

Differential Thermal Analysis

- a low cost, home built apparatus for exploring thermal properties of materials
Part 1: How To Build the DTA Apparatus

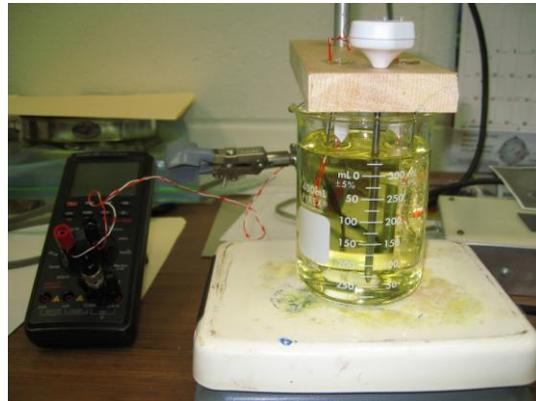
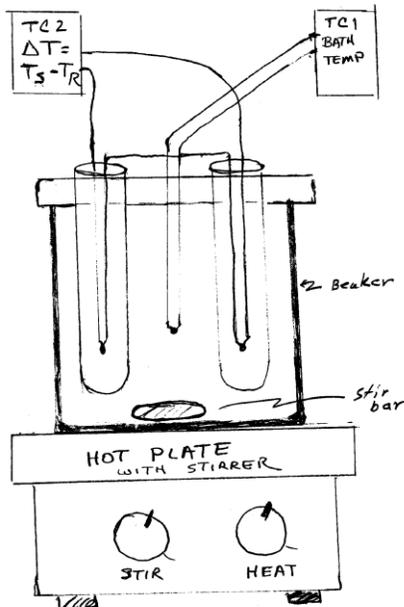
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How To Build the DTA Apparatus - a detailed version

Construction:

Our heating bath consists of a 250 ml beaker filled with about 175 ml of vegetable oil (e.g. corn oil) and resting on a standard laboratory hotplate equipped with a stirring bar to assure uniform temperature within the bath. The student should be advised to exercise caution when working with hot oils and the potential danger of burns from spillage or splashes of hot oil, as well as the dangers of fire, if overheated. (Water can be substituted to limit the bath temperature for safety, but this limits the maximum bath temperature to 100 C and will preclude examination of transitions occurring near or above about 95° C.) A rimmed cookie should be used under the hotplate and apparatus to catch any oil in the event of an accidental spill.



The sample and reference chambers consist of two Pyrex test tubes held by a wooded support attached to a ring stand. We used 100mmx13mm Pyrex test tubes (measuring 0.505 x 4.0 “) with beaded rim for retaining the tube in the wooden holder (e.g. Kimax* Reusable Test Tubes with Beaded Rim and Marking Spot, Kimble # 45042 13100).

The wooden holder was constructed from dimensional lumber to simplify construction and details for our holder are included in the Appendix. The wooden support is simple to

construct, requiring only a few drilled holes and can enhance the student's participation in building the apparatus.

Temperature measurements:

The temperature difference between the sample and reference tubes is measured using a thermocouple pair connected in differential mode as shown in the figure above. For the differential mode we used single strand copper wire (24 gauge, from scraps of telephone hookup wire) for the leads to the meter and a short length of constantan (copper-nickel) wire between the two test tubes. (The copper wire leads to the meter should be of different color insulation to make it easy to maintain polarity when attaching to the meter; we use the convention of having the lead from the sample chamber going to the + side of the meter.) The copper-constantan pair (T-type thermocouple) was chosen for convenience since the copper is readily available leaving only the short pieces of constantan for special purchase and these two metals can be easily soldered to form a stable thermocouple junction. Teflon coated constantan (0.010" diameter wire can be obtained from Omega (<http://www.omega.com>, TFCC-010 – available in 50 ft roll for \$16.) Absolute values of the differential temperature are not at all necessary and thus there is no need for the added expense of using certified thermocouple copper wire. A conversion coefficient of 0.039 mv./°C can be used for calculations for this T-type pair, or alternatively, the student can make their own calibration curve using an ice bath and boiling water as reference temperatures.

