

Calorimetry Experiment For Unknown Material

Assigned ID Number 142

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This project utilized the tools of curve fitting and error analysis and propagation principles to determine material properties and their uncertainties. These tools and techniques were implemented on a given collection of data for a calorimetry experiment and were to be used to find the value of specific heat to identify an unknown sample used in the experiment.

I. Nomenclature

C_s	=	Specific heat of the sample [calories/Gram degree Celsius]
M_c	=	Mass of the calorimeter [Grams]
M_s	=	Mass of the sample [Grams]
C_c	=	Average specific heat of the calorimeter [calories/Gram degree Celsius]
T_0	=	Initial temperature of the calorimeter [Degrees Celsius]
T_1	=	Initial temperature of the sample [Degrees Celsius]
T_2	=	Final temperature of sample and calorimeter at equilibrium [Degrees Celsius]
σM_c	=	Uncertainty in the mass of the calorimeter [Grams]
σM_s	=	Uncertainty in the mass of the sample [Grams]
σT_0	=	Uncertainty in the initial temperature of the calorimeter [Degrees Celsius]
σT_1	=	Uncertainty in the initial temperature of the sample [Degrees Celsius]
σT_2	=	Uncertainty in the final temperature of the sample and calorimeter in equilibrium [Degrees Celsius]

II. Introduction

CALORIMETRY is a technique used to measure quantities of a substance, particularly thermodynamic properties, such as specific heat, heat of fusion, and heat of chemical reaction. Specific heat is defined as the amount of heat per unit mass of a material needed to raise the temperature by one degree Celsius. The property of specific heat is a unique property and is different for different substances. This makes it an excellent identifying characteristic of a certain material. In this experiment, we utilize the fact that specific heat is unique for different substances in order to identify the unknown material being used.

The set of data used in this experiment relates time elapsed in seconds and temperature in degrees Celsius and correlates to a calorimetry experiment done with an unknown material placed in a boiling water bath for approximately 10 minutes. The material was then placed in the calorimeter and approximately 10 minutes of data was recorded before terminating the experiment.

III. Experimental Method

The acquired set of data that relates the the temperature of the calorimeter to time elapsed allows us to ultimately calculate the specific heat of the unknown material placed in the calorimeter using the tools of thermodynamics, curve fitting, and error analysis and propagation.

The overall purpose of this experiment is to use what we know about thermodynamics, error propagation, and curve fitting to determine the specific heat of an unknown substance used in the experiment. To aid us, we are provided a few vital pieces of information, which include the mass of the sample being used, the mass of the calorimeter, and the specific heat of the calorimeter. We are given the uncertainties in these masses and can make the assumption that the given value of the specific heat of the calorimeter is exact. This assumption in coordination with the assumption that the heat lost from the system, or the calorimeter, is negligible, which simplifies our calculations and process. The nature of the data and the given information strongly indicates that the use of weighted curve fitting should be used to determine the specific heat of the sample and its uncertainty.

Ultimately, the goal of this experiment is to expand upon our understanding of thermodynamics and error propagation in order to determine the specific heat of an unknown substance by utilizing a variation on the first law of Thermodynamics. Before we can use this variation however a few things must first be determined using our knowledge of weighted least squares fitting.

The principle behind weighed least squares line fitting is to take a set of data and develop a line of best fit to that set of data. Ideally, This line of best fit accurately models the set of data that it represents. In order to make this line more accurate, we implement a weighted line of best fit. The weight to our line of best fit takes in to account outliers and anomalies in the data that would otherwise severely skew our line, making it less accurate. A weighted line of best fit more accurately represents our data, so it was implemented in three different portions of our total data set. In order to aid my explanation, I will refer to figure one and two below.

