TECHNICAL NOTE

Differential Scanning Calorimetry

Use of Wavelet Analysis for Superior Noise Reduction on Weak Transitions

Introduction

Most phenomena measured by thermal analysis result in a heat-flow effect which is large compared to the noise on a differential scanning calorimetry (DSC) baseline. However, there are applications where high sensitivity is called for, such as when measuring low-concentration components, for example additives or low-concentration phase components. For such applications, it is sometimes useful to use a special signal-processing treatment, like wavelet analysis, to reduce random signal noise. With such an approach, the signal is analyzed in the time domain to identify the periodicity of the components which together add up to the total heat-flow signal. When this is done using a statistical process, the components that are purely random can be removed and the signal reconstituted as the normal DSC output. This is a superior approach than merely averaging over a specific time period – or even over an adjustable time period – because it does not result in shifting the data, reducing the resolution of adjacent events or changing the area of peaks.

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Why Not Conventional Smoothing?

Conventional filtering of data to reduce noise works typically by averaging the data. A simple example of such a filter is a running average such as can be found in the trendline options of Microsoft®'s Excel®. A block of data points is averaged and the block is moved forward one point at a time to produce filtered data points. This filter averages out the rapidly varying noise, leaving the slowly varying signal relatively unchanged. The length of the filter block determines the heaviness of the smooth, so noise components with a period less than the block will be suppressed, and the longer the average, the more noise is eliminated. More sophisticated forms of averaging are also used, but the underlying principle is the same.

The problem with this type of filter is that it can only distinguish between signal and noise based on their relative rates of variation. Provided that signal features are broad and noise features are relatively narrow, the filtering can be very effective. However, if the noise and the signal have similar widths, then both will be affected more or less equally by the filtering. Signal is lost and this is observed by the user as a broadening and reduction of features, leading to loss of both qualitative and quantitative information. This can be particularly problematic for sharp peaks and transitions in thermal-analysis data, where the user may wish to separate closely-spaced events or determine peak parameters rather carefully.

Figure 1 shows data obtained on a PerkinElmer® DSC 8000 from an analysis of a 0.93-mg sample of 98% pure hexatriacontane, a saturated aliphatic hydrocarbon having a formula – C_{36}, H_{74} – that exhibits a solid-solid transition just below the melt. The circles indicate the actual raw heat-flow data points, and the solid line indicates the smoothed data produced by applying a 10 data-point rolling average with a window width of 0.4 ˚C. Even with this seemingly minimal smoothing, there is a clear loss of resolution, as indicated by the reduced peak height and filled-in valley between the peaks.

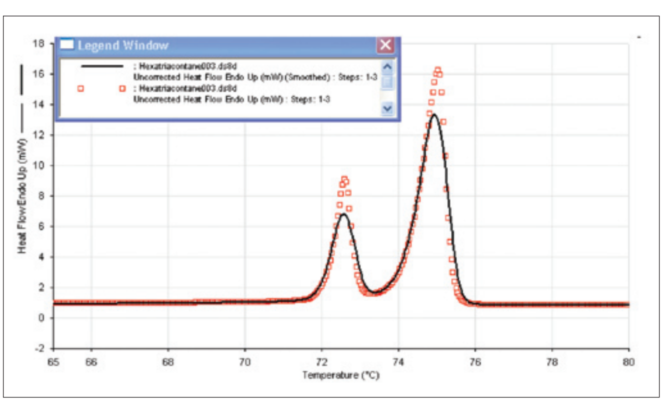

Figure 1. DSC scan of the hexatriacontane melt showing raw data points and conventional smoothing.

The new Wavelet Analysis algorithm from PerkinElmer was also applied to the same data set, as can be seen in Figure 2. The curve fits the raw data with no loss of resolution. Moreover, a calculation of the total peak area and the partial peak areas (not shown) are the same within 0.02%. Clearly, this is a smoothing algorithm we can live with.

