

Evaluation of a New Tritium Calorimeter at Los Alamos National Laboratory

RESULTS AND DISCUSSION:

(continued)



Keithley Model 210 Multimeter

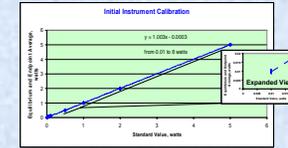


ANTECH Resistor Plate

The accuracy of the ANTECH calorimeter is ensured with the electrical heat standard. The resistance of the standard is referenced against two calibrated resistors on a resistor plate using a calibrated multimeter. The calorimeter was supplied with two multimeter/resistor plate sets to allow instrument operation with one set while the second set is recalibrated. The Los Alamos National Laboratory Calibration Laboratory provides traceability for these calibrations to the National Institute of Standards and Technology (NIST) standards. The multimeter/resistor plate set is changed out on a periodic basis (6 months to 1 year) to ensure the calorimeter stays within its calibration window.

ACCURACY:

Over 200 individual measurements were obtained for the electrical heat standard from October 2005 through May 2006. The selected setpoints for the electrical heat standard ranged from 0.01 Watts to 8 Watts. The average of the observed **Equilibrium** and **Endpoint** values for these measurements was compared to the electrical heat standard setpoint values. This determined the initial calibration of the ANTECH calorimeter with a calibration correction for slope and intercept. During this period, the multimeter/resistor plate set used the original calibration provided by ANTECH.



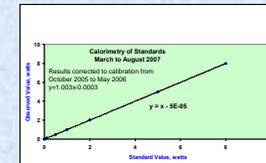
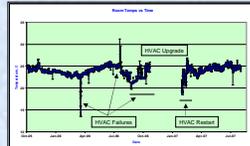
Initial calibration estimate of errors:
slope=1.0030 +/- 0.0003
intercept= -0.0003 +/- 0.0002

STABILITY:

A typical sequence of measurements in the calorimeter is: a Base Power measurement, the measurement of one or two unknown samples, measurement of the electrical heat standard at setpoints bracketing the observed results for the unknown samples, and a final Base Power measurement. The results for the unknown samples and electrical heat standards are corrected for Base Power changes and the initial instrument calibration. A check of the corrected results for the electrical heat standards run from March to August of 2007 against the setpoint values of the standards demonstrated no significant change in the instrument calibration. This was following at least two instrument shutdowns/relocations made necessary from the HVAC upgrade project.



The Base Power of the ANTECH calorimeter drifted over time and experienced sudden shifts due to excursions in room temperature caused by facility HVAC problems. The room temperatures charted show the average value with the high/low values shown in the error bars during ANTECH calorimeter measurements. The change in Base Power from one Base Power run to the next had 1 standard deviation of 0.41 mW due to drift alone.



Recheck of instrument calibration after change-out of the multimeter/resistor plate set.

ERRORS:

Considering the initial errors associated with the slope and intercept values of the calibration, as well as the instrument precision, the errors associated with measuring unknown samples with the ANTECH calorimeter were estimated. Three ranges were defined by the observed instrument performance and the measurement type with the best results. Below 0.01 Watt, the **Endpoint** values (not corrected) were estimated to have an absolute error of three times the precision standard deviation (0.00134 Watts) plus a 0.4% relative error. At 0.01 Watt and above, the average of the **Endpoint** and **Equilibrium** values were used and corrected for the initial instrument calibration. At Wattages between 0.01 Watt and 1 Watt, the unknown errors were considered to include the absolute instrument precision error plus a 0.2% relative error. Above 1 Watt, a 0.3% relative error was estimated. The estimates of the relative errors for these ranges included consideration of the magnitude of the impact of the calibration errors, as well as the influence of other factors influencing the analysis of actual samples, such as heat distribution and the sample mass.

