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Providing Complete Solutions

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VMTS utilization as Serial Thermal Analyzer for determination of phase transitions, boiling points, and chocolate tempering research

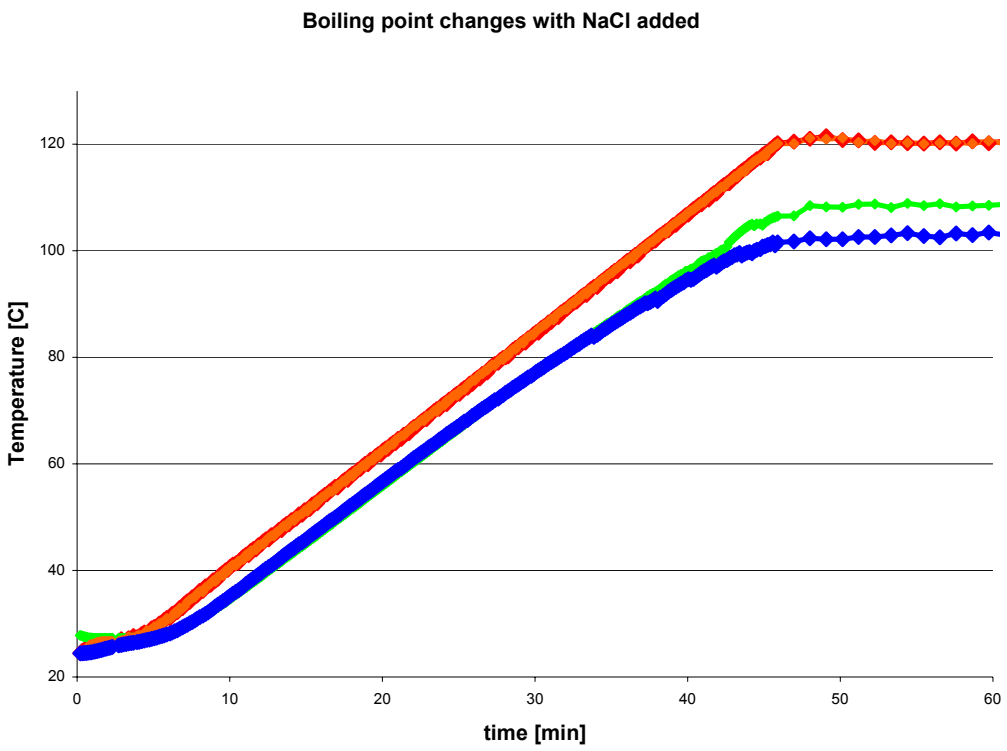
Combining the enhanced version of IQIPyc Helium pycnometer with external hardware created the Versatile Materials Testing Station (VMTS). Since variety of application-specific external sample chambers can be easily interfaced to the pycnometer, one of the choices can be a glass (or metal, ceramic) test tube. Development of multi-port test tube adapter allows for connections to the pycnometer, sensors, or other instruments. Addition of temperature controlling device for the sample chamber, like the Test Tube Heater, increases the pycnometer capabilities to non-isothermal measurements. The temperature of the reference chamber of the pycnometer remains at ambient temperature conditions and is measured by embedded RTD sensor. The temperature of the test tube placed into the test tube heater can be determined from the voltage of the monitoring thermocouple located inside the heater. Placing additional thermocouple into the test tube allows for direct measurements of the sample temperature. Thus, having the two temperatures, one measuring the temperature of the heat source, and the other the sample temperature response, a thermal analyzer can be implemented.

This is not though a typical design, like classical DTA or DSC. In these instruments, deriving the name from differential temperature between the reference and sample, the design can be considered as a parallel approach, as the sample and the reference are subjected simultaneously to the same temperature or heat flow. In our design, the thermal analyzer can be considered as a serial device in a sense, that let say, the reference material can be measured in one run, and the sample in another, using the same temperature profile and all other conditions. Hence, the Serial Thermal Analyzer (STA) name was coined. The reference run can be either a run using empty test tube or some substance in it that can be considered a reference (pure substance). The differential temperature measurements still apply as two thermocouples are used in any run and the sample response to the heater temperature increase or decrease causes differences between the two temperatures. The STA can operate at atmospheric pressure, at pressurized atmosphere depending on test tube material used (up to 340 kPa (50 psia), and at vacuum conditions. If the embedded miniature diaphragm vacuum pump in the pycnometer is used, about 7-10 kPa vacuum is easy to achieve. For lower level of vacuums, an external pumping system needs to be connected to one of the ports of test tube adapter.

