A systematic error in mass flow calorimetry demonstrated

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Abstract

Mass flow calorimetry represents a useful technique for studying calorimetric behavior of a number of systems. However, a systematic error can be introduced at the level of the calibration constant variation. The error is developed directly from linear regression analysis equations, and should be generalizable to any application of the statistical methodology, possibly even for the non-linear variants of regression analysis. This error is developed and illustrated with some recent data purporting to 'prove' cold fusion. © 2002 K.L. Shanahan. Published by Elsevier Science B.V. All rights reserved.

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1. Introduction

Mass flow calorimetry is used to study heat producing or consuming processes by surrounding the test apparatus with a flowing calorimetric fluid of known heat capacity. The fluid temperature is measured before and after contacting the test apparatus and the temperature differential observed is used to calculate output power (P_{out}), i.e.

$$P_{out} = C_p f (T_{out} - T_{in}) \qquad (1)$$

where C_p is the calorimeter fluid's heat capacity and f is its flow rate. Since experimental variations are expected, this equation is usually modified by establishing a statistical correlation between the measured input power (P_{in}) and the variation in the output parameters. Thus, Eq. (1) is applied in practice via a linear regression calibration equation, i.e.

$$P_{out} = m C_p f (T_{out} - T_{in}) + b \qquad (2)$$

where m and b are the standard linear regression coefficients determined by fitting to input power. This statistical process incorporates all errors, such as measurement noise and/or unexpected shifts in calorimeter properties, into the calibration constants.

The 'excess' power (P_{ex}) is defined as the difference between the input power and the computed output power:

$$P_{ex} = P_{out} - P_{in} \qquad (3)$$

Of course, this definition is exactly the statistical residual, and the standard statistical practice of closely examining this residual for non-random patterns is highly recommended. What may not be so well recognized is that the practice of using the linear regression analysis *guarantees* a non-random excess power signal. This will be illustrated herein for a mass flow calorimetry study of heavy water electrolysis.

It is now over 10 years since Pons et al. claimed [1] that electrolysis of heavy water with a palladium cathode and platinum anode produced cold fusion (also known as the Pons and Fleischmann (P&F) effect). In that time, several new variations on the

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original theme have been presented [2]. One of the most recent of these was the claim made by Storms in January 2000 [3] that a *platinum* cathode could be made to show the P&F effect. The raw experimental data and draft papers were made available [4]. Subsequently, the work was presented in [5].

2. Theory

The design goal of a mass flow calorimeter is the total capture of all released heat, and it should *theoretically* not require anything but a single calibration. But perfect design goals are rarely achieved. This is evidenced by (a) the statement that the heat capture efficiency of this mass flow calorimeter approximates 98% [4,5], and (b) the reported calibrations showing small natural variation comprising a few percent of the expected theoretical heat capacities [4,5]. Thus, it seems reasonable that mass flow calorimetry might well display variable calibration constants on a time-to-time or run-to-run basis. Given that some level of natural variation is present, the global coefficients used to interpret any specific run will most probably be numerically different from the coefficients that best represent the specific run. This is the root of the expected artificial excess power signal, and it can be computed algebraically.

In a specific run with no excess power, the expected output temperature in terms of input power, input temperature, and flow rate is computed by solving the run-specific calibration Eq. (2) assuming $P_{out} = P_{in}$, i.e.

$$T_{out} = T_{in} + \frac{P_{in} - b_s}{m_s C_p f} \tag{4}$$

where m_s and b_s are the fit parameters for this specific run. Substituting this expression into the global calibration equation, one finds that the flow rate and input temperature variables drop out. This leaves the expected output power expressed as a function of both sets of calibration constants and the input power. Subtracting the input power from the expected output power gives the excess power as:

$$P_{ex} = \left(\frac{m_g}{m_s} - 1\right) P_{in} + \left(b_g - \frac{m_g}{m_s} b_s\right) \tag{5}$$

where m_g and b_g refer to the linear regression constants of the global calibration equation.

In a perfect situation, both algebraic terms should be zero and no excess power would be expected. However, since the constants are statistically determined, the terms will usually not be identical, and this will produce an excess power signal (either positive or negative). Thus, a +3% calibration difference can produce an apparent positive excess power of 3%, which for 20 W input would mean an excess power of 600 mW.

