EVALUATION OF A NEW TRITIUM CALORIMETER AT LOS ALAMOS NATIONAL LABORATORY

Diana S. West, Kandy J. Frame, Julia Thompson, and Lawrence O. Ticknor

Los Alamos National Laboratory, P.O. Box 1663, Los Alamos, NM 87545, dwest@lanl.gov

The Los Alamos National Laboratory tritium processing facility purchased an ANTECH Series P300 Isothermal Tritium calorimeter from the ANTECH Corporation in 2005. The instrument is used to non-destructively measure the quantity of tritium in an item based on the heat output generated by the tritium beta decay. Instrument performance data collected over the past two years will be presented showing that this instrument can detect as low as 0.001 Watts (0.003 gr. of tritium) within rather large measurement canisters of approximately 170 mm. (6.8 in.) diameter by 610 mm. (24 in.) long. With a manufacturer-stated measurement power range of 0.005 Watts to 15 Watts, this calorimeter has performed beyond the specified purchase requirements. Using a combination of sensors for its thermal element, the P300 calorimeter has demonstrated exceptional sensitivity and precision.

I. PURPOSE

Calorimetry is used for tritium accountability (tracking amounts of nuclear materials) and for waste characterization. The amount of tritium is directly proportional to the heat output of a tritium containing item, about 0.91 mW/TBq. The objective is to accurately measure the tritium content of tritium process beds, such as molecular sieve traps, down to (or below) quantities of regulatory interest (e.g., <37 TBq for a for a “Type A” transportation or waste packaging). To meet safety requirements, these tritium-containing items are placed within quality-tested secondary containers.

NOTE: 0.91 mW/TBq = ~0.324 W/gr. of tritium
1 gr. of tritium equals ~9619 Ci or ~356 TBq).

The ANTECH Isothermal Model 364 Calorimeter[1] (Figure 1) was evaluated for its performance for non-destructively measuring tritium in a variety of samples. The instrument major features are: a thermal element that consists of three concentric cylinders; an air bath with Peltier cooler and fans to control the heat flow through the cylinders; thermometry that is provided by a hybrid of thermopile sensors and Ni-windings; additional negative temperature coefficient thermistors that provide independent cylinder temperature measurement; and dual computers to control the calorimeter, collect raw data, and generate results. Three measurements types are reported from the instrument software[2]: Prediction, Equilibrium, and Endpoint. Both Prediction and Equilibrium use a “fit” to ANTECH software algorithms. Prediction uses the shape of the measurement curve to predict an equilibrium value. An actual Equilibrium result is determined when the instrument run stability is within pre-set parameters. The Endpoint is a user-defined average of measurement data at the end of a user-defined run time.

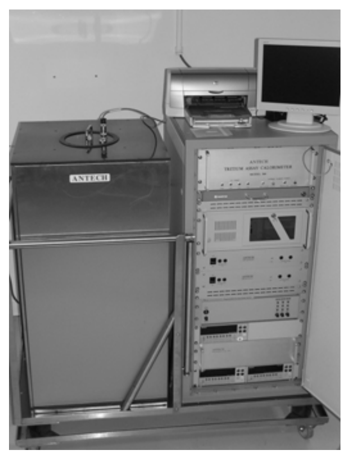

Fig. 1. Photograph of the ANTECH Calorimeter.

II. EXPERIMENTAL

Secondary containers are used for both storage and calorimetry measurement of tritium-containing items. These containers are hermetically sealed, can accept either elastomer or all-metal seals, are pressure rated, and have an access port and pressure gauge. Additionally, newer containers are fabricated and tested to meet current quality standards, including drop testing. The ANTECH electrical heat standard was designed within one of these short tritium sample containers to eliminate differences between tritium samples and the standard due to geometry and heat transfer. These containers and the electrical heat standard are shown in Figure 2.

Fig. 2. Photographs of tritium sample containers and the electrical heat standard.

The electrical standard can be set to any Wattage setpoint within the operating range of the calorimeter with an increment of 0.1 mW. With the instrument in "Auto Mode" multiple runs with different setpoints may be obtained without operator attendance. Using selected setpoints, numerous runs with the electrical standard were used to obtain statistical information to evaluate the quality of the different measurement types; the instrument precision, detection limit, and accuracy; and the calibration stability. Base Powers were run frequently to monitor instrument and environmental stability. The calorimetry results obtained for a variety of tritium-containing items were also compared with results obtained from other calorimeters and other techniques.