Normally, in thermal analyzers the sample and reference holders are kept in very good thermal contact with the heat source and temperatures are measured external to sample. In the STA design, the thermocouple can have direct contact with the sample and usually much larger size of the sample can be used, in grams range. Since the sensor is placed centrally in the test tube, at least qualitative information about thermal conductivity can be obtained. The heat transfer from the test heater can be controlled to some extend. The test tube can be inserted into the heater and rely mainly by transfer of heat via air. A metal insert can be placed into the heater to improve heat transfer. For lower temperatures applications, a suitable liquid can be used to increase heat transfer. For example, refined avocado oil, which has smoke point of about 260-270 °C, can be used for many such applications. To improve throughput, the developed additional hardware like the Peltier based "cold finger" can be used for "ballistic" cooling to bring the heater temperature back to ambient much faster then by natural heat dissipation. Using a different adapter attached to the cooler can also rapidly cool the test tube with sample.

The following applications using this instrument demonstrate preliminary results of typical experiments that can be conducted using the VMTS in the STA configuration. One of the basic experiments that can be done is measuring boiling point elevation when a solute is added to pure water. In the graph below, two

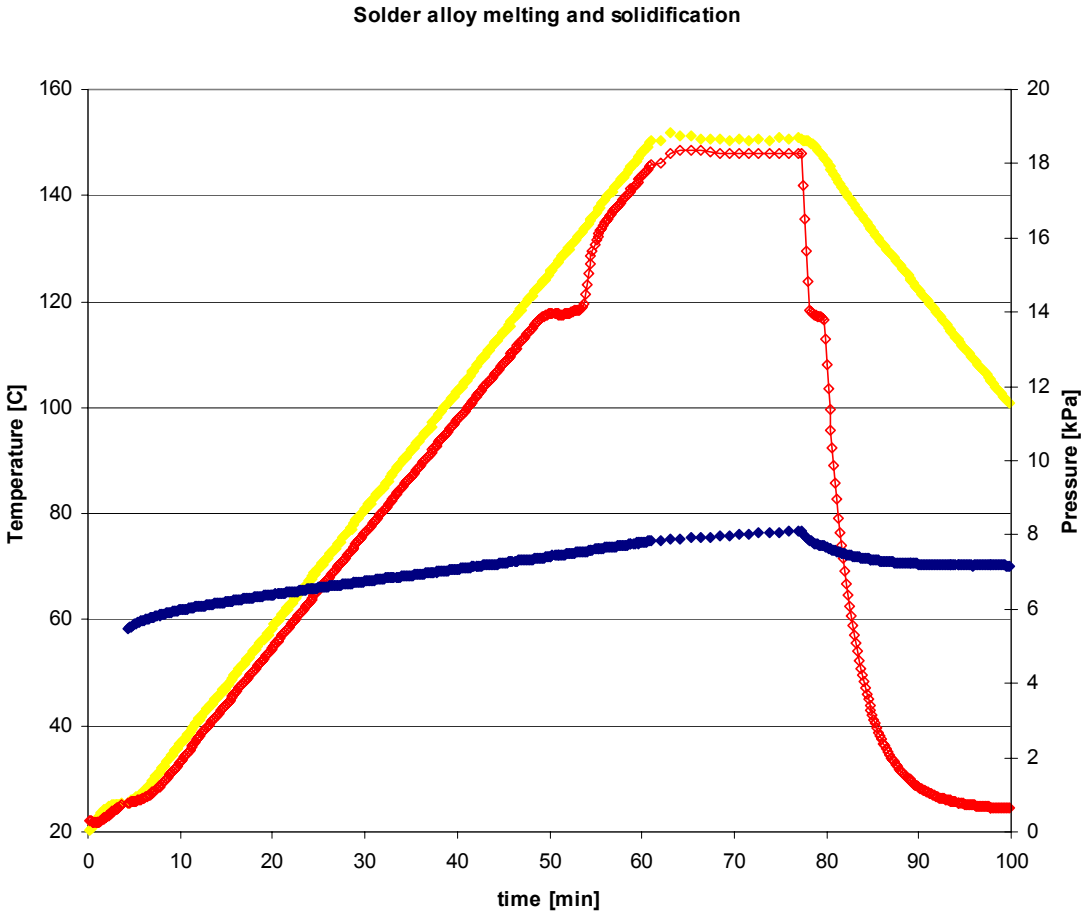
runs, one with water and one with water saturated with NaCl (with some solid NaCl present on the bottom) are presented together.