The bath temperature can be measured using either a digital cooking thermometer (available for ~ \$10 at department store e.g. Sunbeam, digital thermometer) or another thermocouple. The low cost digital cooking thermometer is an easy, low cost approach and is quite suitable for manual measurements using a watch as timer. However, these thermistor based devices have a limited high temperature range, typically less than 170 C. Also the thermocouple can be easily interfaced to the data logger using the same scheme as employed for the Delta T measurement, as will be described in a later section. Thermocouples have a much higher temperature range, a nearly linear response (voltage vs temperature), a small sensing junction and are easy to fabricate. However, their output voltage is rather small (in the millivolt range), requiring microvolt accuracy for a good temperature measurement. Fortunately, many digital voltmeters today include an input for thermocouples with direct conversion into temperature (C or F) and several low cost meters with this thermocouple option are now available on the market (Harbor Freight <http://www.harborfreight.com/> ITEM 37772-0VGA \$40.00). Most of the commercial instruments are designed for the type K (chromel-alumel) thermocouple and thus this type was used for the bath temperature. If the microvoltmeter is used to measure the temperature a suitable conversion factor for the type K thermocouple is 39.7 microvolts per °C above the reference junction.

Datlogging Approach

While manual data collection is the simplest approach for getting started, the data taking requires careful attention to the experiment and gets old after the first few runs.

Automating the data collection allows the student to direct more attention to the visual observations of the sample during the heating run. It also lowers the barrier to repeat runs and exploring the effects of modifications to the experimental conditions such as heating rate, etc. In short, it allows the student to focus more on the interesting science to be discovered.

In keeping with the low cost, hands-on approach we chose to build our own data logging apparatus from a simple but powerful microprocessor, the Basic stamp, from Parallax Inc. (<http://www.parallax.com/>) combined with their thermocouple add-on module.

Many educators and students are already familiar with Parallax's Basic Stamp microprocessors and their associated robotics accessories. The company has a strong education focus and provides a wealth of information and software available free at their website. These microprocessors are programmed using a simple Basic language (called P-Basic) and the necessary editors and sample programs are all available for download at no cost. This platform choice encourages student involvement in the design and implementation of their own data logger with a few simple commands and enables them to modify and extend the program capabilities for this or other projects.

The particular hardware recommended for this application includes the BASIC Stamp 2pe Motherboard (\$80.00) with the DS2760 Thermocouple Kit (\$30 each). The thermocouple kit even includes a few thermocouple pairs. Two DS2019 thermocouple modules were used, one for the differential, ΔT , measurements and one for the bath temperature measurements. These modules measure and the millivolt level signals produced by the thermocouple junctions to a resolution of $15.625\mu\text{V}$

volts, equivalent to a temperature resolution of about 0.4°C , sufficiently adequate for these experiments. The DS2760 sends the results to the microprocessor from a single PBasic serial read command. This device greatly simplifies the software involved. The DS2760 also monitors its own temperature and provide the reference junction voltage appropriate for an absolute temperature measurement if desired as for the bath temperature. (The software aspects will be included later - in a separate document and the P-Basic program used for our apparatus will be available on the IMI website.)

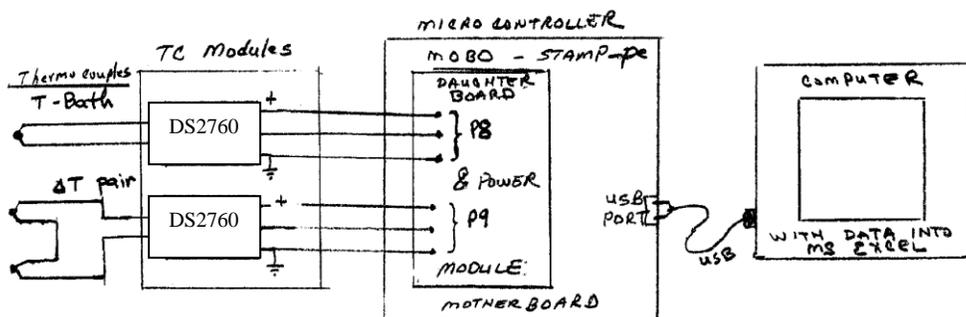


Figure 3. A block diagram of the data measurement and collection approach utilizing the Dallas Semiconductor thermocouple modules (DS2760) and the Parallax MOBO microcontroller board.

