)
\( L \) = thermal leakage (W/°C)
\( T \) = temperature of the thermel (°C)

and the subscript \( j \) refers to the jacket.

Following Sautiez (Sa71), one may identify three conditions or modes under which calorimeters can operate. One may identify other modes of operation, although they are not as important.
1.2.1 Adiabatic mode

The first mode of operation is based on the principle of the elimination of heat transfer between the thermel and its surrounding jacket. Calorimeters of this type are said to be adiabatic, and increases in the temperature of the thermel are therefore solely due to the evolution of heat within the thermel. Adiabatic conditions are generally created by surrounding the thermel with a jacket whose temperature is made to follow that of the thermel. This may be accomplished by externally heating or cooling the jacket, and by the establishment of thermal insulation between the thermel and jacket so that deviations from the adiabatic condition occur slowly. For adiabatic equilibrium, \( T = T_j \) and,

\[
\frac{dQ}{dt} = P = m C \frac{dT}{dt}.
\]  

(2)

Quasi-adiabatic operation is similar to that described above, except that small temperature differences exist between the thermel and the jacket. Constrained quasi-adiabatic operation involves the maintenance of a small and constant temperature difference between the thermel and the jacket. This difference is small and it can be measured, and a correction applied, in order to exactly compensate for the heat loss.

1.2.2 Steady-state (heat flow) and isothermal mode

The second operation mode is known as steady-state or heat flow operation. In this mode, heating or cooling of the thermel is allowed to proceed until a steady-state or equilibrium heat transfer situation exists between the thermel and the jacket. The gap between the thermel and the jacket is designed to have a low thermal conductivity so that a significant and readily-measurable temperature difference will exist. This temperature difference will reach a constant value for a given heat input (heat generation rate) when the heat loss rate balances the heating rate. A constant, temperature-independent thermal
leakage is assumed. This mode of operation is represented mathematically by equation (3),

\[ P = L(T - T_j) \]  

(3)

where the equation applies after the equilibrium heat transfer rate has been established. It is assumed that the jacket temperature remains roughly constant during the measurement period. A disadvantage of this mode of operation is that often, long time-periods are required before the equilibrium heat transfer rate is established.

In some cases it is possible and desirable to maintain an isothermal jacket (constant jacket temperature). Heat flow calorimeters of this type are sometimes incorrectly described as isothermal. The correct term, which is increasing in use, is isoperbol. True isothermal operation requires that the thermal temperature be kept constant. Fuel element calorimeters (Section 3.2) are isothermal and other examples of true isothermal calorimeters include ice (Sw46), and liquid nitrogen calorimeters (Je51), in which the energy deposited by radiation results in a change of state of the material in the thermel.

1.2.3 Kinetic or pseudo-adiabatic mode

In this mode of calorimetry operation, adiabatic and equilibrium (steady-state) conditions apply at different times during the measurement period. The form of analysis appropriate to either adiabatic conditions or steady-state (heat flow) conditions may then be applied when these conditions apply.

1.3 Applications of Calorimetry

In principle, only calorimeters of what has been called the general type are applicable to non-radiometric applications. Although calorimetry has been applied to a very wide variety of applications, only a limited selection will be presented here to serve as examples. The three calorimeter types are illustrated by examples in Figs. 1, 2 and 3. Plutonium assay calorimetry is only mentioned briefly in this section.
1.3.1 General calorimetry

The term 'general calorimeter' has been chosen to describe all calorimeters of the type in which samples of material may be placed in the thermal and the heat evolved from them measured. Virtually all calorimeters used in thermochemistry are of this type, as are radiometric calorimeters used for the measurement of isotope half-lives and for assay purposes.

A wide variety of examples and variations of this type of calorimeter are included in standard references on calorimetry (Sw46, Ro56). Bomb calorimeters of this type are used for measurements of heats of combustion. Microcalorimeters of the general type, operating in a variety of modes, have been employed for the measurement of processes of long duration where only small amounts of heat are evolved. Examples include the measurement of heats of adsorption and of the slow reactions of organic chemistry. Sensitive microcalorimeters have been employed for measurements of biological processes such as the germination of seeds and bacterial growth.

Radiometric applications of general calorimetry have been reviewed most extensively by Gunn (Gu64, Gu70). Their principal use has been in the measurement of α, β and γ active radionuclides. The calorimeters have been used to determine radionuclide half-lives, average β energies and fission product power, as well as for the assay of plutonium-bearing materials including fuel elements.

1.3.2 Radiation beam calorimetry

Radiation beam calorimetry has grown principally out of the need to calibrate gamma-ray sources used for radiotherapy. These calorimeters are used to measure either the local absorbed dose in a beam, or the total beam energy. The field has been extensively reviewed by Gunn (Gu70), and the theory of gamma-ray beam absorbed dose is well understood (ICRU73). Numerous examples of traditional
gamma-ray beam calorimetry for calibrating sources and
detectors may be found in the literature (Do62, Pr62).
Neutron beam dosimetry theory is also well established,
and neutron beam calorimeters have been developed (Bew74,
ICRU77).

Recent developments in absolute radiation beam calorimetry
have resulted in improved performance and measurement
accuracy (Do74, Do82). These developments have been
applied to high energy electron beam measurements and the
determination of improved G-values for chemical dosimeters
(Co80).

1.3.3 Reactor radiation absorbed dose calorimetry

The field of "in pile" calorimetry has been reviewed by
several authors (Li65, Gu70, Sa71, Ma81). Most of the
published work has been directed towards the development
of high-powered calorimeters for in reactor local absorbed
dose measurements of both neutrons and gamma rays. In
a manner similar to beam calorimetry, the absorbed dose
is determined by measuring the temperature rise in a
small sample of material (the thermel). Both the heat
flow and adiabatic modes of operation have been employed.
Thermocouples are most often used for temperature measure-
ments although the use of resistance thermometry is
increasing.

The most difficult problems in this type of calorimetry are
related to the necessarily small size of the thermel or
measurement sample, and the hostile thermal and radiation
environment in which measurements are performed. A par-
ticular problem with many calorimeters of this type has
been a lack of electronic equilibrium between the sample
and its surroundings (Li65, Ma81), and this has led to
significant errors in some absorbed dose measurements.

Dose rates for "in reactor" calorimeters range from a few
k Gy s\(^{-1}\) to a few Gy s\(^{-1}\), (1 Gy s\(^{-1}\) = 100 rad s\(^{-1}\) = 1 mW g\(^{-1}\)).
Examples which illustrate the variety of "in reactor" high-
power calorimeters are to be found in the work of Haack and Petitcoles (Ha72, Pe82).

Recent work at Imperial College is relevant to the "in reactor" calorimetry field. For some time a programme of development of sensitive microcalorimeters for absorbed dose measurements in low intensity radiation fields has been underway (Ma76, Ma78, Ma81, Ma82). Several adiabatic calorimeters with different sample materials (thermels) have been constructed and tested in both a low-power reactor and in the field of a $^{60}$Co source. The aim of the work has been to improve the sensitivity in order that absolute calorimetric measurements can be made in low intensity standard radiation fields, not previously accessible to the calorimetry technique. The use of calorimeters of different materials has made possible a determination of the different components in a reactor-mixed radiation field. Dose rates of a few tens of mGy s$^{-1}$ have been measured in the CONSORT II reactor, and of a few mGy s$^{-1}$ in the Imperial College $^{60}$Co facility. The errors in these measurements depend on the sample materials and they are generally of a few percent.

A novel feature of the calorimeter system is that both the adiabatic electrical heater and the data acquisition are controlled by a microcomputer in the form of a CAMAC-based Harwell 7025 controller. Thermocouple voltages from the calorimeter are amplified by low noise chopper stabilized amplifiers and after digitization, the signals are processed and analysed by the controller.

Current calorimetry development is directed towards two ends. The first is the redesign of the microcalorimeters to improve both their sensitivity and to eliminate systematic errors. The second area of development concerns the control system. The CAMAC controller and system is being replaced by an LSI-II microcomputer system which will provide both improved real-time control, as well as complete data reduction and analysis. The LSI-II microcomputer permits virtually complete automation of the calorimetry measurement process, thus permitting routine use of the device by relatively inexperienced personnel.
2. **CALORIMETRY FOR PLUTONIUM ASSAY**

Calorimetry is an attractive technique for the measurement and assay of plutonium-bearing materials. It is perhaps best to begin this section, in which the technique is described, by summarizing the advantages and disadvantages of calorimetry.

**Advantages:**

(a) Calorimetry is a non-destructive technique.

(b) Sampling or aliquoting is not required. The technique is capable of measuring quantities ranging in size from grams to kilograms.

(c) Weight changes and humidity effects are irrelevant.

(d) Calorimetric determinations of sample power or heat output are very accurate.

(e) The method is unaffected by self-absorption processes in the sample material.

(f) Measurement times are short compared to some other methods of analysis, and range from a few hours to minutes.

(g) No sample preparation is required and sample packaging need not be removed.

(h) Inhomogeneous samples may be measured.

(i) Calorimetry can distinguish between the fissile isotopes $^{235}$U and $^{239}$Pu because of the difference in half-lives.

(j) Calorimetry is an absolute technique.

**Disadvantages:**

(a) The isotopic composition of the plutonium (including $^{241}$Am) must be known or measured by another technique, such as mass spectrometry, neutron counting or gamma-ray spectroscopy.
(b) In some calorimetric measurements, long periods are required for samples to reach thermal equilibrium.

