Comprehensive Performance Analysis of Large Volume Twin Cell Heat-Flow Calorimeters for Tritium Assay

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Abstract

Over a period of five years the Atomic Weapons Establishment (AWE) has performed a variety of measurements using two identical calorimeters. The instruments used were novel, fluid-free, ANTECH model CHF400 series large volume, twin cell, heat-flow calorimeters. Each calorimeter comprises of 53 litre cells, one of which is the measurement chamber and the other acts as a reference. Both calorimeters perform in a consistent manner and achieve a thermal detection level in the order of 500 microwatts (5.50×10^{11} Bq tritium equivalent assuming 3.244×10^{-1} W g^{-1}, 3.57×10^{14} Bq g^{-1}). The analysed measurement data and conclusions represent a comprehensive study of the performance of this calorimeter design. The work includes both the measurement of electric calibration samples and radioactive items containing tritium with a range of masses and thermal power outputs. The studies reported in the paper indicate the performance of the algorithms for predicting end-point and thermal equilibrium compared with the operator-determined result. The analysis further examines the effects of baseline power stability, environmental influences, sample self-heating, instrument recovery time and sample packaging masses. Measurement accuracy and precision data are presented covering a range of sample thermal powers and characteristics. The data generated over five years of operations demonstrate the environmental and sample characteristics have a negligible effect on the instrument performance. The calorimeters have exceeded the minimum performance set out in the design requirements. As a result of their ease of use, sample capacity, baseline stability, significant improvements in safety and efficiency have been made.

Report Contents

1   SCOPE

The work presented includes results taken from factory acceptance and site acceptance testing both utilising electrically powered samples. The sample data from routine operations taken from the proceeding years presents both nuclear powered (tritium) samples and electrically powered samples across the calibrated range of the instrument.

Although reference is made to comparative isothermal calorimeters, all data presented was generated by twin cell heat flow calorimeters.

2   INTRODUCTION

Over a period of five years the Atomic Weapons Establishment (AWE) has performed a variety of tritium measurements using two identical calorimeters. The instruments used were novel, fluid-free, ANTECH model CHF400 series large volume, twin cell, heat-flow calorimeters. The studies reported indicate the performance of the algorithms for predicting end-point and thermal equilibrium compared with the operator-determined result. The analysis further examined the effects of baseline power stability, environmental influences, sample self-heating, instrument recovery time and sample packaging masses. Measurement accuracy and precision data are presented covering a range of sample thermal powers and characteristics.

3   INSTRUMENT PERFORMANCE

3.1   COMMISSIONING

As part of the purchasing process, both calorimeters were required to have undergone commissioning activities. As part of these, precision and accuracy measurements were conducted using electric samples set to varying powers, assayed in triplicate. These tests were carried out at the place of manufacture (factory acceptance tests), and following installation in the laboratory (site acceptance tests).

Table 1:   Site Acceptance Test Results

Test No.	Set Power (mW)	Measured Voltage (mV)	Measured Power (mW)
1	5	0.940	5.08
2	5	0.937	5.06
3	5	0.928	5.01
4	50	9.586	51.76
5	50	9.535	51.49
6	50	9.564	51.65
7	500	96.393	520.52
8	500	96.360	520.50
9	500	96.500	520.85
10	5000	971.928	5248.41
11	5000	970.557	5241.01
12	5000	969.000	5230.75
13	0.5	0.080	0.43
14	0.5	0.090	0.48
15	0.5	0.097	0.52

The calorimeters' performance data exceeds the requirements placed upon them over a wide operational range of several orders of magnitude, as demonstrated in Table 2 below.

Table 2:   Precision Measurements – Site Acceptance Tests

Test No.	Test Value	Precision/µW (1σ)	
		Required	**Act**
1-3	5mW	16	31.9*
4-6	50mW	160	138.1
7-9	500mW	1600	197.5
10-12	5000mW	16000	8867.8
13-15	0.5mW	N/A	45.8

*This test failed during site acceptance testing due to excessive temperature deviations (>10°C), within the room during a heating failure and subsequently passed during future testing.

3.2   BASELINE POWER & STABILITY

The presence of a reference cell in this design of calorimeter gives rise to a significant improvement in instrument stability from external environmental influences. By reducing baseline fluctuations as much as possible, the detection limit may be lowered accordingly.