The orange-red line represents the same temperature profile used for both experiments. The temperature was raised to 25 °C before the linear temperature segment with 2 °C/min started. The temperature ramp ended at 120 °C and was followed by 15 minutes dwell time at the final temperature. The superimposition of the test tube heater temperature profiles shows good linearity and reproducibility. The blue line below the heater temperature represents the temperature data obtained for the 2.6197 g of tap water sample used in this experiment. The green line represents the results for water saturated with sample with NaCl and the excess of salt at the bottom of the glass test tube. It is apparent that the water samples are not quite linear at the higher temperatures thought green line holds better in this respect. The elevation of boiling point is clearly visible. As expected, during the boiling process, the water samples do not get to the higher temperature of the heater but stay relatively flat during this process. Since gas bubbles are emitted from hot water, especially close to the boiling point and for the pure sample, the temperature of the water does not change its temperature sharply in the vicinity of the boiling point. The experiments were carried out at atmospheric pressure.

The next example shows a classical thermal analysis experiment in which melting and solidification temperatures of a solid-state sample can be determined. A low-melting temperature solder alloy was used as a sample. Several pieces of the solder of total mass of 7.2233 g were inserted into the test tubes. The temperature run started at 25 °C with linear rate of 2 °C/min until 150 °C reached. After 10 minutes of dwell time, the test tube was lifted out of the heater and allowed to cool down at room temperature. For the cooling period the heater was left to operate with temperature decrease program with the same rate. The yellow line on the graph is the heater temperature profile. The red line shows the temperature measurements by the thermocouple inside the test tube with its tip inside the molten metal. The melting temperature of 117.5 °C and the solidification temperature of the same value can be easily determined. To avoid oxidation at higher temperatures, the miniature vacuum pump was used to bring the pressure down to about 6 kPa before heating started. The blue color line with units on the secondary Y-axis shows the pressure values inside the test tube during the experiment. It is clearly visible, that due to much better

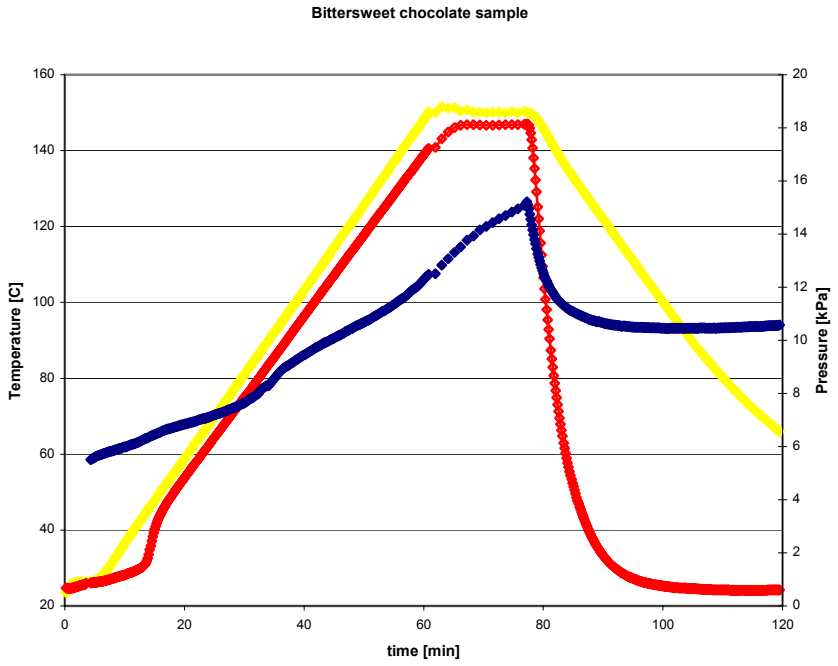
conductivity of metal then water, the sample temperature is much closer to the heater temperature. Obviously, using pure metals like indium and tin, such system can be calibrated within the limits of the test tube heater of 300 °C.