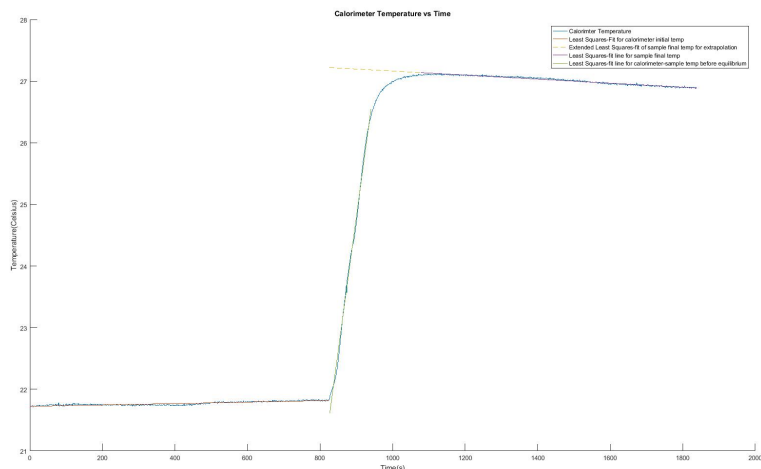


Fig. 1 Calorimeter Temperature as a Function of Time.

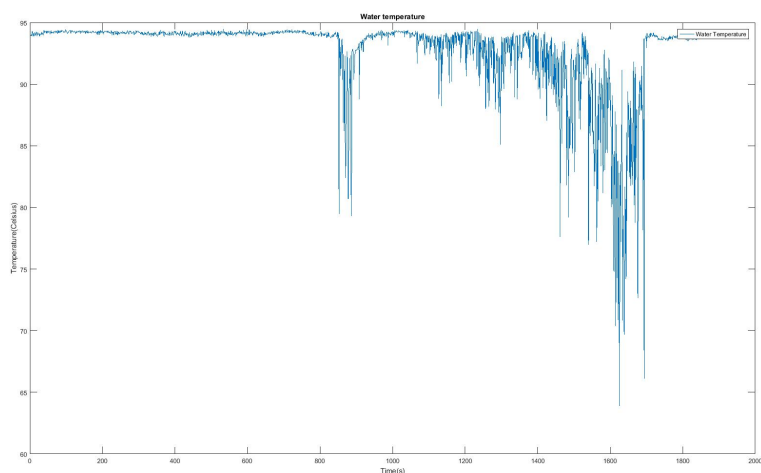


Fig. 2 Water Temperature as a Function of Time.

The first partition of the data is represented in the figure one as data points 1 through 809 and represents the time for which the calorimeter is essentially warming up and coming to equilibrium with the room temperature. A linear weighted least squares line was fit to this portion of the data and used to determine T_0 , the initial temperature of the calorimeter.

The second partition of the data, defined as starting at point 810 and going to point 1057 in figure one, shows us the drastic increase in calorimeter temperature, implying this span of time represents the time period directly after the sample was added and the calorimeter and sample are coming to equilibrium. The line representing this portion of data was also fit in the same manner as described for the first partition of the data, and will later be used to determine T_2 .

The third partition of the data, ranging from point 1058 to the end of the data in figure one, represents the remainder of the experiment after the sample and the calorimeter have come to equilibrium. This partition, like the previous two, was fit with a weighted least squares line.

Looking at figure two, the mean of the first 809 data points of the graph were averaged without a need for a least squares line of best fit, thus one does not appear in figure two.

Once all three partitions of data have been accurately fit with a least squares line, we are able to determine the three desired temperature values T_0 , T_1 , and T_2 , which will allow us to calculate the specific heat of the sample.

T_0 can be quickly calculated by evaluating the equation of the line of best fit of the first partition of the data at the point in time at which the temperature of the calorimeter drastically increases. T_1 can be calculated by taking the average of the 1st to 809th data points of the water temperature, assuming the sample and boiling water are in equilibrium for that portion of the data. The determination of T_2 , however, was slightly more involved.

In order to calculate T_2 , we were required to extrapolate data from an extended best fit line that fits the third partition of the data in figure one. In order to find the X value that corresponded to the desired temperature value we wanted, T_2 , we correlate that temperature value with the average temperature value on the second partition of data, and find the common time value to evaluate the extended line of best fit for the third data partition at in order to extrapolate our desired temperature value, T_2 .

Now that all three necessary temperature values have been determined, it is now possible to determine the value of specific heat of the unknown substance, allowing us to identify it.

