CALORIMETER SIGNAL NOISE ANALYSIS AND SAMPLE POWER PREDICTION IMPROVEMENT

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ABSTRACT

This paper presents some results from an analysis directed towards improving the sample power end-point prediction algorithms (predictors) used with isothermal calorimeters. Simulated and real measurements are given which show how the accuracy of the sample power end-point predictions can be improved. Also the measurement time needed by the predictor to estimate the sample power is reduced, leading to shorter assay times. The improvements in the end-point prediction accuracy are a result of using powerful digital filters. The filters were designed after an analysis of the nature of the noise present on the calorimeter measurement chamber power data. The use of end-point prediction algorithms based on fitting the calorimeter response to a single decaying exponential equation are well established. By extending the fitting function to a double exponential it is possible to estimate the sample power earlier in the measurement cycle, thus reducing the measurement time. Real data is presented which shows the potential of such fitting algorithms by yielding a 50% decrease in measurement time compared to the single exponential end-point predictor.

INTRODUCTION

Isothermal calorimeter temperature servo control is effected by a conventional proportional and integral (P+I) digital controller. The choice of P and I gains determines the transient response of the calorimeter after a perturbation. Higher gains lead to shorter calorimeter settling times, whilst the ratio of P to I determines the nature of the response, i.e. under or over damped.

However, higher proportional gain leads to higher noise levels on the electrical power applied to the temperature controlled cylinders. Because the electrical power delivered to the inner cylinder (measurement chamber) is the variable measured to determine the sample power, higher noise levels are undesirable. The sample power end-point prediction algorithms (predictors) commonly employed to reduce assay times must employ greater amounts of noisy data in order to average out the noise to perform reliable end-point predictions. Increased averaging time leads to lengthened measurement times.

The single exponential end-point predictor is based on fitting the function

\[ P(t) = A + B e^{-\lambda t} \]  \hspace{1cm} (1)

to the early part of the calorimeter decay curve [1]. When the calorimeter response is dominated by a single exponential decay the A term gives an estimate of the final settling value of the calorimeter applied electrical power ahead of sample thermal equilibrium. By estimating the calorimeter steady state end point power value rather than waiting for thermal equilibrium, significant reductions in measurement time can be achieved with little degradation of measurement accuracy.

To perform reliable end-point predictions sufficient data must be gathered to average out the noise present on the measured calorimeter response. A theoretical study of
the nature of the noise present on the inner cylinder power history has lead to the development of digital filters which smooth the noisy data stream more effectively than simple averaging methods.

The digitally filtered data points are used in an exponential end-point prediction algorithm. This enables more reliable estimates to be made of the final settling value of the measurement chamber electrical power than is the case when simple averaging is employed.

SIMULATION AND ANALYSIS

The natural action of the P+I controller is to amplify high frequency noise more than low frequency noise. The frequency characteristics of the electrical noise for a calorimeter based loosely on current ANTECH designs will be as shown on Fig. 1. This assumes that the resistance thermometer Wheatstone bridge is the noise source with a flat frequency spectrum.

The calorimeter power data is sampled every 2 seconds. In order to perform an end-point prediction a large quantity of data must be averaged. This is accomplished either directly by simple averaging which reduces the data to fewer points which are fitted to an analytic exponential decay function. Alternatively, if the analytic exponential decay function is fitted directly to the raw data points, the averaging will be done implicitly by the curve fitting algorithm when the decay curve coefficients are estimated from what is an

![Image of graph]

Figure 1. Theoretical example of relative spectral composition of noise present on the calorimeter electrical power when the temperature error sensor is noisy.

over determined system of equations.

By matching the digital filter response to the calorimeter noise response the performance of the end point predictor can be improved for a given quantity of data. The effect of this is illustrated by Figures 2 and 3 which show the predicted power versus time for a rolling single exponential fit. The averaging time is the same for both cases and for all of the rolling predictions which are evaluated at one minute intervals. The raw
Figure 2. Predicted power versus time using a rolling single exponential predictor in conjunction with simple averaging.

Figure 3. Predicted power versus time using a rolling single exponential predictor in conjunction with digital filtering optimized for the calorimeter frequency response.

Figure 4. Simulated data including realistic noise levels with typical controller gains. Noise level on the electrical power is approximately 5mW peak to peak.

