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Commissioning a Pyris 6 Differential Scanning Calorimeter

by

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Abstract

The object of this project was to commission a Pyris 6 differential scanning calorimeter, or DSC. The DSC unit in question had been unused and unattended for a significant period of time, and so it was necessary to conduct research to find the necessary equipment, then purchase, install, and test that equipment. The subsequent test of this system showed that the system provides accurate measurement of temperature and heat flow, the two main quantities recorded by the analyzer of the DSC, within an acceptable margin of error. This paper also provides a selection of suggestions for proper operation of the system, based on a review of the available literature and manuals for this equipment and the judgement of the experimenter. Finally, this paper provides a small amount of guidance for conversion of the system to the subambient mode of operation, as this project was conducted entirely in the ambient mode.

A large amount of information for this project, and its future applications, is drawn from an operation manual for the Pyris 6 DSC. For the convenience of the reader, a link to this document is provided in Appendix A.

Background

What is a Differential Scanning Calorimeter?

Differential scanning calorimetry is a technique that "measures the energy transferred to or from a sample undergoing chemical or physical change" [1]. This can be used to analyze countless materials, from metals, to polymers such as plastics and resins, and even food. Differential scanning calorimeters measure the temperature of a sample, the heat flow in the sample, and the time. These are generally represented in a single graph of Heat Flow vs. Temperature, which shows the endothermic and exothermic reactions that occur at certain temperatures [2]. An endothermic reaction is a reaction in which the reactant absorbs heat from its surroundings. Examples of endothermic reactions including the melting of metals or the transition from a brittle state to a ductile state at the glass transition temperature (Tg) of polymers. An exothermic reaction is a reaction in which the reactant releases heat to its surroundings. Examples of exothermic reactions include the freezing of metals or the transition from a ductile state to a brittle state at the glass transition temperature of polymers. The information collected by DSCs can be used for many purposes depending on the goals of the researcher. These purposes include, but are not limited to, determining the melting points of materials, observing solid state transitions, and studying the heat capacity of a material as it relates to temperature.

Background and Terminology for the Pyris 6 Differential Scanning Calorimeter

The Pyris 6 DSC is a heat-flux differential scanning calorimeter manufactured by Perkin Elmer, one of the leading manufacturers of lab equipment of this type. Its operating conditions allow temperatures between -120°C and 450°C, with ideal operating temperatures between -30°C and 250°C [3,4]. It has a sensitivity of 0.6 μW, and a dynamic range of ±250 mW. These conditions make it ideal for the analysis of polymers and liquid crystal materials, although it can also be used for metals with low melting points, such as the Zinc reference material tested in this project.

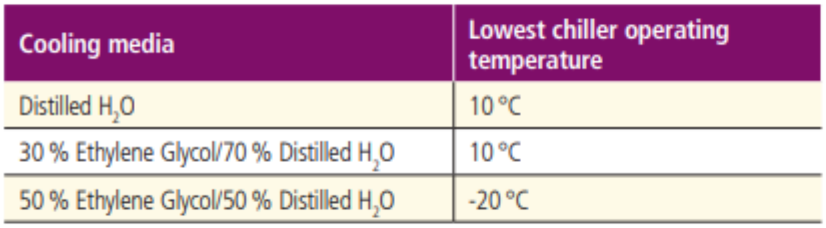
The DSC's system is made up of four essential components. The first of these is the analyzer shown in Figure 1, which serves as the main component of the calorimeter. It contains the furnace where the sample is heated, as well as the electronics necessary to measure the temperature of the sample and the heat flow, the cooling system, and the purge gas system.

Figure 1: A Pyris 6 DSC analyzer [5].

The second component is a computer; or rather, the Pyris Manager software installed on that computer. This software connects to the analyzer through the COM1 serial port on the computer and is used to program, start, stop, monitor, and record all experiments conducted using the DSC.

The third component is the chiller shown in Figure 2. The chiller is a recirculating bath of coolant, connected to the analyzer by a pair of hoses. Multiple coolants are acceptable, as listed in Table 1; the recommended coolants include water and a range of water-Ethylene Glycol mixtures, depending on the desired minimum temperature of the device [6]. For use at the laboratory here on campus, distilled water was chosen as the coolant.

Table 1: A table of acceptable coolants for the Pyris 6 DSC and their lowest operating temperatures.



Cooling media	Lowest chiller operating temperature
Distilled H_2O	10 °C
30 % Ethylene Glycol/70 % Distilled H_2O	10 °C
50 % Ethylene Glycol/50 % Distilled H_2O	-20 °C

Figure 2: A Perkin Elmer chiller, compatible with the Pyris 6 DSC.

It is important to know that the lowest operating temperature of a given coolant does not necessarily reflect the lowest operating temperature of the device. The DSC has two modes of operation, ambient and subambient. The chiller is used in ambient mode, and in ambient mode, the lowest operating temperature is room temperature. So, in order to operate an analyzer being cooled with distilled water at 10°C, the surrounding environment must be cooled to that temperature as well.