The given relationship below allows us to relate the specific heat of the sample to the specific heat of the calorimeter, the mass of the sample and calorimeter, and T_0 , T_1 , and T_2 .

$$\frac{M_c * C_c * (T_2 - T_0)}{M_s * (T_1 - T_2)} = C_s$$

This expression comes from the first law of Thermodynamics through the following simplified derivation

$$\Delta U = Q - W \Rightarrow \Delta U = 0 \Rightarrow Q = W \Rightarrow (M_c * u_{c2} + M_s * u_{s2}) - (M_c * u_{c1} + M_s * u_{s1}) = 0$$

$$\Rightarrow M_s * c_s * (T_1 - T_2) = M_c * C_c (T_2 - T_0) \Rightarrow C_s = \frac{M_c * C_c * (T_2 - T_0)}{M_s (T_1 - T_2)}$$

IV. Results

A. T values

The temperature values required to calculate the specific heat of the sample were calculated by means explained earlier, evaluating the various lines of best fit at determined values of time.

The initial value of the calorimeter, T_0 , was calculated as 21.8168 degrees Celsius with an error of 0.0145 degrees Celsius. The initial value of the sample, T_1 , was calculated as 94.1536 degrees Celsius with an error 0.1253 degrees Celsius. The final temperature of the sample and calorimeter in equilibrium were calculated as 27.1990 degrees Celsius with an error of 0.0013 degrees Celsius.

These uncertainties were calculated using either principles of uncertainty calculation for weighted least squares or for extrapolated data. The uncertainty in a weighted least squares line of best fit involves the utilization of an equation out of John R. Taylor's book of error propagation and uncertainty. The equation listed below allows the uncertainty in T_0 to be calculated where A and B are the calculated intercept and slope values of the weighted least squares fit line, respectively

$$\sigma_y = \sqrt{\frac{1}{N-2} * \sum (y_i - A - B * x_i)^2}$$

Where the summation in the above equation goes from 1 to N.

The uncertainty in the initial temperature of the sample, t_1 , was easily determined by using a built-in MATLAB function called std (Standard Deviation), which was applied to the 1st through 809th data points of the boiling water temperature.

The uncertainty in the final temperature of the sample and calorimeter in equilibrium, t_2 , required the application of uncertainty calculation for extrapolated values. This involves various matrix multiplication operations involving the time value you are extrapolating at along with what is called the Q matrix, which is a matrix of the uncertainties of the slope and intercept values generated in the least squares fit process. Taking X to be the matrix $[X_{extrapolate}]$, Q to be the matrix of uncertainties in m and b, then the resulting uncertainty in the extrapolated y value at the specified x value will be $X * Q * X^T$. The superscript T indicates a transposed matrix.

B. Sample specific heat

Having all necessary information, both calculated and given, the specific heat of the sample can be calculated using the expression for specific heat, C_s , derived from the first law. Once evaluated with all the information, this expression yields a value of 0.2459 Joules/gram degrees Celsius, which is closest to the specific heat of the Tellurium Copper alloy.

The uncertainty in this calculation was yet again pulled from John R. Taylor's book of error analysis and propagation, and is as follows

$$\delta q \leq \left| \frac{\partial q}{\partial x} \right| * \delta x + \dots + \left| \frac{\partial q}{\partial z} \right| * \delta z$$

particular to this experiment, this equation becomes

$$\delta C_s \leq \left| \frac{\partial C_s}{\partial M_c} \right| * \delta M_c + \left| \frac{\partial C_s}{\partial M_s} \right| * \delta M_s + \left| \frac{\partial C_s}{\partial T_0} \right| * \delta T_0 + \left| \frac{\partial C_s}{\partial T_1} \right| * \delta T_1 + \left| \frac{\partial C_s}{\partial T_2} \right| * \delta T_2$$

which yields an error in the specific heat of the substance of 0.0014 Joules/gram degrees Celsius

V. Discussion

A. Algorithm

The developed code begins by reading in the data from an Excel file to acquire the time, calorimeter temperature, and water temperature. It partitions this data up into three partitions as specified in the script to separate it. Then each partition of the data is fed into a Least-Squares function to calculate the slope and intercept values of the weighted least squares line for the specified data partition. These calculated slope and intercept values are then fed into both an uncertainty calculating function and a line equation to plot the line of best fit for each partition. The time value corresponding with the desired temperature value is fed into the respective line equation to determine the desired temperature. Once all desired temperatures are calculated, these in conjunction with the given info can be used to evaluate the equation for specific heat of the sample. The calculated uncertainties in conjunction with the given uncertainties can be used to calculate the uncertainty in the sample specific heat value.

