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**ISOTHERMAL CALORIMETERS APPLIED TO THE MEASUREMENT OF PLUTONIUM RESIDUES
FOR PLANT POST OPERATIONAL CLEAN-OUT**

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ABSTRACT

The Non-Destructive Assay (NDA) of residues is required for material accountancy and criticality control during the post operational clean out decommissioning phase of plutonium pyrochemical recovery facilities. Residues can be problematic for NDA methods using gamma ray and neutron measurement. Errors can be caused by multiplication in lumps and high (α , n) production rates (neutron measurements), and self shielding and matrix heterogeneity in the case of gamma ray methods. The paper describes the application of ANTECH Isothermal Calorimeters to the measurement of the plutonium content of residues from pyrochemical recovery processes.

Almost all of the energy produced in the plutonium decay process is released with the β -particles, the energy released by fission is a very minor contributor due to the much longer half life compared with that for β -decay. The β -particles are slowed down over a very short distance within the material so that almost all the thermal power generated by the decay is deposited within the sample. Thus if the thermal power is measured, and the relationship between power generated and plutonium mass is known, then the plutonium content of the material can be determined.

The ANTECH Isothermal Calorimeter consists of three concentric cylinders, each maintained at a different temperature (innermost highest, outermost lowest) by an automatic control system, so that heat flows from the inner cylinder (measurement chamber) to the outer cylinder where heat is drawn away by a controlled stream of air. The basis of the measurement involves trading precisely measured electrical power for the thermal power produced by the radioactive decay of the sample. A 'power difference' mode is used in which the measurement chamber (the inner cylinder) is maintained at a

constant temperature by electrical heating. When a heat producing sample is inserted into the measurement chamber, the control system reduces the applied electrical power, as it is replaced by the thermal power produced by the sample. At equilibrium, the difference in applied electrical power gives the sample power. The plutonium mass of the sample is determined from this measured power and a knowledge of the sample effective specific power derived from gamma ray isotopic measurement.

Calorimetry is potentially the most accurate NDA method for measuring plutonium. The thermal power is related directly to simple physical quantities (voltage and current) and is immune to the matrix interferences that affect neutron and gamma-ray techniques. Moreover, corrections are not required for sample inhomogeneity or chemical form. The main disadvantage of calorimetry is the time to achieve thermal equilibrium. This can be alleviated by pre-heating of the sample to approximately the internal temperature of the thermal element or by application of an equilibrium power prediction algorithm.

ANTECH have been successfully producing calorimeters for 12 years during which in excess of 20 ANTECH calorimeters have been in service in various USA DoE and UK MoD facilities for the measurement of plutonium residues, achieving a total of almost 250 'calorimeter operational years'. In all approximately 10,000 individual measurements have been carried out making a significant contribution to decommissioning programs.

INTRODUCTION

The Non-Destructive Assay (NDA) of residues is required for material accountancy and criticality control during the post operational clean out decommissioning phase of plutonium pyrochemical recovery facilities. Residues can be problematic for NDA methods using gamma ray and neutron measurement. Errors can be caused by multiplication in lumps and high (α , n) production rates (neutron measurements), and self shielding and matrix heterogeneity in the case of gamma ray methods. The paper describes the application of ANTECH Isothermal Calorimeters to the measurement of the plutonium content of residues from pyrochemical recovery processes.

The ANTECH Isothermal Calorimeter is a precise instrument designed for the measurement of heat producing samples. The principle of operation is based on measuring the heat evolved from the radioactive decay of radioactive material in the sample container. The calorimetry method is particularly effective when the decay process involves the emission of alpha particles or beta particles which liberate a large quantity of thermal energy which is deposited locally.

The basis of the measurement procedure involves trading precisely measured electrical power for the thermal power produced by the radioactive decay of the sample. Electrical power is applied to the surface of the calorimeter measurement chamber in order to maintain its inner surface temperature precisely at a set point temperature, which is specific to the calorimeter. When a canister containing a sample is inserted into the measurement chamber, the calorimeter temperature control system reduces the applied electrical power which is replaced by thermal power emanating from the sample. A measure of the applied electrical power before and after sample insertion is a measure of the thermal power of the sample. The mass of the sample material is determined from this measured power and a knowledge of the sample effective specific power.

