Experiment 7. Material Characterization with Differential Thermal Analysis (DTA)

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Abstract. Importance of including thermoanalytical techniques in the analytical chemistry curriculum is growing due to increasing demands to characterize materials. Our objectives include generating thermograms that show changes in thermovoltage due to changes in phase or structure. Results include melting points for Indium (155C), Crystalline Paracetamol (170C), and Cryatalline Glucose (150C).

I. INTRODUCTION

Importance of including thermoanalytical techniques in the analytical chemistry curriculum is growing due to increasing demands to characterize materials. One particular technique, called DTA, provides information regarding structural changes, phase transitions, and chemical reactions.[6]

DTA stands for differential thermal analysis. It is a technique used to characterize samples based on temperature differences between two materials. In this case one is used for reference and the other is analyzed. Main premise for this technique is based on the existence of two thermocouples connected to the same voltmeter.[1]

Each thermocouple is placed within the reference and the material to analyze. Given the fact that one material is inert, phase changes that occur on the other sample will be recorded as deflections of the voltmeter. This occurs because the input of heat will raise the temperature of the inert substance, but be incorporated as latent heat in the material changing phase.[2]

In order to handle data acquisition and display measurements in real time a program written with LabVIEW was made by the authors of reference [6]. This computer-based instrument panel is more affordable compared to commercial instruments, making DTA measurements accessible to undergraduate laboratories such as ours with sufficient sensitivity for our purposes. So in order to measure phase changes from glucose, paracetamol and sulfur we used the equipment and techniques further developed by them (shared by the university). The setup is shown in figure 1.

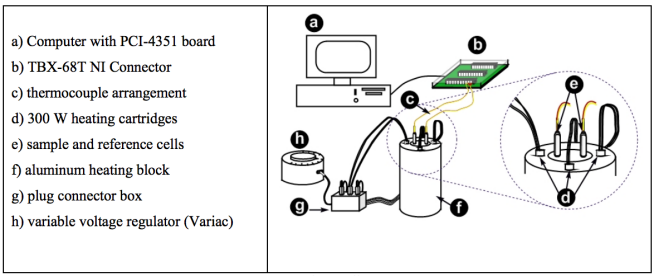

FIG. 1: Graphic schematic for the university DTA apparatus

The data that is displayed in real time is also saved in ASCII code and can be further analyzed using graphing software, in our case Matlab. Our objectives include generating thermograms that show changes in thermovoltage due to changes in phase or structure. This shall then be compared to changes reported in the literature for this materials.

II. EXPERIMENTAL PROCEDURE

During the session two temperature measurement experiments were done. Universities DTA equipment is able to measure the temperature difference of two samples simultaneously, therefore experimental data for 4 samples were created. Materials used for the analysis were crystalline paracetamol, crystalline glucose, amorphous paracetamol and amorphous glucose. Indium and sulfur were used as references. For each sample, thermocouples had to be sealed within the sample's glass tube as indicated within figure 2.

100 mgr Sulfur, glucose and paracetamol glass tubes were made. Prepared samples were then inserted within DTA's heating block and variac was adjusted to create a 10 C/min heating rate. Measurement recorder was connected to a real-time logger interface created by L. M. Martinez.[3] Session one, containing indium as reference and paracetamol and glucose as analyze samples lasted 18 minutes (enough time to head from 37 to 200 degrees C).After the first session the heating block (containing both samples) was promptly cooled down using dry ice until its temperature reached around -40 C. Session two