The last essential component for ambient operation is the purge gas. A purge gas is used when operating a DSC in order to provide an inert environment that surrounds the samples, eliminate thermal "hot spots" that may disturb heat flow, aid in more efficient heat transfer, and aid in the cooling of the system [7]. For the Pyris 6 DSC, the purge gas used is nitrogen with a minimum purity of 99.9%. This purge gas is connected to the analyzer through a system of tubing, the configuration of which depends on the type of operation desired.

Figure 3 shows an image of the actual purge gas setup from this project, including the regulator and flow restrictor.

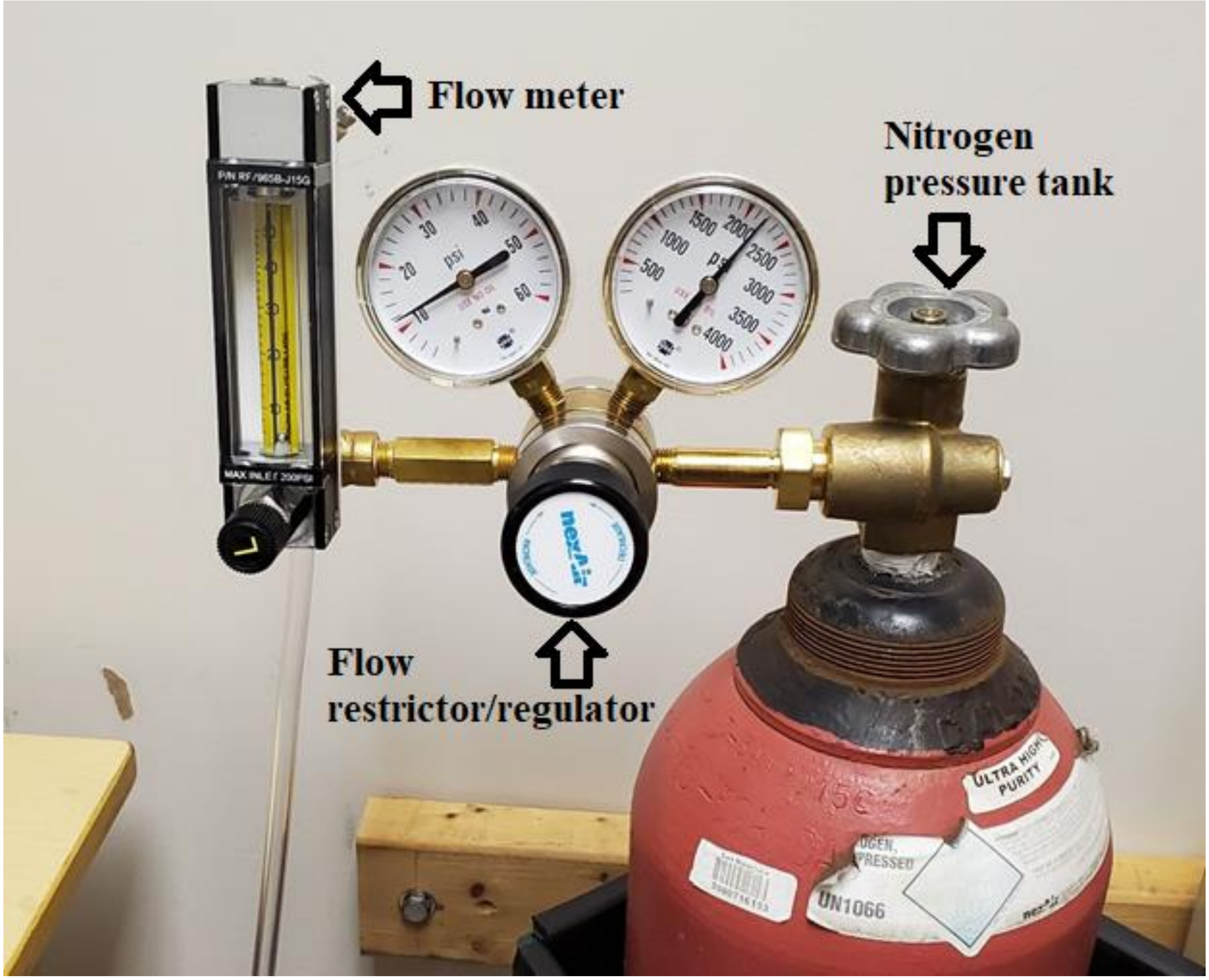


Figure 3: The nitrogen dry purge gas with regulator and flow restrictor.