Figure 5. Noise level on the inner cylinder power readings when the proportional gain is increased by a factor of five - 15mW peak to peak.
data stream was generated from an R-Z geometry time dependent conduction heat-transfer model of the calorimeter incorporating servo control and realistic levels of random noise and instrumentation errors.

A feature of the digital filter is its improved performance when dealing with high frequency noise. This improved noise performance allows the controller gains to be increased. Although this leads to an increase in the noise level on the raw data, it only causes a slight degradation of the accuracy of the predicted power.

In contrast end-point prediction with simple moving averaging suffers from increased uncertainties in the predicted end power for a given averaging time. Figures 4 and 5 show the noise level on a section of raw data for typical controller gains and a case where the proportional gain has been increased by a factor of five. Figures 6 and 7 show the predicted power versus time, again using simple averaging and digital filtering respectively.

**SAMPLE POWER PREDICTION**

As well as work done improving the performance of single exponential predictors attention has been directed towards implementing end-point predictors based around double exponential decay functions to further reduce assay times.

The idea of fitting a double exponential function to the calorimeter decay curve is not new. The single exponential predictor used in conjunction with preheating gives very short measurement times. Consequently, in an earlier study, the improvement in performance using the double exponential predictor with preheated samples was found to be small [2]. In fact the double exponential predictor used in conjunction with preheating tended to pick up the transient response of the calorimeter rather than a thermal decay component associated with the sample [3]. With the digital filters discussed earlier the transient response of the calorimeter can be made very short, so using a double exponential function to allow for the calorimeter response is not necessary.

However, if preheating is not used the calorimeter decay curves become longer and more complex. Although the single exponential predictor significantly shortens measurement times, assay times can still be long. Simulated results with realistic noise levels indicate that the double exponential based predictors have the potential to further reduce measurement times.

It is with the poorer packaged samples that the double exponential based predictors may offer the greatest improvement over the single exponential fitting functions. Figure 8 shows raw data taken from a measurement run performed on a pyro-chemical salt sample. Such samples typically require long measurement times. Figure 9 shows the performance of the double and single exponential predictors when applied to this decay curve.

From Figure 8 it is seen that the time taken for the sample to reach thermal equilibrium is approximately 7 hours. Figure 9 shows that the single exponential predictor yields a reliable estimate of the calorimeter end-point power by approximately 220 minutes after measurement commencement. The off-line analysis of the data indicates that if prediction was performed based on a double exponential decay function the calorimeter end-point could be predicted by approximately 90 minutes after the sample was inserted into the calorimeter. The analysis showed that it was difficult to achieve high precision using the double exponential predictor. However the time taken to estimate the end-point power to within 50 mW could be almost halved using a double exponential predictor in place of the single exponential predictor.

Double exponential predictors, however, are more sensitive to noise, and particularly thermal interference. From studies of the baseline stability of an early experimental ANTECH calorimeter the real system noise has been measured and characterized. By applying noise of a similar nature to analytically generated decay curves
Figure 6. Predicted power versus time using a rolling single exponential predictor in conjunction with simple averaging applied to a data stream with increased noise levels due to higher controller gains.

Figure 7. Predicted power versus time using a rolling single exponential predictor in conjunction with improved digital filtering applied to a data stream with increased noise levels due to higher controller gains.

Figure 8. Power versus time response of the calorimeter inner cylinder electrical power when a pyro salt sample is added to the measurement chamber.

Figure 9. Single and double exponential predicted final power versus time for a pyro salt sample decay curve.
the performance of the end-point predictors under adverse conditions can be readily evaluated. Under certain conditions noise can cause the end-point predictors to behave erratically in a way which is difficult for online expert systems to detect.

CONCLUSION

The present work has demonstrated that a significant reduction in noise in isothermal calorimeter power measurement data can be achieved through the use of optimised digital filtering techniques. This noise reduction permits improved operation of sample power prediction algorithms. The use of the double exponential prediction algorithm can reduce measurement times by as much as 50%.

Work is progressing to try and harness the potential of the double exponential predictor with respect to minimising measurement times as indicated by Figure 9 whilst maintaining full reliability of the predicted end point power in the presence of noise.

REFERENCES

