Differential Scanning Calorimetry
Calibration and Heat Capacity

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Abstract

The Differential Scanning Calorimeter(DSC) is used to find multiple properties of materials such as heat capacity, melting points, crystallization, and more. Fermilab owns the NETZSCH DSC 404 F3 Pegasus to test novel material for a high powered targetry components. The DSC heats up to 1500 C, uses a platinum furnace, and Al_2O_3 crucibles. In order for the DSC to produce consistent and correct data, calibration of the machine was necessary. Testing with the given calibration kit of known metals. Once calibrated, testing on novel materials for their specific heat capacity ensues.

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Contents

1.Background

To understand the DSC and its functions, reading manuals, papers and reports, and procedures is necessary. The DSC is primarily used to examine and test thermal properties of a material such as glass transition, curie points, melting points, crystallization, and heat capacities. The DSC is able to read these properties through the sensors in the measuring head. The sensors are extremely responsive and when a material is absorbing or releasing heat, the measuring head converts the energy to microvolts/mg. (1)

2.Goals

The purpose and goal of the project was to get familiar with the DSC and calibrate the machine to output correct readings. The calibration is done on standard samples provided by NETZSCH. Once fully calibrated the machine is meant to be used on novel materials to find their specific heat capacity. The novel materials are being tested for use in a high power proton beam.

3.DSC 404 F3 Pegasus

Differential Scanning Calorimetry is a tool used to find various properties of polymers, organic material, and metals. It has multiple thermal sensors, a vacuum function, multiple types of furnaces, utilizes a controlled environment, and . The DSC at Fermilab, NETZSCH DSC 404 F3 Pegasus, comes with a platinum furnace, alumina crucibles, and corresponding softwares. Most technical information can be found in the operating manual provided with the machine.

3.1 Capabilities

The Pegasus can provide a controlled environment to the sample and measurement. This allows little to no errors or impurities in the sample and measurement. Any impurity can mess up the measurement through oxidation or reduction. The Pegasus is able to do this by vacuuming the chamber holding the samples, and refilling the chamber with a gas of the operator's choice. It should be noted that the Pegasus is not equipped with the auto-vac system. It should be noted measurements can be done under vacuum, however it cannot go beyond 1400 degrees Celsius. This information can be found on page 46 in the operating manual. The gas for the environment at Fermilab is argon. (1)

The Pegasus has a heating/cooling rate of 5-50 K/min. Testing with the DSC, it was found that a higher heating rate resulted in drifting baselines. A higher cooling rate can be achieved with a NETZSCH liquid nitrogen accessory. This also allows you to go below freezing temperature if your furnace can endure it. At Fermilab, the Pegasus is equipped with a Platinum furnace, temperature range 0-1500 C. The furnace specifications can be found on page 48 to 56 in the operating manual. (1)

The Pegasus uses crucibles to measure the samples. The material of the crucibles affects what samples can be measured as the elements can react with each other when put under heat. In figure 1, you can see what material is suitable with each crucible type provided in page 94 of the operating manual. (1)

	substance										
crucible material	C_5H_{10}	H_2O	Ga	In	Sn	Pb	Zn	$Li_2SO_4 x H_2O$	Al	Ag	Au
corundum, Al_2O_3	0	0	+	+	+	+	+	+	+	+	+
bornitride, BN	0	0	+	+	+	+	+	+	+	?	?
graphite, C	0	0	+	+	+	+	+	+	+	+	-
silicate glass	+	+	+	+	+	+	?	+	-	x	x
fused silica, SiO_2	+	+	+	+	+	+	+	+	-	+	+
aluminium, Al	+	.	-	+	-	+	-	+	x	x	x
Al, oxidized	+	+	+	+	+	+	+	+	x	x	x
silver, Ag	+	+	-	-	-	-	-	?	-	x	x
gold, Au	+	+	.	.	-	-	-	+	-	-	x
nickel, Ni	+	+	.	.	.	.	.	?	-	+	-
iron, Fe	+	.	.	+	.	+	-	?	-	+	-
fine steel	+	+	.	+	.	+	-	?	-	+	-
platinum, Pt	+	+	.	.	-	-	-	+	-	-	-
molybdenum, Mo	+	+	.	?	.	?	.	?	?	?	-
tantalum, Ta	+	+	?	+	?	?	?	+	-	+	-
tungsten, W	0	0	.	?	?	.	+	?	.	+	+

Figure 1 - Compatibility of Substances and Crucible Material. Page 94 of Operating Manual

3.2 Extras

The Pegasus can be equipped with two furnaces. Having two furnaces allows the user to perform a wider range of tests. It can also be equipped with an auto-vac system. This system is controlled via the software.