While not a part of the DSC system, it is important not to forget the sample itself. This sample can be nearly any material, but will generally weigh between 1 and 30 mg depending on the material and test being performed. The sample pan it sits in is generally made of aluminum or ceramic, and is selected based on the maximum temperature of the test being performed and the volatility of the specimen. Figure 4 shows a small, unweighed Zinc sample (≈1 mg) in a standard aluminum sample pan on the left, and an empty reference pan, also made of aluminum, on the right.

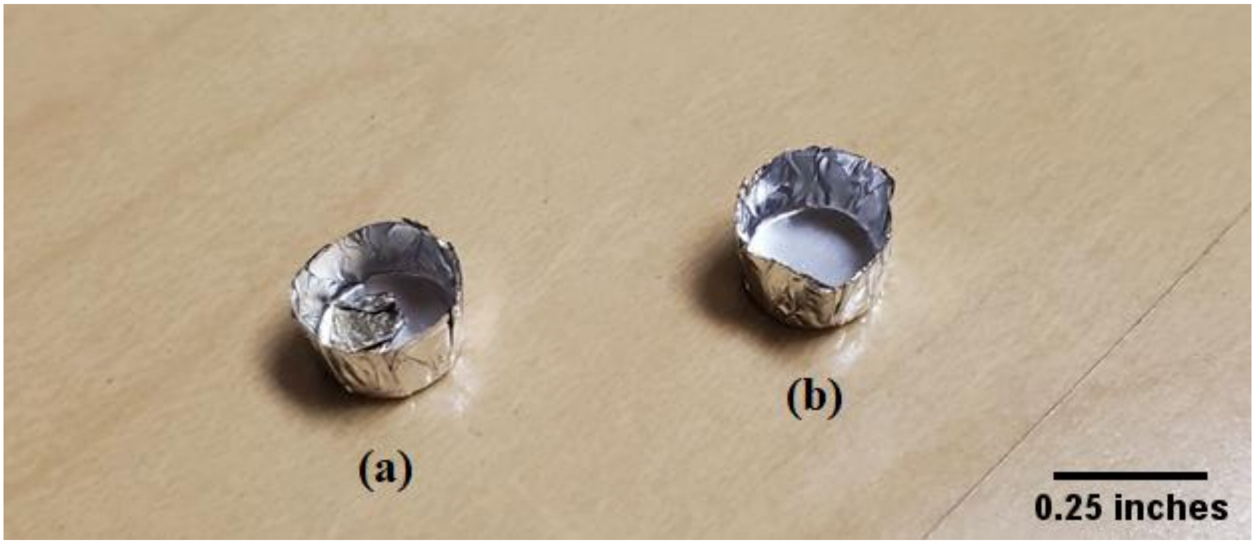


Figure 4: The Zinc reference sample tested in this project (a) and an empty reference pan (b).

Purpose of this Project

The purpose of this project was to commission, or bring into working condition, a Pyris 6 Differential Scanning Calorimeter (DSC), located in the Olin B. King Technology Hall building (OKT.) This particular unit had been in the possession of UAH for several years, and this project was undertaken at the request of my Capstone director and boss, Dr. Judith Schneider.

The long-term benefits and significance of this project were mostly educational in nature. In part, I refer to my own education - I learned quite a few things over the course of this project.

In general, though, I'm referring to graduate studies here at UAH; Dr. Schneider intends to use the DSC as an educational tool for graduate students taking MAE 577, or Experimental Methods. A significant portion of this class is an introduction to new tools and techniques that the students may not have otherwise been introduced to, and the commissioning of this device into something useable will add valuable experience to their repertoire. In addition, this calorimeter could be useful in the study of transitions in polymers or resins, such as the glass transition (Tg), or the point at which polymers experience a transition from a brittle state to a ductile state.

There is currently one other DSC present at UAH in the possession of Dr. Banish. However, that DSC is not immediately available for students and not in ready-to-use condition due to the lack of essential supporting equipment. In addition, the availability of a second machine would still be beneficial due to the chance of failure or other unexpected outages in the first.

The OKT DSC had been left unattended for several years, and was likely not used between its acquisition by UAH faculty and the completion of this project. Before I became involved in the project, the accompanying software for the device had been purchased and installed on the laboratory computer, and a nitrogen tank and chiller had been acquired for the system. My task was to research the system, determine what, if any, software or hardware was missing, install the missing components, determine best practices for running the system, and test the system's functionality.

Methods and Results

Preliminary Research and Preparation

The first step of this project was to research the machine I'd be using in order to ensure that the equipment and software that had already been acquired were sufficient to run the system. Few resources were available regarding the proper operation of the DSC, as its original documentation had been lost, and by far the most useful resources in this portion of the project were the Pyris Installation Help Guide, included as part of the software package for the system, the Perkin Elmer Pyris 6 DSC manual, retrieved from a third-party vendor website, the advice of Stanley Head, a Perkin Elmer employee, and the advice of Dr. Schneider, who had familiarity with the intended functionality of the system.

