



Measuring Specific Heat Capacity Using the Flash Method

Since the introduction of the flash diffusivity method in the 1950's, attempts have been made to extend it to indirectly measure thermal conductivity without reliance on *independently* generated heat capacity data. These properties are interrelated according to the equation:

$$\text{Diffusivity} = \text{Conductivity}/(\text{Density} \times \text{Specific Heat Capacity})$$

To determine specific heat capacity using the same equipment which is used for thermal diffusivity involves measuring the absolute temperature rise of the specimen caused when a known amount of heat is deposited on its front surface in form of a light pulse. Unfortunately, one cannot view this complex process in a simplistic way, especially when attempted at high temperatures. Let us examine some of the parametric components that make up this test.

1) Temperature Rise

As in any calorimetric measurement, the exact knowledge of the absolute magnitude of the temperature rise is mandatory. Any error made in this determination will carry over to the computed specific heat capacity in direct proportion. The type of sensor used for thermal diffusivity tests is selected for its fast response, and is normally operated in a quasi-differential mode. For thermal diffusivity determination it is not important to know the absolute magnitude of the rear face temperature rise, only its time dependent functionality. One may try to calibrate the sensor, but it is a very difficult task to maintain it in calibration over a period of time.

There are no simple ways of doing this except with the use of a second pyrometer trained on the same sample. Since pyrometers can only resolve 0.1°C at best, 1-3°C temperature rise can be determined only with large uncertainties.

2) Quantitative Definition of the Heat Pulse

Equally important to the temperature rise is the exact absolute magnitude of the heat pulse. Any error made in its determination will carry over in direct proportion to the computed specific heat capacity. On repetitive tests over a period of time, the average pulse laser fails rather poorly in terms of power stability because this performance characteristic is of no concern in most applications (including thermal diffusivity testing). The power of a pulse is determined by a great number of independent and interdependent factors, such as:

a) Stored Energy

The energy stored in the capacitor bank and discharged into the flash tube is largely determined by the potential to which the capacitors are charged. Once charged, a certain amount of the charge leaks out before the triggered discharge. This leakage rate will change with such uncontrolled conditions as relative humidity of the air, etc. Thus the energy dumped into the flashlamp one day may not be the same the next day despite having charging levels identical.

b) Flash Tube Efficiency

Upon discharge, the Xenon flash tube converts a portion of the energy into light and the rest into heat, sound, vibration, etc. The proportion among these components is not constant from shot-to-

shot, especially if the repetition is rapid. Tube temperature, humidity, residual ionization, etc. are all among the factors that affect the process. In addition to the percent of total power, the speed at which the discharge will take place is also varied by these environmental factors. These changes make the shots vary gradually during a test and from one day to another.

c) Laser Power

The flash tube's discharge causes the axially located laser rod to absorb the light first and then to re-emit it in form of a coherent monochromatic pulse. A substantial portion of the light is turned into heat. The process is highly temperature dependent. As pulsing is repeated, the rod's temperature rises and both the pulse duration and the total pulse energy changes.

3) Reflections Caused by Intervening Media

For other than ambient testing, it is usually necessary to isolate the sample from the ordinary environment. The window(s) that are placed between the laser and the sample have a certain amount of absorption and reflection associated with them. Even coated windows, (designed to minimize the latter), have serious problems at elevated temperatures. It is not unusual to lose 10 to 15% of the energy per surface in addition to the attenuation caused by the body itself. Mirrors and optics, if used further complicate putting an exact figure on these losses. These properties are also temperature and time sensitive.

