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Whittaker Smoother

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Key words: Data fitting, smoothing penalty

Introduction: Data are often fit to a curve such as a low order polynomial or other basis function. However, at times the fitting functions are too restrictive and don't provide a good representation of the original data. A more flexible approach was developed by Eilers[1] and is further modified to provide additional flexibility as demonstrated by the `wsmooth` function in PLS_Toolbox and Solo.[2]

The Whittaker Smoother: Eiler's paper[1] introduces the following objective function

$$O(\mathbf{z}) = (\mathbf{y}-\mathbf{z})^{\mathrm{T}} \mathbf{W}_0 (\mathbf{y}-\mathbf{z}) + \lambda_{\mathrm{s}} \mathbf{z}^{\mathrm{T}} \mathbf{D}_{\mathrm{s}}^{\mathrm{T}} \mathbf{D}_{\mathrm{s}} \mathbf{z}$$

where $\mathbf{y}$ is a $N \times 1$ vector of measured data, $\mathbf{z}$ is smooth curve to be fit to the data, $\mathbf{W}_0$ is a diagonal matrix of weights (typically $0 \le w_{0,n} \le 1$ for $n = 1,...,N$, $\mathbf{D}_{\mathrm{s}}$ is a second derivative operator (e.g., $\mathbf{D}_{\mathrm{s}}\mathbf{z}$ is the second derivative of $\mathbf{z}$) and λ_{s} is a scalar penalty on the smoothing term. When data are missing, the corresponding weight, $w_{0,n}$, can be set to zero. Once that $\mathbf{W}_0$ and λ_{s} are given (set by default or provided by the user) the corresponding estimate of $\mathbf{z}$ is given by

$$\hat{\mathbf{z}} = \left(\mathbf{W}_0 + \lambda_{\mathrm{s}} \mathbf{D}_{\mathrm{s}}^{\mathrm{T}} \mathbf{D}_{\mathrm{s}} \right)^{-1} \mathbf{W}_0 \mathbf{y} .$$

For example, an optical emission (OES) spectrum is plotted Figure 1 along with two smoothed versions shown for $\mathbf{W}_0 = \mathbf{I}$ and $\lambda_{\mathrm{s}} = 0.1$ (low smoothing) and $\lambda_{\mathrm{s}} = 10$ (stronger smoothing). The optical emission spectra are available at www.eigenvector.com and discussed in References [3,4]. The stronger smoothing (green curve) appears to suppress the noise better than the weak smoothing but it also suppresses the peaks more. With a slight modification to the objective function, the best of both worlds can be obtained.

The Modified Whittaker Smoother: The original smoother can be modified to allow for different smoothness weighting on each of the channels using

$$O(\mathbf{z}) = (\mathbf{y}-\mathbf{z})^{\mathrm{T}} \mathbf{W}_0 (\mathbf{y}-\mathbf{z}) + \lambda_{\mathrm{s}} \mathbf{z}^{\mathrm{T}} \mathbf{D}_{\mathrm{s}}^{\mathrm{T}} \mathbf{W}_{\mathrm{s}} \mathbf{D}_{\mathrm{s}} \mathbf{z}$$

where $\mathbf{W}_{\mathrm{s}}$ is a diagonal matrix of weights with entries $0 \le w_{\mathrm{s},n} \le 1$ and corresponding estimator given by

$$\hat{\mathbf{z}} = \left(\mathbf{W}_0 + \lambda_{\mathrm{s}} \mathbf{D}_{\mathrm{s}}^{\mathrm{T}} \mathbf{W}_{\mathrm{s}} \mathbf{D}_{\mathrm{s}} \right)^{-1} \mathbf{W}_0 \mathbf{y} .$$

For the example, lowering the weights in $\mathbf{W}_{\mathrm{s}}$ from 1 to 0.1 for the wavelengths (λ) with peaks corresponding to 258<λ<280, 307<λ<311 and 393<λ<397, the smoother gives the final smoothed spectrum in Figure 2 (the black curve). The smooth black curve follows the green curve outside the peak ranges and the red curve with the peak ranges.

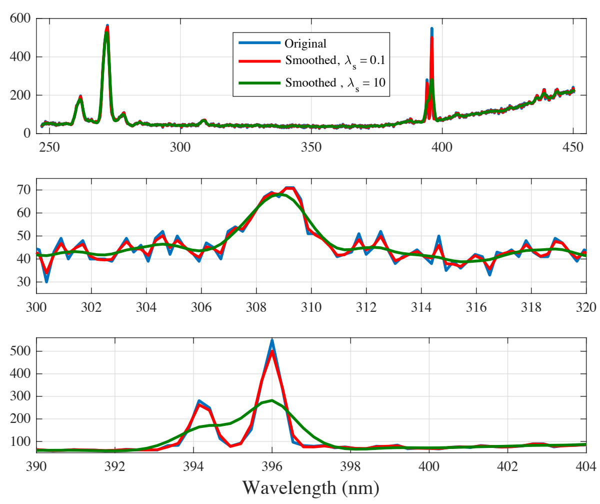

Figure 1: Uncorrected OES spectrum (blue), smoothed spectrum $\lambda_{\mathrm{s}} = 0.1$ (red) and strongly smoothed spectrum $\lambda_{\mathrm{s}} = 10$ (green). Zoom in on a small peak (middle) and significant sharp peaks (bottom).