B. Possible sources of Discrepancy

The final calculated value for the specific heat of the sample was determined to be 0.2459 ± 0.0014 Joules/gram degrees Celsius. Given a list of several different alloys, this calculated value is in closest proximity to the specific heat value of the Tellurium Copper alloy. Observing the calculated value of specific heat, 0.2459 Joules/gram degrees Celsius, and its associated error, 0.0014 Joules/gram degrees Celsius, does not put the accepted value of specific heat of the Tellurium Copper alloy in this range. It is, however, within a range whose discrepancy may be due to the index values at which the data is evaluated and lines are fit to. Considering the method used to select the points at which the data was evaluated and fit was simple observation, a deviation of 30-50 data points is quite possible and could effect the final outcome of the specific heat value and its associated error. Running multiple trials on this set of data, using slightly altered ranges of data points in the three partitions of the data used throughout this experiment, would tell us whether or simple partition range selection is the cause of this discrepancy.

VI. Conclusion

The combined use of a knowledge of Thermodynamics, proper line fitting techniques, and applications of error analysis and propagation is a powerful and effective mixture of principles that can be applied to countless experiments and situations, much like this one. For this particular experiment, the culmination of these principles allowed us to determine the identity of an unknown substance associated with a specific value, and how sure we were in our determination. How cool! This method could be used for many many experiments and procedures. Say you were testing a new aircraft design and taking pressure measurements along the wing. You could use this same general procedure to determine the deviation of the pressure along the wing, what the wing is made of, and how likely it is that it's going to break. Amazing!

Appendix

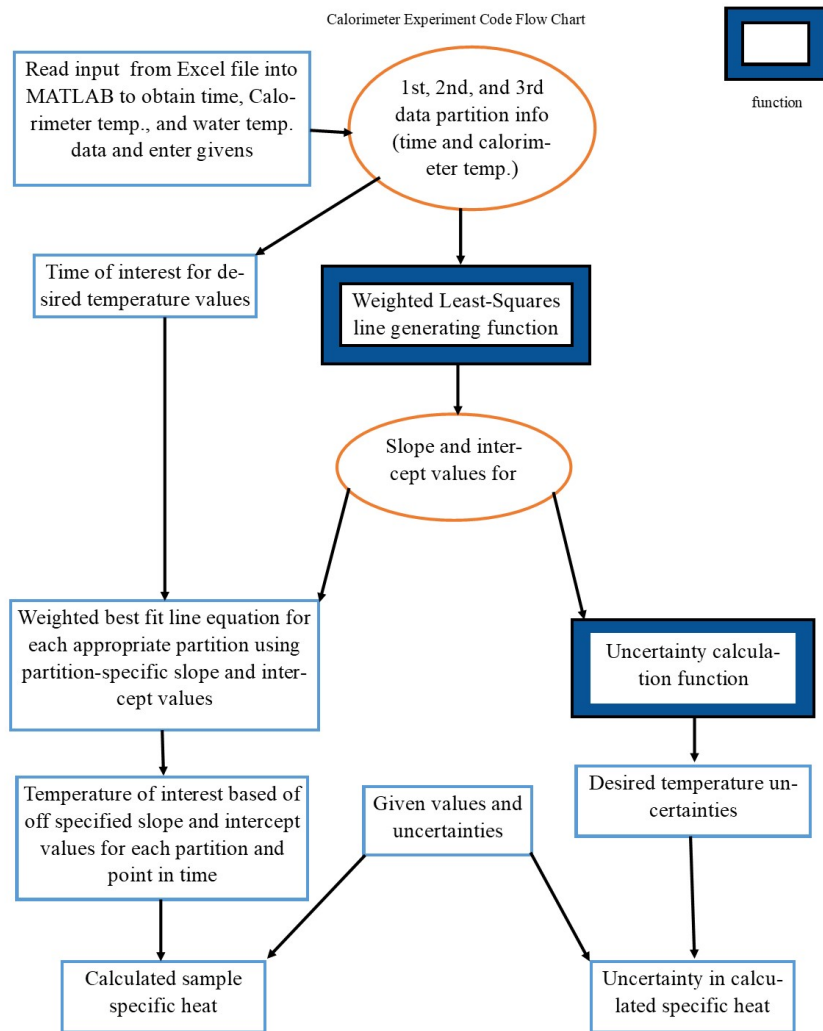


Fig. 3 Developed MATLAB script flow chart.