4.Calibration

Calibration for the DSC was necessary so that it can output the correct data. The following metals were tested for the calibration In, Sn, Zn, Bi, Al, Ag, Au. The points being searched for were the enthalpy change and melting points of each metal.   The data is then imputed into the software for it to compare to known values.

4.1 Procedure

The first step is to load the sample. Measure 10-20 mg of calibration material. Load the material into the sample crucible. The crucible location's are shown in figure 2, a diagram from Daw's manual. Then lower the furnace all the way down. The down arrow should have a green light when the furnace is fully lowered. If not, the software will prevent running a measurement. The state of the furnace can be checked through the diagnostics tab.

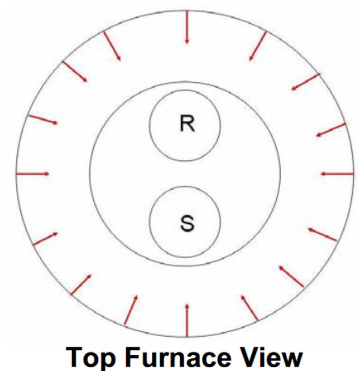


Figure 2 - Crucible Location, Idaho National Laboratory

The second step is creating a pure environment. Once the furnace is down, close the exhaust valve located on the top of the furnace or look at figure 3. Then turn on the vacuum pump. Open the vacuum valve. It will show how much of the chamber is vacuumed on the display. When the chamber has reached a 98% or higher vacuum, close the vacuum valve. Open the backfilling valve slowly until the chamber reaches to a slight overpressure, then close the valve. This system can be seen in figure 4. Open the exhaust valve slowly.

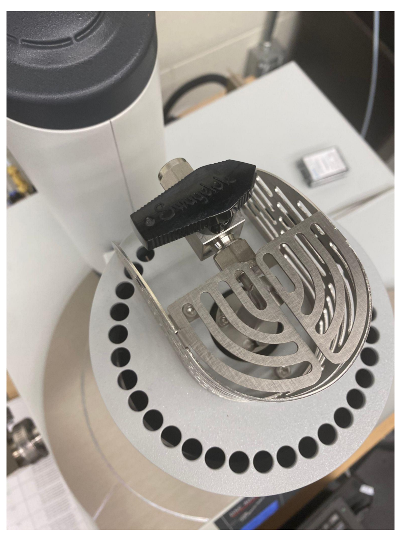


Figure 3 - Exhaust valve closed. Photo taken at MI8

Figure 4 - Vacuum valve in black, backfilling valve on the side, Photo taken at MI8

Next is setting up the measurement the user intends to run within the software. Creating a new measurement, select file and click new. The first tab is the header. This is where the sample mass, crucible mass, purge gas, and flow rates will be defined. At Fermilab, the purge gas used was argon at a flow rate of 50 ml/min for purge gas 2 and 20 ml/min for protective. The header tab can be seen in figure 5. Moving onto the temperature program, each calibration material had its own program that needed to be followed provided by the software manual(2). The temperature programs for each material can be seen in figure 6. The temperature program is set up in three different functions: dynamic, isothermal, and final. Dynamic is the heating/cooling instructions, isothermal is to hold the temperature for a certain amount of time, and final is a failsafe for the machine if it goes over the set temperature. For the calibration the heating and cooling rate were set with dynamic at 5 K/min and the final failsafe was set 25 degrees above the highest temperature. For each calibration material there are 3 heating segments and 3 cooling segments. The temperature program for each calibration material can be found in the software manual on page A6 (2). The calibration tab is where the user can select the temperature, sensitivity, Tau-r calibration however in the runs conducted at Fermilab did not use these and were done manually. Then the final tab is where the user will save the measurement file.