3. Experimental data

The electrolysis cell used by Storms was closed and used a recombination catalyst. The cathode was a platinum foil and the anode was a Pt wire mesh. The cell was placed in a mass flow calorimeter using pure water as the calorimetric fluid. The calorimeter inlet and outlet temperatures were monitored with thermistors. Further, three internal cell temperature thermistors were placed, respectively near the top of the cell, near the bottom of the cell, and near the cathode. Water flow rate was periodically measured by collecting and weighing the water pumped in a measured time interval. Input current (A) and cell voltage were also measured. Input power, P_{in}, is computed as the product of the cell current (controlled in this instance, A) and the cell voltage, which varies depending on many factors such as electrolyte concentration, electrode surface condition, etc. The input current was stepped up, held constant for a time, and stepped again, either up to the maximum or down to zero in a current sweep (a 'run'). All experimental parameters were recorded by a computer data acquisition system. (A more complete description is included in [4,5].)

Calorimetric calibration was effected by the use of a resistive heater in the cell and an 'inert' Pt electrode. (No details about the 'inert' electrode were supplied.) Only one Pt electrode was reported to produce the effect. Once the global calorimeter calibration constants were determined, they were applied to the measurements taken during other specific runs.

Fig. 1 is the input power time profile of the 10 sweeps applied to the active Pt electrode derived by multiplying input current times cell voltage. The global calibration constants reported for the inert Pt electrode and the heater are shown in Table 1. (In this report, numerical results will be for the combined term
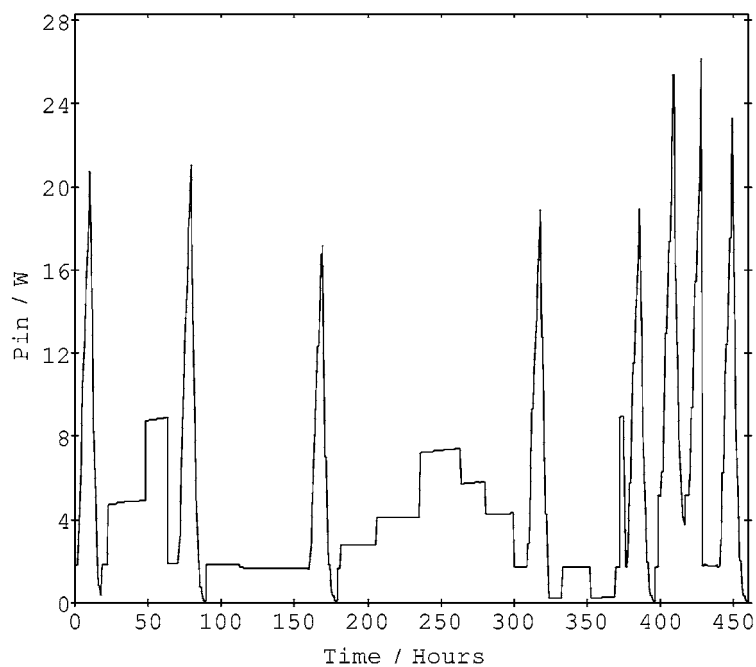
Fig. 1. The experimental input power (W).

Table 1
Computed run-specific calibration constants

	Slope (mC_p)	Intercept (b)	Multiple R^2	S.D. regression	Percent deviation from 20 °C value
Sweep					
1	0.068564	−0.167834	0.999738	0.106	−1.63
2[a]	0.069415	−0.289437	0.999048	0.077	−0.41
3[b]	0.070672	−0.177146	0.999875	0.077	1.40
4	0.067956	−0.187765	0.999728	0.091	−2.50
5[a]	0.068890	−0.174754	0.997721	0.085	−1.16
6[b]	0.071320	−0.131471	0.999950	0.043	2.33
7	0.068622	−0.196223	0.999870	0.070	−1.54
8	0.068751	−0.166957	0.999754	0.101	−1.36
9	0.069961	−0.253006	0.999811	0.081	0.38
10	0.070028	−0.157767	0.999906	0.068	0.47
Average	0.069418	−0.190236			−0.40
Storms					
Electrode, initial	0.071221	−0.18317			2.19
Joule	0.072107	−0.23893			3.46
Electrolysis, final	0.070892	−0.14405			1.71
Theory					
At 20 °C	0.069698	0			0
At 34.5 °C	0.069637	0			−0.09