THE ANTECH ISOTHERMAL CALORIMETER

The ANTECH Isothermal Calorimeter is designed to make measurements using the isothermal power difference mode of operation. The calorimeter Inner Cylinder (the measurement chamber) is maintained at a constant temperature (above the other cylinder constant temperatures) by electrical heating. When a heat producing sample is inserted into the measurement chamber, the control system reduces the applied electrical power, as it is replaced by the thermal power produced by the sample. At equilibrium, the difference in applied electrical power gives the sample power.

Samples to be measured are placed in a canister that is placed in the measurement chamber of the thermal element. The Thermal Element, which contains the Measurement Chamber, is the component used to measure samples in canisters. In Measurement Mode with a sample in place, the action of controlling the measurement chamber temperature

results in a gradual reduction in the applied electrical power as heat from the sample reaches the temperature sensor. The applied electrical power eventually reaches an equilibrium value. At this point the difference between the baseline power (the 'base power') and the new applied electrical power is equal to the sample power. The mass of the sample material is determined from this measured power and a knowledge of the sample effective specific power.

The calorimeter consists of a Thermal Element, Instrumentation Rack and hoist, mounted upon a Transportable Trolley. The Thermal Element contains the Measurement Chamber, into which a canister containing the sample to be measured is placed. System control and measurement electronics, including the control and analysis computers and amplifiers, are based in the Instrumentation Rack. The Instrumentation Rack is connected to the Thermal Element by signal and power supply cables. A Hoist is provided to assist the operator with the loading and unloading of canisters.

The ANTECH Isothermal Calorimeter has a thermal power measurement accuracy better than 0.5% over the operating range (0.5 – 15W) and better than 0.2% at 10 Watts power. (190mm diameter sample). It has a variable measurement chambers operating temperature range from 20°C to 50°C and a measurement power range from 15mW to 50 Watts. In standard configuration, the inner cylinder is capable of accepting sample canister internal dimensions of 190mm diameter x 356 mm high. (External dimensions 210mm diameter x 385mm high).

The standard instrument footprint is 123cm x 69cm x 147cm (L x W x H), with an overall height (including removable hoist) of 187cm. The weight of complete trolley mounted instrument is approximately 300kg. The ANTECH calorimeter measurements have been approved for use by the International Atomic Energy Agency (IAEA) and the Waste Isolation Pilot Plant (WIPP) at Carlsbad, New Mexico.

CALORIMETRY THEORY

The calorimeter is used to measure the thermal power of plutonium samples and, in combination with knowledge of the plutonium isotopic mass ratios, calorimetry provides a convenient, accurate and non-destructive measure of the total plutonium mass of the sample. For plutonium measurement the accuracy of the technique is limited by the accuracy of the plutonium isotopic mass ratio data. As a measurement technique, calorimetry has many advantages and it is generally considered the most accurate non-destructive method for measuring plutonium. In the area of post operational clean out of metal recovery plants, calorimetry can have a role in measuring materials such as pyrochemical residues which can be problematic if measured with neutron or gamma ray based NDA techniques. Alternatively, because of its inherent accuracy and absence of interfering matrix effects, calorimetry can be used either to a) provide confirmatory measurement on items measured by other NDA techniques, or b) provide secondary standards for the checking and calibration of neutron

and gamma ray based NDA techniques. The latter method has been used at the Rocky Flats Environmental Test Facility in the post operational clean out of Building 371. (see later results).

With no sample present and the calorimeter at equilibrium, the electrical power applied to keep the inner cylinder at a constant temperature (i.e. the equilibrium value of the chamber and the heat sink) is a value P_o . This is termed the 'base power'. When a heat producing material is introduced, the calorimeter temperature control system reduces the applied electrical power that is now replaced by thermal power emanating from the sample. Once the system has reached equilibrium a measure of the applied electrical power before and after sample insertion is a measure of the thermal power of the sample, i.e.

$$\Delta P = \text{SamplePower} = (P_o - P_{final})$$

This mode of operation is called the 'Power Replacement' or 'Power Difference' method. Both the measurement chamber (MC) and the heat sink (HS) are isothermal – they are each maintained at fixed temperatures (T) such that: $T_{MC} > T_{HS}$ and there is heat-transfer between them. By this means, an absolute measurement is made since the power of the sample is measured directly and hence there is no requirement for a calibration in this mode of operation. However, in almost all cases with practical calorimeters, a small bias correction is necessary. The mass of the sample material is determined from the measured power and knowledge of the sample effective specific power (see later discussion).