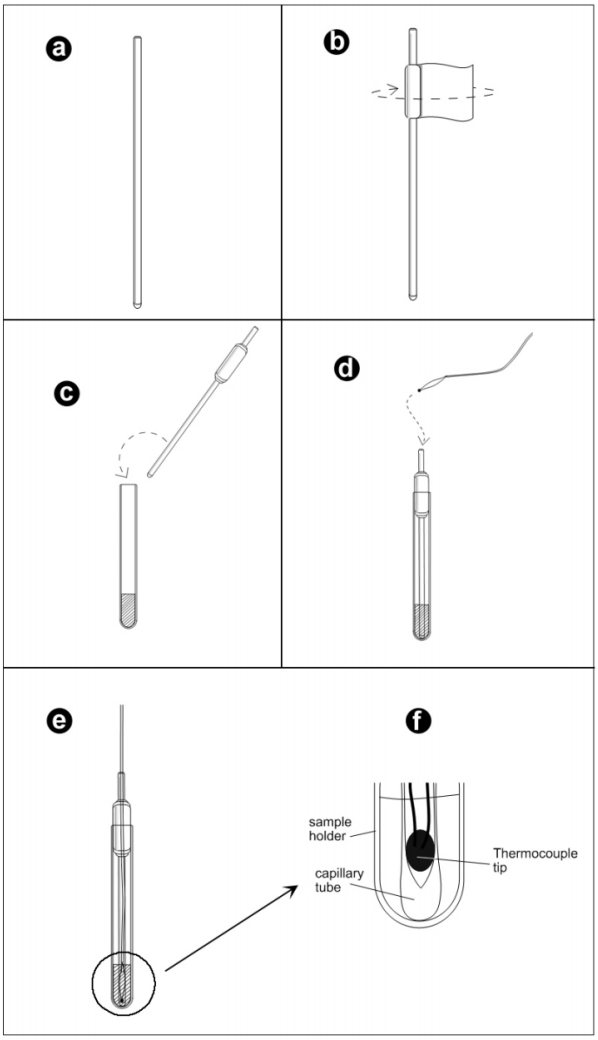

FIG. 2: Graphic schematic for the university DTA apparatus

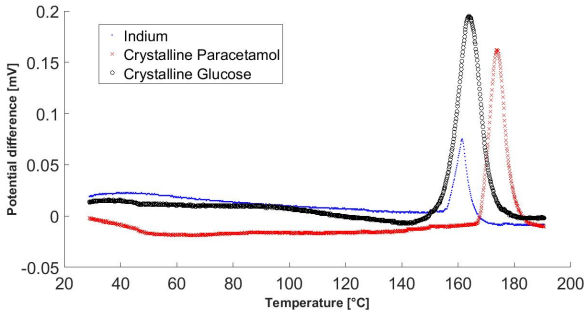

FIG. 3: Thermovoltage vs Temperature curves obtained using DTA equipment provided by lab instructor for Indium, Crystalline Paracetamol, and Crystalline Glucose.

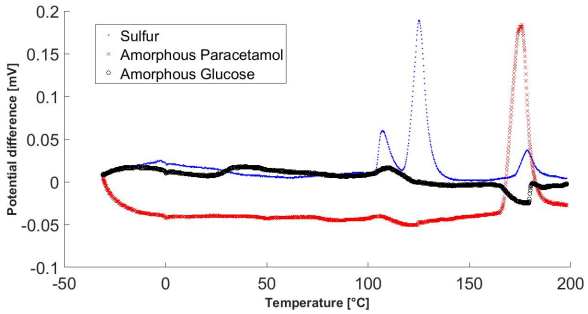

FIG. 4: Thermovoltage vs Temperature curves obtained using DTA equipment provided by lab instructor for Sulfur, Amorphous Paracetamol, and Amorphous Glucose.

contained sulfur as reference and previously frozen glucose and paracetamol as analyze samples. experiment 2 lasted 25 minutes to give enough time to heat from -40 to 200 C.

III. RESULTS

A. Thermograms

Using the ASCII files and a simple program in Matlab that displays values of thermovoltage against temperature the thermograms in figures 3 and 4 were prepared. Features of this program included labeling, scaling, and selecting symbols used for the scatter plots.

B. Determination of Phase Transitions and Structural Changes

In order to know where the phase transitions and structural changes exactly occur, code was used in Matlab to determine accurate starting points in the peaks.This code analyzes the data gathered that was stored in a matrix and it plots the thermovoltage vs temperature graphs. Once the graphs are shown it is easy to determine around which numbers the start of the reactions are. The vertical lines shown in figure 5 were displaced changing values arbitrarily.

The following table shows the starting values registered.

