Automated MP Determinations

Application Note #5

Introduction

OptiMelt was specifically designed to detect and determine melting points with completely unattended operation. What sets this instrument apart from its competition is its reliance on a “built-in digital camera” and sophisticated Digital Image Processing (**DIP**) to detect and determine melting points.

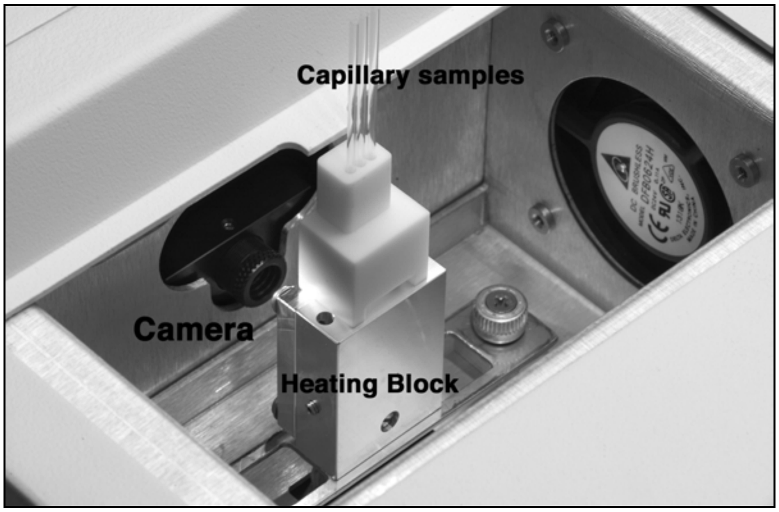

Figure 1. View of the OptiMelt’s heating chamber. A built-in camera faces the samples; a digital image processor calculates melting points and melting ranges.

A very important advantage of the OptiMelt system is its capability to determine melting points automatically while simultaneously visualizing the samples. If required, the capillaries can be viewed at any time, and the melting points can be determined visually. The choice between a time-consuming visual determination and a faster blind automated method is eliminated. Visualization is important for colored or problematic samples, for chemists trying to reproduce published visual observations, and for synthetic chemists generating new, intermediate or exotic compounds.

Figure 2. OptiMelt offers the option to determine melting points automatically while simultaneously visualizing the samples.

Automation offers significant time saving advantages for routine determinations of melting points in production, research and educational settings.

This application note describes the automation capabilities of OptiMelt and compares its Digital Imaging approach to the more primitive optical transmission and reflection methodologies used by its competitors.

Automation Techniques

Most modern automated melting point measurement instruments rely on changes in optical properties of the solid samples during the heating ramp to detect and estimate melting points and ranges.

The three optical techniques used to automatically detect melting point transitions are: 1) Transmission, 2) Reflection, 3) Digital Imaging.

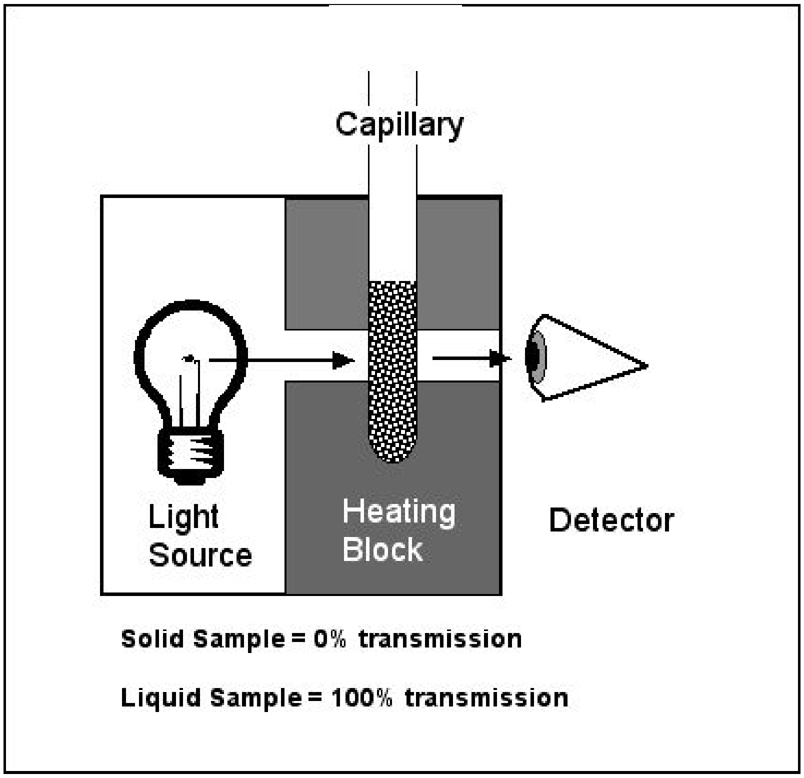

Figure 3. Schematic representation of the transmission method.