The single chamber, true isothermal (air-bath) calorimeter is the most common type of instrument currently in use for the measurement of plutonium in nuclear facilities. In essence, an isothermal air-bath calorimeter consists of three concentric cylinders, each of which is maintained at a different temperature by the automatic control system. In general, the innermost cylinder is at the highest temperature, the middle or intermediate cylinder at a lower temperature and the outer most cylinder at the lowest temperature. In this way, heat flows from the inner cylinder or measurement chamber through the middle cylinder to the outer cylinder.

Heat is drawn away from the calorimeter by a controlled stream of air flowing over the surface of the outer cylinder. Air at ambient temperature is either drawn from the room environment by an air-circulating fan directly or, to improve calorimeter control, via a Peltier cooling system. Using Peltier cooling to provide a thermal sink, allows the calorimeter to operate over a range of temperatures including operation of the inner cylinder or measurement cylinder at room temperature.

The principal of operation of such an Isothermal Calorimeter is as follows: the inner cylinder or measurement chamber is maintained at a constant temperature by the automatic control system which drives a power supply delivering electrical power to a heating element wound around the cylinder outer surface. Similarly the middle cylinder is maintained at a constant and lower temperature by the same

means. The outer cylinder is controlled in the same way, however, its function is simply to provide a guard ring to isolate the inner and middle cylinders from changes in the external ambient temperature.

The automatic control system maintains a constant electrical power supply to maintain constant temperature on the inner cylinder. The constant temperature difference between the inner and middle cylinder means that there is a constant heat flow between the two cylinders. When a heat producing sample is placed in the measurement chamber or inner cylinder, the automatic control system senses the heat generation and reduces the amount of electrical power supplied to the inner cylinder to maintain its temperature.

When thermal equilibrium is reached, the inner cylinder electrical power will be at a lower value and the difference between applied electrical power before sample insertion and after sample insertion, is a direct measure of the thermal power supplied by the sample.

In this mode of operation a controller maintains the calorimeter measurement chamber at a constant temperature slightly above that of the surrounding temperature controlled region thus providing a temperature gradient through which power flows from the measurement chamber in a controlled manner to a heat sink. In most cases the heat sink is a closed cycle air cooling system with a Peltier cooler to control the heat flow from the system. When the heat producing sample is placed in the measurement chamber, less electrical power is required to maintain the constant temperature of the thermal element. The power difference is equal to the sample power. The method has the advantage that the time constant for establishing the temperature gradient throughout the system is eliminated and the time to reach equilibrium is due only to the time constant for establishing the steady heat flow from the sample to the inner surface of the thermal element. If the sample is 'pre-heated' to the temperature of the thermal element then the measurement time can be reduced accordingly

CALORIMETRY APPLIED TO THE MEASUREMENT OF PLUTONIUM

Calorimetry has specific application in the area of nuclear materials accounting, safeguards and decommissioning. Calorimetric measurements of the thermal power of plutonium samples (such as residues), when combined with knowledge of the plutonium isotopic mass ratios, provide a convenient, accurate and non-destructive measure of the total plutonium mass of the samples. The technique has advantages over other measurement methods such as passive neutron coincidence counting, gamma ray measurement and destructive analysis. It does not suffer from self shielding, matrix effects, neutron multiplication effects and it is not biased by inhomogeneity or the presence of moisture in the sample. The technique can be used to validate measurements by other NDA techniques or provide secondary standards to check and calibrate neutron and gamma ray based NDA instruments.

Plutonium bearing materials are measured by means of the thermal energy generated as a result of the absorption of α particles produced by the radioactive decay of plutonium isotopes and the associated isotope ^{241}Am . For the Pu based isotopic mixture, virtually all of the energy liberated in the decay process is absorbed in the sample or associated container and less than 0.01% of the total decay energy (resulting from neutrons and γ -rays) is lost to the calorimetry measurement process. The thermal power of plutonium samples generally ranges from less than 2 W/kg (2mW/g) up to almost 20 W/kg for high burn-up material arising in power reactors.

The accuracy of a determination of plutonium mass depends on the precision of the isotopic data and the relative abundance of the different isotopes of plutonium and americium which have widely varying specific powers. In most practical applications the errors on plutonium isotopic data are the limiting factor in plutonium mass determination. Using high resolution gamma-ray spectrometry and a suitable analysis code (TRIFID, FRAM or MGA) an accuracy in the measurement of Pu and Am isotopic ratios spanning from 0.5% to about 1 % can be achieved for materials of low ^{242}Pu content.