The remainder of this section is devoted to a detailed description of the calorimetry technique as it applies to the measurement of plutonium.

2.1 Plutonium Decay

The heat evolved by plutonium-bearing materials which is measured by calorimetry results from the radioactive decay of the constituent plutonium isotopes and americium-241. In normal reactor grade plutonium, isotopes of the following mass numbers may be present: 238, 239, 240, 241 and 242. All the isotopes decay by α-particle and gamma-ray emission except 241Pu, the β-particle decay of which results in the formation of 241Am, itself an α-particle emitter. The proportions of the isotopes depend on the burn-up of the fuel from which they were extracted, the reactor spectrum in which they were produced, and the length of time from americium separation. Each isotope decays with a characteristic half-life, and each produces heat at a rate which is known as the specific power with units of W g⁻¹. A mixed isotope sample of plutonium (also containing 241Am) may be characterized by an effective specific power which is the sum of the specific powers weighted by the isotopic abundances. This point is illustrated by equation (4),

\[ W_s = M \cdot P_{\text{eff}} = \sum_i m_i R_i P_i = \sum_i m_i R_i P_i \]

where
- \( W_s \) = total power of a plutonium-bearing sample (W)
- \( M \) = total mass of heat-producing isotopes (g)
- \( m_i \) = mass of the \( i^{\text{th}} \) isotope (g)
- \( R_i \) = ratio of the mass of the \( i^{\text{th}} \) isotope to the total plutonium mass (isotopic abundance)
- \( P_i \) = specific power of the \( i^{\text{th}} \) isotope (W g⁻¹)
- \( P_{\text{eff}} \) = effective specific power of the sample (W g⁻¹)

It is useful to consider the two processes of radioactive decay of plutonium in relation to heat production. For
α-particle emitting isotopes, the energy released is the sum of the α-particle energy, the recoil energy of the daughter nucleus and the energy resulting from the transition of the excited daughter nucleus to the ground state. This excitation energy is released through the production of either gamma rays or conversion electrons. The proportion of energy released in the form of gamma rays by plutonium isotopes is very small, less than 0.005%. However, for the α-particle decay of $^{241}$Am a higher proportion of the energy is released in the form of gamma rays (0.38%). These gamma rays are mainly associated with the 59 keV transition and most of the resulting energy is absorbed in the sample. In fact, only the higher energy gamma rays may escape from the sample and this fraction is known to be less than 0.01% of the total decay energy.

In the case of the β-particle decay of $^{241}$Pu, the energy released is the sum of the β-particle energy, the energy carried by the neutrino, a small amount of recoil energy and the transition energy of the daughter nucleus. The neutrino energy is lost completely, although this energy is very small. Also the energy loss due to the production of bremsstrahlung radiation (from the deceleration of β-particles) is negligible for the decay of $^{241}$Pu.

The decay parameters and specific powers for plutonium isotopes and $^{241}$Am are well known (Co65, ANSI75), and the currently recommended values are tabulated in Table 1. References concerning the experimental determinations of these parameters are listed in ANSI75. A list of the isotopic compositions and relative heat contributions for typical plutonium-bearing samples is presented as Tables 2 and 3.

In considering the radionuclide decay of plutonium-bearing samples, it must be noted that the effective specific power is not a constant, but changes due to the decay and growth of the constituent radionuclides. These changes may be calculated using the decay constants in Table 1 and a knowledge of the radionuclide abundances. Using the
TABLE 1
Nuclear Constants for Radionuclides in Plutonium-Bearing Solids

<table>
<thead>
<tr>
<th>Radionuclide</th>
<th>Total Disintegration Energy (MeV)</th>
<th>Principal Decay Mode</th>
<th>Total Energy Emitted as Gamma Rays (%)</th>
<th>Half-Life (years)</th>
<th>Decay Constant (days⁻¹)</th>
<th>Specific Power (W g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{238}\text{Pu}$</td>
<td>$5.5921 \pm 0.0016$</td>
<td>$\alpha$</td>
<td>0.0005</td>
<td>87.79</td>
<td>$2.1617 \times 10^{-5}$</td>
<td>$5.6716 \times 10^{-1}$</td>
</tr>
<tr>
<td>$^{239}\text{Pu}$</td>
<td>$5.2428 \pm 0.0016$</td>
<td>$\alpha$</td>
<td>0.0003</td>
<td>24082</td>
<td>$7.880 \times 10^{-8}$</td>
<td>$1.9292 \times 10^{-3}$</td>
</tr>
<tr>
<td>$^{240}\text{Pu}$</td>
<td>$5.2551 \pm 0.0016$</td>
<td>$\alpha$</td>
<td>0.0005</td>
<td>6537</td>
<td>$2.903 \times 10^{-7}$</td>
<td>$7.098 \times 10^{-3}$</td>
</tr>
<tr>
<td>$^{241}\text{Pu}$</td>
<td>$0.00553 \pm 0.00001$</td>
<td>$\beta$</td>
<td>0.0045</td>
<td>14.35</td>
<td>$1.322 \times 10^{-4}$</td>
<td>$3.390 \times 10^{-3}$</td>
</tr>
<tr>
<td>$^{242}\text{Pu}$</td>
<td>$4.985 \pm 0.010$</td>
<td>$\alpha$</td>
<td>-</td>
<td>379000</td>
<td>$5.01 \times 10^{-9}$</td>
<td>$1.146 \times 10^{-4}$</td>
</tr>
<tr>
<td>$^{241}\text{Am}$</td>
<td>$5.6402 \pm 0.0016$</td>
<td>$\alpha$</td>
<td>0.38 (low energy)</td>
<td>434.1</td>
<td>$4.372 \times 10^{-6}$</td>
<td>$1.1423 \times 10^{-1}$</td>
</tr>
</tbody>
</table>

*(from ANSI75).*
<table>
<thead>
<tr>
<th>SERIAL</th>
<th>SAMPLE DESCRIPTION</th>
<th>PARAMETER</th>
<th>238$_{Pu}$</th>
<th>239$_{Pu}$</th>
<th>240$_{Pu}$</th>
<th>241$_{Pu}$</th>
<th>242$_{Pu}$</th>
<th>241$_{Am}$</th>
<th>TOTAL Pu (g)</th>
<th>ERROR IN TOTAL Pu (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>No. 1, Oxide Sample (Ra81a, Table 1)</td>
<td>Weight % Relative to Total Pu</td>
<td>0.02</td>
<td>93.26</td>
<td>6.43</td>
<td>0.27</td>
<td>-</td>
<td>0.05</td>
<td>4.48</td>
<td>1.12</td>
</tr>
<tr>
<td>1b</td>
<td>As Above</td>
<td>% Heat Contribution Relative to Total Pu</td>
<td>4.6</td>
<td>73.9</td>
<td>18.7</td>
<td>0.4</td>
<td>-</td>
<td>2.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2a</td>
<td>No. 41, Oxide Sample (Ra81a, Table 1)</td>
<td>Weight % Relative to Total Pu</td>
<td>0.05</td>
<td>84.36</td>
<td>13.68</td>
<td>1.70</td>
<td>-</td>
<td>0.41</td>
<td>2181</td>
<td>1.33</td>
</tr>
<tr>
<td>2b</td>
<td>As Above</td>
<td>% Heat Contribution Relative to Total Pu</td>
<td>8.3</td>
<td>47.8</td>
<td>28.5</td>
<td>1.7</td>
<td>-</td>
<td>13.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3a</td>
<td>LWR Oxide Sample (Oh72, Table 9)</td>
<td>Weight % Relative to Total Pu</td>
<td>0.24</td>
<td>75.65</td>
<td>18.42</td>
<td>4.59</td>
<td>1.11</td>
<td>0.74</td>
<td>905.98</td>
<td>2.64</td>
</tr>
<tr>
<td>3b</td>
<td>As Above</td>
<td>% Heat Contribution Relative to Total Pu</td>
<td>26.3</td>
<td>28.8</td>
<td>25.8</td>
<td>3.0</td>
<td>-</td>
<td>16.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4a</td>
<td>FBR Oxide Sample (Oh72, Table 9)</td>
<td>Weight % Relative to Total Pu</td>
<td>0.06</td>
<td>85.68</td>
<td>12.11</td>
<td>1.94</td>
<td>0.22</td>
<td>0.16</td>
<td>985.3</td>
<td>1.17</td>
</tr>
<tr>
<td>4b</td>
<td>As Above</td>
<td>% Heat Contribution Relative to Total Pu</td>
<td>10.6</td>
<td>53.2</td>
<td>27.7</td>
<td>2.1</td>
<td>-</td>
<td>6.4</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
TABLE 2 - NOTES

A. For serials 1 and 2 the uncertainty in the calorimetric heat measurement was typically 0.3%. The isotopic compositions were determined by gamma-ray analysis and the error in the total mass of plutonium was dominated by the errors in the isotopic mass ratios.