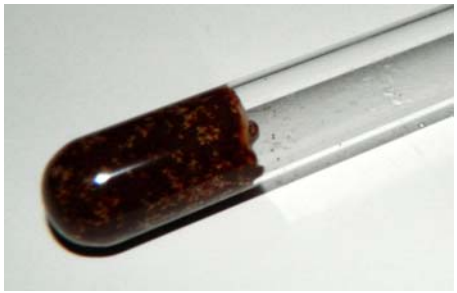
Food samples, opposite to inorganic materials, offer far more complex behavior as many ingredients and complex processing are involved. Everybody knows chocolate, but few may have heard the term chocolate tempering. As it appears, crystallographic studies identify several (5 or 4) forms of crystallization with various temperatures of melting, from about mid twenties to mid thirties (in Celsius), approximately. The higher temperatures melting forms are more desirable as they are more appreciated by consumers for the "melting in the mouth" effect and smooth texture. The chocolate tempering process is basically an elaborated technological process of making the chocolate tastier. Melting the chocolate, "seeding" the crystallization process with un-melted chocolate during cooling with appropriate rate, certain time of storage at final cooling temperature, usage of additives, and perhaps many other proprietary steps are involved for the chocolate production. The final product supposed to have uniform (lustrous) appearance, without the white spots associated with fats separation, and better taste and smoothness then some low temperature melting forms can offer. Reheating to some temperature and residence time in each step are additional factor in the technological process, not to mention origin of ingredients, type of equipment, etc. What is interesting about the whole process of chocolate tempering, that once the given procedure did not result in anticipated results, the chocolate can be re-melted and a modified process can be started again, like a trial and error approach.

A sample of premium baking chocolate with 60% cacao was used for the test using the same experimental procedure as for the solder alloy. The chocolate chips were cut into small pieces and 2.4292 g sample was used for the experiment. The next graph presents the results of the first run. The yellow line represents the heater temperature and the red one the sample temperature response. The blue line shows the pressure