CALORIMETER TECHNOLOGY

The temperature sensor used in the isothermal calorimeter is the nickel winding heat sensor. Nickel resistance thermometry uses fine Ni wire with a known (positive) resistance variation with temperature to measure changes in temperature of the calorimeter cylinders. Nickel, of all commercially available metals, has the highest temperature coefficient of resistivity. The Ni wire is wound in direct contact with the outside of each of the cylinders. The measurement of absolute temperature solely from the nickel winding is inaccurate, but the winding resistance varies in a uniform manner with temperature so once in-situ the winding can be calibrated, used to measure changes in temperature or used to control the temperature of a region.

Nickel sense coils are wound around each cylinder and are connected to resistance bridge circuitry, which produces a voltage related to the resistance, this voltage can be measured directly or amplified before measurement. Nickel sense coils can also be monitored by direct 4-wire resistance measurements. Changes in resistance can be measured accurately to within 0.001 Ω , corresponding to approximately 0.001 $^{\circ}\text{C}$ which is typical for a cylinder winding.

In the unlikely event of a fault with the nickel sense winding, it would be impossible to repair, and so in addition to the nickel sense coils, and to offer redundancy of system, thermistor chains are also employed in the isothermal calorimeter. A Thermistor is a resistor whose resistance varies with temperature. Thermistors can be placed in series to average the resistance to produce a more accurate result. Thermistors can be used singularly to measure the temperature of a point or in chains to measure the temperature across a region.

Electrical heater coils are employed on each cylinder as part of the temperature control mechanism. The inner cylinder or measurement chamber is often provided with an additional heater for precise electrical power calibration. An external electric sample may also be used for precise electrical calibration.

Using calibrated voltmeters and resistors the power applied to a heater winding can be measured to 0.1%. The types of control systems in use can control to a greater accuracy than the temperature measurement methods currently employed. Especially since even in the best designed calorimeter there will be small heat gradients within each temperature controlled region caused by non-uniformity of heat sources within the sample. These non-uniformities lead to errors in the temperature measurement.

The design of the calorimeter ensures that the thermal element is isolated from the environment, except for the controlled heat loss mechanisms, so that all the heat lost by the sample is measured. This is accomplished with insulating materials and long conduction paths. These heat losses will vary in an extremely complex manner with sample temperature and positions of the heat sources thus this is a critical design requirement which is thoroughly modelled and investigated.

The thermal element, which includes the measurement chamber, consists of three concentric aluminium cylinders that serve as temperature controlled regions. A heat-transfer medium fills the gap between the cylinders. The inner cylinder, or measurement chamber, accepts a canister that contains the heat-producing sample.

Resistance thermometry, in the form of a combination of nickel sense coils and thermistors, is used to precisely measure the average surface temperature of the Inner, Middle and Outer Cylinders. Additional sense coils are provided on each cylinder to assure operation, even in the event of the failure of a sense circuit. The nickel sense coils and thermistor chains are used as the sense elements both for resistance bridge measurements and for direct 4-wire resistance measurements. A sensitive digital volt meter (DVM) measures voltages (in 4 wire and 2 wire mode), and resistances, supplied from the output of the Multichannel Scanner Unit.

An independent means of cylinder temperature measurement is provided in the form of linear or non-linear negative temperature coefficient (NTC) thermistors. The mode by which each cylinder temperature can be measured is configurable:

- Nickel Winding Direct - Each cylinder is default set for temperature measurement by Ni Sense Coil A. A 4 wire resistance measurement is made directly by a 4-Wire Scanner card.
- Nickel Winding Bridge Mode - this option enables cylinder temperature measurement to be made by Ni Sense Coil B forming one arm of a Wheatstone Bridge. This is then measured as a 2 wire voltage by the multiplexer through Channel 2 of the Bridge Board (Wheatstone Bridge Circuit).