B. For serials 3 and 4 the uncertainty in the calorimetric heat measurement was typically 0.05%. The isotopic compositions were determined by mass spectrometry. The error in the total plutonium mass was determined solely from the errors in the isotopic ratios because the calorimetric heat measurement error was insignificant by comparison.
<table>
<thead>
<tr>
<th>SERIAL</th>
<th>SAMPLE DESCRIPTION</th>
<th>PARAMETER</th>
<th>238(_{\text{Pu}})</th>
<th>239(_{\text{Pu}})</th>
<th>240(_{\text{Pu}})</th>
<th>241(_{\text{Pu}})</th>
<th>242(_{\text{Pu}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>MAGNOX FUEL 5,000 MW days/tonne 1 year cooled</td>
<td>WEIGHT % RELATIVE TO TOTAL Pu</td>
<td>0.2</td>
<td>68.7</td>
<td>25.3</td>
<td>4.7</td>
<td>1.1</td>
</tr>
<tr>
<td>1b</td>
<td>AS ABOVE</td>
<td>% HEAT CONTRIBUTION RELATIVE TO TOTAL Pu</td>
<td>25</td>
<td>30</td>
<td>41</td>
<td>5</td>
<td>-</td>
</tr>
<tr>
<td>2a</td>
<td>CAGR FUEL 20,000 MW days/tonne 1 year cooled 1.5% initial enrichment</td>
<td>WEIGHT % RELATIVE TO TOTAL Pu</td>
<td>0.8</td>
<td>45.6</td>
<td>34.9</td>
<td>11</td>
<td>7.7</td>
</tr>
<tr>
<td>2b</td>
<td>AS ABOVE</td>
<td>% HEAT CONTRIBUTION RELATIVE TO TOTAL Pu</td>
<td>54</td>
<td>11</td>
<td>30</td>
<td>5</td>
<td>0.1</td>
</tr>
<tr>
<td>3a</td>
<td>PWR (LWR) FUEL WESTINGHOUSE TYPE AS PROPOSED FOR SIZEWELL 40,000 MW days/tonne 1 year cooled 3.2% initial enrichment</td>
<td>WEIGHT % RELATIVE TO TOTAL Pu</td>
<td>1.8</td>
<td>51.8</td>
<td>24.8</td>
<td>13.7</td>
<td>7.9</td>
</tr>
<tr>
<td>3b</td>
<td>AS ABOVE</td>
<td>% HEAT CONTRIBUTION RELATIVE TO TOTAL Pu</td>
<td>75</td>
<td>7.3</td>
<td>13</td>
<td>3.4</td>
<td>-</td>
</tr>
</tbody>
</table>

*Data furnished by Dr. W.B. Hooton, UKAEA, 1982.*
notation of equation (4), and a time-dependent radio-
nuclide abundance \( R_i(t) \), the total heat output as a
function of time may be represented using equation (5),

\[
W_s = M \sum_i R_i(t) p_i,
\]

where

\[
R_i(t) = R_i e^{-\lambda_i t},
\]

and \( R_i \) = initial isotopic abundance
\( \lambda_i \) = decay constant of isotope \( i \).

Using equation (6) a more complicated expression may be
derived for the ingrowth of \( ^{241}\text{Am} \). This relationship is
represented by equation (7),

\[
R_A(t) = R_A e^{-\lambda_A t'} + \frac{R_1 \lambda_1 (e^{-\lambda_A t'} - e^{-\lambda_1 t'})}{(\lambda_1 - \lambda_A)}(e^{-\lambda_A t'} - e^{-\lambda_1 t'}),
\]

where the subscripts \( A \) and \( 1 \) refer to \( ^{241}\text{Am} \) and \( ^{241}\text{Pu} \) res-
pectively and
\( R_A \) = isotopic abundance of \( ^{241}\text{Am} \) at the time of americium
determination

\( R_1 \) = isotopic abundance of \( ^{241}\text{Pu} \) at the time of plutonium
isotopic determination

\( t \) = time between the power measurement and the plutonium
isotopic determination

\( t' \) = time between the power measurement and the americium
determination, and

\( t' = t - t' \).

Using these relationships, the power of a plutonium-bearing
sample may be calculated at any time subsequent to an
initial determination.
2.2 Characteristics of Plutonium Calorimetry

Like other assay and detection techniques, plutonium calorimetry is employed in both the areas of accounting and safeguards verification. Under these broad headings calorimetry may be applied to the specific functions of sample assay, verification of a previous assay, the identification of measurement biases and the calibration of other assay and measurement methods. The technique is applicable to a wide range of plutonium-bearing samples including feed, process and product materials, as well as process scrap and waste. The characteristics of plutonium calorimeters used for the measurement of these materials are considered in the following sections.

2.2.1 Determination of effective specific power

When the calorimeter method is used to determine the total plutonium mass in a sample, two parameters must be determined. The first of these is the power or heat output rate of the sample and this is determined by the calorimetry measurement. The second parameter, from equation (4), is the effective specific power of the sample. This is made clear by equation (8),

\[ M = \frac{W}{P_{\text{eff}}} \]  \hspace{1cm} (8)

If the sample contains only one isotope then \( P_{\text{eff}} \) is simply the specific power of that isotope. In general, the situation is more complicated because several isotopes contribute to the effective specific power of the sample.

Two methods exist for the determination of the effective specific power of plutonium samples. The first, known as the empirical method (ANSI75) is applicable when plutonium-bearing material is processed in uniform discrete batches or blends, or when the isotopic abundances of \(^{238}\text{Pu}\) and \(^{241}\text{Am}\) at low values are not well known. Calorimetry measurements of power are made for random samples of the material and then the plutonium content is determined by mass spec-
trometry or radiochemical analysis. The effective specific power is then computed from equation (8). If this value is to be used over a period of time, other random samples should be retained so that both the growth rate of the power output and the abundance of $^{241}\text{Am}$ may be determined periodically.

The second and more generally applicable method for determining the effective specific power is known as the computational method. It is used when it is possible to measure accurately the isotopic abundances, for example, by the non-destructive technique of gamma ray spectrometry. This method is particularly appropriate when a determination of the effective specific power must be made, individually, for each sample. The effective specific power is computed using equation (9),

$$P_{\text{eff}} = \sum_i R_i P_i.$$  (9)

It should be noted that because of the inclusion of $^{241}\text{Am}$, the sum of the isotopic abundances is greater than one, by the amount of $^{241}\text{Am}$ in the sample.

2.2.2 Plutonium calorimeter types

Plutonium calorimeters are all of the general type described in Sections 1.1 and 1.3.1. They are designed to contain samples of plutonium-bearing material, and to measure the heat evolved by radioactive decay. It is assumed that no significant amount of energy from the decay process escapes and that the daughter isotopes are stable. These assumptions are valid for plutonium calorimeters where the decay of $^{241}\text{Am}$ is also taken into consideration.

Calorimetry requires both the control and measurement of temperature. The former is accomplished either by electrical heating, or the use of isothermal water baths and heat exchangers. The latter is accomplished by thermo-electric or resistance thermometry. Thermocouples have the advantage that they do not deposit heat in the thermal whose temperature they measure. In the form of thermopiles,
they measure the temperature averaged over a number of points. Resistance thermometers, by contrast, average the temperature over the whole region with which they are in contact. They are particularly suitable for minimizing the heat distribution error (Section 2.5) resulting from sample non-uniformity. Both types of temperature sensors may be used effectively with twin calorimeters (Section 1.1) in which temperature drift errors are minimized.

Both the steady state (heat flow) and isothermal modes of operation are employed in plutonium calorimeters of which two basic types have evolved. The first is the twin type using either thermopiles or resistance thermometry, which may be operated in the steady state (heat flow) or isothermal mode, depending on the control system in use. Temperature stability is provided by placing the thermels in a large water bath.

Figure 4 is a diagram of a twin fuel rod calorimeter of this type which has both a measurement and a reference thermel and employs thermopiles for temperature measurement. Figure 5 illustrates the structure of a twin resistance thermometer plutonium-bearing sample calorimeter of the Mound Laboratory design which is reviewed in detail in Section 3.1. The operation of both calorimeters is described in Section 2.3. The thermel of a compact, transportable calorimeter of the Mound design is illustrated in Figure 6. Here the two thermels have been placed end to end, and the water bath has been replaced by a heat exchanger.

The second type of calorimeter is a dry fuel rod calorimeter which is operated only in the isothermal or servo-control mode. It is used for the assay of plutonium-bearing fuel rods and it is both described and reviewed in Section 3.2. A diagram of the device, which was developed at the Argonne National Laboratory, is presented as Figure 7. In the design, temperatures are controlled entirely by electrical heaters, and resistance thermometry is used for temperature sensing.
2.2.3 General characteristics

Calorimeter sensitivity is dependent on a number of factors, including the type of calorimeter, the mode of operation, and the sample size and power. A trade-off exists between the size of the sample and calorimeter sensitivity. The sensitivity also increases with increasing sample power although this factor is less important for large samples. The upper limit of the quantity of plutonium is dictated only by considerations of nuclear safety. The lower limit varies with the types and operating modes of calorimeters but, in general, is less than one gram, even for large sample calorimeters. For example, a 4-litre Mound calorimeter will detect less than 0.2 grams of $^{239}$Pu. The precision of calorimeters is considered in Section 2.5. In order to optimize performance, it is essential that calorimeters be designed for the specific types of measurements for which they are required. The two main factors to be considered in the design are the sample size and power.

2.3 Calorimeter Operation and Calibration Procedures

Calorimeters are usually classified according to their structure and method of operation. In plutonium calorimetry, some confusion exists because calorimeters like those at the Mound Laboratory operate in two different modes, and the distinction between them is not always clear. In this section, the operation and calibration of calorimeters will be described, and the different modes of operation will be related to those described in Section 1.2.2.