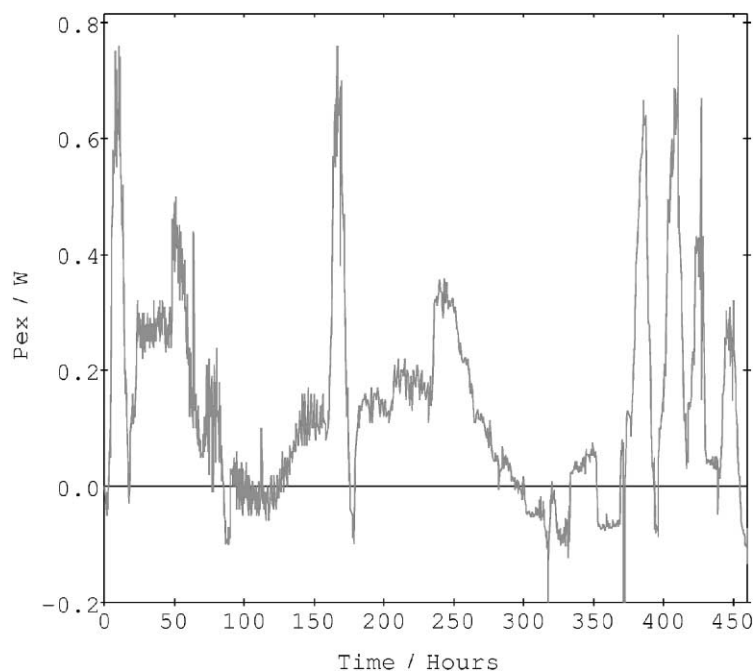[a] Different input power profile.
[b] Low excess power reported.

Fig. 2. The reported excess power (W) derived via a global calibration.

mC_p.) Fig. 2 shows the excess power computed via a global equation using $mC_p = 0.0712$ and $b = 0.13$, which was used in the data files [4]. Figs. 4–6 of [5] show the same data, although they are shown as discrete points instead of a continuous line as in Fig. 2 of this paper.

4. Results and discussion

Calibration data were not collected during the individual runs (current sweeps), so apparent calibration constants are computed by *assuming* the null result, namely P_{out} should equal P_{in} for each sweep. Once the speculative calibration constants are determined, they are compared to the *actual* resistive heater and inert Pt cathode calibration constants and to theoretical expectations. A key point is that the speculative constants must be reasonable, or the power balance assumption would be invalidated.

After assuming no excess power, the specific calibration constants for each individual current sweep (total 10) are computed by simple linear regression. The data span chosen for each run was determined

from the data file by locating the points where the current first began increasing from and first returned to the baseline value. Table 1 presents those constants and statistical fit quality measures, along with the reported resistive heater and inert Pt calibrations and two theoretical values. The theoretical values are the maximal and minimal pure water heat capacity at 20 and 34 °C, respectively for the 20–50 °C range [6], which covers the variation in the calorimeter output temperature. The computed slopes (mC_p term) are roughly centered about theoretical, as shown by the average coefficient values and the percent deviation from the 20 °C theoretical value (Table 1, mean of −0.4% and a S.D. of 1.5%).

Fig. 2 shows the reported ('global') excess power curve [5] and the curve computed using the sweep-specific calibrations is shown in Fig. 3. The power balance assumption and the fit quality leads to the expected reduced excess power in the latter case, statistically centered about zero excess power. It is of interest to note that the excess power peak structure has changed significantly by applying the sweep-specific calibration assumption. Now the largest features seem to be transients associated with peak input power
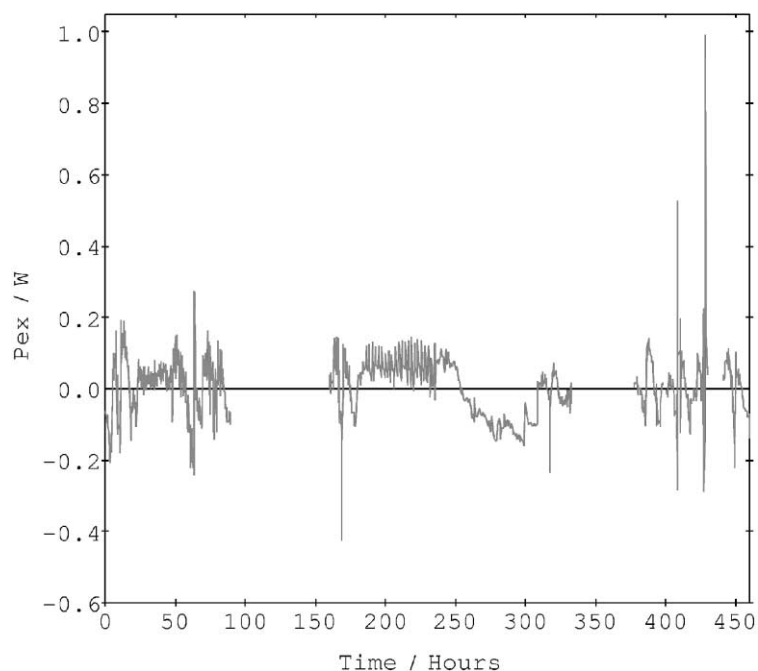
Fig. 3. The excess power (W) computed via individual sweep-specific calibration equations (breaks in the curve indicate unfit regions).