This preliminary research revealed a few optional pieces of software and hardware that were compatible with the system, including a software package that provides additional security to the system; a filter dryer and liquid nitrogen, both of which are only necessary for subambient operation, or operation in the range of -120°C to 200°C; the Thermal Analysis Gas Station, or TAGS, which allows one to use multiple gases as the purge gas; and the autosampler, which attaches to the top of the analyzer with the help of a service engineer and helps to automate the Pyris 6 DSC. It was determined that none of these items were necessary for basic operation of the DSC and that the upgrades would not be used or useful enough to justify the cost and effort of locating, purchasing, and installing them at this time, so the system was left as-is in this regard.

A few minor parts did need to be ordered for the DSC, including a regulator, an SS-200-7-2 Swagelok tube fitting (with a ⅛" tube nut on one end and a ⅛" female NPT thread on the other end), and a set of aluminum sample pans sourced from Perkin Elmer to be compatible with this device. As the various equipment arrived, the regulator was attached to the nitrogen tank, the gas was hooked up to the cell purge and purge A lines, the connection was completed using the ordered Swagelok fitting, and the remainder of the system was cleaned, checked for obvious defects (of which none were found), and prepared for use. In addition to small hardware fixes, the analyzer was connected to the computer with all other systems turned off, connected to the system, and given a unique identity in the management software for easy use in the future.

The next step was to continue researching to determine the best practices for operation of the device. There was no operation guide provided and the manual available was for a slightly different model, but based on the part descriptions and specifications provided and a few educated guesses, both by myself and my my Capstone director Dr. Schneider, the following detailed operation checklist was developed:

It should be noted that, in ambient operation, the Pyris 6 DSC is only capable of reaching temperatures from room temperature to 450°C. This means that, in this mode of operation, the start and end conditions should never be set below the current temperature of the room. For easiest operation, a starting temperature of roughly 5°C or more above room temperature is recommended; 30°C is one example of an acceptable number.

Operational Guidelines

- Shave or clip off a small piece of the test sample.
    - This piece should have a mass of 5 to 30 mg for normal use, or 0.5 to 1 mg for a sample that has not yet been investigated.
- Weigh the empty sample pan and record its mass.
- Add the sample to the pan, weigh, and record its mass. Find the difference in mass to find the mass of the sample.

- Crimp on the lid of the sample pan using the standard sample pan crimper press.
- Open the sample holder (outer and inner covers on the top of the analyzer) and use tweezers to place the sample in the left-hand divot.
- Add an empty sample pan to the right-hand divot as a reference.
- Close both covers of the sample holder.
- Ensure that the analyzer is connected to the COM1 port on the computer.
- Open the top compartment of the chiller (a large square door) and ensure that the inside is clean.
- Fill with approximately one gallon of distilled water. (Non-distilled water can be used if necessary, but distilled is preferable.)
- Close the top compartment of the chiller.
- Ensure that the Nitrogen gas is connected to purge A and the cell purge.
- Open the gas valve using the silver knob on the top of the gas tank, then use the black, front-facing knob to set the flow rate between 20 and 40 cc/min, unless otherwise specified, such as during a baseline correction process. The ideal flow rate for most processes is 20 cc/min.
- Turn on the chiller by first flipping the power switch in the back, then pushing the power button in the front.
- Turn on the analyzer using the power switch in the front.
- Turn on the computer and start the Pyris Manager software.
- Click the second button on the screen, labeled Pyris 6 DSC.

- Go to the Sample tab of the Method Editor interface that appears. Enter the sample ID, the operator ID, any comments on the sample or the test, and the mass of the sample as calculated earlier. If desired, change the file destination.
- Go to the Initial State tab. Enter the desired initial temperature and heat flow.
- Go to the Program tab. Program the desired operation for the sample.
    - The maximum heating rate of the system is 100 °C/min. However, a much slower heating rate is generally preferred, especially near temperature states at which a reaction is expected to occur, in order to prevent overshoot and minimize lag between the system and sample temperatures.
    - Keep in mind that the analyzer will only allow temperatures between -120°C and 450 °C. However, these temperatures do not reflect the actual temperatures attainable by the system. In subambient operation, the system can reach temperatures between -120°C and 200°C. In ambient operation, the system can reach temperatures between room temperature and 450°C.
    - The start and end conditions may be set to any temperature near room temperature; however, these temperatures should be at or above the resting temperature that has been programmed into the device in the Preferences tab.
    - The remainder of the process depends on the material used and the desired testing operations.
- Go to the View Program tab. Ensure that all parameters are set to the desired values.
- Ensure that the gas flow rate is still within the desired range.
- Press the Start/Stop button, which is a large rectangular button set in the DSC 6 Control Panel on the far right side of the screen.

