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# Classical radionuclidic calorimetry

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## Abstract

This brief survey summarizes the principles and practice of classical isothermal microcalorimetry for the primary standardization of the activity of radionuclides. Its advantages and some potential problems are highlighted through the discussion of several standardization examples.

## 1. Overview

Calorimetry (from the Latin *calor* for heat and the Greek *metria* for the process of measuring) refers to the measurement of heat energy absorbed or released in physical, chemical or biological processes. Since there are many different processes that can be studied over a wide range of energies, a large variety of calorimeters have been developed.

The first calorimeter, consisting of a hollowed block of ice, was probably that devised by Black in 1761 [1]. By 1779 to 1784, Lavoiser and Laplace were conducting experiments to measure the quantities of heat evolved during various chemical changes as well as from animal respiration [2]. One of the first quantitative reports was that a guinea pig (genus *Cavia*) placed in the calorimeter for 10 h melted 13 ounces of ice!

Calorimetry became a more standard physical measurement technique around 1840 after Joule and von Mayer independently concluded that heat was a form of energy [3]. This led to a general acceptance of the principle of conservation of energy and of the quantitative interconversion of energy in one form into another. Interestingly, many of the first papers by Helmholtz, Mohr, von Mayer and Joule on these topics, including the first energy conservation hypotheses, were rejected for publication since these views were in conflict with existing thermodynamic beliefs and theories [3].

Heat, as a form of energy, is measured in units of joules; and its time rate of change is a power measured in units of watts. Radionuclidic calorimetry, then, is taken to mean the measurement of the energy released from radionuclides as a result of the radioactive decay process, such that the decay rate is related to the measured calorimetric power. More specifically, as used here, the term will be applied to the kinds of calorimetric measurements that are used for the primary standardization of radionuclides; namely, the realization of the becquerel for specific radionuclides. This paper will primarily focus on the more classical aspects of isothermal calorimetry in the microwatt region, and excludes cryogenic calorimetry [4, 5] and the more recent extraordinary developments in quantum

calorimetry and solid-state bolometry [6–8]. It will become evident, however, that many of the fundamental aspects of calorimetry as applied to radioactivity measurements, as well as its main advantages and shortcomings, are applicable to all of the calorimetric methods.

## 2. History and uses

Calorimetry of radioactive materials has been around for over a century. It was first employed within a few years of Becquerel's 1896 discovery of radioactivity. Collé and Zimmerman [4] briefly summarized some of this early history, noting (i) the use of a Bunsen ice calorimeter for the measurement of radium preparations by Curie and Laborde [9] in 1903; (ii) the use of twin-cup and differential calorimeters by Rutherford and Barnes [10] in 1903–04 and (iii) the early utilization of cryogenic calorimeters at liquid-air and liquid-hydrogen temperatures by Curie and Dewar [11] in 1904. Most of these investigators and many other early workers were primarily concerned with measuring the heat rates arising from the absorption of radiations in the naturally occurring decay series and from radioactive minerals.

The 1910 'radiobalance' of Callandar [12] was perhaps the first precise calorimeter that could be used for radioactivity standardizations. A version of this 'Peltier-effect isothermal microcalorimeter', utilizing twin gold cups and calibrated Peltier junctions, was developed by Mann [13–15] in 1953 and used by our laboratory over the next 40 years for a variety of international radium (Honigschmid) standard comparisons [16, 17] as well as for primary standardizations, such as for  $^{63}\text{Ni}$  [18, 19].

No history of radionuclidic calorimetry, however brief, would be complete without mentioning the crown of glory experiment of Ellis and Wooster in 1925 [20], which verified the need for the neutrino hypothesis in beta decay because of the experimentally observed difference in the maximum energy and average energy of the beta radiation from  $^{210}\text{Bi}$ .

Undoubtedly, one of the first truly important radioactivity standardizations by calorimetry was that of Watson and Henderson [21] in 1928, in which the specific activity of  $^{226}\text{Ra}$  was determined to confirm the value ‘curie’ (the disintegration rate associated with 1 g of  $^{226}\text{Ra}$ ; the original definition) [22, 23]. Their accurate calorimetric power measurement when combined with the known alpha-particle energies gave a value for the specific activity of  $^{226}\text{Ra}$  ( $3.72 \times 10^{10} \text{ s}^{-1} \text{ g}^{-1}$ ) that was in agreement with a result of  $3.69 \times 10^{10} \text{ s}^{-1} \text{ g}^{-1}$  from total charge measurements [24] and with a value of  $3.66 \times 10^{10} \text{ s}^{-1} \text{ g}^{-1}$  from direct alpha-emission-rate measurements [25]. The importance of the agreement amongst these studies may be appreciated by recognition of the fact that the ‘curie’ was historically used as the standard unit of radioactivity from 1910 onwards and was based on an experimentally determined (and variable) value of the  $^{226}\text{Ra}$  specific activity. By 1930, use of a value of  $3.70 \times 10^{10} \text{ s}^{-1} \text{ g}^{-1}$  was recommended [26, 27]. In 1953, the curie was redefined to represent *exactly*  $3.7 \times 10^{10}$  disintegrations per second (37 GBq), and was replaced by the derived SI unit becquerel in 1975 [28].