2.3.1 Operating procedures

The operation of the Mound Laboratory type twin calorimeter in a water bath (Figures 5 and 6) will be considered, and used as an example to illustrate the different modes or methods of operation. The first of these is known as the replacement method. The plutonium sample is placed in the measurement thermal, and the temperature of the thermal
rises. This temperature rise continues until the heat loss across the air gap (between the thermel and jacket, or environmental bath) balances the heat production rate of the sample. At this point, the temperature rise in the thermel is proportional to the heat production rate or sample power. The sample is then removed and the sample heat is replaced (hence the name replacement method), by known electrical heating. In twin calorimeters the temperature difference that is measured is, in reality, the difference in temperature between the two thermels. The method applies to single calorimeters as well, but in that case, the measured temperature must be the temperature difference across the gap. In this method, the calorimeter is operated in the steady state (heat flow) mode.

The second method of measurement is known as the differential method, and it applies to twin calorimeters only. In this case, the temperature difference is measured as before, but electrical heating in the reference side is compared directly to the sample heating, and matched to the sample power. The method is equivalent to a simultaneous calibration, and requires a forehand knowledge of the sample power to within about 1%. It is useful for measuring many samples of approximately the same size. In this method, like the replacement method, the calorimeter is operated in the steady state (heat flow) mode. With an isothermal water bath, both calorimeters could also be described as isoperbol.

The third method is known as the servo-control, or power difference, method. More sophisticated electronics are required, in the form of a servo-controller, to maintain the calorimeter measurement or sample thermel at constant temperature, which is slightly elevated above the surrounding environment or water bath. When the sample is added, less electrical power is needed to maintain the constant temperature of the thermel. The power difference is equal to the sample power. The initial electrical heating power should be chosen so that it is only slightly greater than
the sample power. The method has the distinct advantage that it constitutes a direct measurement of the sample power. An additional advantage is that the time constants of the calorimeter are eliminated and the time taken to reach equilibrium is due only to the time constants of the sample. If the sample can be preheated to the temperature of the therme, then the measurement time will be reduced even further. It should be noted that in this method, the calorimeter is operated in the true isothermal mode.

The servo-control method may also be used for single thermal calorimeters. In fact, this is the case for the ANL dry fast-fuel rod calorimeter which is reviewed and described in Section 3.2.

Several factors affect the time taken for a calorimetry measurement. These include the type of calorimeter, the mode of operation, the thermal conductivity and heat capacity of the therme, the sample and the sample packaging, and finally, the accuracy required. In most cases, the sample packaging controls the time required to reach thermal equilibrium. Also some materials, such as PuO₂ and scrap samples, may require long times to reach equilibrium. Some methods are available, however, to help reduce these times. Improving the geometry of the therme-sample system may improve heat transfer, and end point prediction may reduce the time significantly. Preheating the sample is also useful.

Of all the calorimetry operating methods, the replacement method requires the longest time, although this time is reduced when the methods of the previous paragraph are applied. By far the fastest method is the servo-control method. Combined with the techniques that have been mentioned, times to calorimeter equilibrium in hours may be reduced to minutes.

2.3.2 Calibration procedures

It is necessary to calibrate calorimeters in order to derive the unknown sample power from the calorimeter res-
ponse. Calibrations are normally performed using two types of standards. The first, and perhaps the most obvious, is a heat standard which replaces the sample in the calori-
meter thermel. Well-characterized samples of $^{238}\text{Pu}$ are often used for this purpose. They have the advantage that they exactly simulate the conditions and heat distributions which occur during the measurement of a plutonium sample. The second type of calibration is the electrical calibration. This is normally accomplished using an electrical heater permanently installed in the thermel. Care must be taken to ensure that the temperature distribution from electrical heating closely approximates that produced by the plutonium-bearing sample. In America, it is a requirement that all calibration standards used in plutonium calorimetry be related or traceable to national standards at the N.B.S.

The calibration should be performed over the operating range of the device. If heat sources are employed, several must be used to cover the operating range. The resulting relation-
ship of calorimeter output as a function of sample power is known as the calibration function. This must be checked periodically during a measurement sequence. The calorimeter sensitivity is defined as the derivative of the calibration function with respect to sample power. This function must also be determined.

2.3.3 Typical measurement sequence

Details of the measurement procedure depend to a large extent on the type of calorimeter and the mode of operation. How-
ever, much of the measurement sequence is common to all of the variations of the calorimetry method, and this will be considered here.

Before a measurement sequence is undertaken, a calibration must be performed, as described in Section 2.3.2. The sample to be measured is then placed in the thermel and the calori-
meter is allowed to reach equilibrium at the accuracy level required for the measurement. The time to equilibrium may be reduced using the procedures described in Section 2.3.1. When equilibrium is reached at the required accuracy, the
power is recorded. Depending on which of the three methods is used for the measurement, electrical measurements may have to be made, for example, as with the replacement method. Using the servo-control method, the sample power may be determined directly once isothermal conditions have been restored following the insertion of a sample.

During the course of a sequence of measurements, the calibration of the calorimeter should be tested periodically using electrical or radioactive calibration standards.

Typical measurement times vary considerably, and the factors involved have been considered in Section 2.3.1. Examples of measurement times may be found in the literature review in Section 3.

A particularly useful investigation of the factors which influence equilibration times was conducted by O'Hara (Oh72). His findings are summarized in Table 4, which illustrates the time-savings obtained by servo-control, improved packaging and sample pre-equilibration. It is reasonable to assume that, with computer control and improved calorimeter design, these times could be further improved.

2.4 Instrumentation and Data Analysis

Most plutonium calorimeters have employed very simple instrumentation, and there has been a tendency to avoid the complicated electronics required for the servo-control method of measurement. With the advent of relatively inexpensive minicomputers and microcomputers this situation is now changing. In this section the instrumentation for temperature measurement and control will be described, as well as the role of small computers in the instrumentation of plutonium calorimeters.

2.4.1 Temperature measurement

The use of thermoelectric and resistance thermometry for the measurement of temperature was mentioned briefly in Section 2.2.2. Although sometimes included as a type of resistance thermometer, the use of thermisters should also
<table>
<thead>
<tr>
<th>SERIAL</th>
<th>CALORIMETRY METHOD</th>
<th>SAMPLE DETAILS</th>
<th>MEASUREMENT PRECISION</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.01%</td>
</tr>
<tr>
<td>1</td>
<td>Replacement method</td>
<td>Empty thermel (no sample)</td>
<td>4.8</td>
</tr>
<tr>
<td>2</td>
<td>Replacement method</td>
<td>Poorly-packaged sample; including plastic bags</td>
<td>13.1</td>
</tr>
<tr>
<td>3</td>
<td>Servo-control method</td>
<td>As for serial 2</td>
<td>8.0</td>
</tr>
<tr>
<td></td>
<td>Servo-control method; sample can pre-equilibrated to within 0.007°C of calorimeter measurement chamber temperature</td>
<td>As for serial 2</td>
<td>3.0</td>
</tr>
<tr>
<td>4</td>
<td>Replacement method (ideal case)</td>
<td>As for serial 2. Sample at equilibrium, removed from calorimeter and then re-inserted</td>
<td>3.0</td>
</tr>
<tr>
<td>5</td>
<td>Replacement method</td>
<td>As for serial 2. Heat transfer improved with copper shot between the sample can and thermel inner wall</td>
<td>8.0</td>
</tr>
</tbody>
</table>

TABLE 4
Typical Temperature Equilibrium Times (from Oh72)
be noted. Each type of sensor has advantages and disadvantages and these will be considered.

Thermocouples, especially in the form of thermopiles used in the differential mode, measure the temperature difference averaged over a number of points between two surfaces. These surfaces might be the therme1 outer wall and the jacket of a calorimeter as illustrated in Fig. 4. Thermocouples have the advantage that they do not deposit any heat in the therme1 although great care must be taken to ensure that no additional thermoelectric junctions occur in the thermocouple circuit and that the cold junction is very stable in temperature.

These difficulties are overcome with the use of resistance thermometers and thermisters, where the temperature is determined from the imbalance of a resistance bridge circuit. Although these temperature sensors deposit small amounts of heat in the therme1, this is not a serious limitation and the need for a cold junction is eliminated. Like thermocouples, thermisters are point temperature sensors and, as a result, resistance thermometers in the form of helical windings around the therme1 are most often used in plutonium and fuel element calorimetry. They average the temperature over the whole surface with which they are in contact, and are therefore particularly suitable for minimizing the heat distribution error (Section 2.5). Calorimeters using nickel resistance thermometer windings are illustrated in Figs. 5, 6 and 7. In calorimeters with twin thermels, the resistance thermometers from each therme1 are connected to the same resistance bridge, and differential measurements are then possible.

Resistance bridge circuits have the advantage that the sensitivity may be adjusted by varying the bridge current. The output of the bridge circuit may be set to any desired value through the use of a shunt resistance in one arm of the bridge, or the bridge potential may be amplified. The output is normally measured using a potentiometer or, more recently, a high input impedance digital voltmeter (DVM).
A DVM is able to provide the signal in a digitized form suitable for use and processing by a computer.