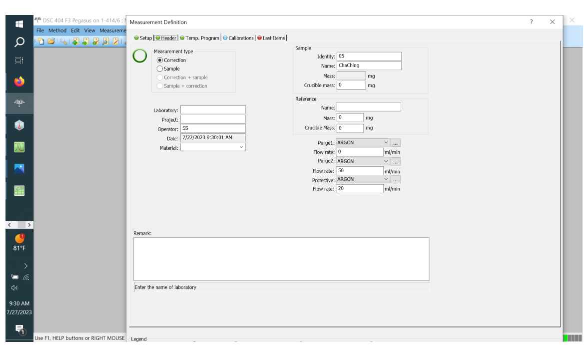


Figure 5 - Header Tab Example, Screenshot Taken at MI8

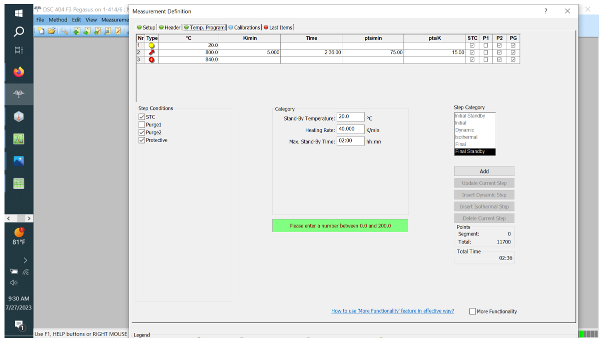


Figure 6 - Temperature Program Tab Example, Screenshot Taken at MI8

Once the measurement file is set, select “set initial gas’s”, then start. The software will give the user information on the time it will take to complete the measurement. When the measurement file is complete, transfer the data to the analyzing program. For calibration the necessary data needed are the melting points and enthalpy change. For the melting point, select the heating segment and select peak and area. The peak will give the exact voltage, temperature, and time of the melting point. This will be put into the temperature calibration. The software integrates the highlighted segment of the curve, hence the name differential, and gives the area in microvolts. This will be inputted into the sensitivity calibration.

To input each value into the calibration programs, select new, then specify the furnace, gas, crucible, and heating rate of the measurements. For the temperature calibration, the most important data are the 2nd and 3rd melting points of the material. Input one or the other into the experimental tab of the graph for the temperature calibration. The sensitivity calibration will be done similarly. Select the second or third segment and input the value into the peak area in the graph. The area is measured in µV*s/mg. The software will convert this value to µV/mW.

4.2 Results

Indium

The experimental result of indiums melting point and enthalpy change was 158.2 C and 1.024 µV/mW. The expected values for indium are 156.2 C for the melting point and 1.081 µV/mW for the enthalpy change. For the melting point the error is calculated to be about a 1.2% difference and for enthalpy change it is about a 5.5% difference.

Tin

The experimental result of tins melting point and enthalpy change was 234.6 C and 0.724 μV/mW. The expected values of tin are 231.9 C for the melting point and 0.892 μV/mW for the enthalpy change. For the melting point the error is calculated to be about a 1.2% difference and for enthalpy change it is a considerable 23.2% difference.

Bismuth

The experimental result of bismuth's melting point and enthalpy change was 274.6 C and 0.872 μV/mW. The expected values of bismuth are 271.4 C for the melting point and 0.839 μV/mW for the enthalpy change. For the melting point the error is calculated to be about a 1.2% difference and for enthalpy change it is about 3.9% difference.

Zinc

The experimental result of zinc's melting point and enthalpy change was 423.3 C and 0.800 μV/mW. The expected values of zinc are 419.5 C for the melting point and 0.704 μV/mW for the enthalpy change. For the melting point the error is calculated to be about a 0.9% and for enthalpy change it is about a 14% difference.

Aluminum

The experimental result of aluminums melting point and enthalpy change was 669.3 C and 0.667 μV/mW. The expected values of aluminum are 662.8 and 0.64 μV/mW for the enthalpy change. The melting point had a 1% difference and a considerable 4% difference for the enthalpy change

Silver

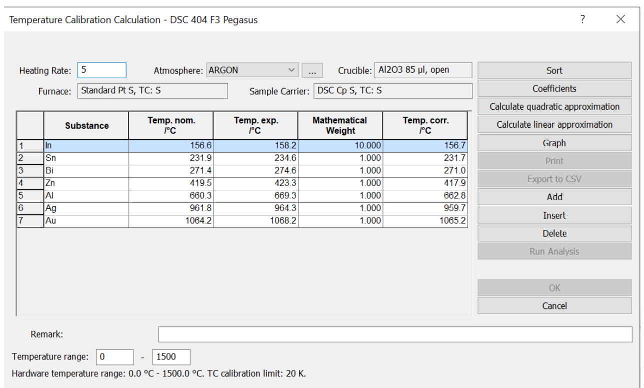
The experimental result of silver’s melting point and enthalpy change was 964.3 C and 0.780 μV/mW. The expected values of silver are 961.8 C and 0.641 μV/mW. The melting point had a 0.3% difference and 21.7% difference for the enthalpy change.