- Wait for the test to end. The length of the test will depend on the test parameters set by the operator; however, it’s a good idea to expect to spend at least half an hour to an hour on most tests.
- After the test has finished, the data can be saved by using the File>Export option and exporting the test files as an Excel file to a flash drive.
- Allow the analyzer and test sample to fully cool before shutting down the equipment.

This checklist may seem excessively detailed, and indeed a simplified one has also been created for lab use. However, I remembered how confusing directions could sometimes be for lab equipment in physics labs and other introductory courses, and I wanted to make a list that anyone could follow, even someone who had never heard of the equipment involved before. I believe I succeeded on that count, but I’m looking forward to any feedback from students in the future. As an additional supplement, a “cheat sheet” with the pictures, names, and functions of each piece of equipment is provided in Appendix B.

The actual program used will depend on the sample in question and the desired results. As an example, here is the program used for the calibration test, which uses 99.998% pure Zinc:

- Pre-Run Actions
    - Start the Run
        - Action occurs Immediately
    - Switch the Gas to Nitrogen at 20.0 ml/min
        - Action occurs Immediately
- Temperature Program

- 1) Heat from 30.00 °C to 200.00 °C at 50.00 °C/min
- 2) Heat from 200.00 °C to 400.00 °C at 20.00 °C/min
- 3) Hold for 5.0 min at 400.00 °C
- 4) Heat from 400.00 °C to 440.00 °C at 10.00 °C/min
- 5) Hold for 1.0 min at 440.00 °C
- 6) Cool from 440.00 °C to 30.00 °C at 20.00 °C/min

It should be noted that plenty of time should be allowed for each test on this machine. The data collection period is relatively short; for example, in the test run described above, this period was approximately 43 minutes. However, the cooldown period is considerably longer. During the test run, this cooldown took approximately three hours. Due to the settings on the device, the program cannot be stopped before this cooldown is complete, nor can a new test be commenced. One way to shorten this turnover period in order to test multiple specimens in less time would be to set a higher end condition and starting temperature. The second starting condition should be equal to or greater than the end condition of the test preceding it.

Data Analysis

The reference material used in this test was 99.998% pure Zinc, with a melting temperature of 419.47°C, according to the data sheet provided by Perkin Elmer. If the differential scanning calorimeter is in working order, an endothermic reaction should be visible at 419.47°C when the sample is melting, and an exothermic reaction should be visible at 419.47°C when the sample is cooling.

Figures 5 and 6 are a visual representation of the data collected by the analyzer during the 43-minute data collection period of the reference sample test.

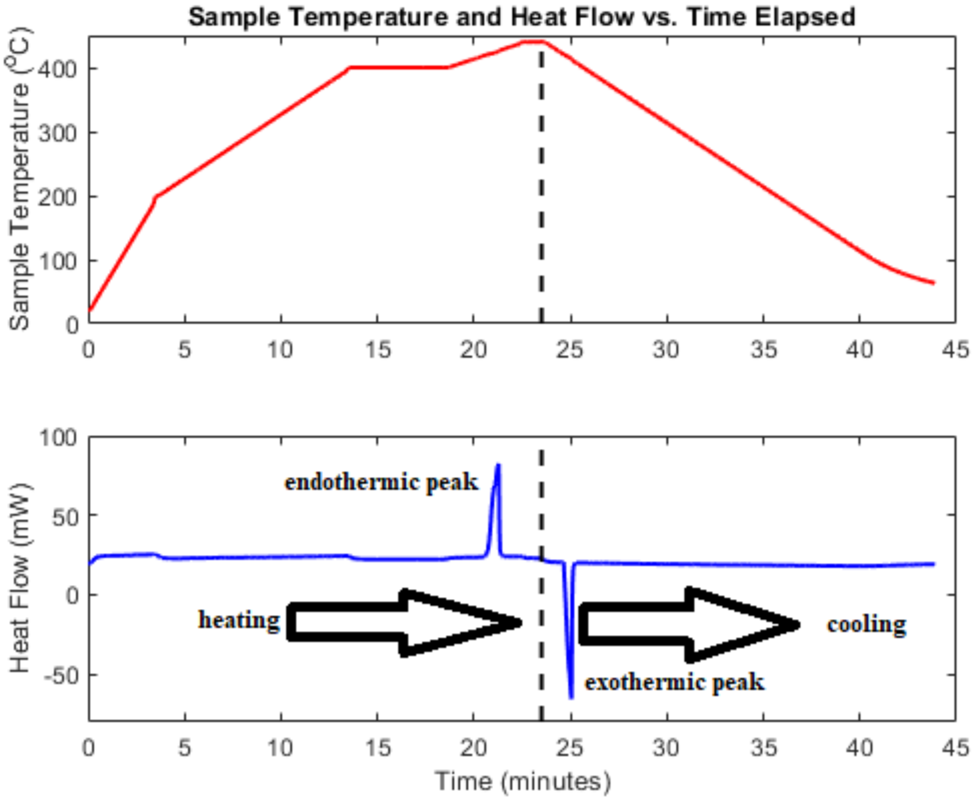


Figure 5: Graph of the temperature of and heat flow in the Zinc reference sample over time.