The baseline ('blank measurement') was recorded by performing an analysis as for a sample with the heat source removed, from a stable state (i.e. a base heat flow of <0.01mV), without disturbance to the instrument. An example blank measurement is shown in Figure 1:
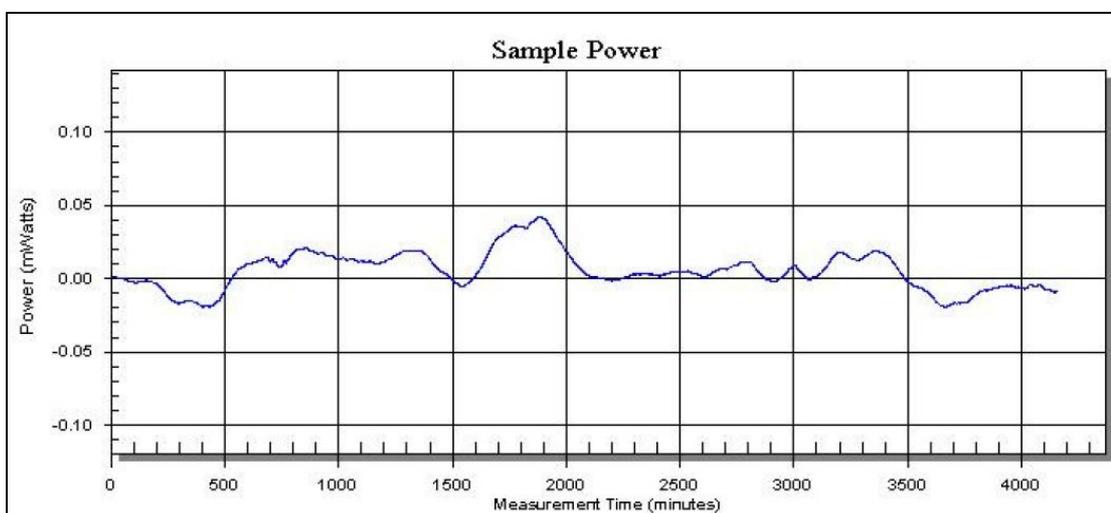

Figure 1: Calorimeter blank measurement

The baseline drift was determined by calculating the difference between the heat flow recorded at the start and end of the run. The graphs below show drift values obtained over a period of two years. Averaged over an extended period and varying run times, both calorimeters showed a small positive heat flow drift of not more than 7×10^{-6} V. Although direct comparison with the older isothermal calorimeters is not possible due to the differing principles of operation, the improvement in drift is approximately two orders of magnitude.
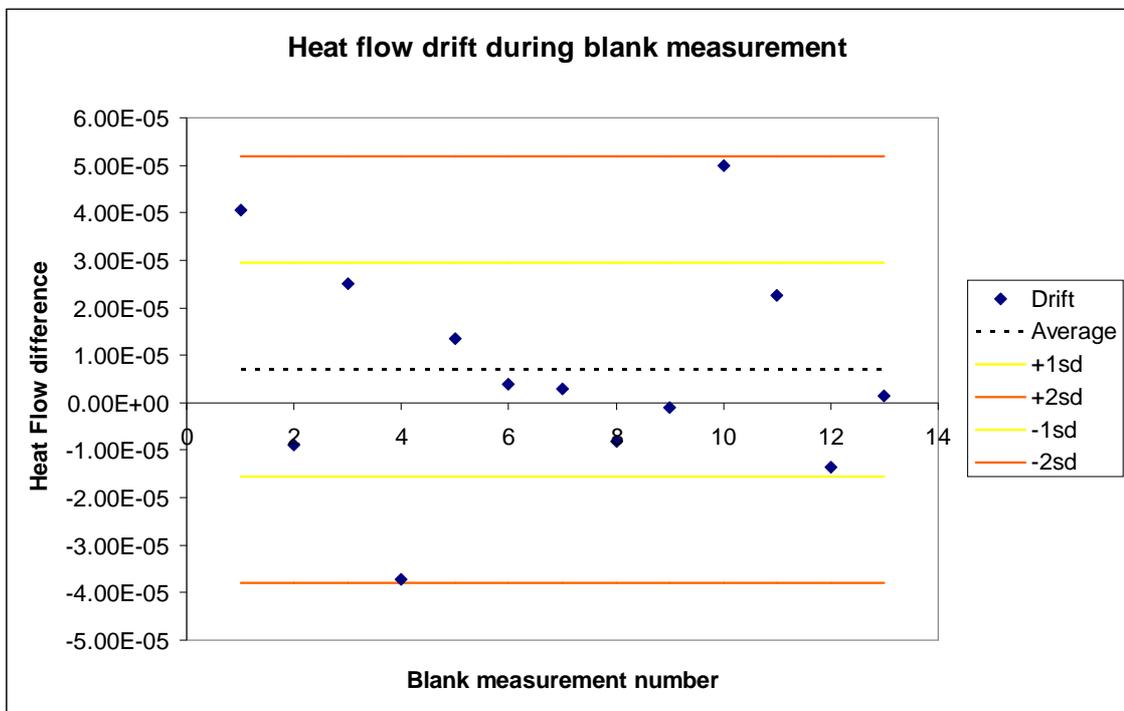
Figure 2: Heat flow drift during blank measurements