III. RESULTS AND DISCUSSION

III.A. Precision

Electrical heat standards were run at selected setpoints ranging from 0.001 Watt up to 8 Watts. These runs were repeated at least five times at higher Wattages and more than twenty times at lower Wattages. The average relative standard deviations obtained are presented over two ranges for each measurement type in Figures 3a and 3b.

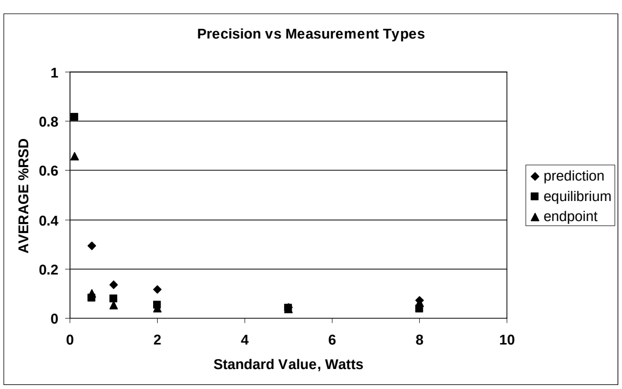

Fig. 3a. Precision results at higher Wattages.

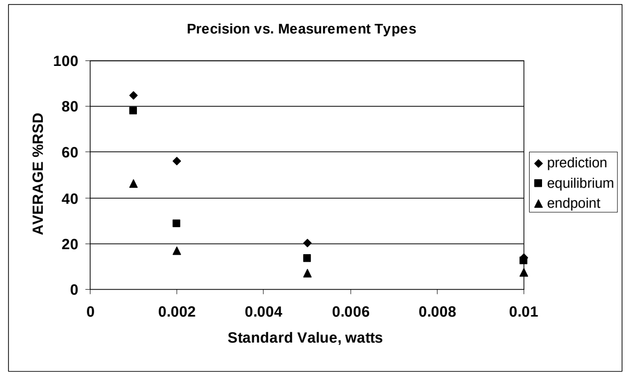

Fig. 3b. Precision results at lower Wattages.

Runs were set to a fixed run time to obtain an Endpoint result. Typically, Equilibrium and Predicted results, as determined by the instrument software, were obtained for most runs. The precision of the Equilibrium results was as good as or better than the Predicted and Endpoint results down to ~10mW. An average of the Equilibrium and Endpoint results at 10 mW and above provided the most precise data.

Predicted results had the advantage of shorter run times, but required a noticeable change in Wattage (>~0.05 Watts) to be consistently observed by the instrument software. Predicted results were, therefore, often not obtained at the lowest Wattages. Furthermore, below 1 Watt, the predicted results were significantly less precise than results obtained by Equilibrium or Endpoint.

Below 10 mW, the most precise results were Endpoint values obtained using 10 hour run times. A detection limit of 1 mW ± 0.4 mW (with 1 standard deviation) was observed. The detection limit and stability at low Wattages is strongly influenced by fluctuations in room temperature and line power. With room temperature stable to within ± 0.5 °C, Endpoint results were obtained from 0.5 mW to 10 mW. The average observed results (at least four measurements) are shown in Figure 4 with 1 standard deviation error bars.

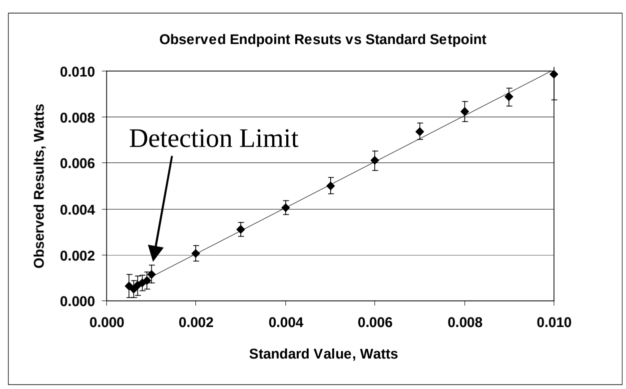

Fig. 4. Endpoint results at the instrument detection limit.

III.B. Accuracy

The accuracy of the ANTECH calorimeter is ensured with the electrical heat standard. The resistance of this standard is referenced against two calibrated resistors on a resistor plate using a calibrated multimeter. The Los Alamos National Laboratory Calibration Laboratory provides periodic re-calibration and traceability to the National Institute of Standards and Technology (NIST).

