Nuclear Calorimetry – "Dispelling the Myths - 10443

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ABSTRACT

Nuclear calorimetry is the quantitative measurement of heat generation (thermal power) from α- and β-emitting radio-nuclides, with the most common examples being plutonium (Pu + 241Am) and tritium. Heat is a penetrating form of energy and since the heat measurement is non-destructive, nuclear calorimetry is one of the three principal non-destructive assay (NDA) measurement techniques for fissile materials assay: nuclear calorimetry, neutron counting, and high resolution gamma-ray spectrometry (HRGS). The measurement of thermal power can often be made with high precision and low bias making calorimetry the superior technique in most cases to other NDA methods, a particular advantage being the relative insensitivity to the sample matrix. The technique provides an accurate measurement of total Pu mass, when coupled to HRGS measurements or other methods used to determine isotopic composition. The principal operational drawback of calorimetry, however, compared with neutron and gamma methods is the long assay time.

In some circumstances nuclear calorimeters present a viable alternative to neutron counters for fissile materials assay given the present shortage of ^{3}He used in most neutron counters. Nuclear calorimetry techniques are quite varied, however, and the performance limitations of nuclear calorimetry have been the subject of recent wide debate. Here, the following technical questions are discussed:

- What is the difference in measurement time between single-cell and twin-cell calorimeters? i.e. how does the time to reach equilibrium vary in each case?
- How does the transition from water bath to air bath instruments impact calorimeter performance and size?
- What is the effect of opening and closing the lid on the measurement time?
- How closely coupled should the item be to the surrounding measurement cell?
- In which scenarios have pre-heated samples been shown to be beneficial?
- How reliable are current end point prediction algorithms?

We highlight common misconceptions regarding the technique based on recent experience and discussion with experts, and also present the research topics that will need to be investigated by the community.

INTRODUCTION

Nuclear calorimetry is the quantitative measurement of heat or rate of heat generation (thermal power) from radionuclides such as plutonium (Pu + 241Am) and tritium. The heat measurement is non-destructive, and calorimetry can provide an accurate measurement of total Pu mass when coupled to gamma-ray spectrometry from which the isotopic composition is determined. While

calorimetry can be used for waste assay, the technique is typically considered to be the "gold standard" for NDA measurements in the safeguards domain [1].

BRIEF BACKGROUND TO THE LVC

Present discussions have been set in the context of developing a large volume calorimeter (LVC) for nuclear applications. The Setaram 3013 Calorimeter [2], which is the next generation active differential isothermal calorimeter, is based on many years of calorimetry experience including previous designs of a LVC [3] as well as microcalorimetry experience. The new design is different in that it uses an air bath heat sink instead of the traditional water bath, and it has an integral Joule Effect heater in both the reference and measurement cells carefully designed to minimize (eliminate) any cable effects. Moreover the power measuring and control circuits and boards have been redesigned. The accuracy is now considerably improved. Instead of the accuracy estimated in the Harwell trials (and reported at WM'09 [4]), the improved design is one to two orders of magnitude better down to 0.05% to 0.1%. The factory calibration for the Sensitivity, S, will now be more extensive so that any non-linearities can be more accurately represented.

In the next generation of large volume differential calorimeters, a series of band heaters surround both the sample and reference cells to heat up and control the measurement temperature. This method of temperature control is active, which means that the equilibrium temperature is reached faster and therefore measurement time is shorter than in previous designs. (Passive methods of temperature control use the heat within the sample to reach measurement temperature). With these design advances measurement times of less than 8 hours can be achieved for a 3013 storage container.

Twin-cell vs. Single-cell: Conventional wisdom and time to reach equilibrium

The common focus of comparison of twin-cell calorimeters versus single-cell designs is the longer measurement time required to achieve the measurement result. What is typically not recognized, however, is the difference in application of the instruments in terms of the desired precision for the measurement, nor the operational design of the instrument which also impacts the time required for the instrument to reach equilibrium.

Single-cell designs have their biggest benefit in being smaller, more compact instruments making them ideal for transport or laboratory applications. To improve accuracy, however, single-cell designs have typically been designed as isothermal calorimeters where the sample chamber is actively held at a constant temperature using a servo-control mechanism. When an item is placed into the single (measurement) cell the temperature of the calorimeter does not change (in the ideal world) and so the dynamics of the instrument do not come into play. Only the item has to come to equilibrium with the cell, so that the assay time is mostly dependent on the thermal time constant of the sample. The power of the sample is then derived from the difference in the power supplied to maintain the constant temperature. Further improvements in assay time can be achieved by also pre-heating the sample, reducing assay times to as little as 4-6 hours. The typical disadvantage of the isothermal calorimeter, however, is that the servo control adds noise to the system thereby making it a less precise instrument (particularly as the control surfaces become larger).