A. MATLAB code

```
%Purpose: To determine the specific heat and its uncertainty of an unknown substance using best
%fit line methods and error propagation and analysis techniques.
%Input:Time, calorimeter temperature, and water temperature in one Excel
%file, calorimeter and sample mass and their uncertainties, calorimeter
%specific heat.
%Output: Sample specific heat and its uncertainty, t0,t1, and t2 values and
%their associated uncertainties.
%Assumptions: Calorimeter specific heat is exact, heat loss from the
%calorimeter is negligible.
%Assigned ID number: 142
%Data Created:10/20/17
%Date(s) modified:10/21/17-10/27/17

clear all;close all;clc
%For excel Data, first column is time, second is calorimeter temp, third is
%water temp. Initial water temp is same as initial sample temp.

Data = xlsread('CalorimeterData.xlsx');

time = Data(:,1); %First column of Excel data, time
calor_temp = Data(:,2); %Second column of Excel data, calorimeter temperature
water_temp = Data(:,3); %Third column of Excel data, water temperature

calor_mass = 313.5; %Mass of the calorimeter in grams
calor_mass_uncert = .05; %Uncertainty in Mass of calorimeter in grams
calor_C = .214; %Specific heat of the calorimeter in calories/gram*C, assumed exact
sample_mass = 91.75; %Mass of sample in grams
mass_uncert = .05; %Uncertainty in the mass of the sample in grams

%By inspection of the graph it appears that the temp rapidly starts to
%increase at the 809th data point => t0 = calor_temp(809)

%Fit the first 809 data points with a weighted least squares line
[m1, b1] = least_squares(time(1:809),(calor_temp(1:809)));
%Calculates uncertainty in line fit to specified portion of data (see
%comment in function)
sigmat0 = uncertainty(time(1:809),(calor_temp(1:809)),m1,b1);
x1 = time(1:809); %First best fit line
y1 = m1*x1 + b1;
%Calculates the initial temperature of the calorimeter
t0 = (m1*time(809) + b1);
%Fit data from the 1057th data point to the last data point with a weighted
%least squares line
[m2, b2, Q2] = least_squares(time(1057:end),(calor_temp(1057:end)));
x2 = time(809:end); %Last best fit line
x3 = time(1057:end); %Last best fit line
y2 = m2*x2 + b2;
y3 = m2*x3 + b2;
t_low = t0; %Assigns t_low as t0 since they are the same, specified in assignment
t_high = y2(1); %Point on extrapolated line corresponding to same t value as t0

t_avg = (t_high + t_low) / 2; %Finds average t on middle portion of graph where the sample is added to
%Fit data from point 840 to 922 with weighted least squares line
```

```

[m3, b3] = least_squares(time(810:922),(calor_temp(810:922)));
x4 = time(810:922);%Middle best fit line
y4 = m3*x4+b3;

t = ((t_avg - b3)/m3); %solves for time value t in order to solve for t2

t1 = mean(water_temp(1:809)); %Average water temperature in first 809 data points
sigmat1 = std(water_temp(1:809)); %Standard deviatio in those data points

t2 = m2*t + b2; %Calculates t2
sigmat2 = sqrt([t 1]*Q2*[t;1]); %Calculates uncertianty in t2 using principles in calculating uncertain
%calculate value of Cs given equation one
Cs = calor_mass*calor_C*(t2 - t0)/(sample_mass*(t1 - t2));

%Convert calorimeter specific heat to J/g*C
Cs = Cs * 4.184; %Using the conversion of 4.184 joules per calories

%Find the uncertainty in the final Cs calculation using partial
%derivatives, given uncertainties, and calculated uncertainties

partialWRS_Mc = (calor_C*(t2 - t0)) / (sample_mass*(t1 - t2));
partialWRS_Ms = -(calor_mass*calor_C*(t2 - t0)) / ((sample_mass)^2*(t1 - t2));
partialWRS_t0 = -(calor_mass*calor_C) / (sample_mass*(t1 - t2));
partialWRS_t1 = -(calor_mass*calor_C*(t2 - t0)) / ((t1 - t2)^2*sample_mass);
partialWRS_t2 = (calor_mass*calor_C*(t1 - t0)) / (sample_mass*(t2 - t1)^2);

sigma_Cs = abs(partialWRS_Mc)*calor_mass_uncert + abs(partialWRS_Ms)*mass_uncert + abs(partialWRS_t0)*s
sigma_Cs = sigma_Cs * 4.184; %Conversion from calories to joules in the uncertainty
hold on
plot(Data(:,1),Data(:,2)) %Plots the temperature of the calorimeter vs time
plot(x1,y1) %Least squares-fit line for first third of data
plot(x2,y2,'--') %Leas squares-fit line extrapolated backwards to find t2
plot(x3,y3) %Least squares-fit line of third portion of data
plot(x4,y4) %Least squares fit of middle portio of data
title('Calorimeter Temperature vs Time')
xlabel('Time(s)')
ylabel('Temperature(Celsius)')
legend('Calorimter Temperature','Least Squares-Fit for calorimeter initial temp','Extended Least Squares
hold off
figure
plot(Data(:,1),Data(:,3))
title('Water temperature')
xlabel('Time(s)')
ylabel('Temperature(Celsius)')
legend('Water Temperature')

%Least_Squares function

%Purpose: To develop necessary slope and intercept values for a weighted
%least squares line of best fit.
%Input:Time and calorimeter temperature
%Output: m and b values for the input partition of the calorimeter data and the Q matrix associated with
%Assumptions: Calorimeter specific heat is exact, heat loss from the
%calorimeter is negligible.

