NPL Report CMMT(A)159

October 1998

# Guide to Smoothing in AES and XPS

by

P J Cumpson
Centre for Materials Measurement & Technology
National Physical Laboratory
Teddington, Middlesex, UK, TW11 0LW

**ABSTRACT**

We examine the smoothing of Auger and X-ray photoelectron spectra, and the most widely used methods of smoothing to improve signal-to-noise ratio, comparing Savitzky-Golay, Gaussian, exponential and moving-average methods. We look at the performance of each of these smoothing methods to make clear what is gained and lost by each, leading to recommendations on when to smooth and how best to apply smoothing to practical situations.

# CONTENTS

# 1 Introduction

There is an extensive literature on applications of smoothing techniques to scientific data in general, and to chemical measurements in particular. Introductory books on the subject include *Data Fitting in the Chemical Sciences* by Gans[1] and from a more statistical point of view *Applied Smoothing Techniques* by Bowman and Azzalini[2]. Here we deal specifically with the application of smoothing techniques to AES and XPS spectra. We shall describe what is gained and what is lost by smoothing. This leads to recommendations on when to smooth and how best to apply smoothing in practical situations.

# 2 Why Smooth?

Smoothing in the general scientific literature has acquired a rather shaky reputation, lying somewhere between respectable data modeling and actually inventing data points. Strangely enough, if the same problem is recast in the Fourier domain, and a Wiener filter applied, this is often viewed as much more rigorous, even though the two processes can be mathematically identical! It can be something of a culture shock for scientists or engineers new to surface analysis to find smoothing is so extensively used. Experienced XPS and AES users know how valuable it can be, so part of the motivation for this guide is to provide enough background to show why smoothing is so useful, and how to obtain the best results from smoothing given your particular analytical problem with the AES or XPS spectra.

## 2.1 When to smooth?

Smoothing is best used as a method of guiding the eye, by using your knowledge of instrument resolution and the noise distribution of electron counting, to eliminate as much as we can of the noise in a spectrum, revealing features which the eye can then identify as being significant. This may be particularly valuable when dealing with large numbers of spectra, for example as part of a montage to be presented to a customer. An intelligent choice of smooth to apply to a set of data of this type may bring out features clearly which would otherwise be lost in the noise, especially for an inexperienced customer. In contrast an experienced analyst has likely already acquired the skill of rejecting the noisy part of the spectrum, when "eyeballing" data. Smoothing can help the less experienced user, or customer, spot some feature which the experienced analyst might spot straight away in the raw data.

One application which proves to be very useful in practice, is the mitigation of errors in software which can make algorithms for spectral processing much more sensitive to noise than they should be. An example is the least squares fitting of a model spectrum to number of chemical states, such as the C1s peak. Some software which is commercially available adjusts the end points which define the background subtraction (typically a Shirley background). Ideally each end-point should be treated as one of the adjustable parameters in the fit. However it is easy to find examples of peak fitting software which simply take the values in the channels at either end of the subtracted background. This makes the area of the background which is subtracted very sensitively dependent on those two, potentially noisy, channels. Though not an ideal solution, the performance of faulty software of this kind can be improved substantially by preceeding the fit with an appropriate smooth.

Quite often in quantitative analysis one wishes to compare properties of a set of peaks which have a simple geometric interpretation. Peak height ratios and full width half maxima are typical examples, but there are many cases where one wishes to compare other measures, such as the height of the peak ratioed to the height of the background in some other region of the spectrum. Experience shows that such simple geometrical ratios, combined with some physical and chemical insight, can lead to very precise measures of systematic variations in surface chemistry across a range of samples. Smoothing can help here, because what is needed is a geometrically simple way of averaging over a small number of channels. If one had the time to set up such a calculation, one might do this by least-squares fitting to polynomials. In practice the time involved in setting up such a fit would detract from the simplicity and speed of the geometrical approach, while smoothing (for example by one of the Savitzky-Golay methods) gives a result which is virtually identical mathematically, but can be performed in seconds using software available on virtually every data system.

Therefore, the most justified use of smoothing in surface analysis is for:

- Presenting noisy spectra for *qualitiative* analysis,

- Mitigating the effects of quantification software which is more sensitive to noisy channels in the spectrum than it should be,

- Improving the precision of simple geometrical ratios taken from spectra, which can often be very precise measures of changes in surface chemistry.