The microprocessor handles the data-logging, it can convert the millivolt thermocouple signals directly into temperatures and it sends the data to the experimenter's computer for final display and graphing. The voltage to temperature conversion can be accomplished using a lookup table (downloadable from Parallax) or one can simply use a fixed conversion coefficient (given earlier) to make the conversion.

Some Experimental Details:

The Basic Stamp's program sends the Bath temperature and differential thermocouple voltage to the PC via a serial or USB cable. Microsoft's Excel was used to capture, monitor and plot the data as it is taken. Parallax provides a sample Excel program (DAT_DAQ.xls) which contains a macro to receive the data from the USB or serial port in real time and provide a time stamp for each entry. Using the Excel program for data acquisition builds on a platform familiar to most students and makes subsequent operations such as plotting much easier for the student to learn.

The heating rate is an important parameter for DTA experiments and it can be adjusted by changing the heat setting of the hotplate. Graphs of both the bath temperature and differential temperature, ΔT vs. time are useful to display and monitor the progress of the experiment. A few trial runs will allow one to obtain an approximate relationship between the sample heating rate and the temperature bath's heat setting. We strongly recommend that the setting required to achieve a heating rate between 5-10° C per minute be determined prior to any serious sample calibration.

If manual data collection is used a watch or timer should be used to record the time at which the temperature measurements are recorded. For manual data collection, measurements taken every 30 seconds to one minute are a reasonable starting point, allowing some time for observations between data taking. For the automated version a shorter sampling time of 10-15 seconds is recommended for heating rates on the order of 5° C/ min.

Whether automated or manual data collection is utilized, the experimenter (student) is advised to record their data in a notebook or data sheet where visual observations, such as melting, softening or boiling, can be also be noted as the experiment progresses, along with their associated temperatures and/or time.

For determining softening points it is useful to have a tooth pick or long wooden stick to probe the sample during the heating scan. A camera is also useful to record some of the interesting visual changes that occur during the heating scan. (Such as the healing of cracks and movement of entrapped air bubbles as softening progresses.)

After the experiment the student should prepare plots of both the T and ΔT vs. time and determine the actual heating rate. Likewise the differential temperature should be plotted vs. the bath temperature, which is the standard DTA graph.

Cooling scans were also possible. The cooling was achieved by placing a sauce pan under the temperature bath after the heat run. By turning off the heat and gradually adding water, and later ice, to the sauce pan one can provide a cooling profile with a

sufficient degree of control to obtain useful results. However, our approach required the transfer of the beaker full of very hot oil into the sauce pan between the heat-up and cool-down cycles. We are reluctant to suggest the cooling experiments for student use until a safer procedure has been refined. However, the data will be included here to show the potential for both heating and cooling.

Calibration and sample preparation:

In order to get a baseline calibration on the performance of the apparatus it is valuable to start with a simple crystalline compound where the melting point and expected thermal behavior are known. This calibration will serve to provide a measure of the accuracy of transition temperatures and also provide a basis for the student to begin their understanding of the physical principles involved and how to interpret the onset of transitions. Stearic acid was selected for having a melting point ($\sim 70^\circ\text{C}$) close to the range of interest as well as for its low cost. Technical grade (Alfa, 90+ %) was purchased to minimize cost and seemed to have a sufficiently sharp melting point for calibration purposes ($69\text{-}71^\circ\text{C}$ on data sheet). An independent determination of the melting was measured using a ____ MP apparatus and found to be 70°C .

Sample preparation

Both the reference and sample tubes should be filled to a level equal to or slightly below that of the oil in the beaker. The reference tube is filled with the same vegetable oil as the bath. Place the tubes in the wooden holder to determine the appropriate level based on your bath; use only about 175 ml of oil in the beaker to allow headroom for stirring and volume expansion on heating. The powdered stearic acid should be added to the sample tube to a height of about 2 cm. above the desired level as the powder's volume will shrink by 30-40% as the particles melt and consolidate. A hair dryer can be used to melt the stearic acid in the test tube consolidating the powder into a liquid which will form a solid crystalline mass on cooling. This should be done before beginning the actual experimental scans. {Additional powder can be added to bring to the same approximate level as the oil in the reference tube.} The differential thermocouple should be paced in the sample and reference tubes while the sample is still liquid. Because this is a differential method, the thermocouple junctions should be immersed to the same level and preferably below the midline of the sample and reference volumes. Allow the sample to cool completely before immersing into the oil bath and beginning the first heating scan.