Gold

The experimental result of gold's melting point and enthalpy change was 1068.2 C and 0.513 µV/mW. The expected values of gold are 1064.2 C and 0.634 µV/mW. The melting point had a .4% difference and a 20% difference.

4.3 Conclusion

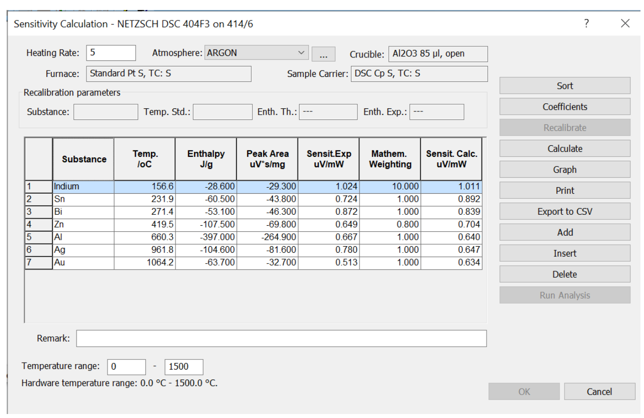
The results of the calibration can be seen in the table and more easily the graph in the figures 7, 7.1, 8, 8.1. The higher the temperature the less of a percent difference there is.. The graph is fitted with a line of best fit. The goal is to be within a 1-3K difference for the melting point and a . Overall the calibration went well and the DSC should be outputting correct data.



	Substance	Temp. nom. /°C	Temp. exp. /°C	Mathematical Weight	Temp. corr. /°C
1	In	156.6	158.2	10.000	156.7
2	Sn	231.9	234.6	1.000	231.7
3	Bi	271.4	274.6	1.000	271.0
4	Zn	419.5	423.3	1.000	417.9
5	Al	660.3	669.3	1.000	662.8
6	Ag	961.8	964.3	1.000	959.7
7	Au	1064.2	1068.2	1.000	1065.2

[1]

Figure 7 - Temperature Calibration Chart



	Substance	Temp. /oC	Enthalpy J/g	Peak Area uV*s/mg	Sensit.Exp uV/mW	Mathem. Weighting	Sensit. Calc. uV/mW
1	Indium	156.6	-28.600	-29.300	1.024	10.000	1.011
2	Sn	231.9	-60.500	-43.800	0.724	1.000	0.892
3	Bi	271.4	-53.100	-46.300	0.872	1.000	0.839
4	Zn	419.5	-107.500	-69.800	0.649	0.800	0.704
5	Al	660.3	-397.000	-264.900	0.667	1.000	0.640
6	Ag	961.8	-104.600	-81.600	0.780	1.000	0.647
7	Au	1064.2	-63.700	-32.700	0.513	1.000	0.634

Figure 7.1 - Sensitivity Calibration Chart

[1] This file can be accessed using the Temperature Calibration software on the computer at MI8. Select open, then select the measurement file with the heat rate and gas described above, same goes for the sensitivity calibration