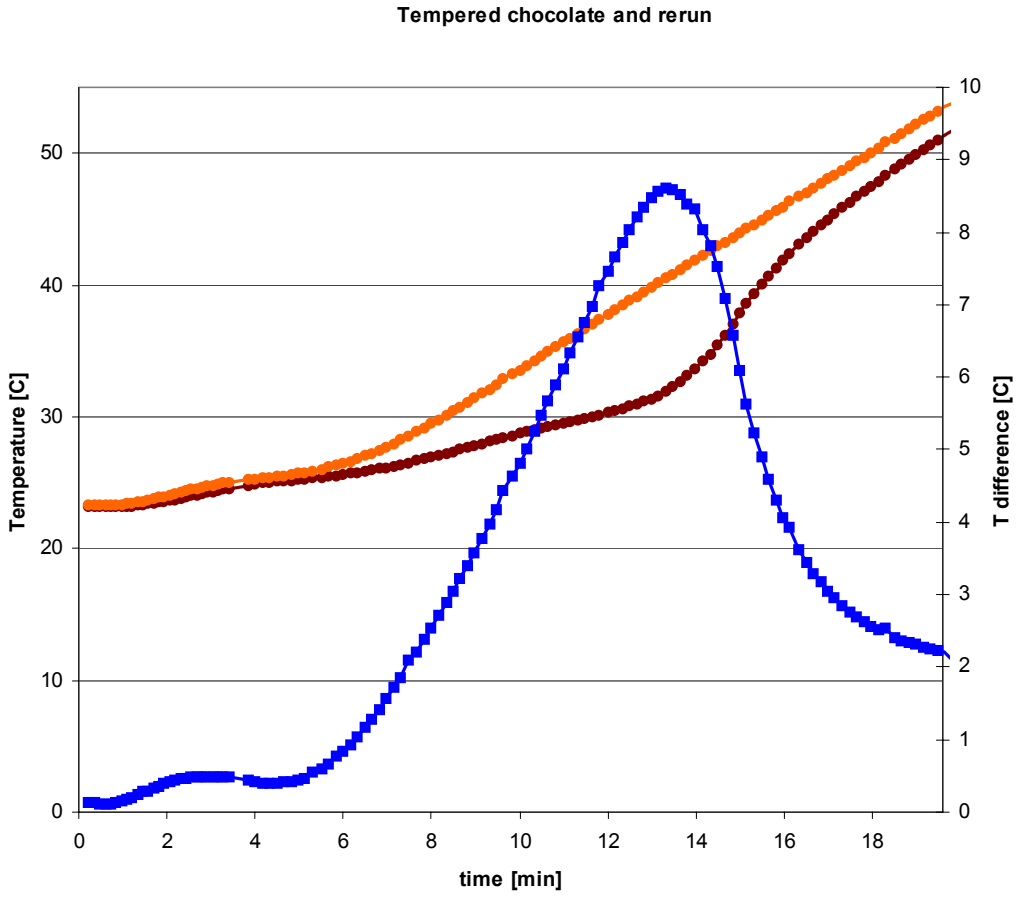
course from the initial vacuum of about 6 kPa. There is clearly noticeable a phase transition in the initial temperature range starting just above 30 °C but the cooling part does not show any such reverse behavior. The non-linear pressure increase at some temperatures indicates evolution of gases from the chocolate ingredients. At room temperature of about 23 C, the chocolate chips are quite hard, but after melting and cooling it back to room temperature, the chocolate remains soft, almost semi-liquid.



A rerun of the same sample using the same procedure and another one with very slow cooling to the room temperature shows no such phase transition which was observed in the first run. Waiting over 24 hours, another run shows some crystallization effects but at lower temperatures then the original one and the large areas of white spots appear on the test-tube walls, typical to the lower grade of chocolate. Although time of settling is one factor, the appropriate cooling temperature and its rate are another. So, for the next experiment, the "ballistic" cooling was used. The described elsewhere on our website, the auxiliary hardware consisting of Peltier based cooler with attached insulated adapter was partially filled with water to improve heat transfer during the rapid cooling. This time the melting of chocolate was carried out to 60 °C, the test tube lifted out of the heater, and immediately immersed in the cooler. The final cooling temperature was about 5 °C, which is below the more optimal temperature, like somewhat above 10 °C used in some processes. Keeping the sample in refrigerator for four hours and later at room temperature for two days resulted in a an interesting appearance shown on the photo below.



Large number of small regions of fat separation appears, instead of few large areas typical for slow cooling to room temperature. The run of the tempered chocolate (same sample) and its rerun are presented together on the graph below. The temperature program from 24 to 60 °C with 2 °C/min rate was used and the experiments were carried out at atmospheric pressure.



The brown line shows the temperature response of the tempered chocolate to the linear temperature profile of the heater. After the experiment was finished the sample was cooled to room temperature and the light brown line shows the result of the rerun. The blue line is the difference between the temperatures of rerun and the tempered sample with temperature scale on the secondary Y-axis. The peak location corresponds to the temperature of 31. 9 °C and is close to the similar value obtained in the first run using the as purchased product.

As it can be concluded from the few experiments, usage of such simple thermal analyzer can be useful in optimizing the technological process of chocolate tempering and many others. One obvious conclusion about the chocolate can be reached, that once the product is subjected to temperature well above 30 °C, its best taste qualities can be lost.

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