In addition to the determination of the activity of radionuclides, calorimetry has had many other uses within the discipline of radioactivity. Only a few examples will be cited, but these applications include calorimetry’s use for the determination of: half-lives, such as that for  $^3\text{H}$  [29],  $^{14}\text{C}$  [30],  $^{210}\text{Po}$  [31],  $^{147}\text{Pm}$  [32] and  $^{226}\text{Ra}$  on many occasions [33]; average beta decay energies, such as for  $^3\text{H}$  [29, 34],  $^{14}\text{C}$  [30] or  $^{147}\text{Pm}$  [32]; alpha emission energies, such as for  $^{239}\text{Pu}$  [35]; and burn-up of nuclear fuels [36, 37]. For the past few decades, calorimetry has been mainly used for the assay of tritium and special nuclear materials in the nuclear-power and -weapons industries and for fusion technology [38–41]. More recently, it has been used to establish standardizations for GBq-range brachytherapy sources [4, 5, 42].

Bibliographic compilations on radionuclidic calorimetry are all quite dated. The first, by Myers [43], was an exhaustive review covering all of the literature up to 1949. Mann [44] extended the references to 1958 in a less-detailed encyclopedic article. The reviews of Gunn in 1964, 1970 and 1976 [45] are broader in scope, covering all radiometric measurements including those for dosimetry. The excellent 1973 survey by Ramthun [46] summarized the classes and basic forms of various calorimeter types and different measurement applications. This latter work is undoubtedly the best available treatment on the metrological aspects of calorimetry as applied to radioactivity measurements.

### 3. Principles and practice

The underlying premise in radionuclidic calorimetry is that the calorimeter will absorb (i.e. and measure) all or a known part of the radiation emitted by the radioactive source. The activity  $A$  of a radioactive source contained in the calorimeter can be related to the energy (or heat) input, or calorimetric power  $P$ , by the basic relation:  $P = c \cdot A \cdot \bar{E}$ , where  $\bar{E}$  is the average energy per decay for the radionuclide and where  $c$  is a proportionality constant that represents the fraction of total power from radioactive decay that is dissipated (and measured) in the calorimeter. In the ideal, if all of the radiation is absorbed and quantitatively converted into heat (and measured), then

**Table 1.** Power  $P$  (in units of  $\mu\text{W}$ ) per unit activity  $A$  (in units of GBq) for various nuclides having an average energy per decay of  $\bar{E}$  (adopted from [4]).

Nuclide	Decay mode	$\bar{E}/\text{keV}$	$(P/A)/(\mu\text{W GBq}^{-1})$
$^3\text{H}$	$\beta$	5.69	0.912
$^{55}\text{Fe}$	EC	5.87	0.940
$^{103}\text{Pd}$	EC	60.8	9.74
$^{63}\text{Ni}$	$\beta$	17.4	2.79
$^{14}\text{C}$	$\beta$	49.5	7.93
$^{33}\text{P}$	$\beta$	76.4	12.2
$^{32}\text{P}$	$\beta$	695	111
$^{90}\text{Sr}$	$\beta$	196	31.4
$^{90}\text{Y}$	$\beta$	934	150
$^{210}\text{Po}$	$\alpha$	5410	869
$^{226}\text{Ra}$ (to $^{210}\text{Pb}$ )	$\alpha/\beta$ chain	—	4340 <sup>a</sup>
$^{210}\text{Pb}$ subseries	$\alpha/\beta$ chain	—	935 <sup>a</sup>

<sup>a</sup> Per GBq of the parent nuclide.

$c = 1$ . The constant  $c$  represents a fractional loss of the radiative energy (from radioactive decay) out of the calorimeter and is specific for a given nuclide and source/calorimeter configuration. This  $c$  is not meant to represent any heat (generated from the radioactive decay) that was not detected and measured or that escaped from the calorimeter. This type of heat loss is normally treated by the calibration and/or corrections used to determine  $P$ .

Table 1 illustrates the power per unit activity  $P/A$  for a selection of nuclides. As indicated, to perform microcalorimetry in the range  $>10 \mu\text{W}$ , large activity-level sources, exceeding 10 GBq are required for very low-energy  $\beta$  emitters and low- $Z$  electron capture (EC) nuclei. Medium energy  $\beta$  emitters still require sources of at least several hundred MBq. The activity levels needed fall into the kBq range only for  $\alpha$  and very high-energy  $\beta$  emitters. These high activity levels are not normally associated with radionuclidic standardization activities, although many such standardizations have been performed in the past and the levels fall within ranges required for radiotherapy calibrations.

For pure  $\alpha$  or pure  $\beta$  emitters, the assumption of  $c = 1$  is usually valid since the short range of their radiations usually precludes their escape from a calorimeter. For nuclides with high  $\beta$  energies, the possible escape of bremsstrahlung may occur and have to be accounted for. Nuclides whose decay is accompanied by photonic emission ( $\gamma$ - and x-rays) can also exhibit losses, except for very low-energy  $\gamma$  radiation or the x-rays from low- $Z$  EC decay, which are likely to be absorbed in the calorimeter.