By contrast the twin-cell differential heat-flow calorimeter design is more precise because residual fluctuations caused by environmental (e.g. temperature) changes are approximately cancelled out in the net (or difference) in signal formed between the measurement and reference cells. For large-volume cells this compensation gives superior performance than can be achieved with the single-cell design because in the single-cell design it becomes progressively harder to control the temperature of the various large surface regions as would be needed. This is related to the complexity of distributing thermometers, heating elements, and other components along with the servo-control mechanism to provide the necessary feedback control to the required finesse. So at some point with size the servo noise gets bigger than can be achieved by simply using a pair of matched cells.

Although potentially more precise, the traditional criticism leveled against a twin cell heat flow design is the much longer measurement time. The reason given as to why the twin cell can never be faster than a single cell isothermal design is because the twin-cell heat-flow calorimeter has to reach equilibrium entirely passively via a controlled and limited thermal path. The thermal path is through the Seebeck thermal elements, and with a few elements the temperature rise will be high and the flow through each will be high, whereas with many elements the temperature rise will be low and the flow through each thermal element will be less. There is therefore a tradeoff in sensitivity (# elements x heat flow per mW per element =μV/mW) as the number of elements is increased, but there is also the possibility that with added elements comes a noise penalty by virtue of a more complicated assembly. Having to reproducibly attach and wire more elements could potentially reduce reliability. On the other hand one may wish to get a rather uniform response by keeping the heat flow per unit area approximately equal over all surfaces. Achieving a high sensitivity is certainly of some interest (and was certainly more of a design goal with small cells when only a few thermal elements were to be placed in near optimum places), but from an assay perspective minimizing the fractional variation in the baseline and at equilibrium level under power is also key. [That is it is better to have 160μV/mW with a ±10mW noise and environmental dependent fluctuation than it is to have 200μV/mW with a 20mW uncertainty in the levels.] In terms of dynamics the approach to equilibrium is therefore made up of two principle components: the impact of the measurement item and the thermal inertia of the calorimeter itself. Since the calorimeter is typically rather massive it can be thought to dominate. Therefore measurement times cannot be faster than the timescale dictated by the calorimeter and hence a twin cell design being larger, is usually considered to be necessarily slower. As a corollary there is usually seen to be little or no benefit to pre-heating the item with such an instrument. With active heating, however, (via band heaters mentioned earlier), the limitation of the traditional passive approach can be tailored.

Air bath (dry) calorimeters vs. Water bath calorimeters

Current design requirements favor the air bath design over the water bath design for purposes of minimizing cleanup at a facility in the event of a major accident. There is also a consideration of minimizing moderator material for criticality reasons at certain facilities, so that here too the air-bath design would be preferred. The question that arises then, is if the same performance criteria are required, would an air-bath design impact the overall size of the system. Since the heat removal in an air bath design might be expected to be less efficient than the water cooled design, will the required compensation of additional fans increase the footprint of the system. In

addition will the calorimeter heat sink have to run at a hotter temperature thereby imposing further requirements on the control of the room environment.

Setaram have laid down a design for a dry (air bath) version based on experience, heuristic rules, and thermal simulations (using SolidWorks® software with the optional CosmosWorks® package). The indications are that the heat removal will be as efficient as the water cooled design. The burden in terms of system size is not expected to be significant.

Effects of opening and closing the lid

Ensuring reproducibility of the calorimeter performance is clearly one of the key factors that influence the time necessary to reach steady-state performance conditions. The opening and closing of the instrument lid and the placement of the sample within the instrument are possibly the two areas that are most susceptible to variation. It is therefore essential to have a mechanism to exactly replace the lid in order to control the heat flow and avoid baseline jumps and response bias between item placements.

The lid opening mechanism has always been a strong point of Setaram's LVC design, given that it is electrically controlled rather than manual. First, one combined lid is used for both the sample and reference cavities thereby preserving the complete function of the reference cell. Second, the lid has a mechanical setup for each cavity that seats snuggly and reproducibly to ensure that the heat flow characteristics are unchanged. The lid is first raised vertically a few centimeters, and then opened to a full 90 degrees to give unfettered access to the cavity. The vertical motion ensures that the lid is always reseated true to the body and cannot be tilted. In addition the temperature control of the lid is under control of a separate proportional integral differential (PID) control because the lid is treated as a separate thermal mass to the walls and floor in order to prevent a thermal gradient at any time (such as the shock following the opening of the unit to the external environment). As a safety precaution the lid also has a laser gate so that the stepper motors are de-energized if the laser gate is disrupted.