The principle of operation of the **transmission** method is simple. The capillary tube standing in a heating block is illuminated from the front with a source of IR light (i.e. LED). A small light channel, drilled into the metal block (directly behind the capillary slot), optically connects the emitter to a photodiode located behind the heater block. A solid sample effectively blocks all light from getting to the photodetector (i.e. 0 % transmission). During the heating process, the light intensity measured by the photocell increases. At a certain transmittance (40 % typical) the sample is deemed to have melted. The melting range is often determined by measuring the temperatures at which the transmission goes above 10 %, and then again when it reaches 90 % (note: thresholds are generally user-programmable). Calibration of the transmission is required and is performed using a capillary with solid sample (0 %) followed by an empty tube (100 %). The transmission technique requires that the melted sample not be opaque, be free of decomposition, and that the compression (density) be uniform from sample to sample to get good reproducibility.

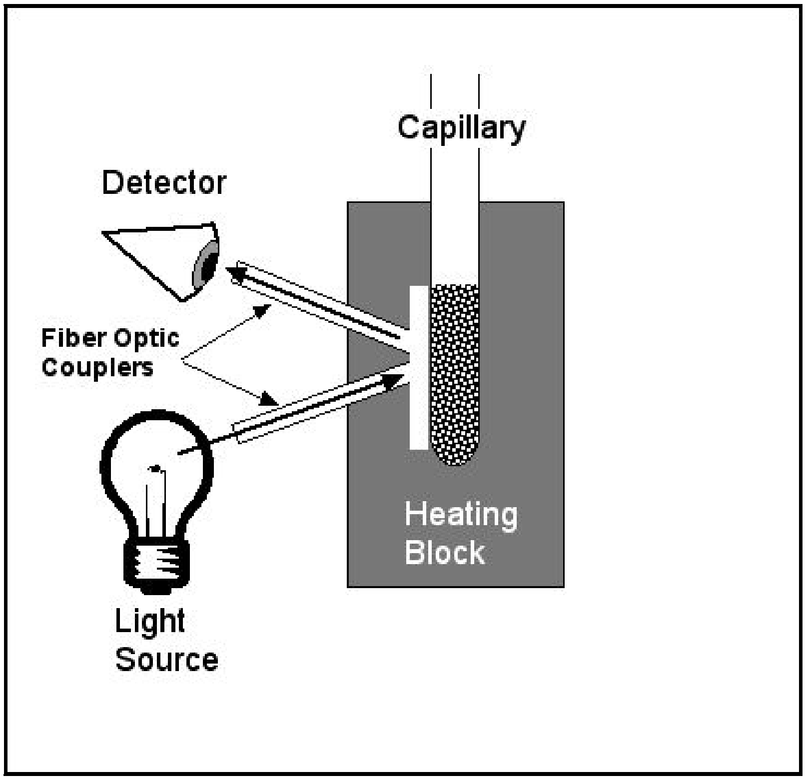

Figure 4. Schematic representation of the reflection method.

In a **reflection** setup, the melting point transition is detected by measuring reflected infrared light. A light source illuminates the front face of the capillary sample and the light reflected "by the crystals" is detected and measured by a photodetector. In order to thermally decouple the heating block from the detector and to block light reflected from surfaces other than the crystals, fine fiber optics are often used to deliver the light and to collect the reflected radiation. Dark, opaque and decomposing samples are often compatible with this method of detection.