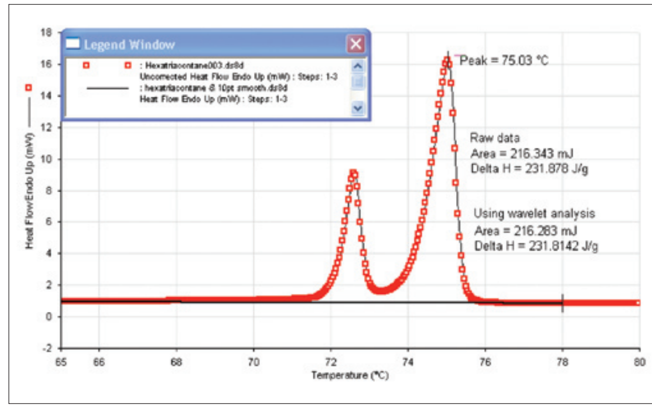

Figure 2. DSC scan of the hexatriacontane melt showing raw data points and wavelet analysis.

How Wavelet Analysis Works

In contrast to averaging, wavelet analysis uses a statistical analysis of the data to distinguish signal from noise. It relies on the fact that despite its random origins, the long-term average character of noise is usually fairly reproducible. Signal, on the other hand, is often quite sparse. There may well be long segments of data with only slowly varying baseline activity (and noise, of course) but only occasional genuine signal. Not only the time character of the signal may be different from the noise – its frequency composition will almost certainly be different. To the eye, this appears as a difference in the character of the shape: signal simply does not look like noise.

Wavelet denoising seeks to break down the combination of signal and noise into its constituent parts as a function of both period (width) and time. The result is a series of time curves characterizing increasingly broader aspects of the original data. A statistical analysis of the time curves then determines the level of the noise components at each width and then de-weights those parts that are clearly noise. The power of wavelet analysis is that the signal can then be reconstructed from the component time curves but minus the noise that was suppressed. The result is effective noise suppression with much less potential for distortion of the signal.

Wavelet Analysis Most Useful for Weak Peaks

One drawback for using wavelet analysis is that *random* noise is sufficiently low that it rarely limits the interpretation of the data. On the other hand, there are sources of noise that are not random and which become more obvious once the random sources are eliminated. Examples of these include: sample motion, pan motion, lid motion, convection effects, imperfect cooler control, and Cp effects due to small variations in the heating rate as experienced by the sample. Trying to interpret small bumps at this level is rarely useful.

An example of a small peak that can benefit from noise reduction can also be seen in the same hexatriacontane analysis at a temperature just below the major peaks. This peak may be due to an impurity or a small amount of material in a different crystalline phase. Figure 3 shows the same DSC analysis presented on a time scale with two regions blown up to better see the reduction in the scatter of the raw data.

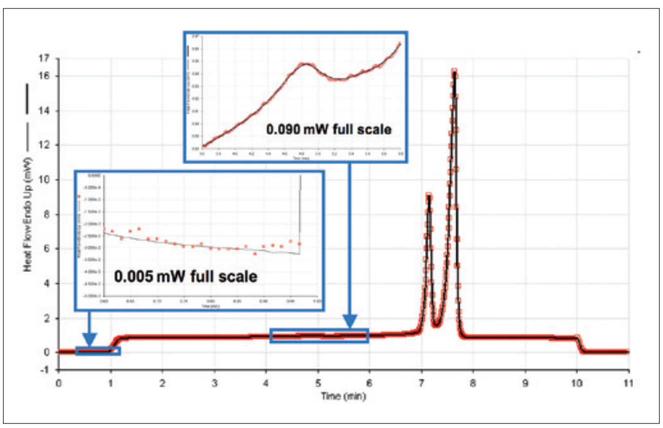

Figure 3. DSC scan of the hexatriacontane melt vs. time with expanded windows to show the fit of the wavelet data in the initial isotherm and in the region of the melting of an impurity.

Conclusion

In summary, smoothing data always carries the risk of losing information or distorting peak shape. However, when using the PerkinElmer DSC 8000 or DSC 8500, wavelet analysis is able to preserve peak shape while reducing random noise.

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