Sample coupling to the measurement cell

A common misconception encountered is that the placement of a small item in a much larger measurement cell (thereby having a large air volume in-between), has no effect on the measurement. Yet, we found from experience that optimizing the size of the measurement cell to the shape of an item allows for reaching faster thermal equilibrium and a shorter measurement time. One possible explanation for the improvement is that reductions in the air volume of the sample chamber reduce convection currents present when an item is loaded, thereby improving the heat transfer to the calorimeter. Another factor is that the conductivity of air varies with temperature and humidity and so it is best to minimize the air volume in the sample chamber. We also feel that ensuring that the sample cavity is closely coupled to the sample of interest also makes the measurement less sensitive to the location of the heat sources and the presence of void spaces within the sample. In all, our experience confirmed the general wisdom that the "physical size of the calorimeter sample chamber and the [relative] diameter of the sample" [5] are important assay time considerations.

Scenarios for which pre-heated samples may be beneficial

The benefit of pre-heating a sample (or 'pre-conditioning) is that the temperature of the sample is raised to match as closely as possible the internal temperature of the sample cavity. This reduces the overall time for the instrument to reach equilibrium and hence the obvious benefit of the practice is to increase throughput. The disadvantages are that there is an added cost in terms of requiring additional floor space to house the pre-heater as well as the additional manpower and coordination required, though one might expect for the latter that some level of automation can reduce the burden. Another overhead of the practice is that the pre-conditioning temperature has to be closely matched to the internal temperature of the calorimeter, so that monitoring and maintaining the calorimeter baseline power level becomes more important. This is typically why the practice is most useful for calorimeters of the servo-control constant temperature design.

Reliability of current end point prediction algorithms

The end-point prediction technique is a mathematical extrapolation of the calorimeter response function that can be used in place of waiting for the instrument to reach equilibrium. The technique can offer as much as a 50% reduction in measurement time, but is clearly only as useful as the accuracy of the mathematical representation and the desired precision for the measurement. The typical limitation of the technique is that the response is usually represented by a single exponential form, whereas in reality there are several thermal gradients in a typical calorimeter each with its own exponential representation. The different gradients between the sample, sample can, chamber walls, and heat sink, should in principle be represented by a sum of exponential response functions, but generally since one term is dominant the single exponential form is used.

If a prediction algorithm is proposed, however, there must be confidence that the approach to equilibrium will be smooth and monotonic and that the result will plateau (not overshoot). In addition the result should not be strongly influenced by the variation in weight and packaging from can to can. Poorly packaged samples and those with high heat capacities can render the prediction algorithms less useful.

In addition, if a Joule-Effect heater is used for calibration purposes it must be ensured that the calorimeter response approaches equilibrium in the same way as if a sample were being measured. Difficulties with the approach to equilibrium can be easily ascertained from test measurements. For example if the initial rise always peaks at a level which overshoots the final 'level', an exponential end-point prediction algorithm can not roll over and so would always tend to over predict. Furthermore, if oscillatory behavior about an equilibrium level is seen, even after long measurement periods, the accuracy of the prediction algorithm will be questionable.

For the reasons outlined above the reliability of current end point prediction algorithms seems questionable for measurements that require high precision.

Further topics of investigation

The topics described above have already been the subject of much debate over the course of history of calorimeter design and performance. New calorimeter designs, however, push the limits to better precision and shorter measurement times. This necessitates the pursuit of other

considerations for which performance data are lacking in the current literature. Some of these topics are listed below:

- To what extent can the simulation of calorimeter response be used to improve performance? What is the impact of simulating the sample contents?
- At higher precision requirements are the effects of room temperature variations a significant factor? To what extent might environmental controls be required in the measurement stations?
- Are the active (Peltier/Seebeck) elements susceptible to neutron radiation damage over the long term and if so to what extent?
- Is the lower limit of detection a valid concept for nuclear calorimetry?

CONCLUSIONS

Based on our experience and exchanges with experts we believe the following conclusions can be drawn:

- Twin-cell designs can be designed to yield shorter measurement times using active controls, and offer the additional advantage of greater precision over single-cell designs.
- There is little difference in the operational performance or instrument footprint between water-bath and air-bath calorimeters.
- The process of opening and closing the calorimeter has a big impact on the time necessary to reach steady-state performance, and hence the design of the lid mechanism is very important. Item removal and replacement must be performed with careful control to ensure reproducibility of the calorimeter performance.
- Close coupling of the sample to the measurement cavity is very important in reducing the time needed to reach steady-state conditions.
- Replication of the sample in the reference cell is a key consideration. Heat capacity impacts the measurement time; heat distribution is very significant in the design.
- The benefit of preheating the item is situation dependent.
- In all cases the availability of performance data and calibration standards is severely limited.

There are clearly additional issues for which further performance data and extended study are required, so that this paper serves only as a beginning to the debate. It is anticipated that future work will expand on these issues to provide quantitative data and results.

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