3.3   ALGORITHM PERFORMANCE

The calorimeter software incorporates prediction and equilibrium algorithms to assist in sample measurement and automated power determination. The equilibrium algorithm uses the power data gathered over a long average, for example 200 data points. New measurement data points must then satisfy a number of fit parameters (variable if desired) for a determined number of times to qualify as being 'stable', and the sample to be deemed at equilibrium.

An operator may also choose to end the sample measurement manually by studying the measured power curve, zooming in where necessary, and determining whether equilibrium has been reached. This method requires a certain amount of training and experience, and may not always be practical.

Electric and tritium sample runs were performed using the manual end point option, with the equilibrium value compared with the operator determined end point. For both types of sample there is good agreement with both end point values. Approaching the limit of detection the variance increases as instrument drift affects the end point determination, however from approximately 5mW upwards, this value is less than 5% of the equilibrium value. When taking the absolute value of the difference between the end point determination methods, the value tends to increase to a larger negative value suggesting that at higher powers the algorithm is ending the sample measurement early. Again, when taking this value relative to the equilibrium determined end point, the difference is much less than 1%.
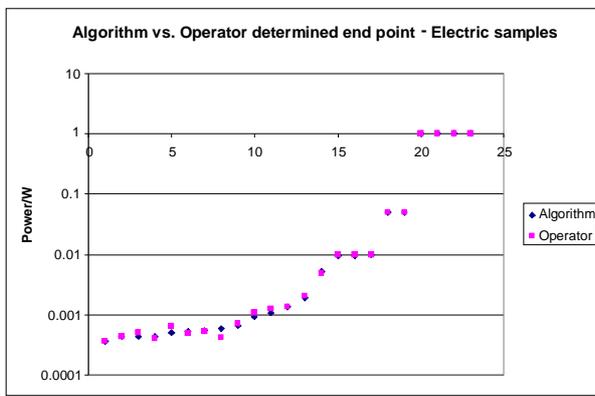
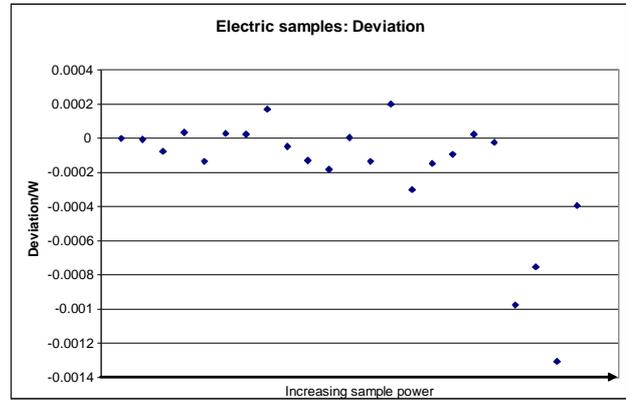**Figure 3: Comparison of algorithm vs. operator determined end points for electric samples**