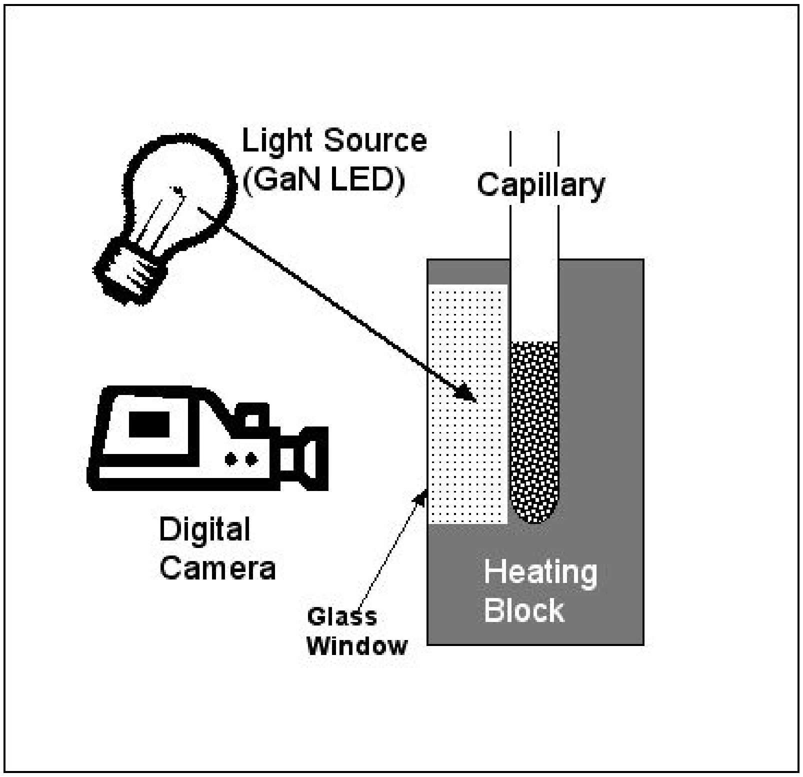

Figure 5. Schematic representation of the digital imaging method.

Digital Imaging is a revolutionary detection scheme found in every OptiMelt system manufactured by Stanford Research Systems. A built-in “digital camera” continuously captures real-time images of the illuminated samples throughout the heating ramp, and sophisticated Digital Image Processing (DIP) technology detects and determines melting points from the analysis of the stored images. The unattended melting points and melting point ranges determined by the OptiMelt system naturally match your visual observations and provide a dramatic improvement over the data generated by units relying on optical transmission and reflection techniques. The high-resolution camera can easily detect and interpret minute changes in the optical characteristics of the capillary samples in a manner very similar to your own eyes. This effectively eliminates the need for the user to be present during the analysis and avoids the subjectivity which is often associated to every visual melting point determination. Colored, opaque and thermally-labile samples can often be analyzed in this fashion.

The three automation techniques described above are generally in good agreement with visual observations on the exact temperature of the clear point. However, since a significant change in sample appearance is required to detect a change in bulk optical properties, the transmission and reflection automation schemes often overestimate the onset temperature. This error in the determination of the onset point leads to a reduced melting range report, which is a cause of concern in purity analysis and QC.

Since melt-point determinations have traditionally relied on visual observation of changes in the physical appearance of solid samples, digital imaging is the most obvious and natural approach to automation. A useful analogy often used to illustrate the limitations of the transmission technique describes this methodology as trying to observe the activity inside a large room by peeking through a keyhole. The limited field of view provided by such a small aperture naturally limits your ability to observe everything that goes on and reduces your power to draw accurate conclusions. At the same time, a high-resolution digital camera, properly positioned inside the same room, would have no problem observing everything going on. A different analogy used for the reflection technique compares the lack of detail in the bulk reflection signals to observing the melts through wax paper. Important details such as sintering points, sublimation and the exact onset point can be lost without a detailed view of the subtle changes that can take place in your samples.

Melt Graphs

In order to provide a real-time display of the changes observed by the digital camera, a graphical representation of the “melting process vs. temperature” can be plotted during the analysis.

The plots (referred to as Melt Graphs in the OptiMelt documentation) are a simplistic representation of the melting process calculated by the digital image processor, and are stored in memory as part of each final Report. Melt Graphs can be displayed during and after a melt on the front panel of the instrument or on a computer screen (using the included Melt View software and USB connection to a host computer). The Digital Image Processor uses the calculated Melt Graphs to detect onset, meniscus and clear points based on user-programmable thresholds (i.e. Onset %, Clear % and Single %) stored in the OptiMelt’s internal memory.

Melt Graphs are generic plots, routinely used to review the changes observed by the camera during a test, and to fine tune automation parameters (i.e. detection thresholds) to better match visual and automated determinations. Melt Graphs are also appended to all printed reports for GLP validation of your analysis results.