The treatment of these potential radiative losses requires consideration of the specific source/calorimeter configurations used in the calorimeter. In large part, one can use Monte Carlo modelling simulations for the specific geometries, using available radiation transport codes, to account for any possible loss corrections. Such calculations were performed for all of the examples cited in sections 4 and 5. In practice, one can use different absorbers (in amount and material) to look for effects, in addition to Monte Carlo calculation verifications. Obviously, the losses and/or corrections can be minimized by maximizing the amount of absorbing material surrounding the source in the calorimeter. The available volume of the source containment space in the calorimeter is often the limiting factor.

An accurate knowledge of  $\bar{E}$ , obtained from available nuclear and atomic data, is required to obtain the source activity  $A$  from the measured power  $P$ . This determination of  $\bar{E}$  is simple in some cases and can be exceedingly troublesome in others, depending upon the complexity of the decay. Ramthun [46] in his survey outlined the procedure for some decay modes. Again, the treatment is relatively straightforward for pure  $\alpha$ - and pure  $\beta$ -emitting nuclides. For the alpha emitters,  $\bar{E}$  can be calculated from the sum of the well-known and tabulated  $\alpha$ -ray energies and the recoil energy of the residual nuclei. For the  $\beta$ -emitters,  $\bar{E}$  can be obtained from measured and tabulated average energies  $E_{\beta(\text{ave})}$  or from Fermi-theory  $\beta$ -spectrum shape calculations. In this case,  $c$  is still taken as unity and we use  $E_{\beta(\text{ave})}$  even though not all of the decay energy is absorbed in the calorimeter. This is merely a convention since neutrino detection in a practical calorimeter is improbable. For nuclides decaying by EC or through multiple branches with accompanying  $\gamma$ -ray emission, conversion electrons and x-rays,  $\bar{E}$  must be obtained by the weighted summation of the individual energies  $E_i$  of all particles ( $\alpha$ ,  $\beta$ , conversion or Auger electrons), recoil nuclei and photons ( $\gamma$ - and x-rays) in the decay:  $\bar{E} = \sum_i f_i E_i$ , where  $f_i$  is the probability per decay for each  $E_i$  component. The summation can, of course, be truncated for  $f_i E_i$  components whose contribution to  $\bar{E}$  is insignificant. These calculations nevertheless can quickly become quite complicated. For multiple-branched  $\beta$  and EC decay, it is usually advisable that one consult an expert in nuclear and atomic data evaluations to obtain a 'best available'  $\bar{E}$  value.

Ramthun [46] has adequately described the three basic forms from which all calorimeters can be derived (namely, heat flow, adiabatic and isothermal) and cited working versions in various metrology laboratories, although few of these calorimeters (if any) are still in operation. The described forms, however, are idealized and most calorimeters of today incorporate more than one of the basic forms. In fact, it is often hard to make distinctions. The identical calorimeter of Calvet and Prat [47] was described by Mathews and Morris [48] as a 'twin isothermal calorimeter', while Ramthun [46] referred to it as a 'so-called heat flow calorimeter'. Adiabatic calorimeters are generally accepted to give the most accurate results, particularly for heat capacity and chemical applications; however, they rarely exist in a pure form or in practice. Historically, adiabatic calorimeters for radiometry were more prevalent, as noted by Ramthun [46], but this is not the case today. A more common variant in use today is likely to be a 'dual cell, near-isothermal (heat flow) calorimeter'. A commercial version of this type is in current use at the National Institute of Standards and Technology (NIST) and will be described below (section 4) to illustrate the practice of radionuclidic calorimetry as used for several recent primary standardizations. Another version of this type of calorimeter has been developed at the Japan Atomic Energy Research Institute and has been described by Genka *et al* [49].

It may be useful to clarify some of the chosen terminology. Although both of the aforementioned calorimeters and similar types are frequently termed 'isothermal', the classification is somewhat of a misnomer. In a true isothermal calorimeter there are, of course, no temperature gradients and hence no heat flow. Instead, a true isothermal calorimeter must rely

upon some type of variable power compensation, such as the cooling or heating from a Peltier current as in the Callandar radiobalance of Mann [13, 14]. So, these types might, more precisely, be described as 'semi-isothermal' or 'near-isothermal' since only the temperature of a surrounding heat sink is kept constant. The descriptor 'heat flow' might also be appended since these calorimeters measure the heat produced in a sample as it flows (due to the temperature gradient) toward the absorbing sink. Almost all calorimeters can be arranged as 'dual cell' (sometimes referred to as 'twin') calorimeters. This configuration allows for a differential measurement that increases the accuracy of the power measurement by rejecting the effect of common-mode perturbations and has obvious advantages that will shortly become apparent.