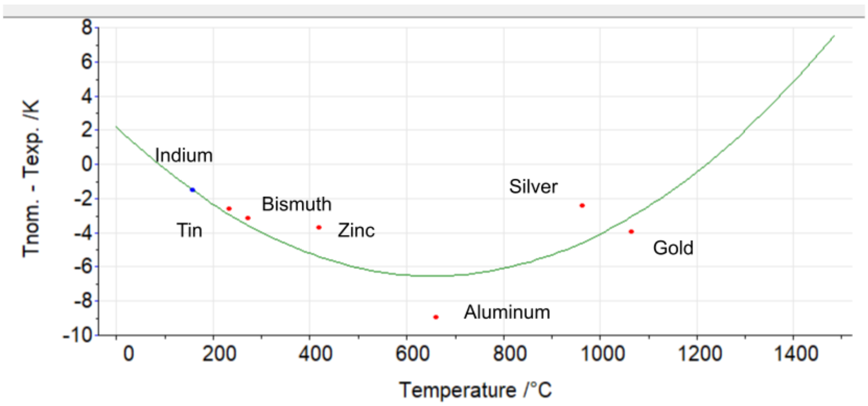


Figure 8 - Temperature Calibration Graph

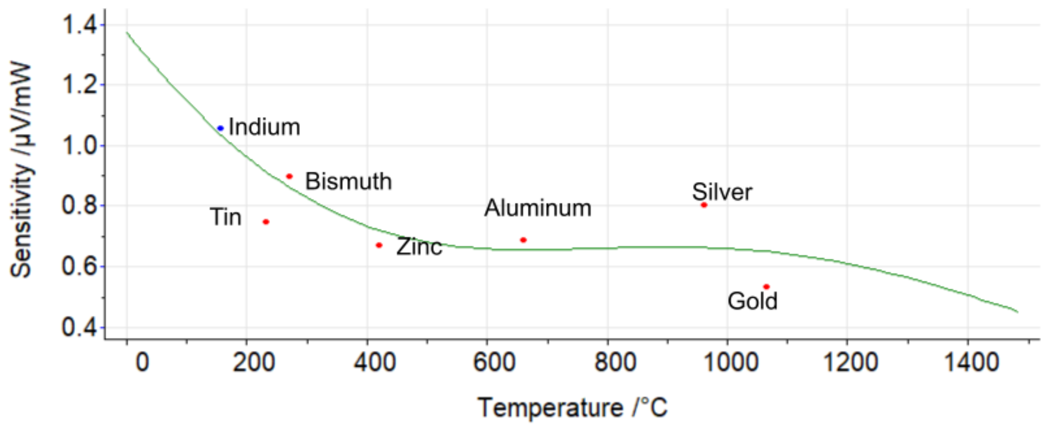


Figure 8.1 Sensitivity Calibration Graph

5.Heat Capacity

The tests for heat capacity had not gone as planned. Tests were conducted on high entropy alloys, HEA's, the DSC outputted what is believed to be the wrong results. So retesting began on standard samples. When testing on a standard sample the machine outputted an incorrect reading on the heat capacity. However this does not mean that the machine is not calibrated. The issue encountered was user error.

5.1 My Procedure

Run the evacuation and backfilling procedure from 4.1 on each of the following runs to create the pure argon environment. For heat capacity, the software needs it to be a sample+correction, or correction+sample to do the ratio method. The following measurements need to be under the same conditions, 1 heating segment, heat rate, and same baseline file. I used the Idaho National Laboratories (3) manual for heat capacity as a reference as they used a NETZSCH DSC.

In Daw's manual (3), the method they use is the three run method. It is a method where the user does 3 measurements. A baseline, standard, and sample. The baseline is a run with both crucibles empty and as mentioned previously, has the same conditions as the following tests. The reference manual (3) states, the baseline should not deviate more than 2 microvolts and be more or less a straight line. Then taking the standard measurement, which is our known value. The known standard used at Fermilab is sapphire, the same as the reference manual (3). The sample is the unknown and is what the user is testing for.

My measurements were conducted with the following conditions. The conditions were, argon gas environment with a 50 ml/min in purge 2 and 20 ml/min in protective. A heating segment to 800 C at a heating rate of 5.00 K/min. Each test went according to plan.

Once all the measurements were complete, I inputted them into the Proteus Analysis program. Selected a segment and clicked Cp:ratio method.

5.2 Conclusion

After testing an HEA, in which multiple tests gave suspiciously high results, retesting for a standard began and the both results given are in figures 9 and 10. This is most likely due to experimentation in procedure or user error. The files used for the analysis program are located in (4) in the references.