2.4.2 Temperature control

The use of electrical heating or isothermal water baths and heat exchangers for temperature control was mentioned briefly in Section 2.2.2. The use of isothermal water baths has been a main feature of Mound Laboratory calorimeter designs for some time (Fig. 5). More recently, the large bath has been replaced by heat exchangers and a temperature controlled water reservoir (Fig. 6). Such systems have large time constants for temperature change, which is an advantage, although it is difficult to control the temperature of the system very precisely. As the precision of a calorimetry measurement is dependent on the precision with which the temperature can be controlled, an upper limit for heat measurement precision is soon reached with these calorimeters. In practice, this is not a limitation as the errors in the isotopic ratio data dominate the overall measurement precision. The physical size and weight, even in the case of the transportable calorimeter, are limitations on the use of these calorimeters as is the presence of a significant volume of water in close proximity to fissile material.

Electrical resistance heating overcomes many of the disadvantages of water bath systems. Coupled with resistance thermometry this form of temperature control has a fast response and very precise temperature control is possible. This system has been exploited to great effect in the ANL dry fast response fuel rod calorimeter illustrated in Fig. 7. Whereas the Mound calorimeter water baths are controlled to about 1 millidegree, the control measurement chamber of the ANL calorimeter is controlled to about 20 microdegrees.

Where electrical heating is used for calibration, highly regulated D.C. power supplies are used to supply known amounts of power to four terminal calibration heaters. Heater wires in this case should have small temperature coefficients.
The control of electrical resistance heaters has generally been accomplished by analogue feedback electronic circuits. More recently, digital control of these heaters has been possible with the advent of programmable constant current sources. This approach is being followed with the Imperial College "in reactor" microcalorimeter system.

2.4.3 Computer control and data analysis

The advent of the inexpensive small computer makes possible significant improvements in plutonium calorimetry. The most important of these is that the technique may be automated so that detailed technical knowledge or skill is not required by an operator.

The critical aspect of calorimeter automation is in the area of temperature control. The computer, in conjunction with programmable constant current generators can replace the complicated analogue feedback electronics required for servo-control operation. Sophisticated software algorithms may be included in the system to improve temperature control in response to temperature signals, acquired from sensors, which have been digitized by a DVM. In this manner, servo-control measurements may be automated and performed to a previously determined precision.

Data is acquired automatically by the computer and other required information, such as isotopic ratio data, may be entered from a keyboard. Data analysis is performed automatically including the calculation of plutonium mass and the analysis of errors. The resulting data may then be either archived or presented in a suitable report form.

The use of a small computer as part of a calorimetry system has other advantages. First the process of electrical calibration may be automated, and the system can be programmed to check for drifts in the calibration and other systematic errors that occur during long-term use. In the case of routine analysis of standard samples, the process of calorimeter loading and unloading may be automated by the use of a computer-controlled robot. Finally, in the
manner proposed by Rakel (Ra81b) and described in Section 3.1, the entire process of calorimetric assay may be autom- 
mated by incorporating a computer-controlled gamma-ray 
isotopic ratio analysis system as part of the calorimeter.

2.5 Measurement Precision and Error Analysis

Errors and uncertainty in the calorimetry technique arise 
from uncertainty in the knowledge or measurement of five 
main parameters. These five parameters are as follows:

(a) Isotopic power constants.
(b) Isotopic half-lives.
(c) The decay period or the time between the isotopic 
    abundance determination and the calorimetric power 
    measurement.
(d) Sample power measured by calorimetry.
(e) Isotopic abundance ratios.

The first two parameters are well established, and accurate 
values are tabulated in Table 1. The error contribution 
from the third parameter is generally insignificant. If 
the decay period is less than one month, it is generally 
not necessary to calculate the decay in the isotopic 
ratios and hence the heat output. The uncertainty in 
these ratios is usually larger than the error introduced 
through sample decay. If a longer decay period is involved, 
or in order to obtain better accuracy when large amounts 
of $^{241}Pu$ are present, the isotopic ratios must be decay 
corrected. This is done using the methods and equations 
described in Section 2.1.

The errors in the last two parameters contribute most of 
the uncertainties associated with the calorimetry method. 
By far the most significant of these is the uncertainty 
in the knowledge of the isotopic ratios which are neces- 
sary in order to determine the sample effective power. 
This uncertainty is always the limiting factor in the accu- 
racy of the calorimetry method. The sources of error in 
the calorimetry power measurement will be considered in 
the remainder of this section.
2.5.1 Sources of error

A variety of sources of error contribute to the uncertainty in the power measurement. The operating conditions of the calorimeter are particularly important. In general, if the time for a measurement is increased, the degree of equilibrium will increase, and hence the precision will improve. Also the operating environment of the calorimeter is important in that large background temperature fluctuations will introduce errors into the process of temperature control. This effect is minimized in twin thermal calorimeters.

Heat absorbing or producing processes such as fission product radioactivity or chemical reactions will lead to erroneous results. The errors due to such interferences can be detected by observations of the time dependence of the heat output, gamma-ray spectrometry of the sample or the use of an independent assay technique.

The heat distribution error is associated with samples whose composition is very non-homogeneous. It is a particular problem with samples of plutonium scrap where the distribution of heat-producing materials is uneven throughout a container. The error is minimized through the use of temperature sensors such as helical resistance thermometers which average the heat flux over the surface of a calorimeter thermal. The heat distribution error may be estimated by measuring the power from a calibrated heat source in extreme positions in the thermal.

Significant errors are associated with the presence of both $^{238}\text{Pu}$ and $^{241}\text{Am}$ in the sample. This is because both isotopes have large specific powers, in fact the specific power of $^{238}\text{Pu}$ is 250 times larger than that of $^{239}\text{Pu}$. For this reason, the uncertainty in the isotopic ratio of $^{238}\text{Pu}$ dominates the overall uncertainty in the plutonium mass determination.

One source of error is particularly associated with electrical calibration. The error arises due to heat loss from the electrical leads connected to calibration heater
elements. The use of four terminal connections minimizes this error and in twin calorimeters, it is less important since the heater current may be made to pass through the leads of both the measurement and reference thermels.

2.5.2 Error analysis

The relationship between the measured heat output, sample mass, specific powers and isotopic ratios was clearly illustrated by equation (4) in Section 2.1. The relationship between the relative errors in these quantities is given by equation (10), from which the relative error in the total plutonium mass may be computed,

\[
\left( \frac{\sigma_M}{M} \right)^2 = \left( \frac{\sigma_{W_s}}{W_s} \right)^2 + \sum_{i=1}^{n} \left( F_i \frac{\sigma_{P_i}}{P_i} \right)^2 + \sum_{i=1}^{n} \left( F_i \frac{\sigma_{R_i}}{R_i} \right)^2,
\]

where \( \sigma_{W_s} \) is the standard deviation in sample power

\[
F_i = \frac{R_i P_i}{P_{\text{eff}}},
\]

and the other symbols have their usual meaning.

The first term is the relative uncertainty in the heat determination. The second term is the relative uncertainty in the specific powers of the constituent isotopes in the sample. The error represented by the sum of these two terms is usually about 0.1%.

The third term is the relative uncertainty in the isotopic abundances (mass ratios) of the constituent plutonium isotopes in the sample. This term is the major component of the error in the total plutonium mass. It should be noted that the relative uncertainty in the mass ratio is weighted by the specific power of each respective isotope. Therefore, in some cases, the uncertainties in the mass ratios of high heat-producing isotopes such as \(^{238}\text{Pu}\) and \(^{240}\text{Pu}\) are of equal importance to the uncertainty in the mass ratio of \(^{239}\text{Pu}\). The significance for the final result of large errors in the determination of \(^{238}\text{Pu}\) content is apparent.
2.5.3 Measurement precision and detection limits

Because of the variations in calorimeter types, methods of measurement and the methods of determining isotopic mass ratios, it is difficult to make definitive statements about calorimetry measurement precision. A useful indication may be obtained, however, by considering typical values from a variety of measurements. Some typical measurement errors are therefore presented in Table 5. The precision in the measurement of sample power is usually greater than that for the isotopic mass ratios and these therefore dominate the overall uncertainty. The precision of the power measurement is virtually independent of the relative isotopic compositions of the plutonium sample.

Detection limits also vary with calorimeter types and modes of operation. Some values are, however, available for Mound type calorimeters and they are quoted in ANSI75. Using resistance thermometry the sample would need to evolve a minimum of 0.1 μW cm⁻² of heat on the inner surface of the thermel. This corresponds to 0.2 grams of \(^{239}\)Pu in a thermel with a 4-litre capacity. A sample of mixed isotopic composition could have significantly smaller mass and still be detectable if it contained a significant amount of a higher specific power isotope such as \(^{238}\)Pu.