## 2.2 When *not* to smooth?

Smoothing needs most care when performed before any kind of quantitative analysis, such as in least-squares fitting, measurement of Full Width Half Maxima (FWHM) or peak-to-peak heights. Even so, the correct choice of smooth can often result in a negligible error in these subsequent quantitative analysis steps. For example, the Savitzky-Golay smoothing methods can be chosen so as to have a negligible effect on both peak height and peak width, while suppressing noise very effectively. However the proper choice of the width this smooth is critical, and the choice of the width for this smooth is an important topic to be reviewed later in this guide.

Smoothing should never be done if one is subsequently to use any statistical method which assumes the counts in each channel to be independent measurements. After smoothing they are no longer independent, but instead are partly correlated. An example of this is in the use of $\chi^2$ to judge goodness-of-fit in peak-synthesis. Many commercial software systems report the "Reduced Chi-Squared" value to the user after fitting, and one quickly learns to recognise that fits which appear good to the user have a reduced $\chi^2$ of about unity. Smoothing before fitting will systematically reduce the value of $\chi^2$ so that it can no longer be used as evidence of the fit being a good one. At worst it could mislead one into accepting a fit which is visually poor, on spurious statistical grounds.

- Avoid, if possible, smoothing before *quantitative* analysis, for example peak-fitting or measurement of parameters like peak height or width.
- If smoothing is unvoidable, choose the number of points in the smooth very carefully to avoid adding a systematic error to the quantity you are trying to measure.
- Treat with special caution statistical measures such as $\chi^2$ values, which can be altered by smoothing.

## 2.3 Why are there so many smoothing methods?

Smoothing eliminates some of the noise present at the expense of distorting the spectrum[3]. One smoothing function may be better than another in a particular application, because it takes advantage of some reasonable assumptions about the form of the spectrum in order to distort it less than might be expected for a given level of noise reduction. For example, over small numbers of channels, true XPS and AES spectra are well fitted by a polynomial, so that Savitzky-Golay smoothing (which is mathematically equivalent to performing this type of fit) distorts the shapes of the peaks very little. Two choices must be made;

- Which smoothing function to use (e.g. Savitzky-Golay[4], Gaussian, etc)
- How many adjacent channels are in the smooth to achieve the best balance between distortion and remaining noise in the smoothed spectrum.

# 3 Savitzky-Golay Smoothing

This smoothing method is mathematically equivalent to fitting a polynomial to $P = 2m + 1$ channels, and taking the value of the polynomial as the value of the centre channel. Popularised by Savitzky and Golay[4] (see also later corrections[5] to their coefficients), the method was used earlier[6], possibly even back to to 19th century[1]. Seah and Dench[7] examined applications of Savitzky-Golay smoothing in AES and XPS. Bromba and Ziegler[8] showed Savitzky-Golay smoothing to give essentially the best reduction of noise in the limit of low peak distortion. Two variants of Savitzky-Golay smoothing need to be discussed in detail. These are the Savitzky-Golay quadratic-cubic smoothing function, and the Savitzky-Golay quartic/quintic smoothing function. It is worth taking a moment to understand why these smoothing functions have the names that they do, since this is seldom explained in the documentation accompanying software which performs smoothing. A detailed mathematical analysis of piecewise polynomial fitting shows that, provided one is dealing with an odd number of points, fitting a quadratic (parabola) function leads to exactly the same equations as a cubic function, and similarly fitting a quartic function leads to exactly the same equations as fitting a quintic[8]. Thus, the Savitzky-Golay quadratic-cubic smooth, for example, could be derived from *either* piecewise fitting of *quadratic* functions to the data *or* piecewise fitting of *cubic* functions to the data.

Ziegler[9] listed a number of important properties of Savitzky-Golay smooths, of whatever order; the first five of those he listed are the most important

- They preserve any symmetry (even/odd) contained in the signal.

  The position of symmetric (spectral) lines of any shape is preserved exactly.

- The area under any signal curve is preserved exactly.

- The center of gravity of any signal curve is preserved exactly.

- For filters with quadratic order and above, the second moment of (spectral) lines is preserved exactly. Since this second moment is the true measure of the line width, this is especially important in spectrometry. In other words, for Savitzky-Golay filters have only a second-order effect on increasing the peak FWHM, not a first order effect as do other filters such as in Gaussian smoothing.