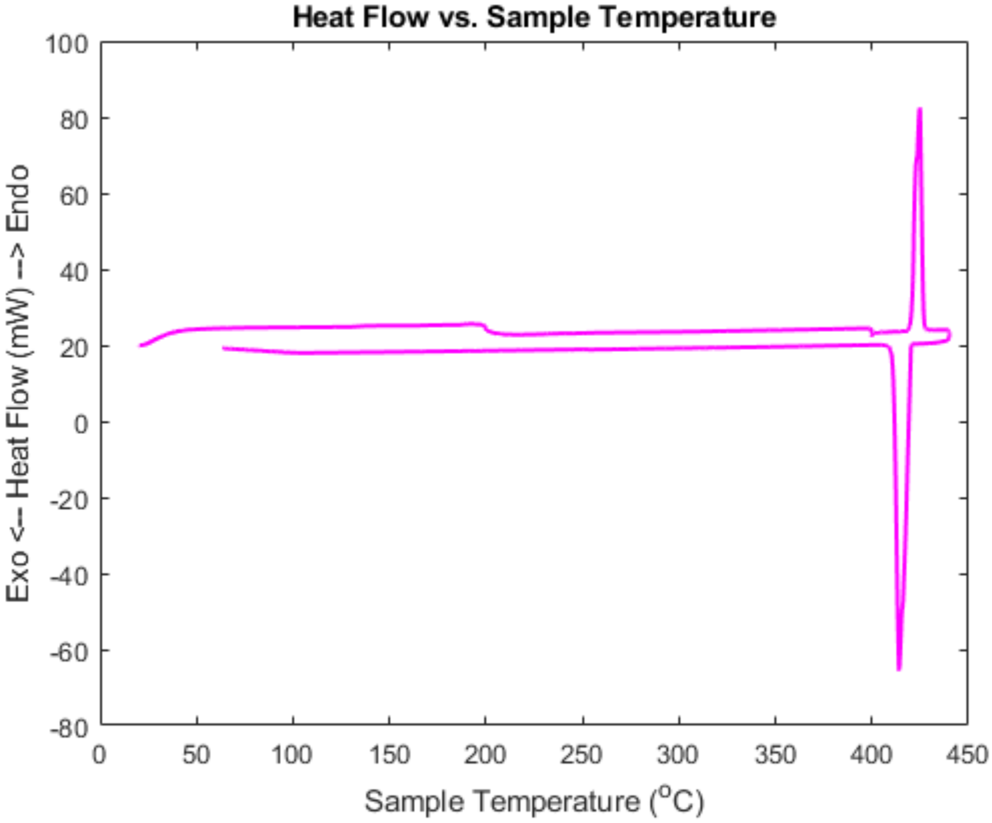


Figure 6: Visual representation of the heat flow vs. the sample temperature for the test of the Zinc reference material.

In this case, an endothermic reaction is characterized by an upward spike in heat flow, and an exothermic reaction is characterized by a downward spike in heat flow. A cursory examination of these graphs shows these spikes beginning somewhere around 420°C, peaking about 5°C after that, and returning to normal 2-5°C after the peak reaches its height.

By examining the raw data exported to the Excel file, these transition points can be found to a higher degree of accuracy. The melting process displays an endothermic peak at 424.78°C with onset at approximately 419.62°C. The freezing process displays an exothermic peak at 413.95°C with onset at approximately 420.25°C. These onset phase change values can be compared with the actual melting temperature of the material, 419.47°C, using the formula described in Equation 1.

Equation 1:

$$percent\ error\ formula = \frac{|experimental\ value - theoretical\ value|}{|theoretical\ value|} \cdot 100\%$$

The use of this equation finds experimental error percentages of 0.036% and 0.18%, respectively, which this study finds acceptable for normal operation of the DSC, although no data on the normal range of acceptable experimental error for this device is available. In addition, the baseline heat flow remained at zero throughout the test, which suggests successful operation. If the error increases significantly or the baseline heat flow deviates from zero, the device may be recalibrated using the Baseline Correction, Temperature Calibration, and Heat Flow Calibration processes described on pages 245-248 of the Pyris 6 DSC manual or by a service engineer approved by Perkin Elmer.

As things stand currently, the Pyris 6 DSC is in working order, properly calibrated, and is ready for use in ambient operation conditions between room temperature and 450°C.

Future Plans for Operation in the Subambient Mode

As described earlier, this differential scanning calorimeter will be used mainly as a teaching tool for graduate level mechanical engineering classes. It may also be used in the study of transitions of polymers. Both of those uses can be accomplished in the current setup of the DSC, which is designed for ambient operation. However, there are some reasons why one might want to set the DSC up for subambient operation as well, depending on the research intended. There are currently two entities, a professor from UAH and a research group from Iowa, interested in using this device in subambient operation mode. For this reason, I will briefly cover the parts and steps required to convert the DSC for subambient use, as well as some suggestions for successful operation.