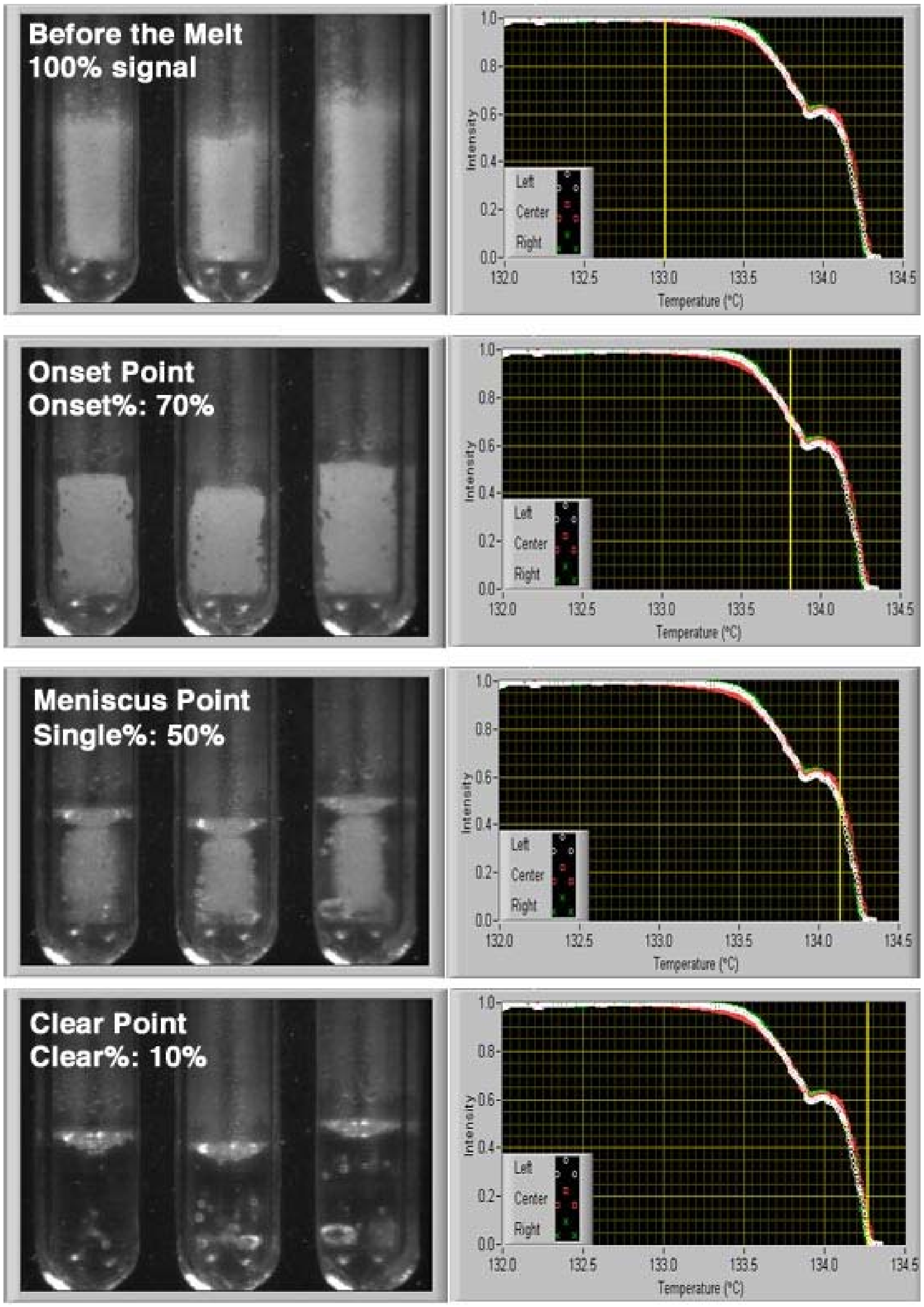

Figure 6. Melt Graphs provide a simplified representation of the melt process. Thresholds are assigned for the onset, meniscus and clear points, and are used by the digital image processor for automated determinations.

The three most important qualities of Melt Graphs, which hold true for most well-behaved chemicals, are that their detection thresholds are (1) very deterministic, (2) ramp independent and (3) shared by samples that behave in similar manner during a melt. For example, most white samples which melt without decomposition share similar MeltGraphs and detection thresholds.