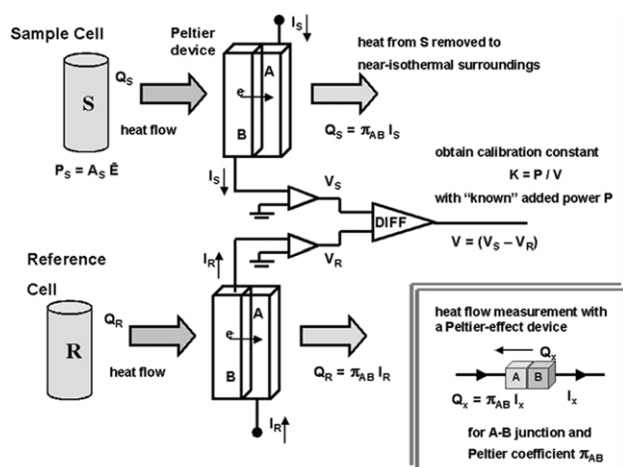
Such a 'dual cell, near-isothermal (heat flow) calorimeter' can have many configurations. Yet, it must rely upon measurement of the heat flow (converted to a power) from the radioactive source contained within the calorimeter, and this power must be determined 'absolutely' (*sic*), traceable to SI quantities and national standards, if the source activity is to be considered to have been determined by a primary measurement method. Section 4 will demonstrate how these requirements can be achieved in practice.

#### 4. The 'isothermal microcalorimeter' at NIST

This specific calorimeter is described mainly as an illustrative example to describe the major features of calorimetry and how it is performed.

The calorimeter, in operation in our laboratory since 2001, was obtained from Calorimetry Sciences Corporation (CSC) of Spanish Fork, Utah and is denoted as the 'CSC 4400 Isothermal Microcalorimeter (IMC)'. It has been located and successfully used in three different physical laboratory locations, which had widely varying ambient conditions. The description that follows is largely taken from [42], which also contain schematics of the component parts and design. The dual calorimeter cells are maintained in a near-isothermal environment with a massive aluminium heat sink that is immersed in a large (about 45 L) temperature-controlled water bath. The temperature of the bath, maintained, for the standardizations presently described in section 5, at a nominal  $T_{\text{BATH}} = 30^\circ\text{C}$ , was regulated, to better than  $\pm 0.001^\circ\text{C}$ , with an internal-heater controller and an auxiliary chiller bath. The auxiliary bath, in turn, was operated at an approximate temperature of  $T_{\text{AUX}} = 22^\circ\text{C}$  (and with a stability of  $\pm 0.01^\circ\text{C}$ ) and was used to circulate (at about  $15\text{ L min}^{-1}$ ) chilled water around a jacket on the primary bath. Thermal equilibrium in this arrangement is achieved by competitive compensation between the auxiliary chilling and the primary bath's heater. The baths can, of course, be operated at other variable temperatures. The calorimeter temperature  $T_{\text{CAL}}$  is continually monitored with a probe that is embedded in the aluminium heat sink. Typical ambient laboratory temperatures in the first two locations were maintained to within  $\pm 0.5^\circ\text{C}$ . The calorimeter has since been moved to a new laboratory having long-term temperature variations of  $< 0.1^\circ\text{C}$ . The stability, and hence power measurement sensitivity, is completely dependent on how 'isothermal' the conditions are maintained. The IMC, as supplied by CSC, is equipped with an 'Auto Calibrate'





**Figure 1.** Schema illustrating the heat flow (power measurement) with Peltier thermoelectric devices as used with dual cells in the NIST isothermal microcalorimeter.

feature that utilizes internal calibration heaters. Since these power-calibration heaters are not located directly within the measurement cells, this calibration feature was not used, except as an approximate confirmation of NIST-provided power calibrations.

A simplistic illustration of the principles underlying the calorimeter's heat flux measurement is given in figure 1. The sensing devices, located between the sample cells and aluminium sink, are Peltier-effect thermoelectric generators that are reported by CSC to be arranged in a kind of modular stack. These semiconductor-based devices can be thought to be like the better-known thermoelectric modules (TEM)—that convert electrical energy into cooling power—working in reverse. Many different types of heat sensors could, of course, be used in similar type calorimeters; e.g. thermopiles, multiple-junction thermocouples, thermistors, Pt-resistance thermometers, etc. They all work.

The calorimeter employs dual cells that are used, in a type of non-compensating 'radiation balance' arrangement [12, 13], to make a differential measurement that is intended to compensate for any heat flux that results from temperature fluctuations in the heat sink or for electronic noise. Power (i.e. the heat change) from a source located within the sample cell creates a temperature difference between the source and the heat sink, which also results in a temperature gradient across the thermoelectric sensors. These Peltier devices, as a result, generate a voltage that is proportional to this temperature gradient and hence to the heat flux. The differential voltage signal ( $V_S - V_R$ ) from the dual cells can then be converted in terms of the heat flux (or power  $P$ ) from a sample by invoking a proportionality constant, or calibration factor  $K$ , that relates  $P$  to  $(V_S - V_R)$ ; i.e.  $K = P/(V_S - V_R)$ . The calibration factor is obtained by performing a calibration with a 'known' added power, e.g. by Joule heating with a resistor.