The following additional parts are required for subambient operation:

- A liquid nitrogen tank capable of providing a pressure between 6.9 and 20.7 kPa.
- A filter dryer accessory, which is a device that attaches to the purge gas line and removes any excess moisture. It is designed specifically for Perkin Elmer's line of differential scanning calorimeters, and is available for purchase at the following website: https://www.perkinelmer.com/Product/ta-filter-dryer-kit-n5370103
- An insulated liquid nitrogen transfer line, long enough to connect the liquid nitrogen tank to the analyzer.
- The following brass Swagelok fittings:
    - Two 5/16 inch elbows
    - Two 5/16 inch tube adapters to 1/4 inch male NPT connectors
    - Two 5/16 inch tube adapters to 1/4 inch female NPT connectors
- Insulation for the connection points
- Teflon tubing

The full instructions for the installation of these parts for subambient operation can be found in pages 248-267. For the most part, these instructions will be omitted from this report, as interested parties would be best served by viewing the document themselves and following the steps carefully. However, there are a few salient points that I find it appropriate to bring up. The first is that, while this manual is for the Pyris 6 DSC, the instructions and illustrations seem to refer to a slightly different model than the one present in the OKT laboratory. Discretion is advised, and changes to the recorded steps may be necessary. If needed, Perkin Elmer support should be able to answer any questions by email. Second, once the DSC is set up for subambient operation, the Swagelok fittings cannot be removed for easy transition back to ambient operation. However, this transition can still be achieved by removing the connection for the cooling liquid, as seen in Figure 8.

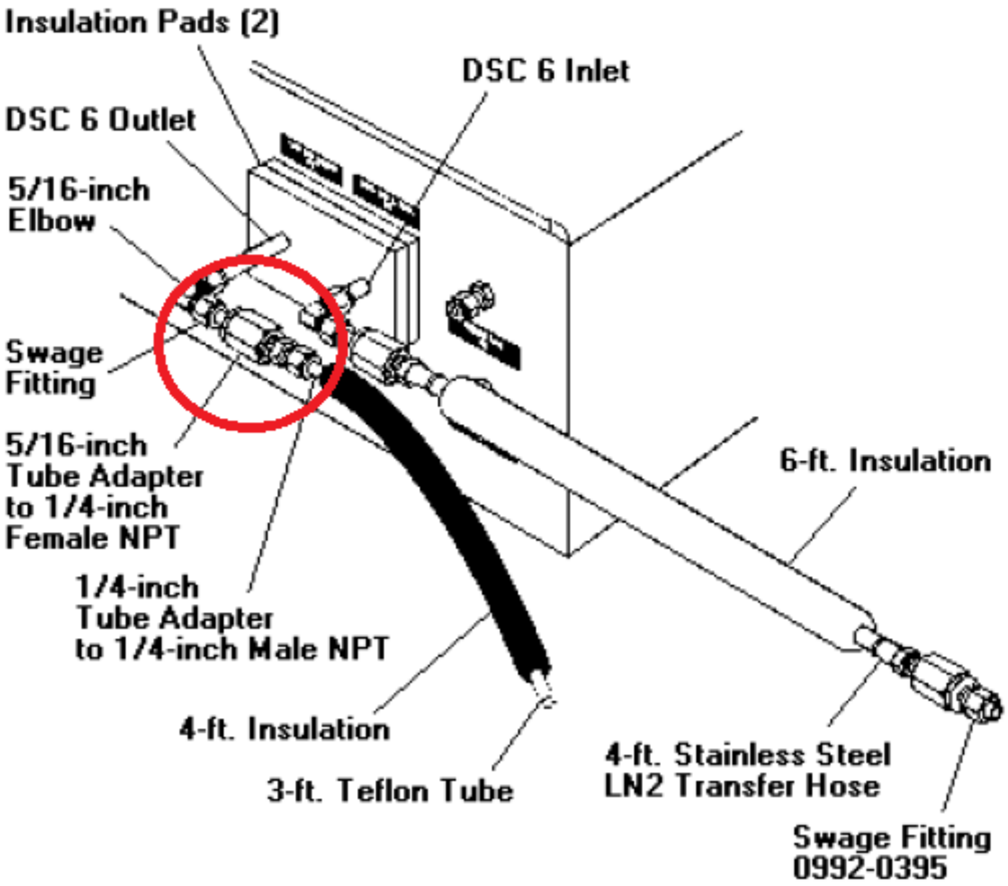


Figure 8: Diagram of the fittings connected to the analyzer for subambient operation, with the removable connection for a cooling liquid highlighted in red.