Based on the difficulties discussed above, one may intuitively say that when all else fails, let's determine the power input with using a known material. Assuming one knows the specific heat, most of the problems are lumped into one, which is then accounted for by a simple correction factor. This simplistic solution, not having anything better, would be an acceptable approach for practical applications as long as the side-by-side comparison is indeed done side-by-side, and within a very short time period (like in the case of the Flashline™ Systems with multiple sample capabilities), and not hours or days apart, sequentially like it is the case for any single sample system. However, this one approach is also riddled with different, but just as devastating problems of its own. These are categorized and discussed below:

4) Problems Associated with the Sample

Equally important to defining the exact overall magnitude of the pulse is the fraction which is actually absorbed by the sample. There are a number of conditions impacting upon this:

a) Configuration

Calorimeters usually consist of a cavity configured to have extremely high internal emissivity to absorb all of the radiation entering it. The sample, on the other hand is a flat disk. By design, one could not have come up with a worse configuration for the purpose of absorbing light than that. Due to being a flat and exposed surface, its light absorbing ability will be solely governed by the emissivity of the surface. This is a dreaded word for anyone who has worked with optical measurements at elevated temperatures. In most cases, this property is not well known and is highly influenced by such hard-to-control items as surface roughness, presence of oxide films, etc., and it is also changing with time and environment. By definition what is not absorbed is reflected. Thus whatever one observes using a "known" material has no rational relationship to the behavior of the unknown material unless it is proven that their emissivities are identical. One only has to consult the Stefan-Boltzman relationship to realize that the energy radiated (or absorbed) by a surface is in linear proportion to its emissivity. Thus a 10% error in estimating emissivity will cause a 10% error in heat input interpretation, and in the resultant specific heat capacity. It is crucial to realize that one can no more make the assumption that a sample will absorb heat at the same rate

as another, than postulating that their heat capacities are the same. This specific problem is considerably broader than what is possible to cover in this discussion, and none of the finer points are favorable for this testing concept.

b) Thermal Limitations

Calorimetric measurements, regardless of the method, have to conform to an adiabatic process. Spurious heat gains or losses must be minimized or nearly eliminated. In the course of this measurement, the sample is at a temperature above that of its surroundings, and consequently will lose some of its stored heat by radiation and/or conduction while equilibration within it is taking place. Since a diffusivity test is a very fast measurement, one may advance the idea that heat losses are minimal during such a short time and therefore can be ignored. This is not so. If this were true then no corrections would be needed for lateral heat flow and heat loss from the sample during diffusivity testing. Yet it is an accepted and needed correction to the test data. Secondary effects, such as having the front surface (due to radiative losses), fall below the rear surface maximum temperature before that level is achieved, is also possible. A longer equilibration period can take care of it, but that will aggravate the overall heat loss even more. Temperature dependence of losses is another serious consideration one must take into account when postulating that two different samples at two different furnace runs (single sample) will behave identically in terms of heat loss. It is clear that this situation is greatly improved with multiple sample side-by-side testing. Again, the Boltzmann-Law defines that the amount of energy radiated from a surface is proportional to the 4th power of its temperature and directly proportional to its emissivity. The net radiative heat transfer will be proportional to the 3rd power of the differential between the sample temperature and that of the environment surrounding it. Therefore, if one material has a slightly higher emissivity than the other, it will absorb a larger portion of a pulse than would a material with lower emissivity. Consequently, its temperature will become higher than the other. Viewing this from the heat loss standpoint, the higher emissivity sample will then radiate at a higher rate due to its higher temperature. This on the other hand may result in a lower final temperature within the same time period. One could conclude that the higher emissivity material reached a lower final temperature; therefore, it has a higher specific heat. This of course is totally wrong as nothing in the foregoing had anything to do with specific heat, only emissivity.

These are only but a few of the most obvious hurdles one has to overcome before the flash method could be used effectively for the determination of specific heat.

CONCLUSIONS

It is clear from the foregoing discussion that specific heat measurements using a single sample flash diffusivity system are fraught with problems and are likely to produce severely erroneous results. Multiple sample, side-by-side testing greatly reduces the severity of these problems, and brings the overall error within the same range as other calorimetric methods (DSC, drop calorimeter, etc.), operating at high temperatures. This is a substantial improvement and the Discovery Laser Flash system is the first one in the world to offer it.

Due to the reasons discussed, TA Instruments offers the capabilities to determine specific heat capacity of samples only with the multi-sample configuration of its Discovery Laser Flash and Discovery Xenon Flash Systems, as the single-sample units would be subject to the same unacceptable errors as all other competitive single sample systems.

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