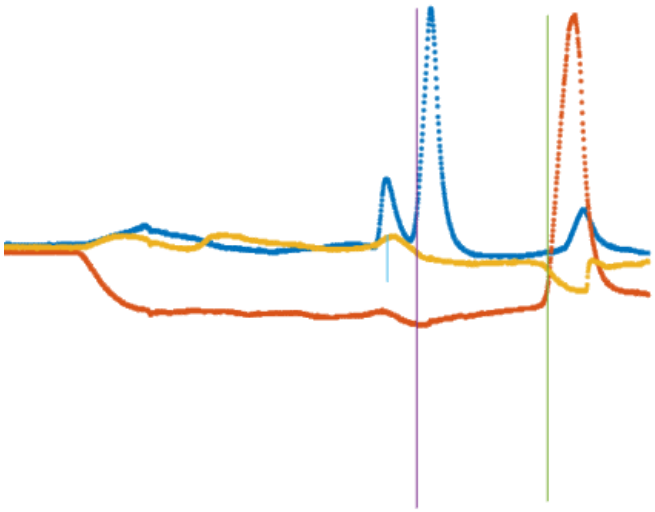

FIG. 5: Demonstration of the vertical lines ploted by the code that were modified in position arbitrarily to find an approximate start of transitions. No axis are shown as this graph only served the purpose of making a better estimation than the naked eye.

TABLE I: Phase transitions and structural changes starting temperature for each substance. Only notable peaks were included.

Substance	Melting[C]	Transitions[C]
Indium	155	x
Crystalline Paracetamol	170	x
Crystalline Glucose	150	x
Sulfur	120	103(glass),175(recryst.)
Amorphous Paracetamol	170	x
Amorphous Glucose	100	170(cryst.)

IV. DISCUSSION OF RESULTS

A. Concerning indium

Indium has a melting point of $T_m = x156.6^oC$. This is consistent with the first test (Figure 3), since the point can clearly be seen.

B. Concerning paracetamol

According to [6], crystalline paracetamol has a melting temperature $T_m \approx 170^oC$. After rapid cooling and reheating the formation of amorphous paracetamol was expected. This had a expected glass transition at $T_g \approx 21.4^oC$, a recrystallization point at $T_c \approx 76^oC$ and again the melting point at $T_m \approx 170^oC$. [6]

In Figure 3 T_m is readily clear. Now, in Figure 4 a glass transition point is not distinguishable at the expected place of T_g. However, it can be argued that the recrystallization point T_c is present since there's a "dip" at that temperature. Again, the melting process happened where it should be. It'll be clear when dealing with the amorphous substances their thermograms, Figure 4, appears to be "noisy", when compared with Figure 3. The team believes that this could be related to the cooling and reheating process. The cooling process may not have been fast enough and other allotropes may have formed along with the expected amorphous materials.

C. Concerning glucose

The melting point of glucose is at $T_m = 146^oC$. According to Simperler2006, a glass transition should be expected at $T_g \approx 52^oC$. This is consistent when dealing with crystalline glucose (Figure 3) but not with amorphous glucose (Figure 4). This behavior can't be explained by the team, as it was completely unexpected. Caramelization of the experimented after the first procedure may be to blame.

D. Concerning sulfur

Sulfur has a phase transition at 98 from alpha to beta-sulfur. The melting point was expected between 114 and 119^oC. It could be argued that this is seed in Figure 4, but with a clear shift to the right. The team couldn't find an explanation for this particular result.

V. CONCLUSION

During this experiment we reported thermogram data for glucose and acetominophen in amorphous and cristalline structure along with indium and sulfur as DTA reference samples. Phase transition data was consistent overall with exception to glucose in amorphous form. We expect this to be a measurement mistake originated from incorrectly adding the thermocouple to the sample's glass tube. Internal structure transitions were reported for sulfur at 98 C, glass transition at 52^oC from glucose and from paracetamol at 170^oC. Due to data quality from paracetamol's thermogram both transition and recrystallization points were difficult to find. Nonetheless, they are still perceivable. Results were consistent with literature [2][6] Differential Thermal Analysis is still used nowadays in the characterization of materials. It is combined with other techniques such as thermogravimetric analysis, and thermomecanical analysis and differential scanning calorimetry for several applications such as crystallization time, phase changes, cure parameter estimation and so on.

VI. REFERENCES

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