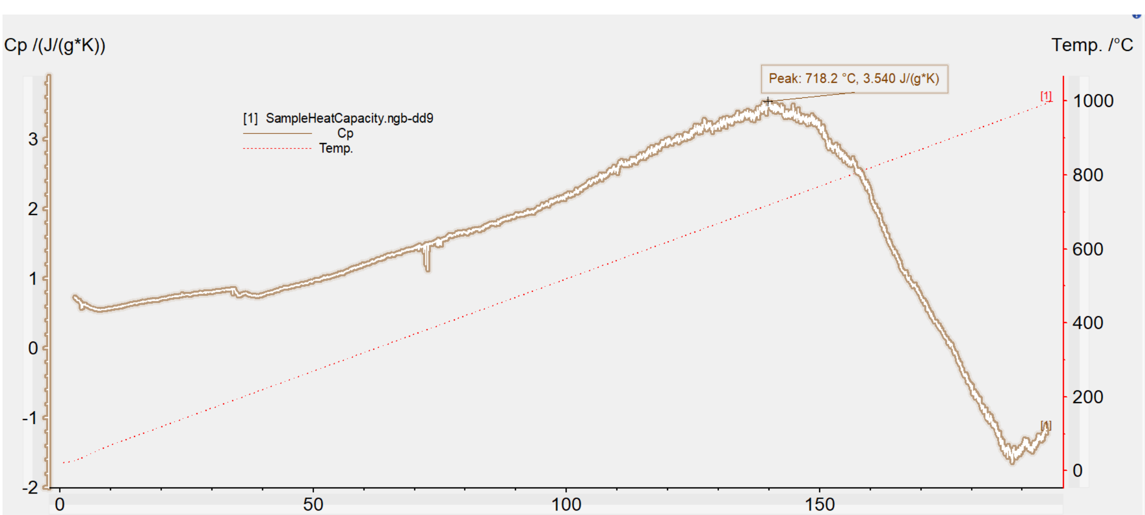


Figure 9 - High Heat Capacity of HEA Sample.

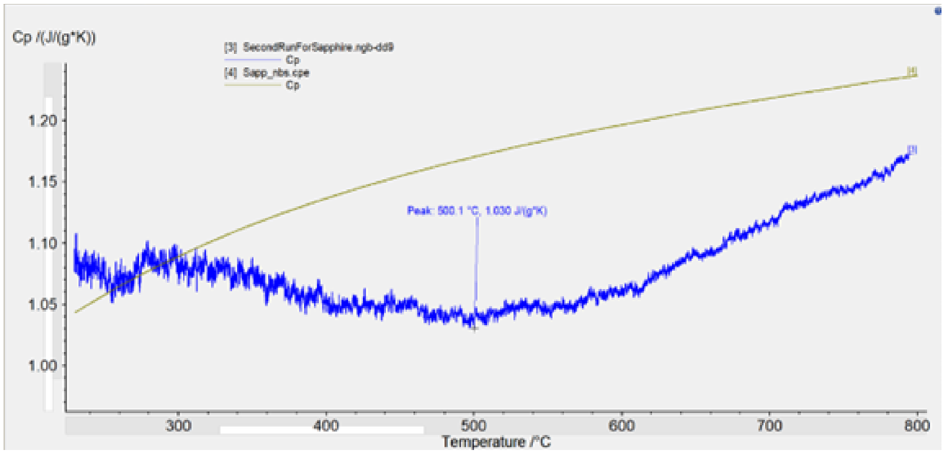


Figure 10 - Exp. Result of Standard in blue compared to Known Value in beige

6.Future Work

Moving forward, Fermilab intends on using this machine to test strictly for heat capacities. The step that is necessary is to use the NETZSCH webinar about heat capacity tests. This will provide valuable information that is not present in the standard manual. When the user understands the procedure, run it on a standard known such as steel or gold. Then running tests on the HEA's should begin.

References

(1) NETZSCH, Operating Instructions DSC 404 Fx Pegasus DSC Apparatus, (2021), https://drive.google.com/file/d/1uSk99mJz5ulkmk8PYnah6BD1-OiNcfW3/view?usp=drive_link

(2) NETZSCH, Software Manual DSC 404 Pegasus - F1 and F3, (2021), https://drive.google.com/file/d/18IkiR-P7XYAFzlp4YvZW8WkXuVxCztA3/view?usp=drive_link

(3) J.E.Daw, Measurement of Specific Heat Capacity Using Differential Scanning Calorimeter, (2008), https://drive.google.com/file/d/18MT2QGbn3VqwHavhCCKGC1yvSoNOH4QD/view?usp=drive_link

(4) Sebastian Szczech, Sapphire Heat Capacity, Sapphiretest, (2023)