```

```
%Assigned ID number: 142
%Data Created:10/20/17
%Date(s) modified:10/21/17-10/27/17
```

```
function [m, b, Q] = least_squares(time,calor_temp)
%Feed in desired chunk of calor_temp and time interval first in main script
%Calcualte standard deviation of calor_temp in range 1:809
W = zeros(length(time)); %Preallocates weight matrix

A = [time ones(length(time),1)]; %Creates A matrix
d = calor_temp; %Creates d column vector
P = inv(transpose(A)*A)*transpose(A)*d; %calculates a non-weighted least squares fit line
m = P(1); %produces m and b values for line equation y=mx+b
b = P(2);
sigma = uncertainty(time,calor_temp,m,b); %Calculates the uncertainty in values using non-weighted least squares
for i = 1:length(time) %populates preallocated matrix of zeros with calculated uncertainty
    W(i,i) = 1/(sigma^2);
end
Q = inv(transpose(A)*W*A); %Calculates Q and new weighted least squares m and b values using created weight matrix
P = inv(transpose(A)*W*A)*transpose(A)*W*d;
m = P(1); %New output m and b values to be used in a weighted least squares fit line y=mx+t+b
```

```
%Uncertainty calculation function
```

```
%Purpose: To calculate the uncertainty in measurements
%Input:Time,calorimeter temperature, m, and b values for weight line of
%best fit for specified partition of data
%Output: Uncertainty sigma of input values
%Assumptions: N/A
%Assigned ID number: 142
%Data Created:10/20/17
%Date(s) modified:10/21/17-10/27/17
```

```
function out = uncertainty(time,calor_temp,m,b)
sigma = [];
for i = 1:length(calor_temp)
    sigma = [sigma (calor_temp(i) - b - m*time(i)).^2];
end
sigma = sum(sigma);
sigma = sqrt(1/(length(time) - 2)*sigma); %Calculates the uncertainty in measured value using equation
out = sigma;
```

References

Taylor, John R., "An Introduction To Error Analysis", Second Edition
 ASEN 2012 lecture slides and online notes