Beginning the Scan:

After the sample has cooled, immerse the test tubes in the bath and turn on the stirring bar. Note the sample appearance of the sample when viewed through the oil bath; you will want to be aware of any visual changes during heating. We often observe that the solid sample usually appears much narrower than the test tube itself when viewed through the oil. This optical illusion occurs because of an air gap at the interface between sample and test tube often formed as re-solidified sample shrinks and detaches from the test tube on cooling. This will provide a useful indicator for the onset of melting, when the air gap disappears and the sample appears to widen.

During the heating record any visual changes in the sample, especially the onset of melting as the molten sample first fills the air gap between the test tube and the solid sample. Other useful observations are the temperature at which the solid falls from the thermocouple and the temperature at which the last solid melts. The ability to visually observe the sample during the heating process is clearly one of the distinct advantages of this simple, transparent apparatus.

Before turning on the heat begin taking some base line temperature and ΔT data. Once you have established a baseline (about 1 minute) turn on the heat, recording the time and temperature at which the heat began. (If you have not previously determined the appropriate heater setting for your desired scan rate then begin with a midrange value.) Continue recording time, bath temperature and differential temperature (or voltage). A heating rate of 5-10 °C per minute is the recommended for the scan rate, the lower the rate the closer the sample's approach to equilibrium with the bath. Of course, this is at the expense of taking longer to run the experiment and at having a smaller differential temperature. Experimentation and experience are the best means to determine the parameters appropriate for your apparatus and your patience. Continue the scan until the solid has melted completely and a flat baseline for the liquid state is established (120 C used here).

Results:

Both the differential temperature ΔT and bath temperature T vs. time are plotted real-time as they are logged in by our data logging software. Example data for our stearic acid sample are shown in the figure below.

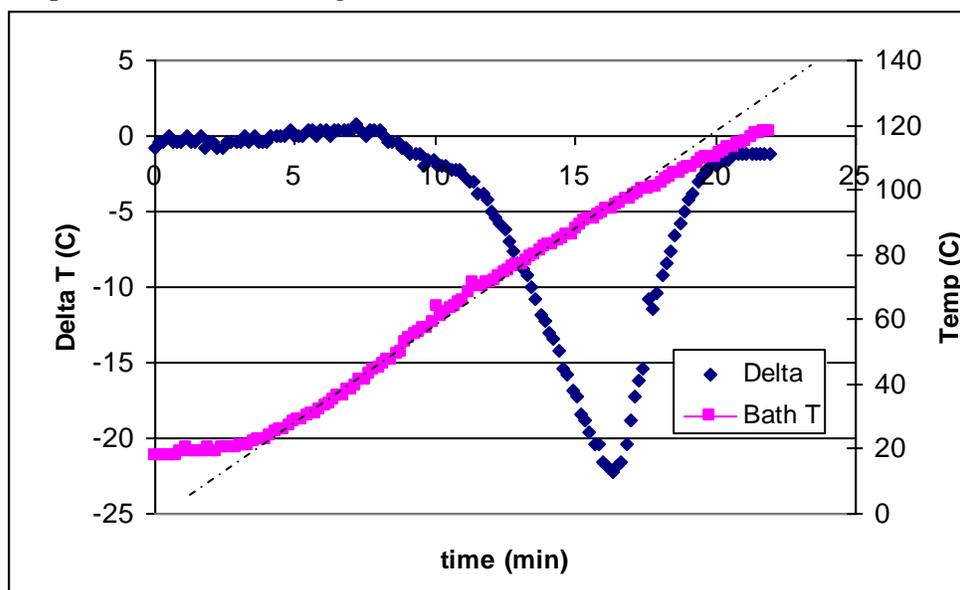


Figure 4. Temperature and Delta T vs. time for the Stearic acid reheat scan. Note that the heating rate is fairly constant over most of the scan. Measured heating rate = 5.2° C/min.