Figure 4: Difference between algorithm and operator determined end points for electric samples as a function of increasing power
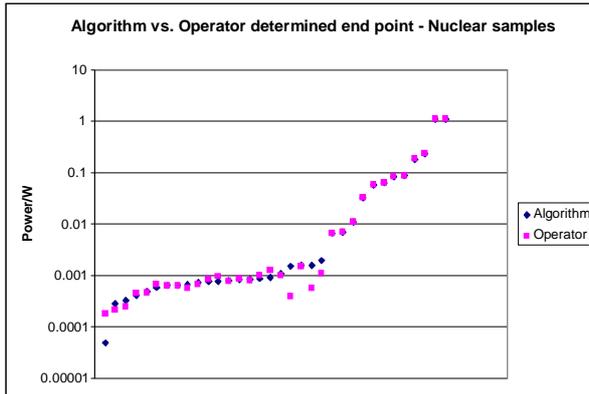

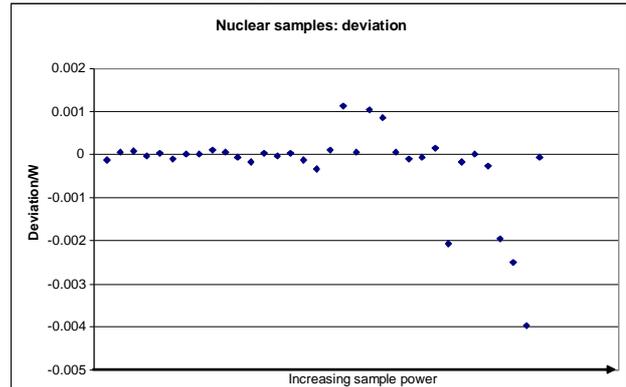**Figure 5: Comparison of algorithm vs. operator determined end points for nuclear samples**

Figure 6: Difference between algorithm and operator determined end points for nuclear samples as a function of increasing power

3.4 MEASUREMENT TIME

Electrically powered sample runs across both instruments were analysed, with the length of time taken to satisfy the equilibrium algorithm compared to the equilibrium power value. The data show a correlation of increasing equilibrium time as the electric sample power is increased over several orders of magnitude. The thermal capacities of the materials surrounding the thermopile sensors may be giving rise to this as it limits the rate of the heat flow increase to a steady state.
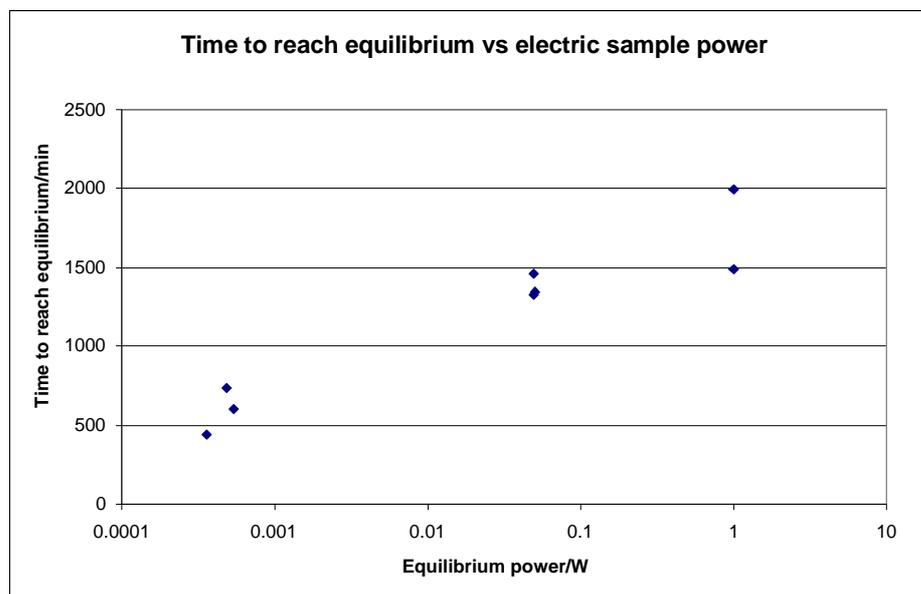

Figure 7: Plot of time to reach equilibrium as a function of electric sample power