The properties of Savitzky-Golay smoothing are neatly summarised by Press *et al* [10]

> Within limits, Savitzky-Golay filtering does manage to provide smoothing without loss of resolution. It does this by assuming that relatively distant data points have some significant redundancy that can be used to reduce the level of noise. The specific nature of the assumed redundancy is that the underlying function should be locally well-fitted by a polynomial. When this is true, as it is for smooth line profiles not too much narrower than the filter width, then the performance of Savitzky-Golay filters can be spectacular. When it is not true. then these filters have no compelling advantage over other classes of smoothing filter coefficients.

Later in this guide, Fig 5 will allow us to fix a firm numerical value for "not too much narrower" valid for AES and XPS.

## 3.1 Coefficients for Savitzky-Golay Smoothing

A table of coefficients was published by Savitzky and Golay[4, 5]. These days the coefficients can be calculated easily "on the fly". There follows a simple MATLAB routine able to calculate the Savitzky-Golay smoothing coefficients for any number of points, for both quadratic-cubic, and quartic-quintic smoothing functions. For derivation and a definition of terms see the 1980 paper by Proctor and Sherwood. This simple code should be easy to convert to other high level languages such as Pascal, Fortran or C.

```
function c = SavGol(n, P);
%
% Calculates the Savitzky-Golay
% convolutional smoothing functions
% n = order of fitting polynomial (2, 3 ,4 or 5)
% (note that n=2 and n=3 give identical
% results as do 4 and 5)
% P = number of points in the smooth
%                   - must be an odd number
%
m=round((P-1)/2);
c=zeros(1,P); %pre-alocation of vectors...
y=zeros(1,P); %a useful step peculiar to MATLAB
% NOTE: vectorization of code is not attempted
% here, to allow easy re-writing into conventional
% compiled languages such as Fortran, pascal
% or BASIC. Calculation of these coefficients
% in MATLAB is fast even without it.
 if n<3.5,  %Savitzky--Golay quadratic/cubic
   NORM=m*(4*m* m - 1)*(2*m+3)*(m+1)/3;
```

```
    RecipNORM=1/NORM;
    for k=-m:m,
       c(m+k+1)=m*(m+1)*(3*m*(m+1)-1 -5*k*k)*RecipNORM;
    end;
else %Savitzky--Golay quartic/quintic
    NORM=4*(4*m*m-1)*(4*m*m-9)*(2*m+5)/15;
    RecipNORM=1/NORM;
    for k=-m:m,
         c(m+k+1)=(((((15*m + 30)*m - 35)*m - 50)*m +12

       35*((2*m + 2)*m - 3)*k*k + 63*k*k*k*k)*RecipNORM;
    end;
end;
%c is the vector (with P elements) of S-G coefficients
```

## 3.2 Properties of Savitzky-Golay Smoothing Functions

Savitzky-Golay smoothing offers two main families of related smoothing functions which differ only in the number of channels over which the smooth takes place. However, if one plots each family in reduced form, as shown in Fig 1, one can see that as the number of points in the smooth increases, The smoothing functions rapidly become very similar.

The Savitzky-Golay quartic/quintic smooth shows this property too; as shown in Fig 2, the number of points increases a limiting functional shape is quickly approached.

One can easily see from figures 1 and 2 that convergence to a consistent smoothing function is relatively rapid as one increases the number of points in the smooth. The conclusion we should draw is that the performance of the smoothing functions depends not so much on a number of channels chosen, but on the total width of the smoothing function, especially in relation to the size of features in the spectrum to be smoothed. It is therefore useful to compare the noise reduction performance of the quadratic-cubic and quartic-quintic Savitzky-Golay smooths when applied to spectra with the range feature size, specifically peaks with a range of full width half maximum. What the previous two figures tell us, is that the number of points in the smooths does not strongly affect performance, so we will plot the results assuming a very large number of points in the smooth.

To compare the effects of different kinds of smooth let's look at the separate effects of the smooth on the spectrum and on the noise. Measured spectra, of course, are an inextricable mixture of the two. Therefore we shall compare the effects of different smooths on model spectra and model noise plotted separately. The model spectrum we shall use, shown in Fig. 3, consists of nine peaks, of progressively larger full-width at half maximum, each having a peak height of 1000 counts per channel, on a background