Some additional details:

The bath temperature shows a relatively uniform heating rate of approximately 5.2° C per minute for most of the heating scan. {There is a slight reduction to this uniform heating rate above 110° C but this is of no significant effect on the DTA response.}

At the heat setting used here (producing 5° C/min) it takes about 2.5 minutes after the heat is turned on before the bath temperature begins to rise. (This thermal lag is a consequence of the appreciable thermal mass between the heating element and the bath thermocouple, but this lag is of no special consequence for our measurements.) It typically takes another 1.5 minutes on average before a response in the differential temperature (ΔT) can be detected. This latter sample lag will depend somewhat on the position of the thermocouple within the test tube and will be shorter the closer the thermocouple is to the test tube wall as well as for a higher heating rate.

In the scan shown the on-set of the differential response is not very obvious. The pre-exotherm region is sensitive to the thermal history of the sample and can even have an initial exothermic excursion if the previous cooling did not allow full crystallization (more on this later). In this particular scan one can see a slight trace of such an exotherm.

A more noticeable change in ΔT for this sample begins above 40° C. The differential temperature curve in the time plot shows a clearly defined endothermic peak associated with the absorption of heat during the melting of the crystalline phase. This peak begins at about 70° C where the sample appears to “widen” as the initial melt fills the gap.

Note that the sign of the ΔT is negative for the endothermic melting event because we have connected our thermocouple pair to record $T_{\text{sample}} - T_{\text{ref}}$. This is the most common convention, although the opposite sign convention is also used and one must always be careful to note the direction of the endothermic event. If you observe the crystallization peak to occur in the opposite (upward) direction, it is recommended that you check and reverse the connection of your differential leads to maintain the same convention.

Conventional DTA represents the data as a plot of the differential temperature (ΔT) vs. the bath temperature as shown in the figure below. Because of the lower heat capacity and thermal conductivity of the solid compared to that of the liquid in the reference, the sample temperature is expected to be below that of the reference during the initial heating. This explains the region of low negative slope above 40 C. The melting point is marked by the kink in the slope of the DTA curve where the endothermic melting peak begins. It is determined by extrapolating the linear regions above and below to their intersection as shown in the figure. The 70° C extrapolation is in excellent agreement with the manufacturer's reported range of 69-71° C. Repeat scans on this sample provided consistent results for the onset of crystallization; four separate scans ranged from 69-71 in spite of some significant differences in their pre-exotherm region behavior (which is dependent on thermal history).

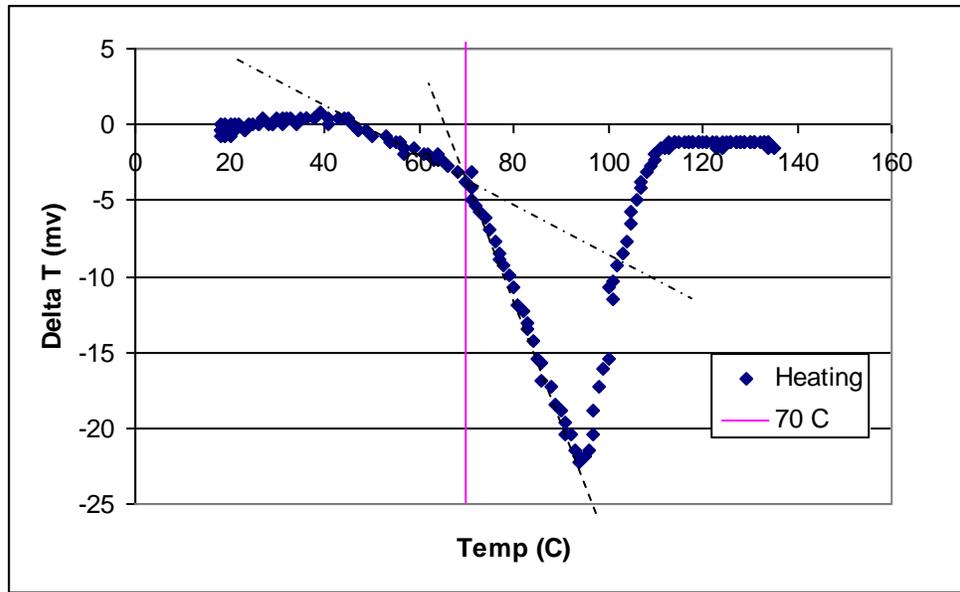


Figure 5. Heating DTA curve for reheated stearic acid (#28) at 5.2° C/min.