The same comparison was performed on tritium containing samples. Less of a definitive correlation is seen, as there are no high inventory samples in this data set in addition to the different physical sizes of sample requiring different containers, each with their own thermal transfer properties. Across this range of samples the average time to reach equilibrium was approximately 28 hours.
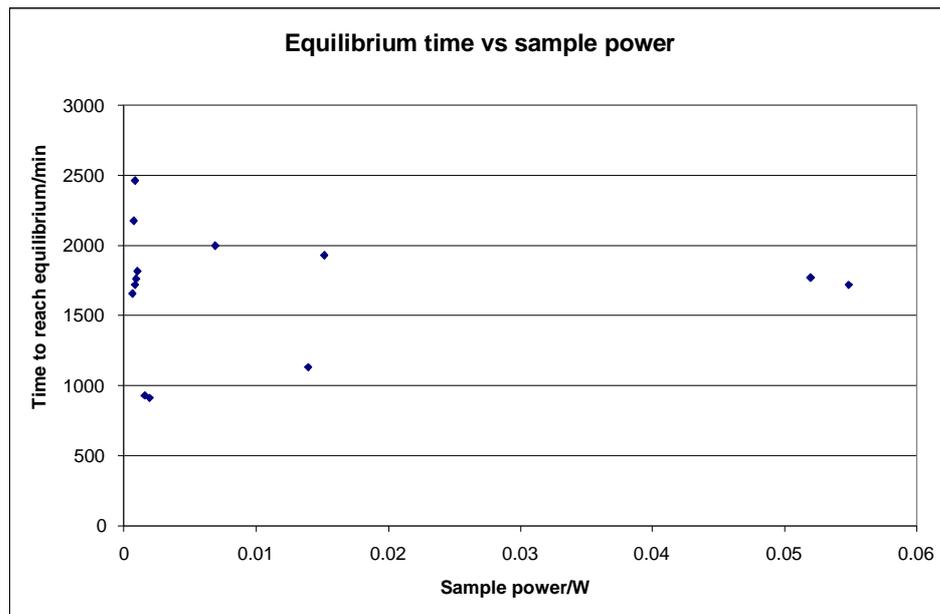

Figure 8: Plot of time to reach equilibrium as a function of nuclear sample power

3.5   RECOVERY TIME

Subsequent to a measurement and removal of the sample, the calorimeter must be allowed to remain idle for a period of time in order to achieve a stable base heat flow. This can be recorded using a 'settle' run: essentially the same as a blank measurement. The operator can determine when a stable baseline has been reached and deem the calorimeter suitable for the next analysis. The typical time taken to reach a stable baseline, averaged across recorded settle runs is approximately 1100 minutes. Therefore the calorimeter is generally able to accept a sample within 24 hours of removal of the previous.

4   MEASUREMENT CONTROLS

4.1   ENVIRONMENTAL INFLUENCES

A recognised limitation of many calorimeters is the thermal power drift associated with the small variations in the environment conditions leading to an increase in the limit of detection. The dual-cell design of the HF calorimeters mitigates the effect of these changes with the implementation of a reference cell. Experience has shown this to be very effective in eliminating this and providing an extremely stable instrument baseline.

Over time it has been shown that external temperature and pressure variability does not impact the capability of the instruments to assay samples. Two primary examples of this are noted.

The calorimeters were designed to operate in a temperature controlled environment. On numerous occasions relatively minor changes in the room temperature ($<\pm5°C$) where the heating has failed have been shown (with equivalent electric samples) to be negligible over the course of the measurement.