Insertion assemblies for the dual cells are matched, as nearly as possible, for both physical dimensions and material compositions. This is done so that heat transfers from the two cells to the surrounding envelope shall be as nearly equal as possible, when the cells are at the same temperature. Inner-cell holders, consisting of various materials and whose designs

are optimized for each radionuclide and source geometry, are used to contain the radioactive sources and to serve as absorbers for the ionizing radiations. In order to relate a measured power to the activity of a source contained in a cell, these absorbers must be able to absorb all (or a well-determined known part) of the radiative energy, including that due to secondary radiation, e.g. bremsstrahlung. For the standardizations described in section 5, the sources were contained in either aluminium or brass (Cu63/Zn37) holders of varying lengths, having a minimum wall thickness of 12 mm. These specially fabricated absorbers fit snugly within screw-capped cells. These cells are composed of heat-resistant Hastelloy-C (Ni57/Mo17/Cr16/Fe/W/Mn) and have 4 mm thick walls. The cells, in turn, are inserted deep into the aluminium heat sink (using a removable threaded rod) to a depth of about 43 cm and are seated within isolated, thin-walled, aluminium blocks. The well shafts are thermally shielded from the ambient room air with a series of three aluminium discs and the access ports are sealed with high-density resin caps. Precision resistors are embedded both within the reference (R) and sample (S) cells. These are wired to power-calibration instrumentation using four-wire leads (of 36 AWG gauge, low-heat conductivity, phosphor-bronze wires) that snake up the well assemblies through miniscule clearance holes. The lead wires inside each cell are sufficiently long so that the resistor can be positioned in various locations (with respect to the interior source absorber-holder) within the cell.

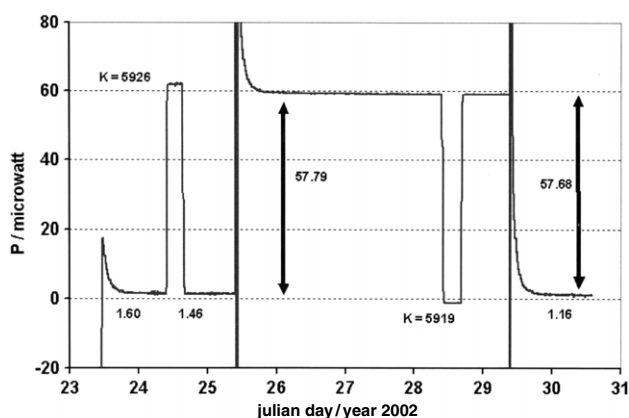
The power-calibration circuitry, using the embedded resistors for Joule heating, used for this calorimeter has also been described in detail in [42]. This independent power-calibration feature was instituted since we felt that the IMC 'Auto Calibrate' heaters might not adequately simulate the power dissipated from a sample within a cell. There are, of course, several alternative ways to provide such a power calibration. For this calorimeter, a variable-waveform signal generator (with a variable, but preset, voltage) is used to provide a dc current through the precision resistor  $R$ . To eliminate thermal EMF effects, the voltage (and hence current direction) from the generator is reversed every 50 s to 100 s. This is achieved by setting the generator to produce a square waveform with an appropriate frequency, e.g. 0.01 Hz. A second set of lead wires is used to continuously measure the voltage  $V$  across the resistor using a calibrated digital voltmeter (DVM), such that the applied calibration power at any time is  $P_{CAL} = V^2/R$ . Calibration powers over a wide range can be obtained by varying the voltage from the signal generator. Using voltages typically in the range of  $\pm 1$  V to  $\pm 5$  V, calibrations up to  $250 \mu\text{W}$  could be obtained. The resistors used for the power calibrations are Vishay (Malvern, PA) H series Foil Resistors, model VHP-202, which are oil-filled, hermetically sealed, ultra-precision resistors. Each has a certified resistance of  $100.00 \text{ k}\Omega$  with relative initial resistance 'accuracy' (tolerance) of  $\pm 0.001\%$  at  $25^\circ\text{C}$ . These resistors are often used as secondary standards in metrology laboratories. The DVMs that have been used to measure  $V$  across  $R$  are calibrated and certified to have a dc voltage measurement 'accuracy' at  $(23 \pm 5)^\circ\text{C}$  of about  $\pm 0.004\%$ . For assurance purposes, the voltage is usually monitored with two separate DVMs in parallel. Both the DVM and signal generator

are controlled by a LabView (Austin, TX, USA) program that communicated with the instruments over a General Purpose Interface BUS (GPIB) interface connected to a PC-compatible computer. The program accumulates DVM readings at a desired sampling rate and calculates suitable averages of the applied power [42].

Power calibrations could also be obtained from voltage and current measurements with a calibrated electrometer, which is a method used at other laboratories [50].

Calorimetric measurement of a source is effected by measuring the difference in the apparent power  $P = (P_S - P_B)$  between a baseline determination  $P_B$  and the power  $P_S$  after a source is inserted into the cell assembly. Both  $P_S$  and  $P_B$  must be measured under steady state conditions when the power levels are at a state of thermal equilibrium in the calorimeter.