- Thermistor Direct – in this mode cylinder temperature measurement is made by a chain of thermistors (Thermistor Chain A) wired in series and distributed evenly across the cylinder. Each thermistor is inserted into a hole drilled into the wall of the cylinder, and potted in thermal grease. A 4 wire resistance measurement is made directly by the 4-Wire Scanner card.
- Thermistor Bridged - Cylinder temperature measurement is made with Thermistor Chain B as a 2 wire voltage measurement by the multiplexer through Channel 1 of the Bridge Board.
- Ni/Thermistor Bridged Amp – The voltage produced by either of the Wheatstone Bridges can be fed into the amplifier circuit by selecting with a jumper on the Bridge Board. The amplified voltage is then measured as a 2 wire voltage through the multiplexer.

CALORIMETER PERFORMANCE CHECKING

There are two manners in which an isothermal calorimeters performance can be measured:

- Use of plutonium samples of known specific power (known isotopic content)
- An electric heater with accurately measured voltage and current.

The use of electric heater samples is common and convenient since they can be used to confirm the correct operation of the calorimeter whenever necessary without the need for a radioactive heat generating source.

Periodically, a check of the calorimeter is performed in which a sequence of electrical powers is injected into a measurement region and the applied power compared with the measured power. This verifies correct operation of all the instrumentation, although it does not take into consideration heat distribution errors and thermal leakage associated with samples which are located at different positions in the measurement chamber.

Calibration aspects of the calorimeter components are straightforward. The electrical power is measured by using calibrated electrical measuring components. These usually consist of a digital volt meter (DVM) for measuring voltage and a combination of the DVM and a calibrated precision resistor, to measure current. The product of current and voltage is of course, electrical power. The DVM and calibrated precision resistor is calibrated against national standards, such as those held by the National Institute for Standards and Technology (NIST) in the United States and the National Physical Laboratory (NPL) in the United Kingdom.

Electrical heat standards (resistor chains), which accurately represent both the physical geometry, and the thermal characteristics of the samples employed in the measurements are used to check the calorimeter performance. The

performance checking involves applying a pre-selected and measured power and then measuring the power which that sample evolves in the measurement chamber, as one would do in a normal measurement. Because the electrical power used for the calibration is user selectable, the calorimeter is checked over its entire dynamic range.

FACTORS AFFECTING MEASUREMENT

Sample Thermal Conductivity

The physical nature of the sample and the distribution of heat generating material within it (metal billet, high density oxide powder, scrap and heterogeneous item with large voidage) will affect the overall measurement time. Moreover, the measurement precision as a result of measurement time will also be affected. Typically, 1 kg of plutonium oxide can be measured successfully in under four hours, while the equivalent weight of pyrochemical salt (containing 100 to 200 g Pu) can take up to 20 hours to measure. The measurement time is also highly dependent upon sample packing.

Sample Packaging

The thermal conductivity of the material which separates the heat generating components of the sample from the sample container wall (the sample packaging) will affect the time required for the flow of heat to reach thermal equilibrium and hence the overall measurement time. The measurement time is very dependent on the nature of the sample packaging.

Sample Chamber Size

The size of the sample chamber also affects the time required to reach thermal equilibrium since the larger the chamber the further from the chamber wall the heat producing sample is located. The sample size and thermal conductivity are the major factors affecting measurement time. The type of material to be measured, and hence the thermal conductivity, is defined by the particular application and cannot be altered. In principle, the sample size could be optimised to achieve a balance between the conflicting requirements of throughput and measurement accuracy.

Effective Specific Power

The majority (99.99%) of the energy generated through the decay is released with the α and β particles, which are slowed within the material in a very short distance resulting all the power generated through the decay being deposited within the sample. Thus if the power generated by the sample is measured and relationship between the power generated and the amount of material is well known then the amount of material in the sample can be calculated by dividing the measured power (in Watts) by the Effective Specific Power (Watts/gram) the latter being derived from the isotopic composition.

Additional Sources of Heat

The calorimeter cannot distinguish heat produced by radioactive decay from that produced by any other mechanism, such as chemical reactions. This is usually not a problem for two reasons:

1. the production of heat from long lived Pu isotopes is effectively 'constant',
2. chemical reactions by their very nature tend to have relatively short half lives and the time dependence of the heat output can be used to detect the presence of such reactions.

In the special case of pyrochemical materials where chemically reactive species might be present, it is estimated that the heat of reaction would have a negligible effect on the overall heat measurement. In most cases, the use of hermetically sealed containers excluding air and moisture will mitigate against this problem. Procedural controls can also prevent such effects adversely affecting measurements.