A primary objective of smoothing, and preprocessing in general, is to increase the signal-to-noise (or more precisely signal-to-clutter). The eigenvalue distribution from PCA for a set of 46 OES spectra is

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shown in Figure 3 for the original data and the three different smoothing approaches. The eigenvalue distribution for principal components (PCs) ≥6 are mostly attributable to noise. A proxy for S/N is the ratio of the sum of the eigenvalues 1 to 5 to the sum of eigenvalues ≥6 shown in the figure. The original spectra and the low smoothing appear to have the lowest S/N while the higher smoothing has the biggest S/N. Interestingly, relaxing the smoothing on the peaks appears to lower the S/N slightly compared to including smoothing over all the wavelengths.

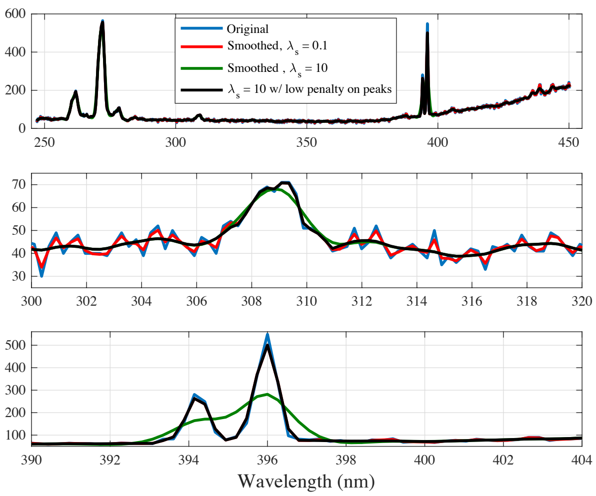

Figure 2: Uncorrected OES spectrum (blue), smoothed spectrum $\lambda_s = 0.1$ (red) and strongly smoothed spectrum $\lambda_s = 10$ (green). Strong smoothing except for the peaks (black) Zoom in on a small peak (middle) and significant sharp peaks (bottom).

Conclusions: Smoothing is a useful tool for providing interpretable trends given by the smoothed signal and has the potential to improve signal-to-noise.

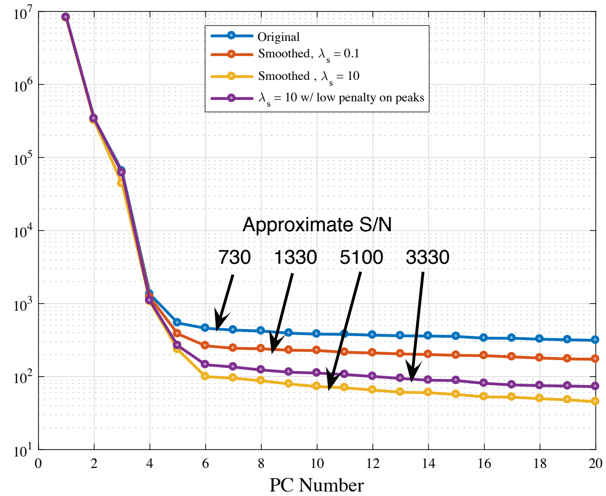

Figure 3: Eigenvalue distributions for the original signal and three versions of the smoothed signal for a set of 46 OES spectra.

References:

[1] Eilers, PHC, "A Perfect Smoother," *Anal. Chem.* 2003, **75**, 3631-3636.

[2] PLS_Toolbox and Solo. Eigenvector Research, Inc., Manson, WA USA 98831; software available at http://www.eigenvector.com.

[3] Wise, BM, NGallagher, NB, Butler, SW, White D, Barna, GG, "A Comparison of Principal Components Analysis, Multi-way Principal Components Analysis, Tri-linear Decomposition and Parallel Factor Analysis for Fault Detection in a Semiconductor Etch Process," *J Chemom*, 1999 **13**(3-4), 379-396.

[4] Gallagher NB, Wise, BM, Butler, SW, White, D, Barna, GG, "Development and Benchmarking of Multivariate Statistical Process Control Tools for a Semiconductor Etch Process: Improving Robustness Through Model Updating," IFAC ADCHEM'97, 78-83, Banff, Canada, June 1997.