The design of the HF calorimeters is such that the measurement cells are not airtight. This leads to an interesting observation of three distinct peaks on the measurement plot during short-term pressure changes within the laboratory caused by ventilation plant switchover of the three main fans.
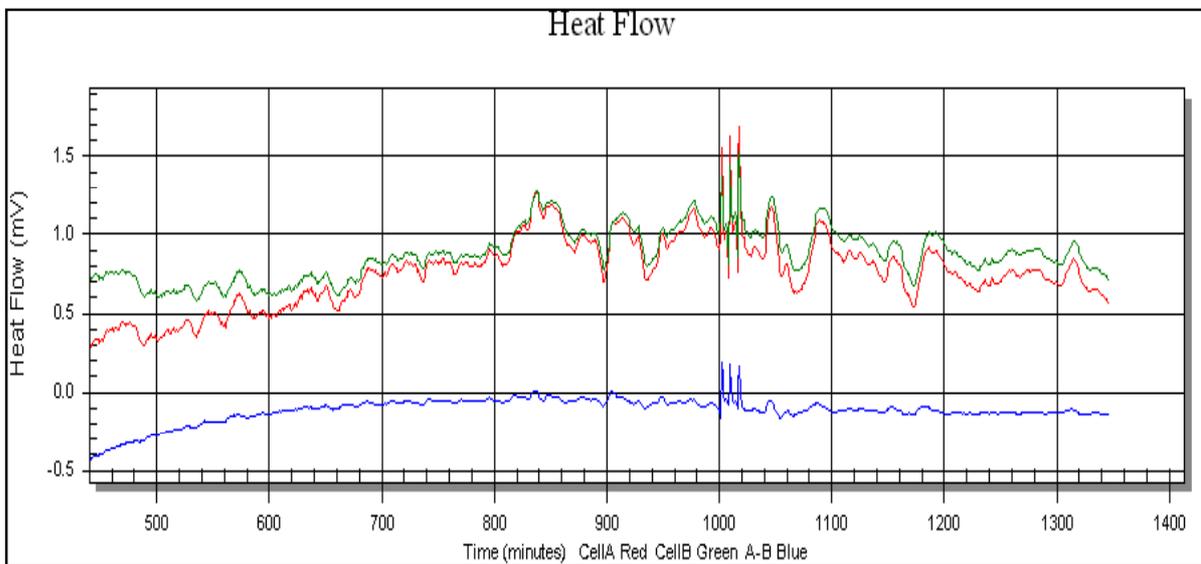
Figure 9: **Heat Flow plot demonstrating three short timeframe peaks**

As can be seen, the resulting trend of the plot does not change when comparing either side of the anomaly.

4.2 THERMAL STUDIES

Due to the high performance of the calorimeter insulation, concerns were raised that should a high inventory tritium containing sample be left within for the length of the measurement, the temperature of the item may increase to unsafe levels.

It is standard practice to use heat-conducting foil to increase the rate at which thermal equilibrium is met. As a worst-case example this was not used.

The following sections detail the experiments carried out, the results and conclusions.

4.2.1 Experimental

The CHF400-5300 calorimeter had a stable heat flow of less than 0.01mV prior to sample insertion and the room temperature was remained within the range of 26-28±0.5°C. A surface temperature probe (Testo 0628 7507), mated with a Digital Indicating Logger (Testo 177-T3) was attached to the external circumference of each tritium storage bed using electrical tape. A second surface temperature probe assembly was similarly attached at mid-height to the external circumference of the containment vessel (30.9kg, o-ring sealed, stainless steel). The tritium storage bed and temperature logger were sealed within the containment vessel which was then loaded in to the calorimeter. The system was monitored in each case for a period of >6 days, twice the expected measurement time. Storage beds with a range of inventories were used to enable a trend to be established.

4.2.2 Results

The sample vessel wall and containment vessel wall were monitored with the Testo data logger and thermocouple providing a resolution of 0.1 °C, the calorimeter measurement cell walls (inner and outer) were monitored by in-built thermocouples logging data on the in-built control computer with a resolution of 0.01 °C.