Physical and Chemical Form

Calorimetry is most precise for materials with relatively high Pu concentrations, consequently calorimeters are normally used for measuring bulk solids such as plutonium oxide, plutonium metal (billets, buttons) and pyrochemical materials containing significant quantities of metal 'shot' or species such as plutonium trichloride.

Because of the restricted size for optimum performance of the calorimeter sample well, measurement tends to be on the packet scale with a normal upper limit of 30 litres capacity.

Use of Sample Pre-Heating

In the case of the isothermal calorimeter measurements, pre-heating of the sample to approximately the internal temperature of the thermal element can be used to reduce the measurement time.

The advantage of this method of pre-heating is reduced time leading to equilibrium and increased throughput. To have any benefit, several samples must be pre-heated at the same time. This may not be possible in the case of plutonium samples because often criticality safety rules do not permit multiples packages in the same pre-heater. In this case, the advantages of pre-heating are lost.

The disadvantages of pre-heating are that a) the instrument has a larger foot-print (required to accommodate the requirements of the pre-heater cylinder and control equipment), b) the instrument is more expensive, and c) the pre-heating can make matters worse if the sample is pre-heated to the wrong temperature.

Equilibrium Power Prediction

In order to reduce measurement times, isothermal calorimeters employ equilibrium power prediction algorithms. Theoretical justification exists which suggests that the decay of the applied electrical power can be treated as an exponential function consisting of a number of terms with different time constants. The calorimeter response function is thus dominated by the exponential of the form:

$$Y = A + Be^{-\lambda t}$$

where Y is the time-dependent calorimeter output, A is the equilibrium output signal, B is a scaling constant and λ is the final decay constant of both the calorimeter and sample.

After a period of time, a single exponential remains once the short decay time exponential terms have died away. The calorimeter software detects the point at which a single exponential can be used to describe the decay of the applied electrical power. At this point the system fits either a single or a double exponential function to the power decay data. Using the fit, an extrapolation is employed to determine the final equilibrium electrical power, and hence the sample power.

The time for a measurement depends on the thermal properties of the sample and may be significantly reduced by the use of the sample power prediction algorithm.

CALORIMETER SOURCES OF ERROR

The Effective Specific Power for Plutonium (P_{eff}) is the product of the specific power P_i for each isotope multiplied by the relative amount R_i of each isotope, and an extra term for the specific power of ^{241}Am and relative amount of ^{241}Am (R_{Am241}) which also generates power through its decay.

$$P_{eff} = \sum_{i=238}^{242} P_i R_i + Am_{241} R_{Am241}$$

Values for the Effective Specific Power P_i for each isotope are taken from reference data in the literature [3]. The values of R_i can be derived from historical plant records, γ -spectrometry, or mass spectrometry. In order to determine the Effective Specific Power experimentally, an accurately known amount of the material to be assayed is measured and the power measured (W) divided by the mass to give the Specific Power.

$$P_{eff} = \frac{W}{Pu}$$

Chemical analysis can be used to accurately derive the amount of the material. The error is, then:

$$\Delta Pu^2 = \Delta W^2 + \Delta P_{eff}^2$$

and from the isotopic information:

$$\Delta P_{eff}^2 = \sum_i \left[\frac{R_i P_i}{P_{eff}} \right]^2 [\Delta R_i^2 + \Delta P_i^2]$$

The accuracy of the calorimeter measurement is dependent on the accuracy of the isotopic measurement. It is essential that plant operators identify all significant heat producing nuclides that may be present in the sample. This is especially important in the assay of plutonium bearing materials where the heat output can be dominated by the presence of ²³⁸Pu and ²⁴¹Am.

Isotopic Composition

Potentially, errors are introduced when significant quantities of nuclides having high specific powers such as ²³⁸Pu and ²⁴¹Am are present in the sample. The uncertainty in the isotopic ratios of these nuclides dominates the overall error in the determination of the Pu mass.

Quantitative Determination of Errors

For the measurement of Pu, the main elements of the quantitative errors associated with calorimetry are then:

- Errors on measurement of the sample power,
- Errors on determination of the isotopic ratios and specific power of the sample,
- Uncertainty on date of Pu isotopic measurement,
- Uncertainty on date of Am measurement.