As mentioned previously, one can visually note the onset of melting through the widening of the sample resulting from the initial melt filling the test tube /sample air gap. Another interesting observation is that, as the solid melts, it eventually breaks free from the thermocouple. When this occurs we always observe a differential temperature jump similar to the one shown here at about 99° C. Once the entire crystalline solid has melted the ΔT trace flattens, usually at zero. The non-zero value in the scan shown here was due to the thermocouple moving upward in the solution on melting, where the solution was in fact slightly cooler.

We also recorded the cooling traces for the above sample using the sauce pan and filling with water and ice as described previously. This data provides some additional insight and interpretation for the heating data. Note the constant and near zero value of the differential temperature of the cooling curve above 60° C. There is a slight jump at about 115° C where the thermocouple was repositioned to match the reference sample, illustrating the significance of thermocouple placement. More important is the exothermic crystallization peak that occurs at 60° C, considerably below its equilibrium temperature. It is this non-equilibrium super cooling that accounts for some of the variation observed on heating prior to the melting endotherm. With this much super cooling it is likely that some of the mixture does not achieve the full equilibrium crystalline state, but gets frozen in at the lower temperatures. And this small non-equilibrated part may again begin to crystallize as the sample is reheated, producing the initial slight rise in ΔT observed in many re-heat runs.

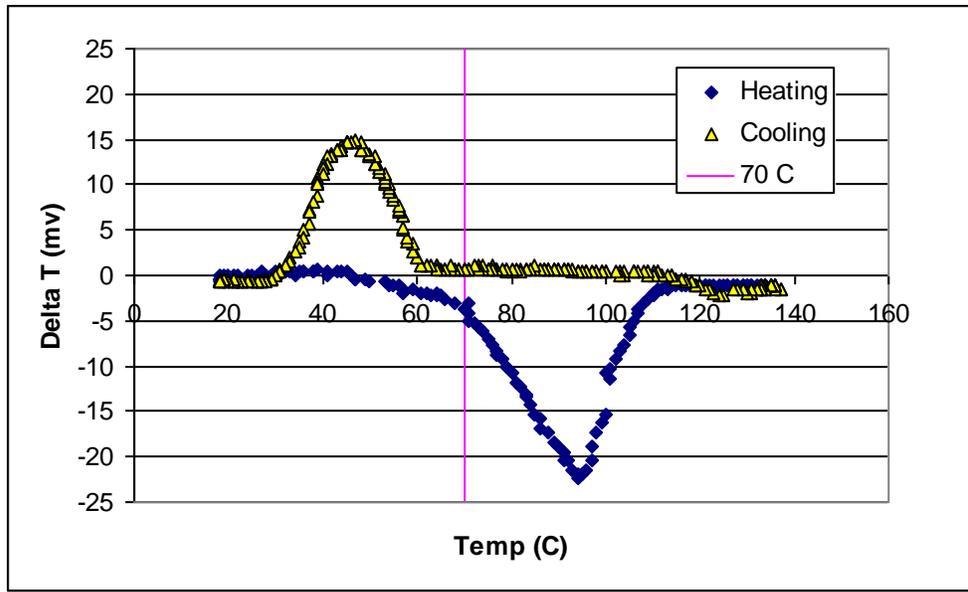


Figure 6. Heating and Cooling rate data for the stearic acid calibration sample.

Plotting vs Sample Temperature:

It should also be noted that the temperature of the sample can be quite different (usually lower on heating) than the oil bath due to the differential offset. This needs to be taken into account when comparing onset of crystallizations where the measured ΔT at the downturn is appreciable. Using the data in Excel format it is easy to correct for the offset by simply plotting the ΔT vs. the sample temperature, which can be estimated as $T_{\text{sample}} = T_{\text{bath}} - \Delta T$. In the figure below we plot the differential temperature vs. the sample temperature using this approach and one can see a striking difference between this and figure 5. The onset of crystallization remains much the same but the drop after reaching the maximum ΔT is much sharper.