Figure 2 shows the results of two calibrations performed during the course of such a measurement of a  $^{90}\text{Sr}$  source (with its  $^{90}\text{Y}$  daughter in radioactive equilibrium). The ordinate scale is strictly proportional to the voltage difference ( $V_S - V_R$ ) and is somewhat arbitrarily in microwatt units since it depends on the chosen  $K$  value, which is determined during the measurement by an internal calibration. The average baseline was initially at  $P_B = 1.60\ \mu\text{W}$  and a calibration power (matched to the approximate power level of the source) of about  $P_{\text{CAL}} = 60\ \mu\text{W}$  was applied to the S cell to obtain a well-determined  $K = 5926\ \mu\text{W V}^{-1}$ . The baseline on removing the applied power went to a value of  $P_B = 1.46\ \mu\text{W}$ . This inability to reproduce the power level after any change in the calorimeter's condition is the severest limiting factor in the measurement precision. The  $^{90}\text{Sr}$  source was then inserted and the power difference due to the source was  $P = (P_S - P_B) = 57.79\ \mu\text{W}$ . After opening the calorimeter to insert the source, a long time period is required for restoration of thermal equilibrium. The time depends on how long the calorimeter was opened and on the masses in the cell assemblies. Restoration can typically require 6 h to 12 h, and can be as long as a few days. A second calibration was then performed by applying a calibration power of  $P_{\text{CAL}} = 60\ \mu\text{W}$  to the R cell, which returned the calorimeter's power level to near a baseline value with the source still inside. This second calibration factor



**Figure 2.** Typical calorimetric data for the standardization of a nominal 300 MBq  $^{90}\text{Sr}$  (with its  $^{90}\text{Y}$  daughter in radioactive equilibrium) source, showing the baseline determinations, power level with the source inserted, and applied power calibrations of  $60\ \mu\text{W}$  in the S cell from baseline and in the R cell with the source inserted.

( $K = 5919\ \mu\text{W V}^{-1}$ ) was within 0.12% of the first. The source was then removed, and after restoration resulted in a new baseline  $P_B = 1.16\ \mu\text{W}$ . The second power difference ( $P = 57.68\ \mu\text{W}$ ) was 0.2% different than the first. Obviously, there are many other possible calibration schemes that could be used to establish the power of this source. In fact, for this sequence of  $^{90}\text{Sr}$  measurements, 22 separate power calibrations for  $K$  were performed over a range from  $15\ \mu\text{W}$  to  $250\ \mu\text{W}$  in both S and R cells under both baseline and inserted source conditions, and the relative standard deviation of the mean for these was 0.06%. Two things from this example are readily apparent. First, calorimetry is *slow*, requiring many days to perform even one power determination of a source with an internal calibration. Second, precise measurements of source strength are attainable only by getting a good central value after many insertion trials. Baseline stabilities with this calorimeter were typically of the order of about  $0.2\ \mu\text{W}$  or less over the typical short measurement time intervals used to obtain the power level at one condition. However, this variability excludes unpredictable and unexplained power transients of as large as  $1\ \mu\text{W}$  that occur irregularly and unexpectedly. Other laboratories [50] using similar instruments have also observed this disturbing behaviour.

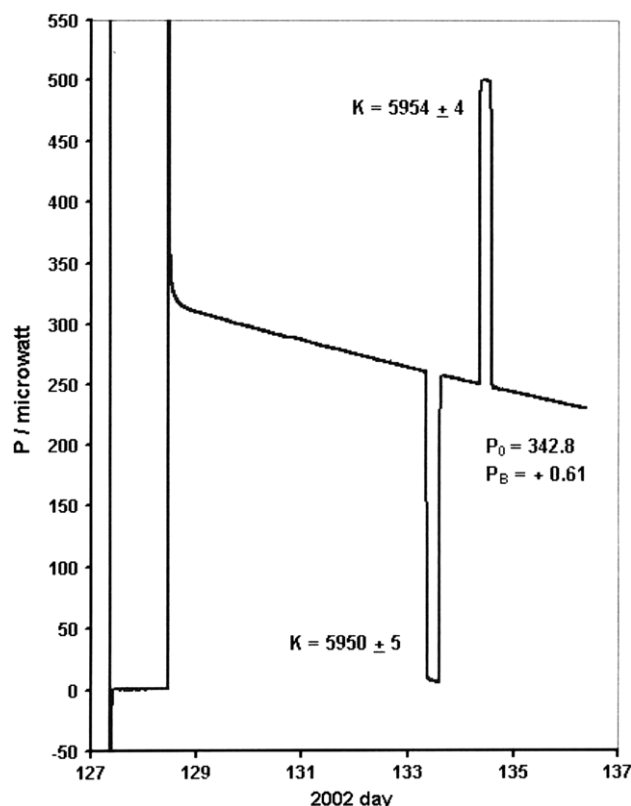
Fortunately, the measurements and determinations of baseline conditions become decidedly easier for sources that exhibit substantial decay during the measurement intervals. In this case, both a baseline power  $P_B$  and the source power  $P_0$  at some  $t = 0$  reference time can be obtained from regressions of the measured power  $P$  as a function of time  $t$ , as given by  $P = P_B + P_0 e^{-\lambda t}$ , where  $\lambda$  is the usual decay constant for the nuclide. Figure 3 gives an example of such a determination for a  $^{103}\text{Pd}$  source. As indicated, the nominal  $300\ \mu\text{W}$  source was calibrated with a power of about  $P_{\text{CAL}} = 250\ \mu\text{W}$  in both the R and S cells, and a fit of the data to  $P_B + P_0 e^{-\lambda t}$  using the known  $^{103}\text{Pd}$  decay constant yielded both  $P_B$  and  $P_0$ .

## 5. Some recent primary standardization results

Between 2002 and 2006, five calorimetric-based primary standardizations were performed at NIST.