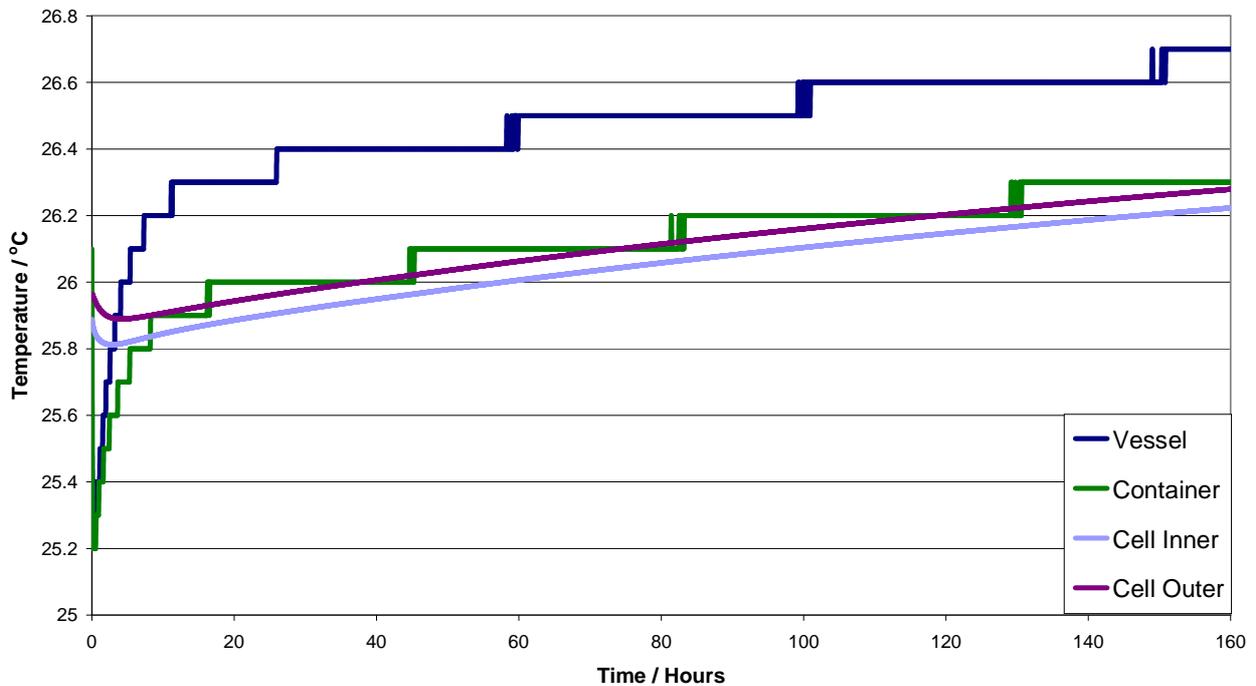## Thermal Trial Depicting Wall Temperatures

Figure 10: Thermal Trial – Sample vs Calorimeter Wall Temperatures

The result in the plot above clearly show that after the first 24hours the increase in storage bed temperature is minimal. The rate of 'self-heating' is <0.1°C d^{-1}.

4.2.3   Comments

It must be noted that a separate measurement was carried out to enable omission of the thermal output from the temperature logger equipment as this may have potentially altered the result; however, the analysis in this case retuned a <Limit Of Detection (LOD) result and was therefore ignored in the calculations.

4.3   SAMPLE PACKAGING

The large sample cells of the CHF400-5300 allow for measurement of a large variety of sample sizes. This often includes measuring tritium containing samples from within an amount of containment and packaging which increases the safety to operators and the environment. However it was expected that with increased packaging mass would come a delay in the calorimeter and sample reaching thermal equilibrium.

4.3.1   Experimental

In each case the calorimeter base heat flow was recorded prior to measurement at <0.1mV. The samples were loaded in to the calorimeter and the measurement ended at the instrument determined equilibrium point.

4.3.2 Results

Run Time (min)	Container Description	Decay Corrected Inventory (g)
927	plastic bag	0.708
1126	plastic bag	0.708
1415	5kg aluminium vessel	0.698
2265	13kg steel vessel	0.713
2264	31kg steel vessel	0.663
2280	31kg steel vessel	0.652
3761	31kg steel vessel	0.650

4.3.3 Comments

As was expected, the length of time taken to reach equilibrium increases with the mass of the packaging. It must be noted that these measurements took place during the initial active-commissioning of the first CHF400 instrument and as a result were ended using unmodified fit-parameters that have since been updated to allow for the slow equilibration of more massive samples.

4.4 EFFICIENCIES

A known downside to the CHF series calorimeters in comparison to their single cell isothermal forebears is the extended time taken to reach thermal equilibration although as stated previously, their accuracy and stability is shown to be greater with larger sample cells and equilibration times improving safety by removing the need for unpacking sample vessels from containment vessels.

The pre-treatment of samples and their containment vessels is an option if large thermal variations in storage/delivery temperatures are found when inserted into the internal thermal environment of the calorimeter sample cell, providing decreased thermal equilibration times if high throughput is an operational requirement.

5 CONCLUSIONS

The introduction of Heat Flow calorimeters to replace Isothermal instruments has resulted in an improvement in safety to operators, reduced the potential impact on the environment and the burden on operators' time, with respect to sample unpacking and handling prior to testing, offsetting the increase in measurement time.

6 ACKNOWLEDGEMENTS