points, possibly pointing to some other experimental problem. Also, the non-random shape of the residual peaks suggests that a slightly different form of the calibration equation (non-linear?) might reduce the residual excess power even further.

The global calibration constants show some of the largest deviations from the theoretical values, thus positive excess power signals can be anticipated simply from this based on Eq. (5). The two sweeps that showed anomalously low excess power (third and sixth sweeps in the Fig. 2) can be seen to have specific calibration constants very similar to the global one used.

Other parts of the experimental data may suggest possible causes of the divergence between the global and specific calibrations. The internal cell temperature profiles for the resistive heater calibration and the electrolysis sweeps are different. The difference between the top thermistor output and the bottom one varies systematically with input power. For electrolysis runs, at near zero P_{in} the difference is 0.1 °C, while at peak input power ($\sim$26 W), the difference increases to, approximately 1.8 °C. However, during the resistive heater calibration this differences increases

to, approximately 7 °C for a 12.5 W input power, which scales to 14.5 °C at 26 W. Clearly, a much stronger thermal gradient exists in the heater case, which may be a key to understanding a contributing factor in the constant's variation.

5. Conclusions

A potential systematic error in mass flow calorimetry has been described. It arises from the application of a global calibration equation to data where run-specific variation in that calibration exists. Eq. (5) shows it to be a potentially significant error term, easily approaching the magnitude of many reported excess power signals in typical 'cold fusion' experiments, for example.

Reanalysis of data presented by Storms to support the claim that platinum produces a P&F effect has clearly demonstrated the proposed systemic error. Because no sweep-specific calibration data were recorded, the implied sweep-specific calibrations were computed based on the zero excess power assumption and found to be scattered about the theoretical expectations. The

reported Pt electrode calibration constants also fall within that variation. Thus, there seems to be nothing particularly unreasonable about the computed constants, suggesting that the Storms' interpretation simply fails to recognize the statistical character of the experiments.

The resulting excess power curve showed significantly reduced excess, but still contained residual signal. This is possibly due to one or more other factors, such as the need for a more sophisticated calibration model, other physical/chemical process affecting the apparatus, or perhaps the actual presence of an excess power source (of reduced magnitude). More sophisticated analysis was not attempted here, as it simply complicates this analysis without adding insight.

Therefore, a simple reinterpretation produces the conclusions that the cell would seem to be close to power balance as expected, and the excess power detected by Storms was likely due to the systematic error involving calibration constant variation. The root causes of the calibration constant variation remain unclear. A significant difference in internal cell temperature gradients between the electrolysis runs and the resistive heater calibration is suggestive. In fact, if one assumes the 'active' electrode as the correct calibration electrode, the net result would be that the 'inactive' electrode would show noticeable heat losses. This would be a much more reasonable conclusion from this data, as heat losses of a few percent with a different electrode would not be unexpected. Additional data must be acquired and further analysis performed before the claim of Storms that platinum shows evidence for cold fusion can be taken seriously.

This paper delineates a fundamental systemic error possible with regression analysis calibration methodology of which all researchers should be aware. It establishes the requirement that the statistical variation in calibration constants must be explicitly determined and considered, since any variation in those constants can be reflected through the residuals as non-random features, which can apparently lead to misinterpretation of the results.

Acknowledgements

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