2.6 Calorimetry and Other Plutonium Measurement Techniques

Although a discussion of other plutonium measurement techniques is beyond the scope of the present report, some techniques are relevant in that they are used to determine plutonium isotopic composition. The most accurate method for isotopic ratio determination is mass spectrometry (Pi74), although it requires sample destruction and is time-consuming. Other useful techniques include neutron interrogation, especially using \(^{252}\)Cf sources (Ba72, Me72, Ha80), and gamma-ray spectrometry (Ha74, Bra77, Cow80, Fi80). The use of gamma-ray analysis for plutonium assay is non-destructive although the accuracy of the technique is not high.
TABLE 5  
Typical Errors Associated With Plutonium Calorimetry

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Relative Error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Isotopic Ratio Determination by Mass Spectrometry</strong></td>
<td></td>
</tr>
<tr>
<td>- isotopic concentration &gt;10%</td>
<td>0.3</td>
</tr>
<tr>
<td>- isotopic concentration 0.1%-1%</td>
<td>1</td>
</tr>
<tr>
<td>- isotopic concentration &lt;0.1%</td>
<td>5</td>
</tr>
<tr>
<td><strong>Calorimetric Power Determination</strong></td>
<td></td>
</tr>
<tr>
<td>- usual</td>
<td>0.3</td>
</tr>
<tr>
<td>- good</td>
<td>0.1</td>
</tr>
<tr>
<td>- best</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td><strong>Isotopic Specific Powers</strong></td>
<td>0.1 - 0.2</td>
</tr>
<tr>
<td><strong>Heat Distribution Error (worst)</strong></td>
<td>&lt;0.1</td>
</tr>
<tr>
<td><strong>Determination of Pu Mass</strong></td>
<td></td>
</tr>
<tr>
<td>- transportable calorimeter with portable gamma-ray detector for isotopic determination</td>
<td>1.3 - 4.4</td>
</tr>
<tr>
<td>- transportable calorimeter, isotopic ratios from mass spectrometry</td>
<td>0.98</td>
</tr>
<tr>
<td>- Mound Calorimeter (long equilibrium time)</td>
<td>0.1</td>
</tr>
<tr>
<td>- Rocky Flats Calorimeter, routine factory use</td>
<td>&gt;2</td>
</tr>
<tr>
<td>- ANL MKIV dry fuel rod calorimeter</td>
<td>0.13</td>
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By contrast, the combined technique of gamma-ray isotopic ratio analysis and calorimetric power measurement shows considerable promise as a completely non-destructive assay system. Recent work at the Mound Laboratory, which is described in Section 3.1, has been directed towards the development of an integrated assay system combining both techniques in one device (Fl81, Ra81). The computer used for calorimeter control and data analysis (Section 2.4.3), could also form the basis of the gamma-ray spectrometer and perform the necessary analysis on the gamma-ray spectrum data required to compute the isotopic ratios. In this manner, the complete process of non-destructive plutonium assay may be automated.
3. CRITICAL REVIEW AND ASSESSMENT OF THE LITERATURE OF PLUTONIUM ASSAY AND FUEL ELEMENT CALORIMETRY

The literature review in this section is not exhaustive and includes only those references considered to be significant in that they describe the current state of plutonium calorimetry, or contain information on new techniques and improvements. A substantial proportion of the available sources of information are laboratory research reports. Although some plutonium calorimetry work has been published, it is probable that development work in some laboratories goes unreported.

Work on plutonium calorimetry appears to have developed along two separate lines. The first of these involves the assay and verification of plutonium in a variety of forms. The second is concerned exclusively with the assay of plutonium-bearing fuel rods. These two categories are considered separately in the following sections. For convenience, the references are considered in chronological order.

Two recent safeguards papers of a general nature are relevant to plutonium calorimetry. In proposing goals for safeguards measurement systems, J.M. de Montmollin et al. (Mo80) demonstrated the usefulness of plutonium calorimetry in the context of IAEA safeguards. In a paper on safeguards verification methods in the U.S., C.S. Smith et al. (Sm80) cited numerous examples of the use of calorimetry by both safeguards inspectors and contractors.

By far the most important single reference for plutonium calorimetry is the American National Standards Institute report, ANSI N15.22-1975 (ANSI75). It should be regarded as the definitive standard for calorimetry in this area, and will be considered in the next section.
3.1 Calorimetric Assay of Plutonium-Bearing Materials

The vast majority of development of the technique of plutonium assay has been done in America and particularly at the Mound Laboratory, Ohio, which is operated by the Monsanto Research Corporation for the U.S. Department of Energy. Most plutonium calorimeters used in the U.S. are either Mound calorimeters or they are derived from Mound designs.

Early work in this area has been reviewed by Gunn (Gu70). The present review will be concerned with work since 1970. In that year V.W. Schneider et al. (Sc70) reported the design of the ALKEM twin steady-state (heat flow) calorimeters of different sizes. They use thermopiles as heat sensors and they all employ a large constant temperature water bath. Calorimeters of different sizes have been used for measuring PuO$_2$ in cans, scrap material, and fuel pins and sub-assemblies of up to 3.6 m in length. The accuracy of measurements with these calorimeters is better than 1%, although long times are required for thermal equilibrium to be achieved.

An excellent general description of the calorimetry technique applied to plutonium was presented by O'Hara et al. (Oh72) of the Mound Laboratory. The work was undertaken as a study of the feasibility of the calorimetric assay technique for safeguards purposes. A twin heat flow calorimeter in a water bath using resistance thermometry was employed and measurements were performed using two 1 kg samples of PuO$_2$ feed material with isotopic compositions typical of plutonium from fast-breeder reactors and light water reactors. The paper contained useful information including the time-saving which results from pre-equilibrating the sample and the use of servo-control. The average error in the measurements, including the error in the isotopic ratios, is less than 0.1%.

W.W. Strohm et al. (St73) reported a series of plutonium calorimetry measurements at the Mound Laboratory with Pu content ranging from 0.8 to 2200 grams. The samples inc-
luded plutonium in metal, oxide, fluoride and alloy forms, as well as various forms of plutonium scrap and waste. The calorimeter described by O'Hara et al. (Oh72) was used for the measurements and an average accuracy of 0.1% was achieved. In the case of large samples, contained in gallon cans, the quoted detection limit is 0.5 grams of plutonium. The paper included a list of another 18 radio-nuclides that have been assayed at the Mound Laboratory by calorimetry.

W.W. Rodenburg (Ro74) presented calorimetry fundamentals in a useful paper based again on work at the Mound Laboratory. An investigation of calorimeter sensitivity led to the conclusion that a direct relationship exists between the accuracy and the time per assay in an unautomated calorimeter. It was found that if the insulation between the thermel and the water bath was increased, then both the temperature difference and the time to equilibrium increased. Additional sample packaging also increased the time to equilibrium. This is due to an increase in both the heat capacity of the thermel and the thermal resistance of the sample. A table of equilibrium times was presented for various packagings. As an example, for a calorimetry measurement of 0.1% accuracy, a time of 3.6 hours was required for an empty calorimeter to come to equilibrium, while for a can of plutonium oxide, packaged in a plastic bag inside a second can inside a second plastic bag, a time of 10.2 hours was required. The use of servo-control subsequently reduced this time by 40% to 6.1 hours. When the same sample was allowed to pre-equilibrate, the time to equilibrium was reduced to less than 1.5 hours. Placing copper shot in the thermel vessel to increase the heat transfer rate should improve the time still further.

Mention was also made of a small research calorimeter used for making accurate half-life measurements. One standard deviation for measurements with this device was quoted as approximately 5 ppm.
Plutonium calorimetry at Dow Rocky Flats was reviewed by F.L. Oetting (Oe74). The calorimeters described are similar to those at the Mound Laboratory in that they are of the twin cell, heat flow, water bath type, and use a helical nickel resistance thermometer. Their principal use is for half-life measurements. The importance of the heat contribution from $^{238}$Pu was emphasized by an example in which the presence of the isotope in a concentration of only 115 ppm produced 2% of the total heat output of a plutonium sample.

Further work at Dow Rockly Flats was reviewed by G.P. Minges et al. (Mi75), who described the use of a 4 litre calorimeter for the assay of packages of plutonium-bearing waste and scrap residue. The calorimeter was of the twin, heat flow type and, like those of the Mound Laboratory and that described earlier (Oe74), it employed a helical nickel resistance thermometer. The constant temperature environment was provided by a temperature-controlled 500 litre water bath. Initially, the calorimeter was not automated and the times to equilibrium ranged from approximately 9 to 16 hours for large waste samples, with an overall average measurement error of less than 2%. The main purpose of the calorimeter was to aid in the calibration of package counting equipment used for routine assay purposes where appropriate standards are difficult to fabricate. The detection limit of the device was less than one gram of plutonium and the operating range extended to samples of larger than 1 kg.

As mentioned earlier, the most important reference for plutonium calorimetric assay is the American National Standards Institute document on the subject, ANSI N15.22 (ANSI75). It is an extremely useful reference which covers most aspects of the subject, and it is now the basis of all plutonium calorimetry for safeguard or accounting purposes in America. Although much of the content of the reference was considered in Section 2 of this report, a summary will be presented here. In view of the contri-
butions of the Mound Laboratory, it is not surprising that several members of the committee responsible for ANSI N15.22 were from the Mound. Much of the content of ANSI N15.22 was drawn from an earlier Mound report by O'Hara (Oh72) who was chairman of the committee.

The principles of the calorimetric method applied to plutonium assay are described in detail, and standard data for use in calorimeter calculations is provided. The types of calorimetry equipment, modes of operation and operating procedures are described, and calibration techniques are discussed. The method of determination of the plutonium content from power measurements is described, and a thorough analysis of errors, both in the measurement and calculation procedures, is presented.

In an Appendix, data for the half-lives and specific powers for plutonium isotopes and $^{241}$Am is presented with references.