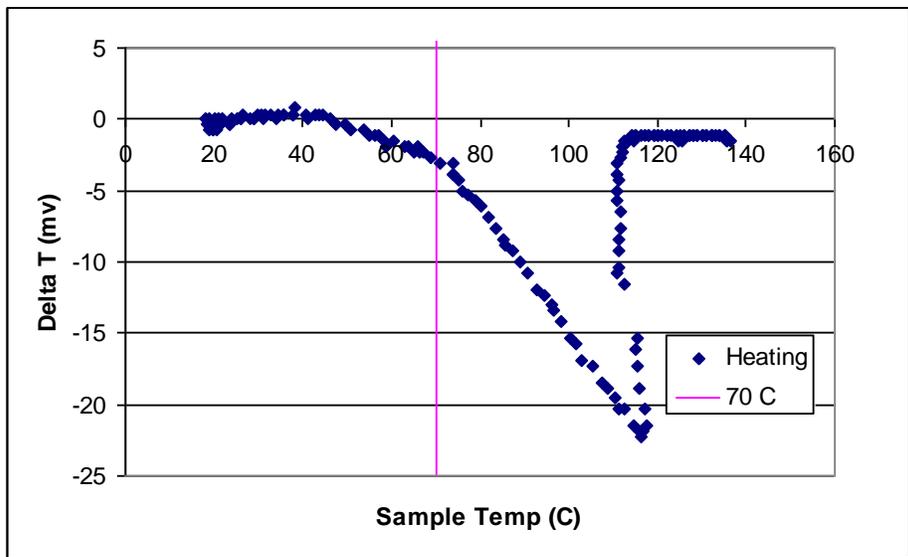


Figure 7. Same stearic acid heating data shown in figure 5, but with actual sample temperature as the abscissa rather than bath temperature.

Using the DTA to measure glass transitions in candy glass

In our final section we will show some results for a simple glassy material made for sugar, our candy glass, a.k.a. hard candy. A much more complete description of the glass transition phenomena and the materials will be given in Part 2 of this series, however, I would like to present some of the interesting results here.

Candy Glass

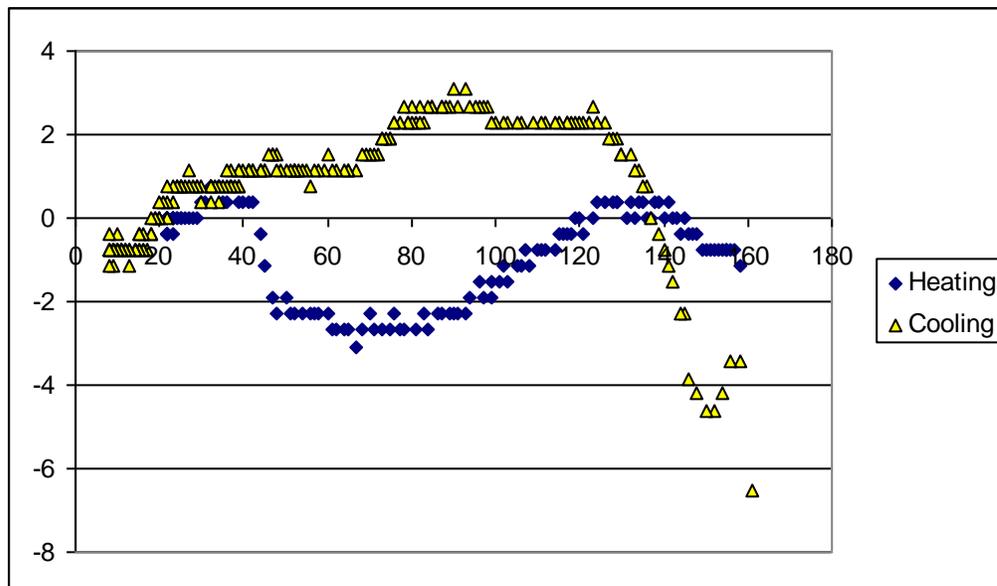


Figure 8. Heating and cooling scans taken during the initial phase of experimenting with the candy glass materials.

The figure above shows some of our initial results using candy glass samples. The glass transition was indeed observed in this and other samples. In this case it is associated with the abrupt step down that occurs near 40° C. However, several problems plagued the measurements. The major issue was an enormous run to run variation of the results, especially in the heating scans. Inconsistent behavior at lower temperature was especially problematic as it often obscured the Tg entirely. The other concern was the appreciable amount of noise in the ΔT data compared with that of the stearate sample, likely owing to smaller signal size.

