Locating Exotherms in Differential Thermal Analysis with Nonparametric Regression

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Differential Thermal Analysis (DTA) is a technique used to quantify cold tolerance in plants. Plant tissue is cooled and the ambient temperature and the temperature differential between tissue and ambient measured. Freezing episodes, called exotherms, can be identified as changepoints, local minima, or selected inflection points in a plot of differential temperature against ambient temperature. The primary exotherm typically manifests itself as a changepoint and can be identified using techniques similar to those described by Müller (1992). Modifications for locally weighted polynomial regression are proposed here to locate additional exotherms through estimation of first and second derivatives. These techniques involve an innovative combination of local and global bandwidth selection. Finally, the estimators are applied to crepe myrtle (Lagerstremia indica) and pecan (Carya illinoensis) DTA data.

Key Words : bandwidth; changepoint; derivative estimation; local polynomial .

1. Introduction

Differential Thermal Analysis (DTA) is a technique used to assess cold tolerance of plants. Samples of plant tissue are placed in an enclosed, temperature-controlled structure and the temperature is gradually decreased. The air or reference temperature within the enclosure and the differential between the temperature of the tissue and the air are measured at specified sampling intervals. The reference temperature is sometimes measured using a sample of dry or dead tissue. When water within the tissue freezes, heat is released resulting in what is referred to as an exotherm. Multiple exotherms are often observed as water in distinct parts of the tissue freezes. If the reference temperature is placed on the horizontal axis and the differential temperature on the vertical axis, the exotherms can be identified by examining features such as changepoints, local minima, and certain inflection points of the resulting curve. Since water freezing within the tissue is often the cause of injury to the plant, the temperatures at which these freezing points occur are important in determining the level of cold tolerance of a given cultivar or genotype. Plants with exotherms at lower temperatures are typically more tolerant to cold conditions. This information can be used in selection of more cold tolerant genotypes or cultivars. More information on DTA can be found in Barney (1989) and Quamme et al (1972). Section 2 of the present paper provides some details of DTA and defines the exotherms within the framework of a mathematical model.

It is not unusual for hundreds of tissue samples to be subjected to DTA. The primary method of locating exotherms is currently by visual inspection of the raw data or the curves described above. Since each sample typically generates several hundred pairs of reference and differential temperatures, this can be a very costly and time consuming exercise. Hence, an automated, objective means of locating exotherms is desired. Nonparametric regression estimators, particularly locally weighted polynomial estimators (Hastie and Loader, 1993; Ruppert and Wand, 1994), provide the tools necessary to identify exotherms without resorting to a parametric structure in the proposed model. Section 3 provides an overview of these estimators as well as their implementation in exotherm estimation. Section 4 provides details of exotherm location in crepe myrtles (Lagerstroemia indica) and pecans (Carya illinoensis) and Section 5 provides conclusions, discussion, and some alternatives.

2. Differential Thermal Analysis

Tolerance to cold is a limiting factor in the adaptation of plants to new geographical areas. Many cultivars are not viable alternatives in colder climates due to their inability to withstand the harsher temperature conditions. Most cold weather damage to plants occurs when the plant freezes. This often occurs in stages as water in different tissues freezes. Determination of the temperature at which these freezing episodes occur provides information about the minimum temperatures that the plant can withstand. This information can be useful in breeding for improved cold tolerance or cultivar selection for colder climates. One method of determining these critical temperatures is Differential Thermal Analysis (DTA).

In DTA, plant tissue samples are placed in a closed, temperature-controlled environment. The temperature of the air, or other reference temperature, is measured as is the difference between the reference and sample temperature, known as the differential temperature. The temperature is then reduced at a specified rate and both the reference and differential temperatures recorded. As water within the tissue freezes, heat is released causing an increase in differential temperature. Certain changes in the differential temperature versus reference temperature curve during freezing episodes are called exotherms. Figure 1 is an example of a curve with three obvious exotherms. The most prominent exothem occurs at approximately -7.5 °C. The large jump in the curve at that reference temperature is indicative of a significant freezing episode. A different exotherm is located at approximately -18.6 °C and appears on the curve as a local minimum. A less noticeable exotherm occurs earlier at approximately -12.9 °C. The freezing episode associated with this exotherm is more moderate in nature and is manisfested by a "shoulder" on the curve. These three exotherms represent the three types of exotherms commonly seen in DTA. Note that the chronological order of the exotherms is from right to left on the plot. The temperature record was sampled at equal time intervals to produce a total of 431 pairs. Typically, the number of exotherms that are evident varies from sample to sample. The first type appear with virtual certainty and the other two types are seen in many, but not all, samples.

A model describing the relationship between the differential temperature (y_i) and the reference temperature (t_i) is

$$y_i = m(t_i) + \varepsilon_i \ , i = 1, \dots , n, \tag{2.1}$$

where ε_i are random variables with mean zero and common variance σ^2. The function $m(\cdot)$ is assumed to be smooth with continuous derivatives up to some specified order at every t_i with the exception of a changepoint at $t = \tau$.

The three types of exotherms can be defined in terms of the model as follows. The first corresponds to a changepoint and, hence, occurs when the reference temperature is equal to τ. The "shoulder", occurs at reference temperatures where m'' changes from negative to positive and $m' > 0$. The remaining one corresponds to a local minimum and hence corresonds to reference temperatures where m' is zero as it changes from negative to positive.

A general overview of locally weighted polynomial regression is given in the next section. Subsequently, we include details on using these estimation techniques to locate exotherms.

3. Estimation of Exotherms

In this section, the use of nonparametric regression techniques in the location of exotherms is outlined. Section 3.1 provides a brief overview of locally weighted polynomial estimation. Section 3.2 gives details on applying changepoint estimation to exotherm location. Sections 3.3 and 3.4 demonstrate how exotherms that are characterized by local minima and "shoulders" can be located.

3.1 Locally weighted polynomial curve estimation

Locally weighted polynomial estimators have become a realistic choice for data analysts wishing to estimate the relationship between two variables without requiring that the functions fall into a parametric framework. An appropriate model is given in (2.1). Without loss of generality, it is also usually assumed that $t_i \in [0,1]$ for $i = 1, .. n$.

One method proposed (Stone, 1977; Müller, 1987; Fan, 1992; Hastie and Loader, 1993; Ruppert and Wand, 1994) for estimation of $m(\cdot)$ is locally weighted polynomial estimation. A p^{th}

order estimator, $\hat{m}_{lp}(t;h)$ is the appropriate element from the familiar solution to the normal equations, namely

$$\hat{m}_{lp}(t;h) = \mathbf{e}_{1,p+1}(\mathbf{X}'\mathbf{W}\mathbf{X})^{-1}\mathbf{X}'\mathbf{W}\mathbf{y}, \tag{3.1}$$

where $\mathbf{X} = \left(\mathbf{1}\mathbf{Z}\mathbf{Z}^2 \ldots \mathbf{Z}^p\right)$, $\mathbf{W} = diag\left(K\left(\frac{Z_i}{h}\right)\right)$, $\mathbf{Z}^j = \left((x_1-t)^j, \ldots, (x_n-t)^j\right)'$,

and $\mathbf{y}' = \left(y_1, \ldots, y_n\right)$. The vector $\mathbf{e}_{i,j}$ is a vector of length j with a one in the i^{th} location and zeros elsewhere. The function $K(\cdot)$ is a symmetric, positive, 2^{nd} order kernel function defined on [-1,1] such that

$$\int_{-1}^{1} K(u)du = 1, \quad \int_{-1}^{1} uK(u) = 0, \quad \int_{-1}^{1} u^2K(u)du = k_2 \neq 0, \quad \text{and} \quad \int_{-1}^{1} K^2(u)du = Q < \infty.$$

A commonly used function that satisfies these requirements, which has been shown to possess good theoretical properties is $K(u) = .75(1-u^2)$ (Epanechnikov, 1969; Benedetti, 1977).

Essentially, this curve estimator consists of a weighted least-squares fit of a polynomial of degree p at each desired point of estimation. The weights are determined by the function $K(\cdot)$. Most reasonable weight functions place more weight on points closer to the point of estimation and less on those farther away. How much of the data set is included when calculating the estimator is controlled by the parameter h, called a bandwidth. Only those values within the interval $[t-h,t+h]$ are used by the estimator. Hence large values of h result in more data being used and give a smoother estimated curve and small values of h yield a less smooth curve. Optimal choice of h is addressed in the next section.

Derivatives can also be estimated with locally weighted polynomial regression. Estimation of the r^{th} derivative of $m(\cdot)$ at t with a p^{th} order locally weighted polynomial fit ($p \geq r$) yields

$$\hat{m}^{(r)}(t;h) = r!\mathbf{e}_{r+1,p+1}(\mathbf{Z}'\mathbf{W}\mathbf{Z})^{-1}\mathbf{Z}'\mathbf{W}\mathbf{y},$$

with all quantities defined analogously as in (3.1). The next section describes how these estimators can be used in changepoint estimation of the first type of exotherm.

3.2 Changepoint estimation and location of the first exotherm

The first type of exotherm exhibited as the temperature is reduced is characterized by a changepoint in $m(\cdot)$. That is, there exists a reference temperature τ such that $\lim_{t\downarrow\tau} m(t) \neq \lim_{t\uparrow\tau} m(t)$. Typically, there is only one exotherm of this type for a given sample. Müller(1992) proposed a method of estimating a single changepoint using kernel regression estimators (Gasser and Müller, 1979). The technique involves calculating the absolute difference between two regression estimators (p=0) at each candidate value of the explanatory variable using only data to the left and to the right of that value, respectively. The value of the explanatory variable corresponding to the largest such absolute difference is taken as the estimate of the changepoint. However, to calculate this estimator, it is necessary to compute curve estimates at the very edge of the data used for the right and left fits. Clearly these points fall in the boundary area, i.e., within one bandwidth of the edge of the range of the explanatory variable. Kernel regression estimators are known to have increased bias within the boundary region, requiring specialized boundary kernels to overcome this difficulty. Locally weighted polynomial estimators of degree one or greater adapt automatically to the boundary (Fan,1992) and the use of special weighting functions is typically not required. Hence, we use a changepoint estimator employing locally weighted linear regression (p=1) to locate the first type of exotherm.

The proposed procedure consists of stepping through the dataset and at each step dividing the data into left and right portions. Estimation of the mean function at that point using the data to the left and the data to the right separately is then carried out with locally weighted linear regressions. The reference temperature with the largest positive difference between the left and right fits is the estimated exotherm, $\hat{\tau}$. The largest positive difference is used here rather than the largest absolute difference, because only a positive change is indicative of heat being released. Before any estimation can be done, however, bandwidths must be chosen. A local bandwidth selection scheme is proposed.

Bandwidths can be chosen either globally or locally. Global bandwidths employ the same smoothing parameter at each estimation point but local bandwidths allow for a different bandwidth at each point. Thus, a small bandwidth can be used when the function is changing rapidly and not much smoothing is possible. A larger bandwidth is to be used when the function is not changing rapidly and more smoothing is allowable. Müller and Stadtmüller (1987) showed that local bandwidths are more efficient in terms of asymptotic mean squared error (AMSE). A method of local bandwidth selection from Schucany (1995) is adapted here for use in the changepoint problem.

One criterion for local bandwidth selection is to choose a bandwidth that minimizes the AMSE at the point of estimation. The AMSE of the left fit, $\hat{m}_l(t;h_l)$, using bandwidth h_l is (Fan, 1992)

$$AMSE\left[\hat{m}_l(t;h_l)\right] = \left(\frac{1}{2}k_2^* m_l''(t) h_l^2\right)^2 + \frac{\sigma^2 Q^*}{n_l h_l f(t)}, \tag{3.2}$$

where n_l = number of pairs to the left of the point of estimation,

$$k_2^* = \frac{s_{2,0}^2 - s_{1,0}s_{3,0}}{s_{2,0}s_{0,0} - s_{1,0}^2},$$

$$Q^* = \frac{\int_{-1}^{0}\left(s_{2,0} - us_{1,0}\right)^2 K^2(u)du}{\left(s_{2,0}s_{0,0} - s_{1,0}^2\right)^2},$$

$$s_{i,0} = \int_{-1}^{0} u^i K(u)du,$$

and $K(\cdot)$ is a weight function described in Section 3.1. The quantity $f(\cdot)$ is called the design density and is the probability density function of the reference temperatures. The density is taken to be uniform ($f(t)$=1 for all $t \in [0,1]$) for the discussion that follows. In general, the model is $F(t_i)=i/(n+1)$, where F is the cumulative distribution function corresponding to f. In the exotherm application, the uniform density may not hold exactly throughout the entire range of temperatures, but is still a reasonably good approximation. The derivation of (3.2) requires the existence of a finite second derivative, $m_l''(t)$. It should be noted that the first term in (3.2) is the squared asymptotic bias and the second is the asymptotic variance of the estimator. Hence for this estimator to be consistent, the bandwidth must shrink as the sample size increases such that $\lim_{n_l \to \infty} n_l h_l = \infty$. An analogous expression holds for $\hat{m}_r(t;h_r)$.

Differentiation of (3.2) yields an optimal bandwidth of

$$h_{l,opt} = \left[\frac{\sigma^2 Q^*}{\left(k_2^* m_l''(t)\right)^2 n_l} \right]^{1/5}.$$

Since Q^*, k_2^*, and n_l are known, if consistent estimates of σ^2 and $m_l''(t)$ can be obtained, a plug-in estimate of each bandwidth can be calculated. A consistent estimate of σ^2 can be computed using a method developed by Gasser et al (1986). Hence the only real difficulty lies in estimation of $m_l''(t)$.

Schucany (1995) proposed a method of estimation motivated by the form of the squared bias in (3.2)

$$bias\left[\hat{m}_l(t;h_l)\right]^2 = \left(\frac{1}{2}k_2^* m_l''(t)h_l^2\right)^2 = Bh_l^4,$$

which can be viewed as a regression model with independent variable h_l^4 and parameter B. If the bias were known for a fixed grid of h_l's, then least squares could be used to estimate B. However, the bias is not known and must be estimated. One consistent estimator, $\hat{b}$, is

$$\hat{b} = \hat{m}_{l2}(t;h_l) - \hat{m}_{l1}(t;h_l),$$

where $\hat{m}_{l2}(t;h_l)$ and $\hat{m}_{l1}(t;h_l)$ are locally weighted quadratic and linear regression estimators, respectively. Gerard and Schucany (1996) showed that the resulting bandwidth estimator of the form

$$\hat{h}_l = \left[\frac{\hat{\sigma}^2 Q^*}{4\hat{B}n_l}\right]^{1/5} \tag{3.3}$$

is consistent under fairly general regularity conditions for estimation in the interior. It follows also that on the edge of the estimation interval (3.3) is also consistent. See Schucany (1995) for details on the choice of bandwidth grids. An analogous procedure can be followed to determine bandwidths for $\hat{m}_r(t;h_r)$. Now $\hat{\tau} = \arg\max_t(\hat{m}_l(t) - \hat{m}_r(t))$ and we have our estimated exotherm.

Since samples typically have no exotherms prior to this changepoint and only one exotherm of this type is present in a single DTA analysis, the data can now be separated into two disjoint parts. The portion with reference temperatures greater than $\hat{\tau}$ is not searched for exotherms of the other two types. The data with reference temperatures less than $\hat{\tau}$ are investigated for additional exotherms. The next section presents details on locating exotherms that are represented by local minima.

3.3 Local minima exotherm estimation

The second type of exotherm is manifested by a local minimum in $m(t)$, the differential by reference temperature curve. Hence, estimation of first derivatives is required over the range of reference temperatures less than $\hat{\tau}$. The estimated first derivatives can be scanned and those points where the sign changes from negative to positive classified as local minima exotherms.

The use of local polynomial estimation (Ruppert and Wand, 1994) allows for estimation of the derivatives of the underlying mean function. The regression coefficient for the r^{th} order term in a p^{th} order local polynomial fit ($p \geq r$) is an estimate of $m^{(r)}(t)/r!$. For p-r odd, the expression for the asymptotic bias of the derivative estimator is less complicated. Hence we use a locally weighted quadratic estimator and the coefficient of the linear term is our estimate of the first derivative, $\hat{m}^{(1)}(t)$. Under general regularity conditions, the asymptotic bias and variance are

$$\text{bias}\left[\hat{m}^{(1)}(t)\right] \approx \frac{1}{6} m^{(3)}(t) \frac{k_4}{k_2} h^2 = B_1 m^{(3)}(t) h^2$$

and

$$\text{var}\left[\hat{m}^{(1)}(t)\right] \approx \frac{\sigma^2}{nh^3 k_2^2} \cdot \int_{-1}^{1} K^2(u)\,du = \frac{\sigma^2 V_1}{nh^3},$$

where

$$k_i = \int_{-1}^{1} u^i K(u)\,du. \tag{3.4}$$

Since neighboring estimates are compared to determine the location of local minima, it is desirable that the estimates have an equal amount of smoothing. With this in mind, we use a global bandwidth procedure suggested by Gasser et al (1991) and modified by Herrmann (1994) for derivative estimation. The procedure attempts to find the bandwidth that minimizes the Integrated Mean Square Error of prediction using a fixed number of iterations. The procedure outlined by Gasser et al (1991) uses exactly eleven steps. For derivative estimation, the number of iterations varies depending on the derivative to be estimated. The steps for first derivative estimation are outlined below, making use of the asymptotic equivalence of this local polynomial estimator and a third-order kernel estimator.

1. Set h_0=2/n.

2. Iterate the following step for i=1,...,16.

$$h_i = \left(\frac{3}{4n} \frac{V_1 \hat{\sigma}^2}{B_1^2 \left(\int_0^1 v(t) \left(\hat{m}^{(3)}\left(t; \hat{h}_{i-1} n^{1/14}\right) \right)^2 dt \right)} \right)^{1/7}.$$

3. Stop after 16 iterations and set $h = h_{16}$.

The estimate of the third derivative is obtained from the coefficient of the cubic term of a locally weighted third-order fit. The function $v(t)$ is a weight function used to eliminate boundary effects, taken here to be an indicator function for $t \in [.1,.9]$. The estimate of σ^2 is again found using the method of Gasser et al (1986). Using the global bandwidth, the estimates of the $m'(t_i)$ can be evaluated on a grid of points and local minima located approximately. For convenience, the values of t are scaled to lie in the interval [0,1]. Though the estimates of derivatives are also scaled, the methods proposed are invariant to these scale changes. These estimates are also subsequently used to locate the third type of exotherm discussed in the next section.

3.4 Estimation of shoulder exotherms

The third type of exotherm is identified by the second derivative changing signs from negative to positive while the first derivative remains positive. This gives the appearance of a "shoulder" on the curve. Since the first derivatives are found to locate local minima exotherms, all that remains is estimation of the second derivatives. A third-order locally weighted fit is used and the coefficient of the quadratic term is $\hat{m}^{(2)}(t)/2$. Hence, twice the regression coefficient estimates the required derivative.

Under general regularity conditions, the asymptotic bias and variance of the estimate of second derivative are

$$\text{bias}\left[\hat{m}^{(2)}(t)\right] \approx \frac{1}{24} m^{(4)}(t) B_2 h^2$$

and

$$\text{var}\left[\hat{m}^{(2)}(t)\right] \approx \frac{\sigma^2 V_2}{nh^5},$$

where

$$B_2 = 2\frac{k_4^2 k_6 + k_2^2 k_6 k_4 - k_2 k_6^2 - k_2 k_4^3}{k_4^3 + k_2^3 k_6 - k_2 k_4 k_6 - k_2^2 k_4^2},$$

$$V_2 = 4\frac{\left[\begin{array}{l}\int_{-1}^{1} K^2(u)\left(k_4^2 k_6^2 + k_2^2 k_4^4 - 2k_2^3 k_4^2 k_6\right)du + \int_{-1}^{1} u^4 K^2(u)\left(k_4^4 + k_2^2 k_6^2 - 2k_2 k_4^2 k_6\right)du \\ +2\int_{-1}^{1} u^2 K^2(u)\left(k_2^2 k_6 k_4^2 - k_2 k_4^4 + k_2^2 k_4^2 k_6 - k_2^3 k_6^2\right)du\end{array}\right]}{\left(k_4^3 + k_2^3 k_6 - k_2^2 k_4^2 - k_2 k_4 k_6\right)^2},$$

and the k_i are defined in (3.4).

As with the first derivative, a global bandwidth is used to estimate the second derivative. The procedure of Gasser et al (1991) as modified by Herrmann (1994) is as follows.

1. Set h_0=4/n.

2. Iterate the following step for i=1, .. ,21.

$$h_i = \left(\frac{5}{4n}\frac{V_2\hat{\sigma}^2}{B_2^2\left(\int_0^1 v(t)\left(\hat{m}^{(4)}\left(t;\hat{h}_{i-1}n^{1/18}\right)\right)^2 dt\right)}\right)^{1/9}$$

3. Stop after 21 iterations and set h=h_{21}.

The estimate of the fourth derivative, $\hat{m}^{(4)}(t)$, is from a fourth-order local polynomial fit. The estimate of σ^2 and the function $v(t)$ are as in the previous section. Using this bandwidth estimator, the second derivatives are estimated and points where the sign changes from negative to positive accompanied by a positive first derivative are selected as "shoulder" exotherms. These techniques are applied in the next section to identify exotherms for crepe myrtles and pecans.

4. Application : Location of Crepe Myrtle and Pecan Exotherms

The results of differential thermal analysis of a tissue sample (n=431) from crepe myrtle are plotted in Figure 2. For completeness the curve from Figure 1 is reproduced as Figure 2a. In keeping with the algorithm in Section 3.2, the first type of exotherm that is located is the changepoint exotherm. The differences between the left and right boundary fits are plotted against reference temperature in Figure 2b. The largest difference corresponds to a reference temperature of -7.54° C, which agrees closely with the jump seen in Figure 1. This value locates $\hat{\tau}$, the first estimated exotherm, and reference temperatures larger than this value are not searched for additional exotherms. The estimated first derivatives and second derivatives for the reference temperatures less than -7.54° C are plotted in Figure 2c and Figure 2d, respectively. The exotherms characterized by local minima are shown in Figure 2c to be -31.44° C and -18.61° C. The shoulder exotherms are shown in Figure 2d to be -24.64° C, -15.10° C, and -12.88° C. The two shoulder exotherms at the lower temperatures are difficult to see in Figure 1 without close inspection of the data. Further, the local minimum exotherm at -31.44°C is also not obvious and might be missed in a quick inspection of the plot.

The results of differential thermal analysis of pecan tissue (n=690) is shown in Figure 3. Plots providing details of the location of exotherms are found in Figure 4a-d. The first exotherm is estimated to be -9.065 °C. Searching reference temperatures less than -9.065 °C yields local minimum exotherms at -10.58 °C and -23.56 °C and a shoulder exotherm at -14.02 °C. These are in close agreement with exotherms determined from a close visual inspection of Figure 3.

5. Discussion

The nonparametric regression techniques described and illustrated in the previous sections provide a fast, automatic method of locating exotherms used to evaluate cold tolerance in plants. Changepoint estimation techniques provide an accurate method of locating the first exotherm, where the most damage to the plant is usually sustained. Subsequent, less dramatic, freezing events are located by searching estimates of first and second derivatives to find their corresponding exotherms. The methods proposed here tend to locate more exotherms than would be found using the naked eye. This is especially true in areas where the curve is flat, which can lead to estimates of the first derivative that fluctuate about zero, or where the curve is essentially linear, which can lead to similar fluctuations in the second derivative estimate.

In many instances, this increased sensitivity is desirable, at least as a screening mechanism, so that the scientist may choose critical exotherms from a list of candidates. In the event that location of only the strongest freezing episodes is desired, there are ways to remove some candidate exotherms from consideration. First, since most of the less obvious exotherms occur in an area where more smoothing is required, local bandwidth techniques could be used for derivative estimation as well as in changepoint location. The method of Schucany (1995) could be extended to provide the required local bandwidths. These local bandwidths would allow for more smoothing to be done in those areas where undersmoothing may be causing spurious exotherm location.

Another method to reduce the number of candidate exotherms involves confidence intervals. Since the derivative estimators are linear functions of the data, central limit theorems (Müller, 1988) are available for the asymptotically equivalent local polynomial estimators and kernel estimators. Gasser and Kneip (1995) proposed such a method by constructing confidence intervals on $m'(t)$ and $m''(t)$, whenever the bias in these estimators is negligible. One way of eliminating spurious exotherms would be to disregard those candidates that do not have a significantly nonzero derivative from all of the simultaneous confidence intervals between the proposed exotherm and the nearest zero on the derivative curve. In the crepe myrle example of the previous section, this would eliminate all exotherms except those three mentioned in the Introduction. No exotherms would be eliminated from the pecan example. A system involving quick visual inspection of a set of candidate exotherms as well as subjecting these exotherms to an objective criterion using confidence intervals would provide the scientist with a substantial amount of information for informed judgements regarding these locations.

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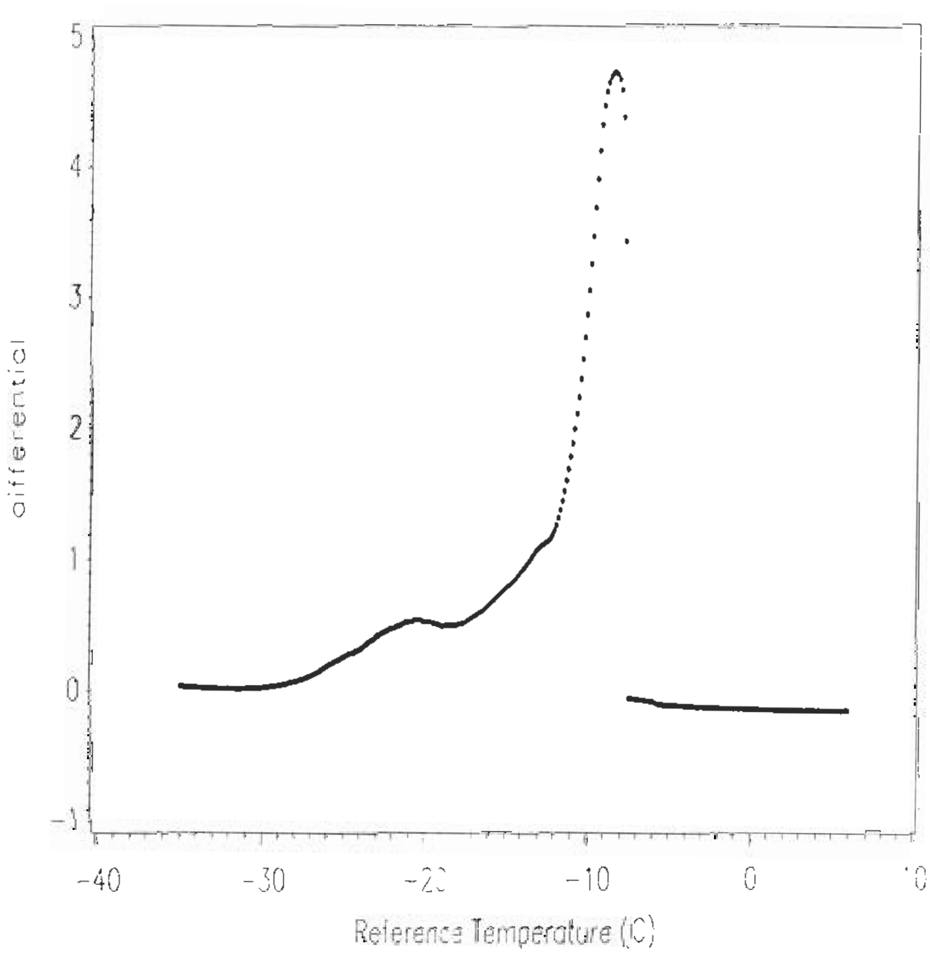

Figure 1. Crepe Myrtle plot of differential versus reference temperature.

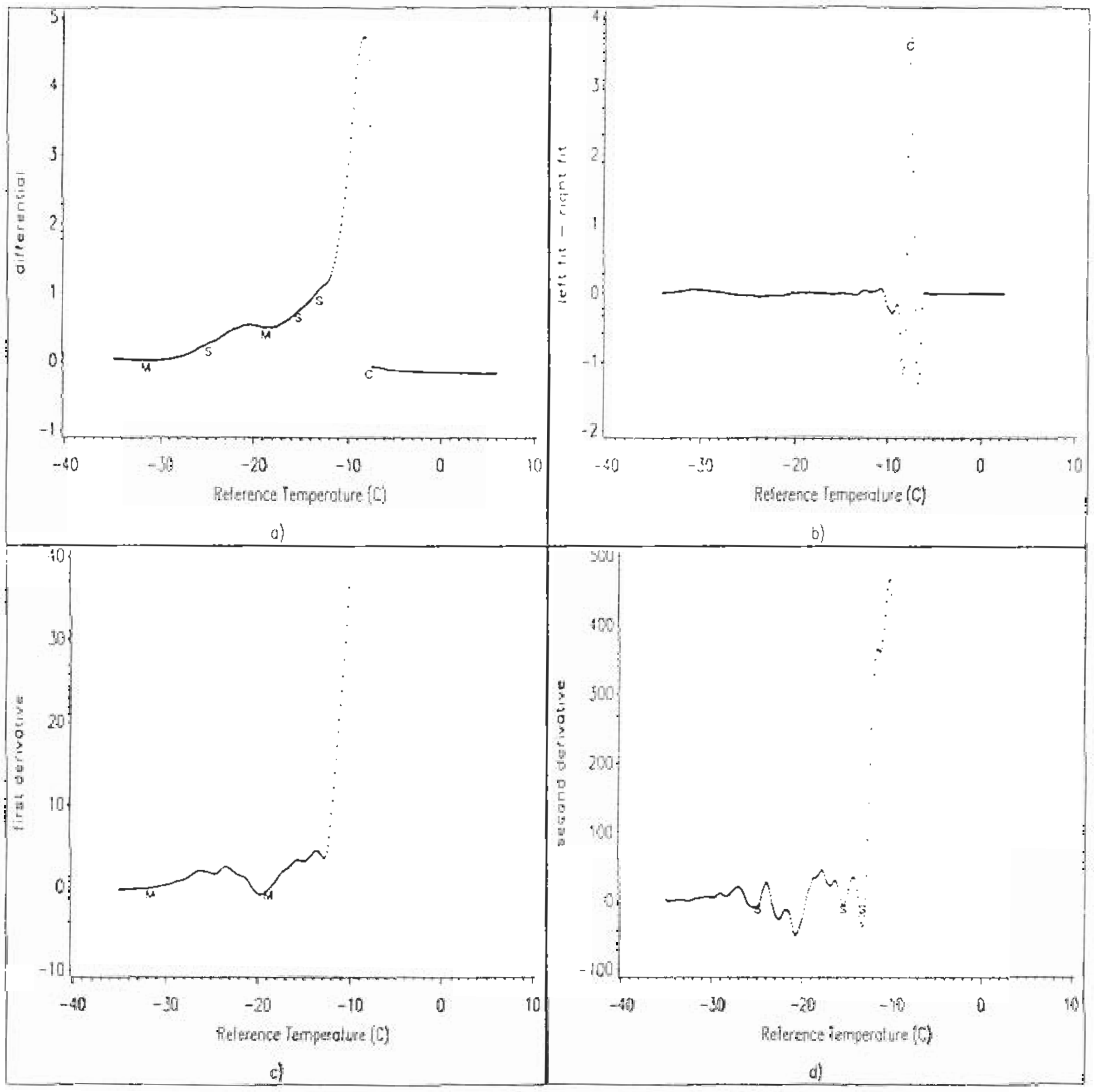

Figure 2. Plot of Crepe Myrtle (a) differential,(b) difference of left and right fits,(c) first derivative, and (d) second derivative versus reference temperature. The changepoint (C), local minima (M), and shoulder (S) exotherms are noted.

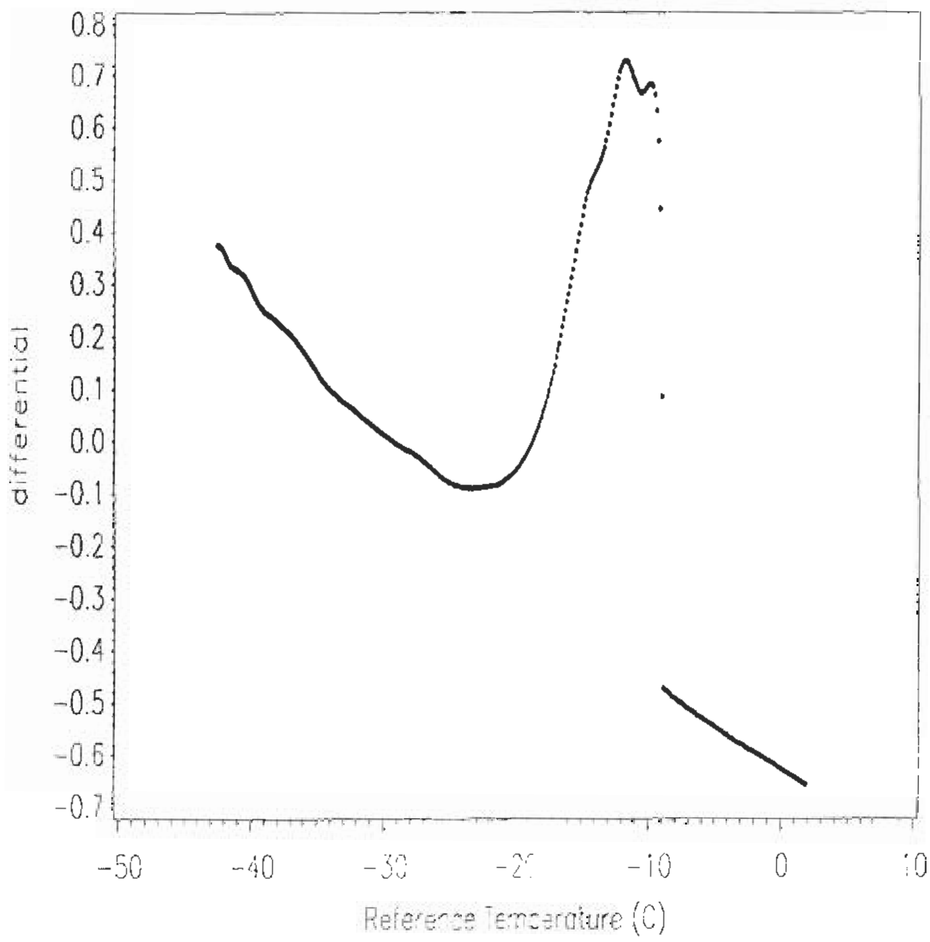

Figure 3. Pecan plot of differential versus reference temperature.

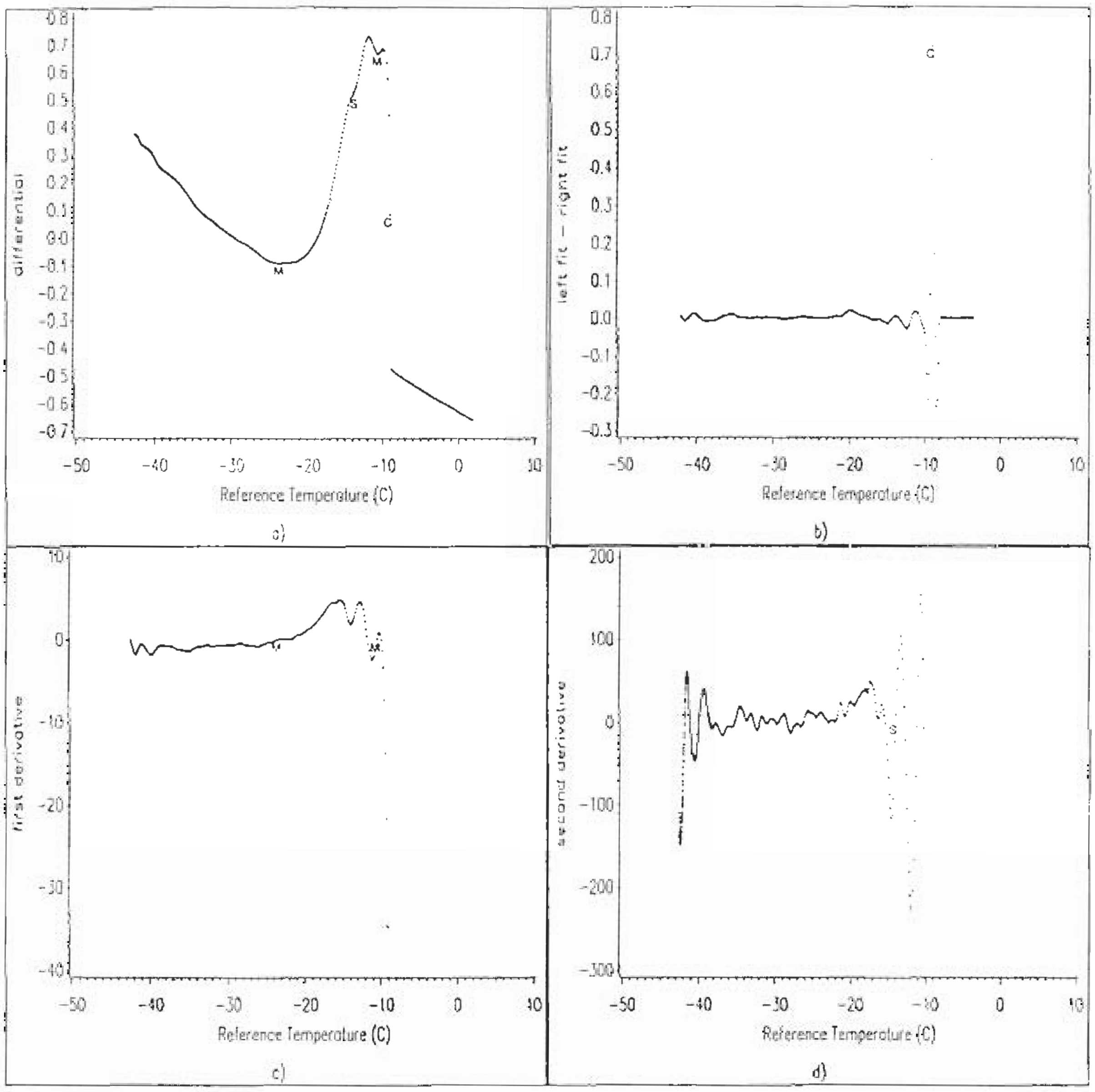

Figure 4. Plot of Pecan (a) differential,(b) difference of left and right fits,(c) first derivative, and (d) second derivative versus reference temperature. The changepoint (C), local minimum (M), and shoulder (S) exotherms are noted.