In a useful report on calorimetry measurement reliability, Reilly et al. (Re77) examined the various sources of measurement error. The report suggests that the range of error in heat determination is from approximately 0.25% to 0.01% or less. It is noted that very high precision in the measurement is unnecessary as the total error is dominated by the uncertainty in the isotopic ratios. The problem of the larger errors associated with calorimetry measurements of waste and scrap materials is emphasized, as well as the longer times required to reach thermal equilibrium with such materials. Errors due to the uncertainty in the $^{238}$Pu concentration may be significant. An example is considered in the report where 80% of the total heat output of a sample is due to $^{238}$Pu heating. Finally, the usefulness of the calorimetry technique for samples with isotopic inhomogeneity is considered. Such samples pose problems for other assay methods.

Rodenburg of the Mound Laboratory published two reports on plutonium calorimetry in 1977. The first (Ro77a) is of a general nature and provides a convenient introduction to
the technique including a literature survey. The second report (Ro77b) deals exclusively with calorimetry errors and provides a number of worked examples of error calculations.

In 1979 Fellers et al. (Fe79) of the Mound Laboratory published a paper describing an algorithm for the real time prediction of calorimeter equilibrium. The method was applied to three different calorimeters with a variety of different heat sources. Over all of the tests, an average reduction in the time to equilibrium of 55% was obtained, without instrument modification, for calorimeters using the replacement method.

All of the calorimeters considered thus far in this literature review are static installations, generally of significant size and weight. In 1980 Lemming et al. (Le80) of the Mound Laboratory published a paper describing the development and testing of a prototype transportable assay calorimeter. The device was intended for use by Department of Energy inspectors as part of the safeguards verification programme, and could be moved from one site to another. The usual large, temperature-controlled water bath was replaced by two heat exchangers, a centrifugal pump and a small temperature-controlled water reservoir. The calorimeter was mounted on an aluminium cart and had overall dimensions of 2 ft. wide by 4 ft. long by 6 ft. high. The total weight was 450 lbs. A diagram of the calorimeter thermal and heat exchanger is included as Fig. 6.

The whole of the assay process was made portable by using the calorimeter in conjunction with a portable gamma-ray spectroscopy system which was used to determine the isotopic composition data for each sample. The calorimeter could accommodate sample cans of 5 inches by 8 inches and this was later increased to 6 inches by 13 inches. Powers of between 0.5 and 10 watts were measured with an average uncertainty in heat determination of 0.3%. This gave a total measurement error of 0.98% for eleven hour measurements and of 1.64% for short measurements of a three-hour duration. The equilibrium prediction technique (Fe79) was used to decrease these measurement times.
A review of recent work at the Mound Laboratory was published by Fellers et al. (Fe80). It included details of the equilibrium prediction technique (Fe79), and an improved transportable calorimeter of the twin type where the two thermels were placed end to end. Data acquisition was controlled by a computer. An analytical plutonium calorimeter for samples of between 1 and 5 grams was also described. It employed a heat exchange system like the transportable calorimeter and included the facility for pre-equilibrating samples so that measurement times were reduced to approximately 30 minutes. The calorimeter was intended for use in conjunction with chemical assay.

Further development and testing of the transportable plutonium calorimeter was reported by Rakel et al. (Ra81a). Once again, the calorimeter was employed as part of a portable assay system as it was used in conjunction with a portable gamma-ray spectrometer.

The development of a completely portable plutonium assay system was taken to a further stage in work reported by Rakel (Ra81b). In this work, the thermel was modified to incorporate a gamma-ray detector so that heat determination and isotopic composition measurements could be performed simultaneously. The work included a detailed study of the transmission of gamma rays through the materials of which the walls of the thermel were constructed. The average uncertainty in the power measurements was approximately 0.3% and this value, combined with the uncertainty in the isotopic composition determination gave a range of uncertainty of between 1.3% and 4.4% for simultaneous assay.

3.2 Fuel Element Calorimetry

As was the case with calorimetry for plutonium-bearing materials, fuel element calorimetry has developed mainly through the efforts of one group. This group is the Non-destructive Assay Section at the Argonne National Laboratory (ANL) in America. Although Mound-type calorimeters have been used for fuel element assay, a different and
novel approach to the problem has come from ANL. This approach is complementary to the usual approach to plutonium assay calorimetry and it is for this reason that fuel element calorimetry has been included in the present study. In this section, the highlights of these developments will be reviewed.

In an early paper, Bishop et al. (Bi74) described calorimetry measurements performed on LWR recycle fuel by the General Electric Company. Calorimeters similar to those of the Mound design were employed and the large variation in plutonium isotopic composition was noted for fuel-recycled plutonium, due to variations in burn-up of the original fuel. The error in the power measurements was again dependent on the amount of $^{238}$Pu and $^{241}$Am with their higher specific powers, although the presence of uranium was not important as it does not contribute significantly to total heat output.

The development of fuel element calorimetry at the Argonne National Laboratory is described in several reports and papers. The basis of the method is the use of a series of long, horizontal, concentric, cylindrical measurement chambers whose temperatures are entirely controlled by helical electrical heating coils which are wound around the periphery of each cylinder. The need for a water bath or heat exchanger is eliminated entirely because the system is maintained at a higher temperature than its surroundings. The number of concentric temperature-controlled cylinders and the method of temperature-sensing varies with the different designs. A common feature, however, is that as one moves from the outer cylinder to the innermost cylinder, the temperature increases slightly, but more important, the extent of temperature control and regulation increases. In other words, the temperature in the inner cylinder is held constant to a high degree of precision, typically much better than a millidegree centigrade. The power or heat output of plutonium-bearing fuel placed in the inner cylinder is determined by noting the difference between the power measured when the cylinder is empty, and when it
contains a heat-producing fuel rod. This difference is
equal to the electrical equivalent of the power produced
by the plutonium in the fuel. The cylinder is maintained
at a constant temperature during both parts of the measure-
ment. The ANL fast response fuel rod calorimeter is an
example of a calorimeter operated in the isothermal or
constant temperature mode. In the terminology of ANSI75,
this is also called the servo-control, or power difference
mode. The general features of the device are illustrated
in Fig. 7.

Although ANL fast-response rod calorimeters have been under
development for some time, significant improvements were
reported by Beyer et al. (Be74) in a paper that described
the MKIII, 36 inch fuel rod calorimeter. This device
employed helical resistance wire temperature sensors,
except on the outer cylinder surface where thermisters were
used. The signals from the temperature sensors were used
by analogue feed-back electronic temperature control cir-
cuits that, in turn, operated the helical heating coils
associated with each cylindrical region. The central
measurement cylinder (the thermel) was extended at one
end to form a preheater, which served to pre-equilibrate
fuel rods before they were pushed into the measurement
region. Within the measurement region of the control
cylinder, the temperature was controlled to a tolerance of
$2 \times 10^{-5}$ °C.

The device was designed for the measurement of 1/4 inch
diameter mixed oxide fuel columns of up to 36 inches in
length and containing between 1 and 100 grams of plutonium.
Typical measurements took between 13 and 23 minutes to
complete. The accuracy of the device was determined to be
0.13% as a result of comparisons made with Mound calori-
meters and NBS certified heat standards. The precision
in the measurements was 0.02% to 0.04%.

As a result of experience gained with the MKIII calorimeter,
the MKIV device was developed and it has been described by
Beyer et al. (Be75, Be76). Design improvements included
the use of nickel helical resistance temperature sensors throughout and additional temperature-controlled regions or thermal guards at either end of the measurement region of the central cylinder. A novel feature of the MKIV design was the use of an HP45 electronic calculator which was interfaced into the circuitry of the readout controller. It was programmed to periodically monitor the thermal power and to compute the point at which thermal stabilization was sufficient for a precision of 0.1%. It then calculated the mean thermal power, errors in the measurement, and the final result of plutonium mass in grams. With this system, measurements were performed using FFTF fuel rods with an uncertainty of 0.2% and an average measurement period of 15 minutes.

A theoretical investigation of the behaviour and performance of the ANL isothermal fuel rod calorimeter was published by Perry et al. (Pe76). An electrical analogue mathematical thermal control model was proposed and it was developed and used to investigate the performance of the device and to optimize the design.

The use of the electrical analogue model contributed to the improved design of the four meter calorimeter which was discussed in an ANL report by Brumbach et al. (Br77). The device was controlled with four concentric temperature-controlled cylinders with a total length of 15 feet. The preheater, which is an extension of the central measurement cylinder, was an additional 14 feet in length. The electronic control system was improved to include control by microcomputer and a terminal input/output device which included magnetic cassette data storage. Temperature control was accomplished by the computer using a prediction algorithm.

A small sample analytic calorimeter was also reported. It was intended for use with 1 to 2 gram samples of solid plutonium compounds or mixtures encountered in plutonium recycle fuel fabrication. The main use of the calorimeter is in conjunction with chemical analysis to determine the
specific power of plutonium samples. Like the four meter calorimeter it is microcomputer-controlled and an error prediction technique is used as part of the temperature correction process. The measurement goal of the device was a single measurement precision of 0.05%, with a thermal power measurement error of 0.01% or less.

3.3 Summary and Assessment of the Calorimetric Technique for Plutonium Assay

The use of calorimetry for the measurement of plutonium has developed to a high degree of sophistication in recent years. Particularly as a result of work in America, it is employed as a routine non-destructive assay method for both accounting and safeguards verification purposes.