Since the Pu mass M, is determined from the total power of the Pu bearing sample, W_s, and the effective specific power of the sample P_{eff} by:

$$M = \frac{W_s}{P_{eff}}$$

Then the overall uncertainty of the measurement is given by:

$$\left(\frac{\sigma_M}{M} \right)^2 = \left(\frac{\sigma_{W_s}}{W_s} \right)^2 + \sum_i \left[\frac{R_i P_i}{P_{eff}} \right]^2 [\Delta R_i^2 + \Delta P_i^2]$$

The accuracy of a determination of plutonium mass depends on the precision of the isotopic data and the relative abundance of the different isotopes of plutonium and americium which have widely varying specific powers. In most practical applications the errors on plutonium isotopic data are the limiting factor in plutonium mass determination, since the sample power as measured by the calorimeter can be determined with an error less than, and usually much better than, 0.3% (relative standard deviation (1σ)). Using gamma-

ray spectrometry and a suitable analysis code an accuracy in the measurement of Pu and Am isotopic ratios spanning from 0.5% to about 1 % can be achieved for materials of low ²⁴²Pu content.

MEASUREMENT PERFORMANCE

The ANTECH Isothermal Calorimeter has been used to measure Pu oxide, metal or pyrochemical recovery residue material in practical situations.

Inter-comparison results from the measurement of pyrochemical salts using an ANTECH Tomographic Gamma Scanner (TGS) and an ANTECH Isothermal Calorimeter ('Cal'), combined with isotopic measurement ('Iso') are shown in Fig. 1 (below).

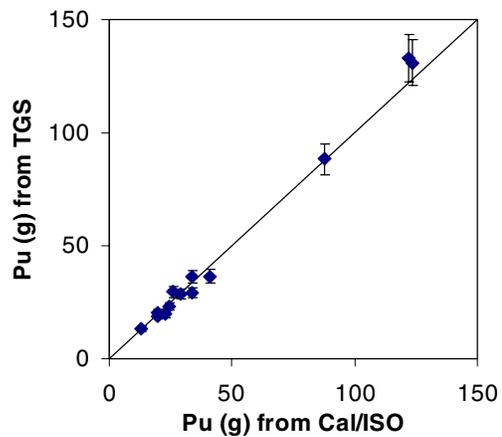


Fig. 1. Pyrochemical Salts Measurements

Table I below shows actual performance data from a single cell isothermal air bath calorimeter designed to measure plutonium. The 'Set Power' values are from electric heat standards.

Table I. True Isothermal Calorimeter Performance Data (electric heat standards)

Set Power (W)	Equiv. Mass 'A' Grade Pu (*)	Equiv. Mass 'O' Grade Pu (*)	Accuracy % (1σ)	Precision % (1σ)
0.015	6g	1.9g	8.5	7.4
0.3	120g	38g	1.0	0.3
1.5	600g	188g	0.3	0.3
10	4 kg	1250g	0.04	0.04
15	6kg	1875g	0.2	0.08

(*) based upon an assumed, average composition of (Pu isotopes + ²⁴¹Am) in each case. Approximate values given for guidance only.

The results given in Table II below are based upon the measurement of Pu metal samples of known isotopic composition. The Pu isotopic composition of the Pu metals samples is measured by High Resolution Gamma Spectroscopy or is the result of destructive sampling and assay using more accurate techniques such as Mass Spectrometry. From the isotopic composition can be derived the effective specific power from reference data. The isotopic content of the Pu is ~94% ²³⁹Pu and ~6% ²⁴⁰Pu. The nominal specific power given a fixed isotopic content and ²⁴¹Am grow-in from the decay of ²⁴¹Pu is therefore ~ 2.5 mW/gram. The results in Table II below are for a calorimeter operating in isothermal mode. The equilibrium result was achieved in a timescale of between 5 and 8 hours.

Table II. Isothermal Measurement of Plutonium Samples

Pu Sample Mass (or heat standard)	(*)Predicted Value (mW)	(*)Equilibrium Value (mW)	Accuracy % (1σ)	Precision % (1σ)
5.0g	11.0	11.1	16.8	13.2
75g	186.2	188.1	0.63	0.53
800g	1603.3	1603.9	0.53	0.08
300mW Electric Heat Standard	302.5	300.6	0.82	0.78
10W Electric Heat Standard	10035.5	9999.1	0.05	0.05

(*) mean of three independent measurements and based upon an assumed, average composition of (Pu isotopes + ²⁴¹Am) in each case.

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