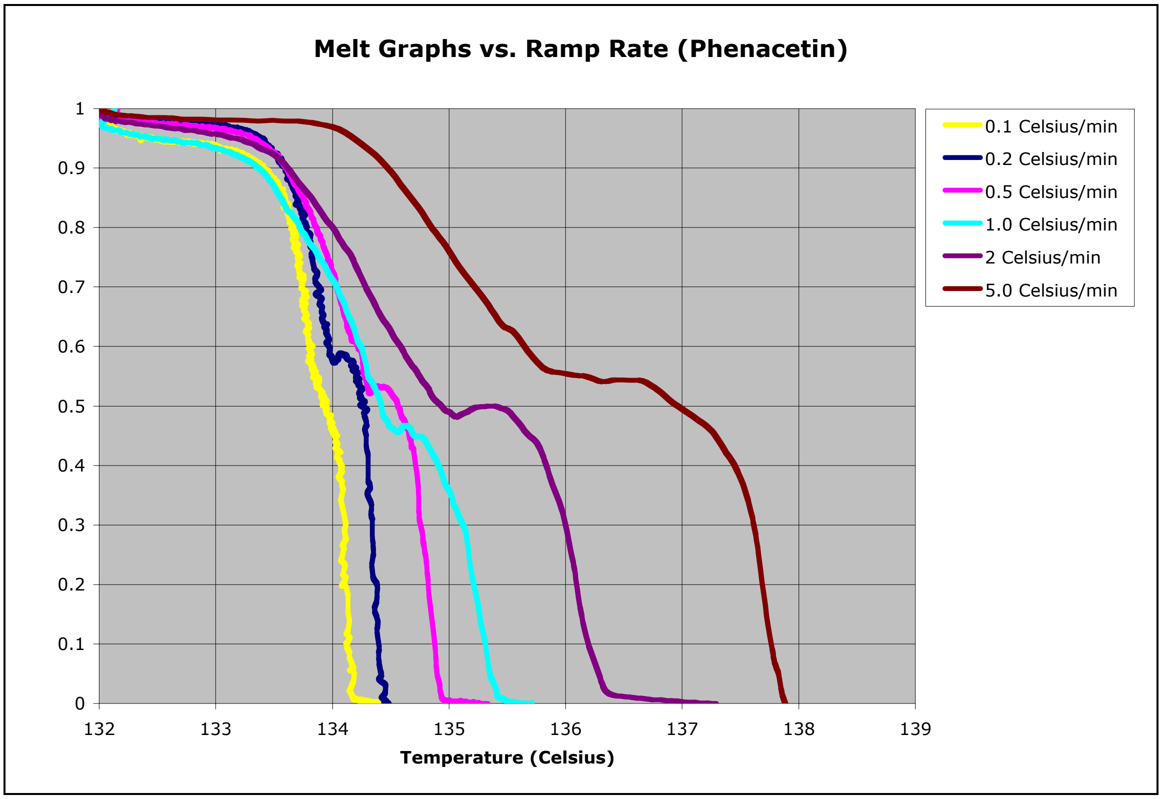

Figure 7. Melt Graph for phenacetin as a function of heating ramp rate.

Melt Playback (MeltView Software)

The sample images captured by OptiMelt's digital camera (which are used by the Digital Image Processor to determine unattended melting points and ranges) are also available for real-time transfer to a PC over the USB interface.

The MeltView software package provided with your OptiMelt can handle real-time image transfer, allowing you to display and store high-resolution digital images of the samples (including relevant information such as temperature, time and date) on your computer screen during analysis. All sample images transferred to the PC are bundled together as a single package and automatically stored in the computer's hard disk when the test is completed. This option provides the most powerful and definitive documentation infrastructure available from any commercial melting point apparatus. Stored images may be recalled at any time, and melts can be played back frame-by-frame or as movie, by simply moving a cursor back and forth with your mouse. Being able to replay a test movie after the fact is an invaluable tool for GLP documentation, fine tuning of results, and laboratory demonstrations in educational settings.

The combination of excellent image resolution, high magnification, and the power to carefully step back and forth through a melt provides dramatically enhanced accuracy compared to visual determinations. The ability to display the melt so that several people can view it at once makes the MeltView software package ideal for teaching and lecturing.