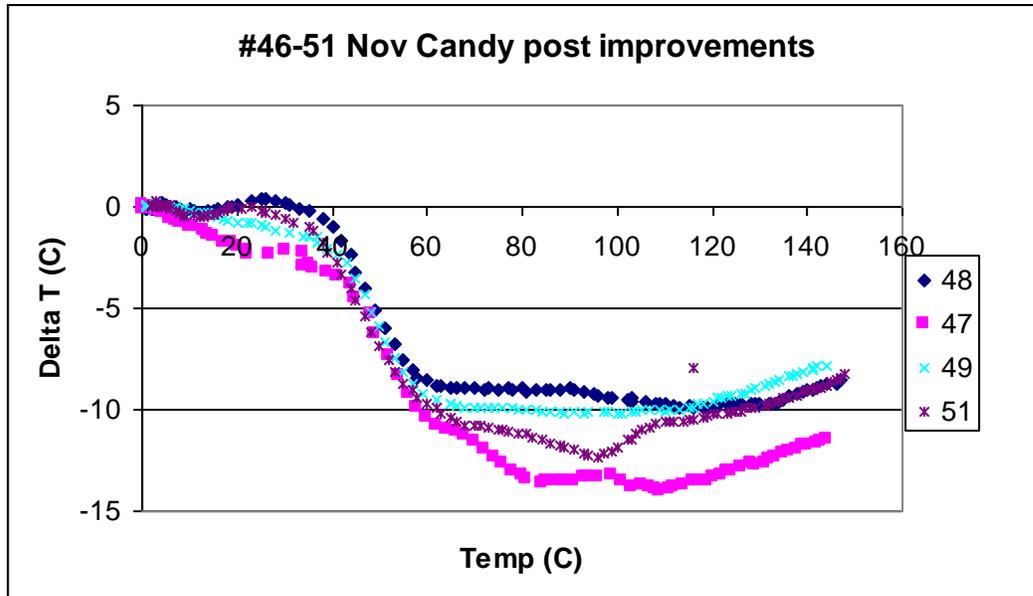
Three important improvements were a) understanding the considerable impact prior thermal history can have on the DTA of a candy glass.

b) learning how to control the sample history to obtain a good glass transition trace and

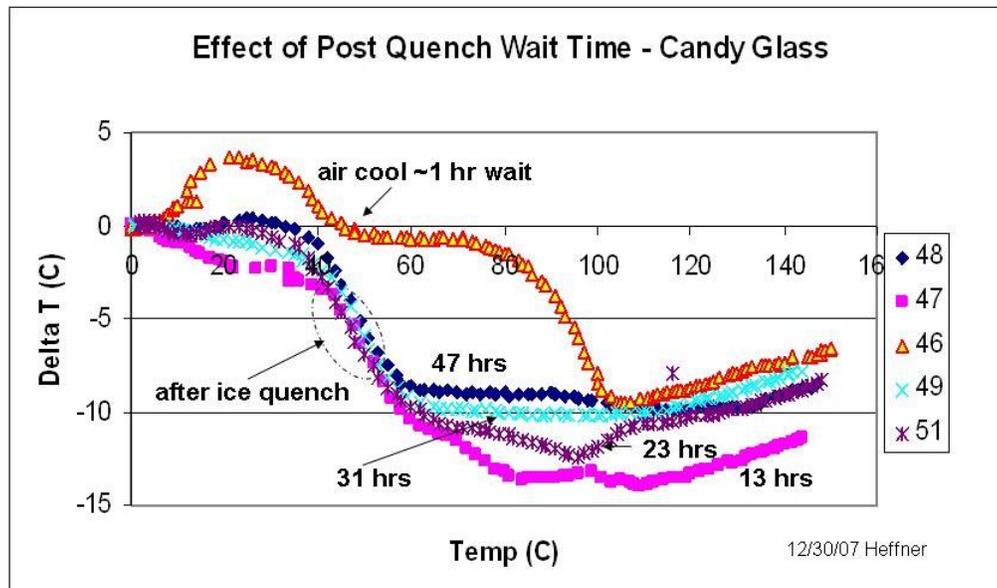
c) modifications to the apparatus for improved signal quality.

But these will be the details explained in the next chapter of this story. For now I leave you with the results from one of my last series of scans on the same candy glass. All show similar behavior with a nice Tg signature and in fact even the differences can be

explained by differences in thermal histories. You will need to read on to get the rest of the story.



A partial answer for those who can't bear to wait.



Appendix 1: Design for wooden test tube holder:

