Peak Estimation of a Spectrum from Noisy Measurements by Least Squares Piecewise Monotonic Data Approximation

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***Abstract*—We consider the application of the piecewise monotonic data approximation method to some problems that are derived from peak estimation of univariate spectra contaminated by random errors. This method makes the smallest change to the data such that the first differences of the smoothed values change sign a prescribed number of times. The algorithms that we have developed for this challenging combinatorial calculation are very efficient providing optimal solutions in quadratic complexity with respect to the number of data. We present examples that show the efficacy of the method in peak estimation to data from a Raman spectrum. Our results exhibit some strengths and certain advantages of the method. Therefore, they may be helpful to the development of new algorithms that are particularly suitable for peak estimation in spectroscopy calculations.**

***Index Terms*—data smoothing, divided differences, peak finding, piecewise monotonic approximation, Raman spectrum, spectroscopy.**

I. Introduction

Peak estimation problems appear inherently in spectroscopy. In proton spectroscopy, for example, magnetic resonance allows examining the metabolism of mass lesion areas due to the height of the peaks. Infrared and Raman are the most common vibrational spectroscopy techniques for assessing molecular motion and fingerprinting species. For the Raman spectra, the location of peaks and their intensities are the signature of a sample of an organic or an inorganic compound. In general, the detection of peaks and troughs in time series is a long-standing problem in many applications. Peaks and troughs represent the most interesting trends in time series analyses.

We consider the important problem in which a number of values of a univariate spectrum have been measured, but the measurements include errors and the data are to be used to estimate the peaks of the spectrum. We assume that if the spectrum has turning points, then the number of measurements is substantially greater than the number of turning points. Therefore we apply a method that smooths the data by imposing a limit on the number of sign changes in the sequence of the first differences. To be precise if $k-1$ is the limit, then the piecewise linear interpolant to the approximated values is composed of at most k monotonic sections.

The positions of the joins of the monotonic sections are integer variables of the optimization calculation whose optimal values have to be found automatically, but, if n is the number of data, about $O(n^k)$ combinations of positions can occur that makes it impossible to test each one separately. This problem was studied in depth by Demetriou and Powell [10] and furthermore some highly efficient algorithms and software have been developed by Demetriou [5], [6] and [8]. The algorithms calculate efficiently a global solution in $O(kn^2)$ computer operations, a complexity which reduces to only $O(n)$ when $k = 1$ or $k = 2$. The piecewise monotonicity method decomposes the spectrum into at most k monotonically increasing and decreasing sections. Each peak is the join of an increasing and a decreasing section.

Some advantages of our technique over other smoothing techniques are as follows. First, there is no need to choose a set of approximating functions as for example in splines or wavelets [1], [11], [14]. Second, the smoothing process is a projection because, if it is applied to the smoothed values, then no changes are made to. Third, it is not inefficient to run the algorithm of [10] for a sequence of integers k if a suitable value is not known in advance. An immediate consequence is that due to the nature of the smoothing condition that is defined by the constraints on the components of the approximant, irregular errors in the data do not cause piecewise monotonic approximation to ripple. Moreover, a feature of the piecewise monotonic approximation is that the presence of a peak does not introduce any perturbation away from the peak. In other words, the method avoids Gibb's ringing and is able to represent the data at a peak without becoming less accurate away from the peak. This makes the method highly suitable for the peak estimation purpose.

The paper is organized as follows. In Section II we outline the method for piecewise monotonic data approximation. In Section III we present an example that illustrates the estimations of peaks in a Raman spectrum sample. The results are instructively analyzed and the estimation capability of the method is demonstrated. In Section IV we present some concluding remarks and discuss on the possibility of future directions of this research.

More generally one could apply piecewise monotonic approximation to a variety of situations in which peak estimations are required but we do not have sufficient information to state a parametric form. Such situations are quite common so applications of piecewise monotonic approximation may arise in several fields.

Fortran software packages that implement different versions of the method were developed by the author [6], [9]. They are quite suitable for processing large numbers of data in real time. In order to apply the piecewise monotonicity method to a sequence of data, only one parameter, namely

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k, must be set by the user. Then the method automatically obtains the optimal turning points and the smoothed values. The calculations were performed on a HP 8770w portable workstation with an Intel Core i7-3610QM, 2.3 GHz processor, which was used with the standard Fortran compiler of the Intel Visual Fortran Composer XE2013 in single precision arithmetic operating on Windows 7 with 64 bits word length.

II. Least Squares Piecewise Monotonic Data Approximation

This section presents some background results and notation. For proofs of our statements one may consult [10] and [5]. The user provides the data $\{\phi_i : i = 1, 2, \ldots, n\}$ and an integer k, which is an upper bound on the number of monotonic sections of the smoothed values. The method seeks values $\{y_i : i = 1, 2, \ldots, n\}$ that minimize the sum of squares of residuals

$$\Phi(y_1, y_2, \ldots, y_n) = \sum_{i=1}^{n} (y_i - \phi_i)^2 \tag{1}$$

subject to the piecewise monotonicity constraints

$$\left.\begin{array}{l} y_{t_{j-1}} \le y_{t_{j-1}+1} \le \cdots \le y_{t_j},\ j \text{ is odd} \\ y_{t_{j-1}} \ge y_{t_{j-1}+1} \ge \cdots \ge y_{t_j},\ j \text{ is even} \end{array}\right\}, \tag{2}$$

where the integers $\{t_j : j = 1, 2, \ldots, k-1\}$ satisfy the conditions

$$1 = t_0 \le t_1 \le \cdots \le t_k = n. \tag{3}$$

Without loss of generality we assume that the first section is increasing. Assuming that the data do not satisfy the constraints, it follows that the optimal integers $\{t_j : j = 1, 2, \ldots, k-1\}$ are all different. Their values are calculated by a dynamic programming method, whose basic version is described below.

The efficiency of the method depends on two main properties of the optimal fit. One is that if $1 \le j \le k-1$ then the optimal value of y_{t_j} is independent of $\{y_i : i \ne t_j\}$ and at the turning points (local extrema) of the fit we have the interpolation conditions

$$y_{t_j} = \phi_{t_j},\ j = 1, 2, \ldots, k-1. \tag{4}$$

These conditions are fundamental to the peak estimation problem. Secondly, the associated optimal piecewise monotonic approximation consists of separate optimal monotonic sections of adjacent components that increase and decrease alternately between adjacent integers of the sequence $\{t_j : j = 0, 1, \ldots, k\}$. Thus, the components $\{y_i : i = t_{j-1}, t_{j-1}+1, \ldots, t_j\}$, $1 \le j \le k$, minimize the sum

$$\sum_{i=t_{j-1}}^{t_j} (y_i - \phi_i)^2 \tag{5}$$

subject to the increasing monotonicity constraints

$$y_i \le y_{i+1}, i = t_{j-1}, t_{j-1}+1, \ldots, t_j, \quad \text{if } j \text{ is odd} \tag{6}$$

or subject to the decreasing monotonicity constraints

$$y_i \ge y_{i+1}, i = t_{j-1}, t_{j-1}+1, \ldots, t_j, \quad \text{if } j \text{ is even.} \tag{7}$$

For all positive integers s and t such that $1 \le s \le t \le n$, we define $\alpha(s, t)$ to be the least value of (5) subject to (6), after we replace t_{j-1} by s and t_j by t, and analogously we define $\beta(s, t)$ to be the least value of (5) subject to (7). The calculation of the best monotonic increasing fit on $[t_{j-1}, t_j]$ together with all the numbers $\alpha(t_{j-1}, i),\ i = t_{j-1}, t_{j-1}+1, \ldots, t_j$ is achieved in only $O(t_j - t_{j-1})$ computer operations. This surprisingly little work contributes heavily to the efficiency of the calculation of an optimal piecewise monotonic fit.

These two properties lead to the important characterization of the problem that the first t_{k-1} components of an optimal fit with k sections to the data $\{\phi_i:\ i = 1, 2, \ldots, n\}$ give an optimal fit with $k-1$ sections to the data $\{\phi_i:\ i = 1, 2, \ldots, t_{k-1}\}$ and the last $n - t_{k-1} + 1$ components give the optimal fit to the data $\{\phi_i :\ i = t_{k-1}, t_{k-1}+1, \ldots, n\}$ subject to the constraints $y_{t_{k-1}} \le y_{t_{k-1}+1} \le \cdots \le y_{t_k}$, if k is odd, or subject to the constraints $y_{t_{k-1}} \ge y_{t_{k-1}+1} \ge \cdots \ge y_{t_k}$, if k is even.

Hence introducing the notation

$$\gamma(m, t) = \min_{z_i, i=1,2,\ldots,t} \sum_{i=1}^{t} (z_i - \phi_i)^2,\ 1 \le t \le n,$$

where the components $z_i, i = 1, 2, \ldots, t$ have m monotonic sections for $m \in [1, k]$, the integer t_{k-1} at an optimal fit satisfies the equation

$$\left.\begin{array}{l} \gamma(k, n) = \gamma(k-1, t_{k-1}) + \alpha(t_{k-1}, n), k \text{ odd} \\ \\ \gamma(k, n) = \gamma(k-1, t_{k-1}) + \beta(t_{k-1}, n), k \text{ even} \end{array}\right\}. \tag{8}$$

where $\gamma(k, n)$ is the least value of (1).

Provided that the sequences $\{\gamma(k-1, s) :\ s = 1, 2, \ldots, n\}$ and $\{\alpha(s, n) :\ s = 1, 2, \ldots, n\}$ are available, the right hand side of (8) when k is odd is the least value of $\{\gamma(k-1, s) + \alpha(s, n) :\ s = 1, 2, \ldots, n\}$ and can be found in $O(n)$ computer operations; similarly when k is even. Therefore in order to calculate $\gamma(k, n)$, we begin with the values $\gamma(1, t) = \alpha(1, t)$, for $t = 1, 2, \ldots, n$ and proceed by applying the dynamic programming formulae

$$\gamma(m, t) = \left\{\begin{array}{l} \min\limits_{1 \le s \le t} [\gamma(m-1, s) + \alpha(s, t)], m \text{ odd} \\ \min\limits_{1 \le s \le t} [\gamma(m-1, s) + \beta(s, t)], m \text{ even,} \end{array}\right. \tag{9}$$

for $t = 1, 2, \ldots, n$, for every value of $m \in [2, k]$. It follows that $\gamma(k, n)$ can be found in $O(kn^2)$ computer operations.

We let also $\tau(m, t)$ be the value of s that minimizes expression (9), for each value of m and t. When $m = k$ occurs, the value $\tau(k, n)$ is the integer t_{k-1} that is required in equation (8). Hence, with $t_0 = 1$ and $t_k = n$, we obtain the sequence of optimal values $\{t_j :\ j = 1, 2, \ldots, k-1\}$ by the backward formula

$$t_{m-1} = \tau(m, t_m), \text{ for } m = k, k-1, \ldots, 2. \tag{10}$$

Finally, the components of the best fit are calculated by independent monotonic approximation calculations. They are monotonic increasing on $[1, t_1]$ and on $[t_{j-1}, t_j]$ for odd j in $[2, k]$ and monotonic decreasing on $[t_{j-1}, t_j]$ for even j in $[2, k]$.

Formulae (9) provide the basis for the calculation, but far more efficient formulae are employed in practice by restricting the search for the optimal values of $\{t_j :\ j = 1, 2, \ldots, k-1\}$ to certain subsets of the data. To be specific, we define $t \in [1, n]$ to be the index of a local minimum of the

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data if, moving to the left or right from ϕ_t in the sequence $\{\phi_i : \ i = 1, 2, \ldots, n\}$, we find either $\phi_i > \phi_t$ or the end of the sequence before $\phi_i < \phi_t$ occurs, and analogously for a local maximum. The indices of local minima and local maxima of the data are collected in the sets $\mathcal{L}$ and $\mathcal{U}$ respectively. Both the sets $\mathcal{L}$ and $\mathcal{U}$ can be formed in $O(n)$ operations, their elements are in strictly ascending order and their interior elements interlace. Usually each of these sets has fewer than $n/2$ elements. Therefore, restricting s and t to the sets $\mathcal{L}$ and $\mathcal{U}$ or $\mathcal{U}$ and $\mathcal{L}$, formulae (9) require $O(k|\mathcal{U}|^2)$ computer operations, which is a reduction in the amount of work at least by a factor of 4. Further, an alternative application of the dynamic programming formulae by a binary tree algorithm [8] reduces substantially this complexity to only $O(k|\mathcal{U}| \log_2 |\mathcal{U}|)$.

III. Estimation of Peaks of a Raman Spectrum

In this section we present an example of our method intended to illustrate the estimation of peaks in a Raman spectrum sample. As was noted already, the location of peaks and their intensities for the Raman spectra are the signature of a sample. Raman spectroscopy is a powerful tool for analysis and chemical monitoring of solids, liquids and solutions, as well as for providing information on physical characteristics [19]. For medical and industrial applications see Renishaw plc [20]. The complexity of the underlying physical laws make this a good test of the power of the piecewise monotonic approximation method in peak finding.

We downloaded the datafile named "amylose" from SPECARB, an experimental database containing Raman spectra of carbohydrates, which is freely available on the website [22] of the Department of Food Science, Faculty of Science, University of Copenhagen. This spectrum was sampled on a Perkin Elmer System 2000 interferometer with a Nd:YAG laser using excitation 1064 nm, laser power 400 mW, Raman shift 3600-0 cm^{-1}, accumulations 256 and resolution 4 cm^{-1}.

The amylose datafile contains two-column data, where the first column keeps the Raman shift (cm^{-1}) and the second column keeps the intensity, which provide the values $\{x_i : \ i = 1, 2, \ldots, n\}$ and $\{\phi_i : \ i = 1, 2, \ldots, n\}$ respectively for our calculations. The abscissae $\{x_i : \ i = 1, 2, \ldots, n\}$ are irrelevant to our calculation, except that they are used in our plots. The file contains 3401 pairs of data (having $|\mathcal{U}| = 404$ and $|\mathcal{L}| = 405$), far too many to be presented as raw numbers in these pages. However, we may easily capture the main features of this data set by looking at Fig. 1. Indeed, we can see, for instance, very small deviations, some very distinguishable peaks, sharp increases and several peaks with lower intensity.

We seek turning points that might reveal major monotonic trends. We fed the data to our computer program with $k = 20$ without any preliminary analysis. The resultant fit and the peaks with the corresponding intensities are displayed in Fig. 1. We see that the fit to the data is much smoother than are the data values themselves and the sum of squares of residuals is equal to 11.25.

In case that the first attempt at estimating suitable turning points of these data is not entirely satisfactory, we carried out two more runs with larger numbers of turning points in order to give more emphasis to minor monotonic trends. The piecewise monotonic approximation with $k = 32$ was calculated giving 31 turning points and having sum of squares of residuals equal to 2.39. Fig. 2 displays the data, the fit and the turning points. The new fit maintained the turning points of the fit presented in Fig. 1, while the extra turning points have indices $441, 459, 691, 709, 735, 761, 1081, 1095, 1264,$ $1284,$ 1364 and 1382.

Further, the piecewise monotonic approximation with $k = 36$ gave automatically four extra turning points with indices $339, 357, 405$ and 419 that enhance the left hand side of the fit in Fig. 2. The fit is presented in Fig. 3, the extra peaks are highlighted and the sum of squares of residuals is equal to 1.58.

We see that the piecewise monotonic approximation has revealed the most important turning points (peaks and troughs), while it interpolates the data at these points. By increasing k, piecewise monotonic approximation had the freedom to make the sum of the squares of residuals smaller, while it maintained the most important turning points.

Therefore we investigate further this behavior of the approximation by presenting in Table I the turning point positions by piecewise monotonic fits to the amylose data for various values of k. In the right hand side part of Table I we give the positions of the turning points of each optimal fit for $k \in \{2, 4, 8, 12, 16, 20, 24, 28, 30, 32, 34, 36\}$ in correspondence with the column labeled "t_j", which is derived when $k = 36$. For example, when $k = 4$ the turning points occur at positions 481 (peak), 2454 (trough) and 2905 (peak) as indicated by the times signs in the column labeled "4". A comparison of the k-columns shows the differences in the final fits to the given Raman spectrum with respect to the values of k. It is noticeable that as k was increased to an adjacent value, the extra turning points of the optimal fit occurred between adjacent turning points of the associated optimal fit for the previous k. Although it is usual in practice that the turning points of an optimal fit with k monotonic sections are preserved by the optimal fit with $k + 2$ monotonic sections, it should be noted that this depends on the specific calculation and need not happen generally. Indeed, it has been shown by [4] that any algorithm based on local improvements of an optimal approximation with k monotonic sections cannot succeed in finding more than a local minimum of (1), which need not be a global minimum.

Two points are worth emphasizing with respect to this example. Firstly, the method effectively captured the trends of the data and detected appropriate peaks as required by the values of k. Moreover, by comparing Figs. 1, 2 and 3, there seems that as k increased, the method detected subtle trends in the data, which are not detected for smaller values of k, because they are rather conservative. Secondly, the problem of systematic differences between piecewise monotonic approximations for consecutive values of k to the same data needs attention, which is likely to lead to the development of more efficient algorithms. Further, if there exists appropriate *a priori* information to be taken into account about the required number of peaks, it is very useful that the analyst may well combine it with the automatic feature of our method.

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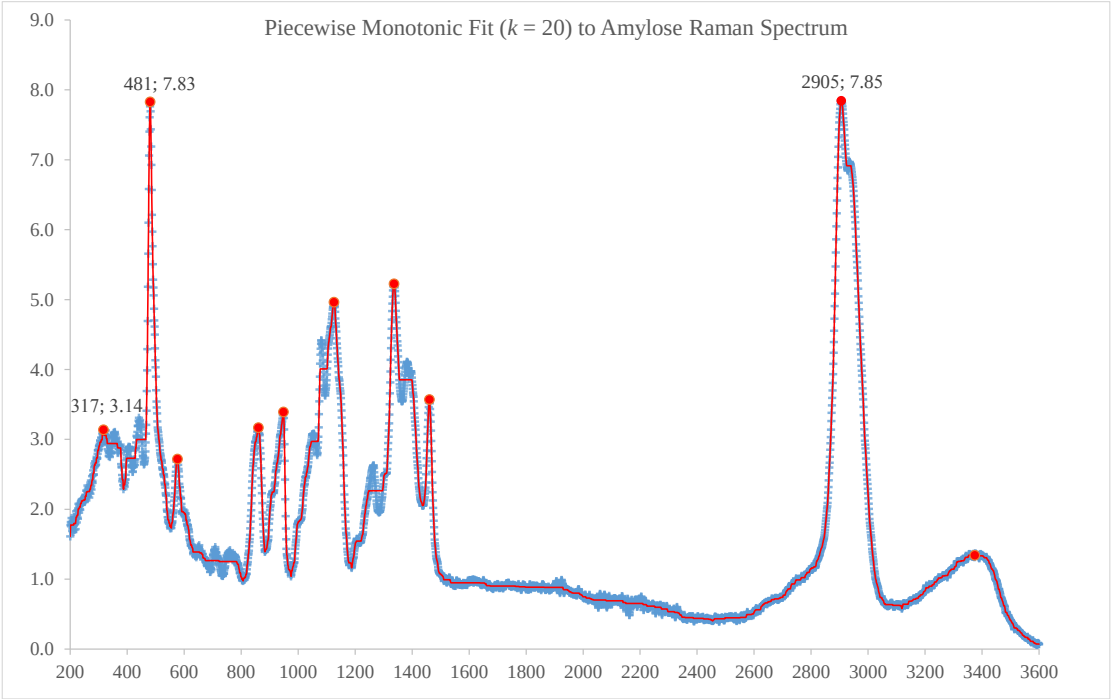

Fig. 1. Detected peaks (circles) by a best piecewise monotonic fit with $k = 20$ to 3401 data points (plus signs) of the amylose Raman spectrum. The solid line illustrates the best fit. The numbers give the intensities at the corresponding Raman shifts (cm^{-1}).

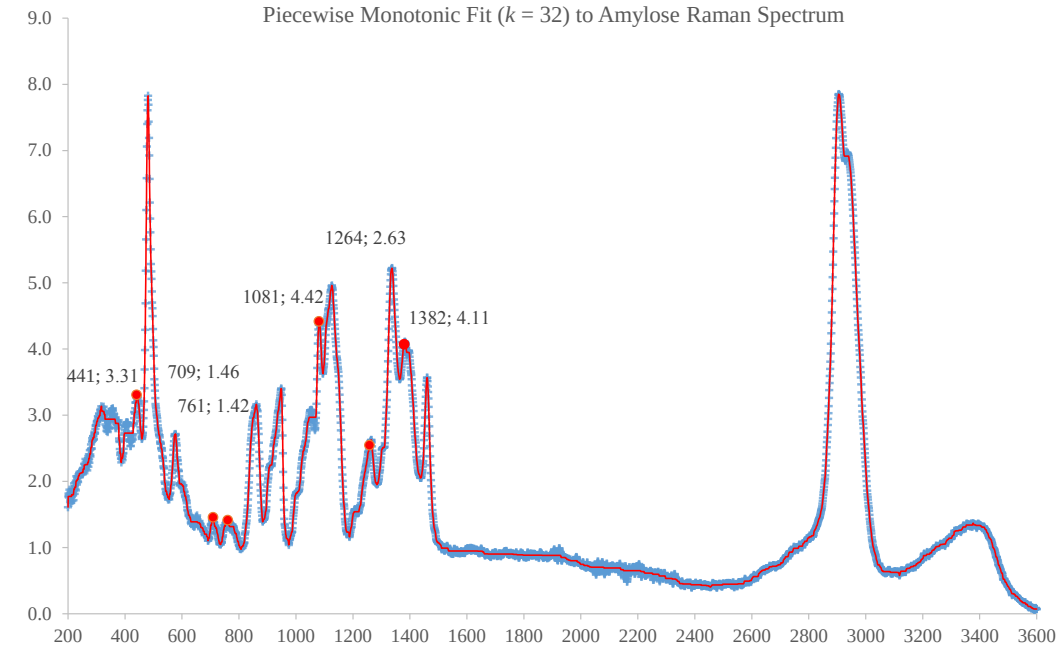

Fig. 2. As in Fig. 1, but $k = 32$. The extra peaks as compared to Fig. 1 are indicated by circles.

IV. Conclusions

Piecewise monotonic approximation as a data smoothing approach can have many applications. In this work we have presented an application that shows the effectiveness of piecewise monotonic approximation to peak estimation of spectra that are represented by some noisy measurements of their values. The optimization calculation may have a very large number of local minima, but we have procedures that obtain a global solution in quadratic complexity with respect to n. Several improvements of the calculation are available in [5] and [10], which have been taken into account by the software package [6] as well as by the unpublished as yet software [9]. These software packages are far faster in practice than the complexity indicates in theory. They are suitable for calculations that involve very large amounts of data points and they would be most useful for real time processing applications. In view of the effort and time that was needed to develop the Fortran software, it is expected that these packages will be of value to many computer calculations.

The method achieves the piecewise monotonicity property it sets out to achieve and, generally, any degree of undulation

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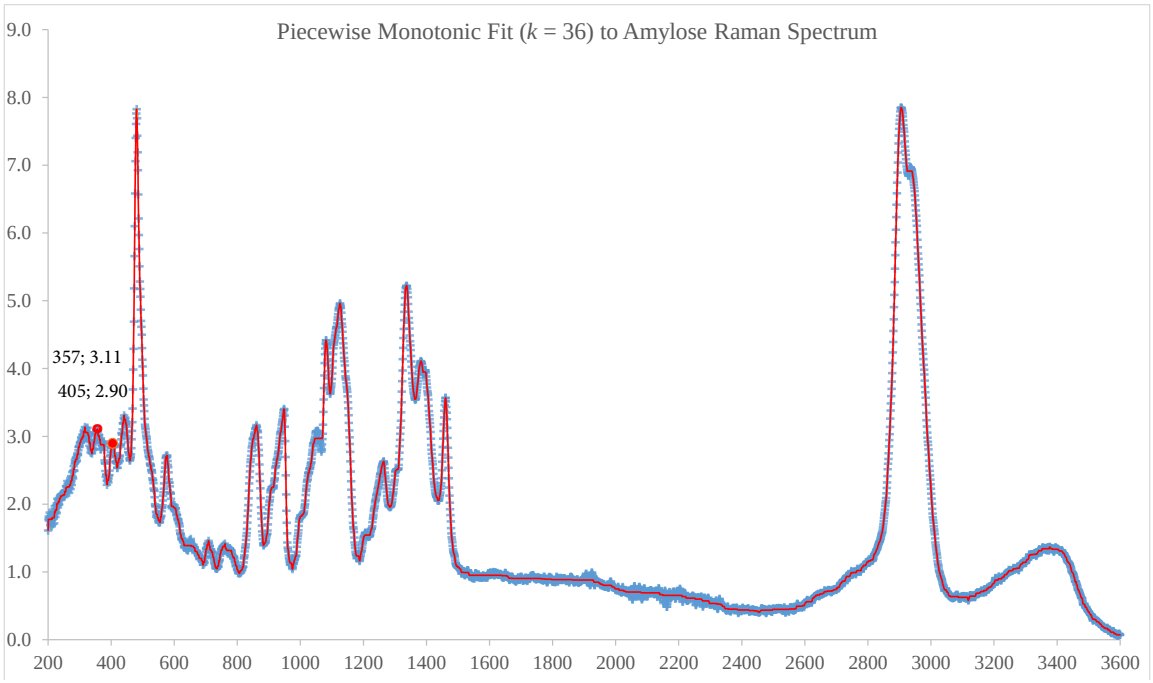

Fig. 3. As in Fig. 1, but $k = 36$. The extra peaks as compared to Fig. 2 are indicated by circles.

TABLE I
LEFT THREE COLUMNS: TURNING POINTS IN THE AMYLOSE SPECTRUM BY A BEST FIT WITH $k = 36$ MONOTONIC SECTIONS. RIGHT TWELVE COLUMNS: THE TURNING POINT POSITIONS OF THE OPTIMAL FIT FOR VARIOUS VALUES OF k ARE INDICATED BY THE TIMES SIGN

j	t_j	Intensity (ϕ_{t_j})	$k =$	2	4	8	12	16	20	24	28	30	32	34	36
0	200	1.61		×	×	×	×	×	×	×	×	×	×	×	×
1	317	3.14							×	×	×	×	×	×	×
2	339	2.75												×	×
3	357	3.11												×	×
4	387	2.29							×	×	×	×	×	×	×
5	405	2.90													×
6	419	2.53													×
7	441	3.31									×	×	×	×	×
8	459	2.64									×	×	×	×	×
9	481	7.83			×	×	×	×	×	×	×	×	×	×	×
10	555	1.73							×	×	×	×	×	×	×
11	577	2.72							×	×	×	×	×	×	×
12	691	1.10											×	×	×
13	709	1.46											×	×	×
14	735	1.05										×	×	×	×
15	761	1.42										×	×	×	×
16	807	0.98				×	×	×	×	×	×	×	×	×	×
17	861	3.17					×	×	×	×	×	×	×	×	×
18	883	1.39					×	×	×	×	×	×	×	×	×
19	948	3.41					×	×	×	×	×	×	×	×	×
20	975	1.04					×	×	×	×	×	×	×	×	×
21	1081	4.42									×	×	×	×	×
22	1095	3.63									×	×	×	×	×
23	1126	4.96				×	×	×	×	×	×	×	×	×	×
24	1188	1.16				×	×	×	×	×	×	×	×	×	×
25	1264	2.63									×	×	×	×	×
26	1284	1.95									×	×	×	×	×
27	1337	5.22				×	×	×	×	×	×	×	×	×	×
28	1364	3.54									×	×	×	×	×
29	1382	4.11									×	×	×	×	×
30	1437	2.05						×	×	×	×	×	×	×	×
31	1461	3.57						×	×	×	×	×	×	×	×
32	2454	0.40			×	×	×	×	×	×	×	×	×	×	×
33	2905	7.85		×	×	×	×	×	×	×	×	×	×	×	×
34	3118	0.58					×	×	×	×	×	×	×	×	×
35	3377	1.37					×	×	×	×	×	×	×	×	×
36	3600	0.07		×	×	×	×	×	×	×	×	×	×	×	×

in the data can be accommodated by choosing a suitable k. Besides the efficiency of the algorithms, an advantage of the piecewise monotonic approximation method is that it smooths the data as little as possible, it leaves increases or decreases unchanged and both sharp and smooth increases remain unchanged as noted by [25]. Another advantage of

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the piecewise monotonic approximation for peak estimation is that the presence of a peak in the data does not introduce any perturbations at all into the approximation. Instead, in wavelet or spline approximation it is difficult to represent the data at a peak, because the presence of a peak causes the propagation effect to introduce substantial perturbations away of the peak. Hence piecewise monotonic approximation provides a considerable advantage over low-pass filtering or over the use of basis functions to represent the data, which usually result in ringing artifacts [12], [13], [15], [16].

The algorithms that we have developed may be applied to *any* data set. However, it would be very helpful to try to solve particular peak estimation problems, in order to receive guidance from numerical results and, for instance, from medical imaging practices [2], [7], [21] or from other application areas [23], [24]. In some applications, such as nuclear magnetic resonance and Raman spectroscopy we often have good estimates of k [16] as well as databases [18] which keep estimates of peak positions that can be further utilized for developing automatic procedures. In addition, one may well combine certain features of our method with, for example, wavelets [14], [15] and splines [1], [11] or other smoothing techniques [3] or pattern recognition techniques [17] if there exists an opportunity for improved practical analyses in peak estimation.

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