The first two were used to confirm the extant calibration factors for ionization chamber measurements on two types of brachytherapy sources: (i) stainless-steel-encapsulated, ceramic-based  $^{90}\text{Sr}$ – $^{90}\text{Y}$  intravascular brachytherapy sources and (ii)  $^{32}\text{P}$  ‘hot-wall’ angioplasty-balloon-catheter sources. Both of these were originally standardized by liquid-scintillation (LS)-based quantitative destructive analyses [51–53]. The original standardizations that were used to establish the ion chamber calibration factors had combined standard uncertainties of between 0.5% and 0.8%. The calorimetry results for both types of sources were in agreement with ion chamber measurements to within 1.5% and 0.5%, respectively [42].

The third calorimetric standardization was on a newer version of the ceramic-based  $^{90}\text{Sr}$ – $^{90}\text{Y}$  brachytherapy sources. In this case, a direct comparison was made between an LS-based destructive assay and calorimetry. The relative combined standard uncertainty on the calorimetric result was 1.6% and differed from the assay result by  $-1.1\%$ . The calorimetry's major source of uncertainty (see section 7) was the power



**Figure 3.** Typical calorimetric data for the standardization of a 35 GBq  $^{103}\text{Pd}$  source, with applied power calibrations in the R and S cells. Both the baseline  $P_B$  and source power  $P_0$  can be obtained by regression fitting of the decay data.

measurement reproducibility for replicate insertions, which included the embodied baseline determination variabilities.

The fourth standardization was for  $^{103}\text{Pd}$ . Again, direct comparisons were made between calorimetry and LS-based assays performed on gravimetrically linked solutions obtained from the digested brachytherapy seeds. The LS assays were performed using both a CIEMAT/NIST efficiency tracing (CNET) method with  $^{54}\text{Mn}$  as the efficiency monitor and by the triple-to-double-coincidence-ratio (TDCR) method [54]. An example of typical calorimetric data for this standardization was shown in figure 3. The calorimetric results agreed with the CNET values to about 2% and with the TDCR results to about 4%. Even larger differences were seen between any of these measurement results and that obtained from photonic-emission spectrometry. These findings suggested that there were problems with the currently available  $^{103}\text{Pd}$  decay scheme data, particularly with the photon emission probabilities per decay. These suggested decay scheme problems were also noted from measurements at LNHb on the same  $^{103}\text{Pd}$  solutions [55].

The fifth standardization [56], initiated in 2004 and completed in 2006, was for  $^{55}\text{Fe}$ , a low-Z EC nuclide. For this work, a specially fabricated solid 30 GBq source of  $^{55}\text{Fe}$  was prepared and gravimetrically linked to an  $^{55}\text{Fe}$  master solution. Many replicate trials of coupled baseline and inserted source determinations were required to obtain a precise average power. Thirteen independent insertion trials were performed, and independent power calibrations were performed for each

trial. The calorimetric power result was converted into an  $^{55}\text{Fe}$  activity through use of an assumed average energy per decay. This activity for the source was in turn linked to the master solutions, which had an assigned standard uncertainty of 0.39%. This standardization was used as a basis for calibrating a new  $^{55}\text{Fe}$  solution standard (SRM 4929F) [57] as well as for measurements of a BIPM-distributed  $^{55}\text{Fe}$  solution that was part of an international measurement comparison [58]. The calorimetrically standardized master solution was linked to the SRM and BIPM-intercomparison solutions by comparative LS measurements. Although the results of the international comparison are not as yet compiled and available, it is known that the NIST calorimetric results are in good agreement (<2% differences) with several other national metrology laboratories [58].

The primary standardization of  $^{63}\text{Ni}$  by NIST [18] in 1968 is perhaps one of the most enduring pieces of evidence of how well classical isothermal calorimetry can be performed. Solutions linked to this calorimetric result have been followed by LS measurements for the past 38 years [19, 59]. These results also served as a verification from decay data of the calorimetrically established  $^{63}\text{Ni}$  half-life. Recent 2006 LS-based re-standardizations at both NIST and LNHb on solutions linked to the original 1968 calorimetric source are in agreement with the decay-corrected calorimetry to better than 0.1%.

## 6. Limitations and potential problems

Although many different types of calorimeters are commercially available, few are suitable for radionuclidic metrology since they are primarily designed for use in material, chemical, biological and pharmaceutical studies.

In addition to the CSC 'isothermal microcalorimeter (IMC)' described in section 4, the same company (CSC) vends an 'Isothermal Nanocalorimeter (INC)' of similar design. An INC is in use for radioactivity measurements at LNHb in France [50]. The principal difference between the IMC and INC is that the latter calorimeter is more sensitive, measuring in the nanowatt range. This is achieved by using much smaller sample cells and wells in the INC. The available volumes for sources in the two are approximately 85 cm<sup>3</sup> and 3.5 cm<sup>3</sup>, respectively. In fact, the sensitivity and baseline stability of the two instruments scales by almost this same factor of 25.

The only other known manufacturer of a commercial calorimeter that may be suitable for radionuclidic standardization is Setaram Instrumentation (Caluire, France). They make a variety of different sized calorimeters, based on the heat flow principle of Calvet [47], in which a differential power measurement is made by surrounding the sample and reference with a three-dimensional array of heat flow sensors with up to 120 thermocouples (depending on the model). Like the INC from CSC, these Setaram calorimeters are more sensitive than the IMC, but they too can only be used with small source volumes.