Third, the DSC should not be turned off while configured for the subambient operation mode. When not in use, the temperature of the furnace should be left at 50°C, and the purge gas should be left running. As this unit is unlikely that this unit will see constant operation in the subambient mode, it is recommended that tests be performed in batches, and that after all desired tests have been run, the DSC be reconfigured for ambient mode.

Finally, the acceptable calibration reference materials for subambient operation are different from those of ambient operation. The list of acceptable reference materials, which consists of high purity (99.999% or above) organic materials, can be found on pages 266 and 267 of the DSC manual. These samples must be tested in special pans called “volatile sample pans”, which are available for purchase on Perkin Elmer’s website: https://www.perkinelmer.com/Product/aluminum-volatile-pans-covers-pkg-400-02190062.

Conclusions

Improvements can certainly still be made upon this project. For example, another student or researcher will have to pick up where I left off in the preparation for subambient mode setup, and do the requisite tests for that mode to ensure proper operation. In addition, it should be noted that the referenced sample tested in this project was not weighed due to a lack of access to a scale of sufficient accuracy, and thus the correct sample weight was not entered into the Pyris Manager software prior to operation. It is unlikely that this changed any results; however, for the sake of completeness, a second test should be conducted with the correct weight recorded. In general, however, I am satisfied with the results of this project. The initial goals of this project - to set the differential scanning calorimeter up for ambient operation, test the system, and create a set of guidelines for future use - were all satisfactorily completed. The Pyris 6 DSC unit located in the composites laboratory in the Olin B. King Technology Hall building is commissioned and ready for use.

References

1. Karoui, R. (2012). Chapter 15 - Food Authenticity and Fraud. In *Chemical Analysis of Food: Techniques and Applications* (pp. 499–517). Academic Press. Retrieved 4/30/2021 from https://www.sciencedirect.com/topics/materials-science/differential-scanning-calorimetry
2. Perkin Elmer (2013). Differential Scanning Calorimetry: Frequently Asked Questions. Retrieved 4/30/2021 from https://www.perkinelmer.com/CMSResources/Images/44-74542GDE_DSCBeginnersGuide.pdf
3. Perkin Elmer. Chapter 3: Pyris 6 DSC. Retrieved 2/26/2021 from https://www.artisantg.com/Scientific/63719-6/Perkin-Elmer-Pyris-6-DSC-Differential-Scanning-Calorimeter
4. University of Pittsburgh. (2021). *Perkin Elmer Pyris 6 Differential Scanning Calorimeter*. Shared Research Support Services | University of Pittsburgh. http://researchservices.pitt.edu/instruments/perkin-elmer-pyris-6-differential-scanning-calorimeter.
5. LabX. (2021). *Perkin Elmer Pyris 6 DSC*. Perkin Elmer Pyris 6 DSC | For Sale. https://www.labx.com/item/perkin-elmer-pyris-6-dsc/4287434.
6. Perkin Elmer (2015). Differential Scannin Calorimetry: Cooling Solutions. Retrieved 4/30.2021 from https://www.perkinelmer.com/lab-solutions/resources/docs/TCH_CoolingAccessories.pdf
7. TA Instruments. THERMAL APPLICATIONS NOTE: Purge Gas Recommendations for use in Modulated DSC. Retrieved 4/30.2021 from http://www.tainstruments.com/pdf/literature/TN44.pdf

Appendix A

What follows is a link to the document referenced in source number three, which is an operation manual referenced often in this paper [3]. For the reader’s convenience, a link to this document is provided in this appendix so that the document is still accessible should its original source be taken down, as this document is a vital resource for those wishing to do further work with this device: https://drive.google.com/file/d/1AMM1j-FDFYc9pupnLVbemaBi_rDHcfYp/view?usp=sharing

Appendix B

What follows is the operational checklist for quick reference when operating the DSC.

- Weigh the sample pan with and without the sample; find the mass of the sample and record.
- Load the pan with the sample and the reference pan into the furnace.
- Ensure that the analyzer is connected to the COM1 port on the computer.
- Ensure the chiller is filled with water.
- Ensure that the Nitrogen gas is connected to purge A and the cell purge.
- Set the flow rate between 20 and 40 cc/min unless otherwise specified.
- Turn on the chiller.
- Turn on the analyzer.
- Turn on the computer and start the Pyris Manager software.
- Click the second button on the screen, labeled Pyris 6 DSC.
- Enter the sample information and the desired program in the Method Editor interface.
    - Max heating rate = 100 °C/min, max temperature range for ambient operation = room temperature to 450°C, max temperature range for subambient operation = -120°C to 200°C. Lower heating rates are preferable. Start and end temperatures must exceed the resting temperature.
- Ensure that the gas flow rate is still within the desired range.
- Commence the test by pressing the Start/Stop button. When finished collecting data, export to a flash drive using File>Export.
- Allow the analyzer and test sample to fully cool before shutting down the equipment.