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 to 8 Watts. The average of the observed Equilibrium and Endpoint results was compared to the electrical heat standard setpoint values. (Figure 5). This determined the initial calibration of the ANTECH calorimeter with a calibration correction for slope and intercept. The initial calibration estimate of errors were: slope=1.0030+/-0.0003 and intercept= -0.0003 +/- 0.0002.

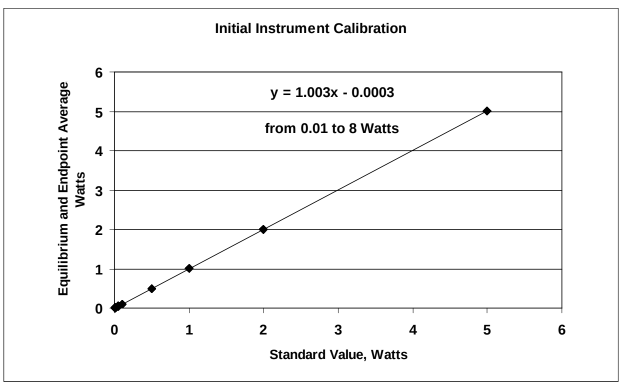

Fig. 5. Initial calibration results for the ANTECH calorimeter.

III.C. Stability

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 change in Base Power from one Base Power run to the next had 1 standard deviation of 0.41 mW due to drift alone. 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. There was no change in the calibration slope and the intercept showed only a 0.05 mW change. This was following at least two instrument shutdowns made necessary from the HVAC upgrade project and after the re-calibration of the multimeter and plate resistors.

III.D. 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 0.1% 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 was developed for each range, but only the low Wattage range control chart is provided in Figure 6. The upper and lower control limits (3 standard deviations) are shown in solid lines and the upper and lower warning limits (2 standard deviations) are shown in dashed lines. These limits are based on the ANTECH calorimeter performance from October 2005 through May 2006, but the data points are the results of electrical heat standard runs from March to August of 2007. The data shown indicates that the instrument performance has remained constant (in control). Furthermore, the data distribution around the mean and above/below warning limits indicates the initial error estimates for the instrument are reasonable in this range. Similar results were observed with the mid-range control chart; 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.

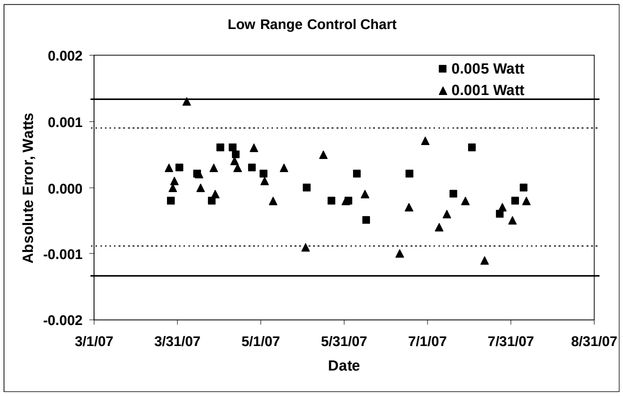

Fig. 6. Low Wattage range control chart.

III.E. 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 sample. This is the only technique with a precision and accuracy similar to the ANTECH calorimeter. This data is shown in Figure 7.

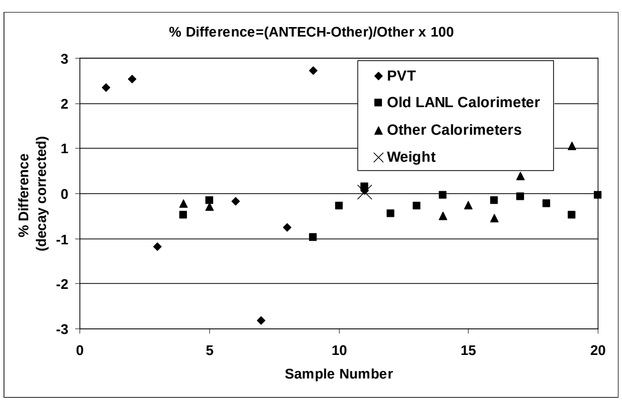

Fig. 7. Cross-comparison of data for unknown samples.

The ANTECH calorimeter result 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.

IV. 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 reported by the calorimeter software: 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 resistors 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.

ACKNOWLEDGMENTS

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2. *Factory Acceptance Test Plan for ANTECH High Sensitivity, Large Sample, Tritium Calorimeter*, ANTECH Corporation, August 8, 2004.