Although increased sensitivity is desirable in being able to measure lower levels of activity, the tradeoff is almost always made with the available volume for containing the source. Selecting sensitivity over size can in many cases be a poor choice. As noted in section 3, it is necessary that the



source containment absorb all of the radiative energy. This may be difficult to achieve in small volumes for even high-energy pure  $\beta$  emitters because of bremsstrahlung production. The problem is not just the radiation losses, which might be accounted for with good radiation transport modelling, but the unaccountable effects of radiation on the heat sensors. NIST chose to use a larger volume calorimeter for these reasons, and since it had hoped to be able to accommodate large high-Z absorbers (like tungsten alloys) in the source cells to capture most of the energy from even some photon-emitting nuclei.

A potential problem with unaccounted heat losses from a calorimeter must be considered. This is usually addressed and handled in the original design and construction of the calorimeter and in the design and implementation of the power-calibration protocol. Nevertheless, it can be a component in a final uncertainty analysis.

An exceedingly important aspect of all calorimetric measurements is that the calorimeter will not only measure the energy from the radioactive decay, but also from any other physical, chemical or biological process occurring within the calorimeter. This is a serious consideration that had to be accounted for in each of the standardizations of section 5. No solutions can be measured directly because of the so-called ‘heat defect’ in water calorimetry [60], which is the loss of energy due to radiation-induced chemical reactions in water. These chemical effects, which result in a difference in the absorbed radiative energy and the energy appearing as heat in the calorimeter, can show up as either a heat loss or gain. The first measurements on the  $^{32}\text{P}$  ‘hot-wall’ balloon mentioned in section 5 exhibited large excess heat due to the radiation-induced breaking of chemical bonds and re-polymerization in the polyethylene balloons. This problem was eliminated by encapsulating the balloon in a sealed glass ampoule and reducing the balloon to graphite and graphitic tars in a muffle furnace. From this, one can conclude that calorimetry is not always a non-destructive analysis method. Similarly, the solid  $^{55}\text{Fe}$  source of section 5 was initially prepared as a dried ferric chloride deposit. This was a poorly conceived choice, resulting from last-minute changes to the experimental design. The initial calorimetric power levels exhibited massive enthalpic changes, in the milliwatt range, due to the adsorption of waters of hydration and the subsequent deliquescence. This too was resolved by re-drying the deposit and encapsulating the source in a glass capsule, which thereby contained a fixed quantity of water. This sealed source became a closed thermodynamic chemical system, and eventually, after the passage of a few weeks, reached an equilibrium that then allowed measurement of the energy due to the  $^{55}\text{Fe}$  radioactive decay. Other possible interfering effects can be more subtle, such as energy losses or gains due to oxidation of metals, condensation of water, or growth of moulds in humid calorimeters.

The last limitation or potential problem to consider is that any activity determination by calorimetry requires the assumption of a well-known average energy per decay,  $\bar{E}$ . Even if the power is measured very accurately (‘absolute’ power measurements of better than 0.05% are achievable), one still needs an  $\bar{E}$  to get an activity. The inconsistencies in the  $^{103}\text{Pd}$  work cited in section 5 demonstrate that the available decay data for  $^{103}\text{Pd}$  may not be adequate to obtain accurate activity standardization. Similarly, the recent NIST

$^{55}\text{Fe}$  primary standardization for  $^{55}\text{Fe}$  [56] is wholly dependent on the assumed  $\bar{E} = (5.87 \pm 0.02)$  keV.

## 7. Uncertainties and concluding comments

Much of the content of this paper can be summarized, in concluding, by tabulating the major contributors to the uncertainty of a calorimetrically based standardization. They are: (i) the precision and reproducibility in the power levels for replicate insertions, including the embodied uncertainty in baseline determinations; (ii) corrections for non-absorbed radiative energy losses; (iii) required decay corrections to the calorimetric data; (iv) uncertainty with the power calibrations; (v) systemic heat losses not accounted for with the power calibration; (vi) preparation of the solid calorimetric source; (vii) chemical/physical stability of the solid calorimetric source; (viii) gravimetric linkage of the calorimetric source to subsequent master solutions or transfer standards; (ix) possible heat defect/excess effects due to physical, chemical or biological processes and (x) decay data needed to determine the assumed average energy per decay.

Radionuclidic standardization by classical calorimetry can be a powerful tool in our suite of metrological methods. Comparison agreement with other primary methods has been shown to be in the range of 0.5% to 2%, and have overall uncertainties that rival other methods. It may in fact be a method of choice in some cases, depending on available nuclear and atomic data. It is important to keep in mind, however, that calorimetry is slow and it is not necessarily a non-destructive method. But, it is fun to do.

## Disclaimer

The National Institute of Standards and Technology (NIST) is an agency of the Technology Administration of the US Department of Commerce. Certain commercial equipment, instruments and materials are identified in this paper to foster understanding. Such identification does not imply recommendation or endorsement by NIST, nor does it imply that the materials are the best available for the purpose.

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