The technique provides a very accurate means of determining total plutonium mass from a sample power measurement. Typical accuracies achieved range from 1% to 0.1%. Calorimetry may be used to measure all types of plutonium bearing materials in all types of packaging including sealed containers. It is particularly useful for the measurement of inhomogeneous samples. Although no literature references to the calorimetric assay of liquid plutonium nitrate samples were found, there is, in principle, no reason why the technique cannot be applied to such samples.

In some cases, calorimetry is employed as a routine laboratory assay technique and, in other cases, calorimeters are employed in a factory environment for routine accounting purposes. Probably most plutonium calorimeters are used as a non-destructive means of calibrating other assay techniques.

Calorimeters may be either fixed or transportable. Although most of the calorimeters described in the literature are of the fixed installation type, the development of a transportable instrument is well advanced at the Mound Laboratory. The performance of this device is only slightly degraded in comparison to fixed calorimeters, and trans-
portable calorimeters can be made to measure the complete range of sample sizes and sample types. The device may be either vehicle mounted or movable within the confines of a factory or laboratory.

The various modes or methods of calorimeter operation, (replacement, differential and servo-control), have been described in Section 2.3.1 of this report. Although more sophisticated instrumentation is required, it would appear that, on balance, the servo-control method is the one that should be adopted for use in a U.K. calorimeter. There are powerful reasons for this choice. First of all, the servo-control method of operation requires the shortest equilibration time, and hence the shortest measurement time. Combined with sample preheating, the total measurement time can be significantly reduced. If implemented by means of computer control, then all of the advantages of computer control of measurement precision, automatic data analysis and automatic error calculation accrue as well. As was described in Section 2.4.3, a computer-automated calorimeter may be operated in a routine fashion by semi-skilled technicians.

The two main types of plutonium calorimeters of the Mound and ANL designs have been described in Sections 2 and 3. Although designed for the different purposes of plutonium sample and fuel element assay, the two types of calorimeters may be used interchangeably within their respective design specifications. Each calorimeter type has advantages although, on balance, the ANL type dry, fast response design appears to be superior.

The first advantage is that the need for either a water bath or water reservoir and heat exchangers is eliminated. This immediately implies a substantial reduction in weight which has implications as far as transportability is concerned. Secondly, the temperature of the thermal may be controlled to a higher degree of precision than was possible with water bath calorimeters. In cases where the
isotopic mass ratios of the sample are very accurately known, greater overall measurement accuracy is therefore possible. Sample preheating or pre-equilibration may be done without the necessity of removing the sample from the device.

There are other advantages to the ANL design. For example, it is more suitable both for automatic loading, perhaps by means of a computer-controlled robot, and also for simultaneous gamma-ray isotopic ratio analysis. It is potentially more readily transported. A single computer control system may be employed with different calorimeters designed for different sample types and sizes.

A crucial parameter in the use of calorimetry is the time required for a measurement. Clearly, for one-off sample measurements including the preheating time, the total measurement time is likely to be of the order of an hour, assuming a measurement precision of 1%. For the measurement of a number of roughly similar samples, where the preheating and measurement of successive samples may take place simultaneously, measurement times may be a few tens of minutes. Obviously factors such as sample size and power, and especially packaging, greatly influence these times which are, of course, estimates.

The calorimetry technique is well suited to samples of different sizes and powers. For optimum performance, the calorimeter thermal should be designed with a particular sample size and power in mind. The detection limits of calorimetry were considered in Section 2.5.3 and are typically fractions of a gram. The upper limit of sample size is dictated exclusively by considerations of nuclear safety. Because the technique relies on a measurement of the heat evolved from a sample, it is not possible to measure samples where other heat production or absorption processes occur. For example, plutonium samples containing significant amounts of fission products cannot be accurately assayed by calorimetry.
Two factors limit the usefulness of the calorimetry technique for plutonium assay. The first of these is the time required for a measurement. In many cases, this is not a serious limitation and modern calorimetry techniques have improved the situation considerably. Measurement times are likely to be a limiting factor, however, where the calorimetry technique is applied to plutonium assay in a production line or factory environment.

The second factor is by far the most serious limitation. It is the fact that the calorimetry technique depends on an independent knowledge or measurement of the isotopic mass ratios of the constituent plutonium isotopes in the sample. Generally the errors in the isotopic ratios also constitute the largest part of the error in the plutonium mass.

One possible solution to this difficulty is the combined calorimetry and gamma-ray spectrometry isotopic ratio measurement systems. The system was reviewed in Section 3.1 and consists of a simultaneous calorimetry sample power measurement and gamma-ray spectroscopy analysis of the plutonium isotopic ratios. Such an approach shows promise and may lead to a reliable, portable and completely non-destructive plutonium assay system.
4. **DESIGN OF A PLUTONIUM ASSAY CALORIMETER**

The design of plutonium calorimeters is complicated by the variety of plutonium-bearing materials to be measured and the requirements of different types of measurements. The overriding consideration in calorimeter design is that the device must be specific both to the type of sample to be measured and the type of measurement required. There is no such thing as a general-purpose plutonium assay calorimeter, although generally applicable design features and principles may be identified. The purpose of this section is to consider, first of all, design principles and subsequently to apply these to the general design of a calorimeter instrument.

4.1 **General Design Considerations**

The most important factors in plutonium calorimeter design are the types, masses and powers of the samples to be measured. These factors will determine the dimensions of the thermel, the type of temperature sensor and the methods of calibration. Another essential consideration is the type of measurement, whether calibration or assay, and the accuracy required. Assay measurements may be either one-off or of a routine production-line type. The accuracy required of the device will also be determined by the accuracy of the isotopic mass ratio data available for the samples being measured. Two additional general considerations are the time available for the measurement, and whether the device is to be transportable or fixed.

In Section 2.3.1, the different methods of calorimeter operation were considered and the servo-control method emerged as the one involving the shortest measurement times and most suitable for automation by computer. The advantages of computer control and data analysis were considered in Section 2.4.3. It is appropriate then, that in future, accurate, short measurement-time plutonium calorimeters
employ the computer-automated, servo-control method of operation.

Although the details of the design of calorimeter thermels (thermal elements) are dependent on the factors considered in the previous section, an optimum general design may be selected. Following the assessment presented in Section 3.3, a thermel design based on the thermel of the ANL dry fast-response fuel rod calorimeter appears to be most appropriate. It is this design that is considered further in Section 4.2.

4.2 Proposal for a Fast-Response Plutonium Calorimeter

It is convenient to consider the calorimeter as consisting of the two parts of a computer control system and a thermel element. The first part, the computer control system, is illustrated in block diagram form as Fig. 8.

The computer hardware consists of a processor, memory, serial ports and a console terminal, a data and program storage unit, and a parallel interface. Additional instruments include a multiplexer and a digital voltmeter (DVM). The parallel interface is the means by which the computer communicates with, and controls, the other instruments. Measured temperatures, which result in voltage signals, are multiplexed, digitized and transferred to the computer memory. The temperature-controlling electrical heaters are driven by programmed current sources which, in turn, are controlled through the parallel interface. Operator intervention and result-reporting is accomplished through the console terminal.

The computer software, which may be permanently loaded into read-only memory, operates in a real-time environment. In response to measured temperatures, heater control is exercised through the heater control programmed current sources. Once the sample has been loaded into the device, the measurement sequence is controlled by the computer and the measurement proceeds until a predetermined precision is achieved. Automatic data reduction may be carried out,
using operator-entered values of the isotopic mass ratios, and measurement errors automatically calculated. The system may be programmed to be self-checking, and long-term error analysis may be carried out by the software to detect instabilities in the calorimeter and long-term drift. In the case of samples where decay errors are significant, the decay corrections may be calculated by the computer.

The procedures for sample pre-equilibration and calibration can be automated using the computer. Sample preheating may be hastened by computer-controlled overheating, and electrical calibration checks may be performed routinely and automatically without the need for operator intervention.

The design of the thermel is based on the ANL dry fast-response fuel rod calorimeter design and it is illustrated in Fig. 9. In this particular case, it is shown containing canisters of plutonium-bearing material in the preheater and measurement chamber. A detailed design would have to consider the sizes and types of samples, as described earlier, and this information would influence the dimensions of the chambers, the heating and temperature-sensing windings, and the details of the operating procedures. The construction details of the thermel would be similar to those proposed by Brumbach et al. (Br77).

It is difficult to estimate the cost of constructing a plutonium calorimeter of the sort proposed. Based on experience with other computer control systems, the computer control hardware is likely to cost approximately £10,000. This figure might reduce for subsequent post-prototype systems. The cost of construction of the thermel element is very difficult to estimate without considering a very specific design, although it is likely to be of the order of £5,000.
Example of a General Calorimeter

Example of a Radiation Beam Calorimeter
The Imperial College "In Reactor" Microcalorimeter
FIGURE 4

Twin Thermoelectric Fuel Rod Calorimeter

FIGURE 5

Mound Twin Resistance Bridge Plutonium Calorimeter
Thermal and Heat Exchanger of the Mound Transportable Twin Resistance Bridge Plutonium Calorimeter
FIGURE 8
Calorimeter Computer Control and Data Analysis System
FIGURE 9

Proposed Single Isothermal Servo-Controlled Plutonium Assay Calorimeter
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<th>Title</th>
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