Based on these error estimates, control charts were developed for selected setpoints of the electric heat standard. A control chart is given for each range with the upper and lower control limits (3 standard deviations) shown in solid lines and the upper and lower warning limits (2 standard deviations) shown in dashed lines. For the low and mid-range control charts, the absolute error of these limits changes with the setpoint selected, so these charts show the limits for the lowest setpoint of the standards plotted. The error estimates and control charts are based on the ANTECH calorimeter performance from October 2005 through May 2006. The control charts show the results of electrical heat standard runs from March to August of 2007. The data shown within all three control charts indicate that the instrument performance has remained constant (in control) during the time period shown. Furthermore, within the low and mid-range control charts, the data distribution around the mean and above/below warning limits indicates the initial error estimates for the instrument are reasonable. However, for the high range control chart, the data distribution indicates that the actual errors may be less than initially estimated. However, other variables such as container size and sample geometry are still being evaluated.

Error Estimates for Unknowns based on Initial Antech Performance

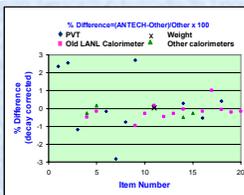
Measurement Type Used	Range	Error (3 standard deviation)
Endpoint (no correction)	0.001 to < 0.01 Watt	± 0.00134 Watts & 0.4%
Average of Equilibrium and Endpoint (corrected)	0.01 to < 1 Watt	± 0.00134 Watts & 0.2%
Average of Equilibrium and Endpoint (corrected)	≥ 1 Watt	± 0.3%



DATA CROSS COMPARISONS:

There were twenty unknown samples that were measured in the ANTECH calorimeter for which other measurement data was available. Pressure-Volume-Temperature (PVT) data, including tritium composition, was available for eight of these items. Thirteen were also measured on an older LANL calorimeter (Ni-windings and water bath) and seven had data from other calorimeters (items from other DOE locations). None of these other measurement techniques have precision and accuracy comparable to the ANTECH calorimeter, so only measurements in the mid and high ranges of the ANTECH calorimeter were considered for comparison. A high-accuracy weight, including tritium composition, was obtained for just one item. This is the only technique with a precision and accuracy similar to the ANTECH calorimeter.

The ANTECH calorimeter measurement was just 0.04% higher than the high-accuracy weight measurement, indicating an excellent cross-comparison of results by these two methods. The average measurement differences of the ANTECH calorimeter were compared with the other measurement techniques. The ANTECH results averaged 0.05% lower than calorimetry measurements obtained from other DOE locations and 0.26% lower than the older LANL water bath calorimeter. The ANTECH measurements averaged 0.35% higher than measurements obtained by PVT.



SUMMARY AND CONCLUSIONS:

- A detection limit of 1 mW ± 0.4 mW (1 standard deviation) was observed for the ANTECH calorimeter which has a rather large (610 mm. long by 170 mm. diameter) measurement chamber.
- There are three of types of measurement results available with this calorimeter; **Prediction**, **Equilibrium**, and **Endpoint**. Although Predicted results were obtained faster, the best precision was observed with an average of **Equilibrium** and **Endpoint** results over most of the operating range of the instrument that was evaluated (from 0.01 Watt to 8 Watts). The **Endpoint** values were the most precise results below 0.01 Watts.
- The instrument accuracy is ensured by calibrating the multimeter and reference resistor plate to recognized national standards.
- Calibration of observed results for the electrical heat standard versus the setpoint values for these standards was stable over many months and two instrument shutdowns/relocations.
- Error estimates based on the precision and calibration of the instrument were made for three operating ranges. Control charts of electrical standard runs relative to these error estimates show excellent instrument performance and adequate error estimation for the low and mid-ranges of instrument operation. The error estimates for the high range of instrument operation may be reduced depending upon the results obtained evaluating other variables.
- Cross-comparison of results for a variety of measurement techniques and unknown samples demonstrate the excellent accuracy and detection limit of the ANTECH calorimeter.