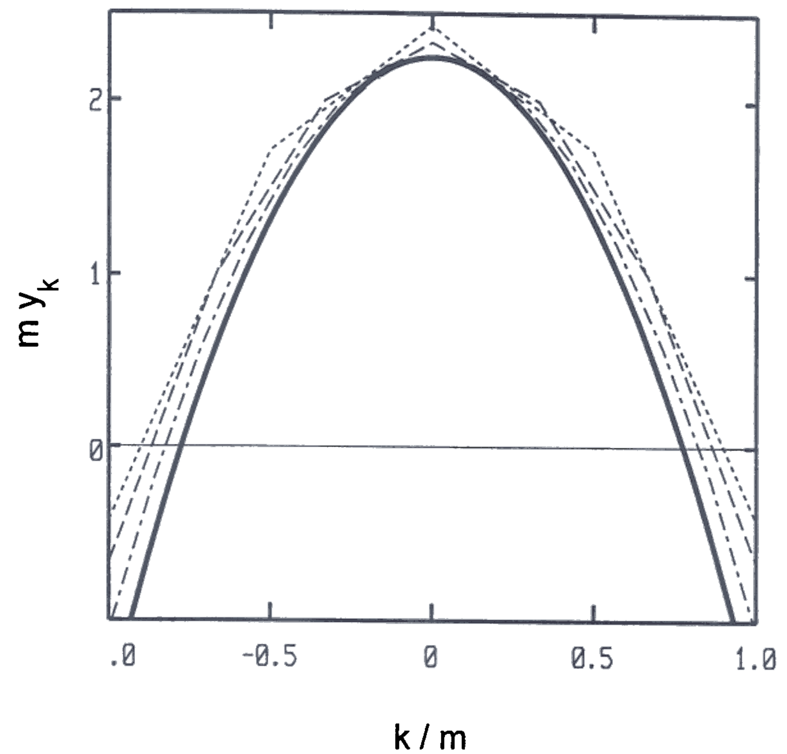


Figure 1: Savitzky-Golay quadratic/cubic smoothing functions, for smooths of $P = 5$ points (dotted), 7 points (dashed), 15 points (dash-dot) and 1001 points (continuous line). To emphasise how closely related these smoothing functions are, we have plotted them on axes scaled by $m = (P-1)/2$, otherwise the normalisation of their areas tends to obscure their similarity. $k = -m, -m+1, \ldots, m-1, m$ is the channel number with respect to the channel being smoothed, so that the centre channel corresponds to $k = 0$. Clearly an asymptotic shape for this filter function is reached rapidly.

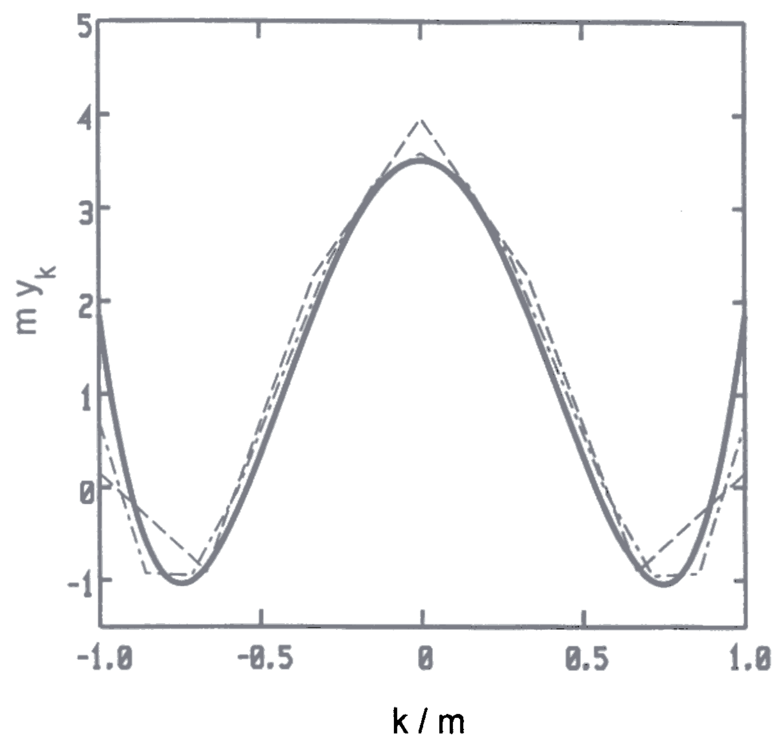


Figure 2: As for Fig. 1, but plotted for the Savitzky-Golay quartic/quintic smoothing function, for $P$ = 7 points (dashed), 15 points (dash-dot) and 1001 points (continuous line). As was the case with the quadratic/cubic function, an asymptotic shape for the quartic/quintic function is reached rapidly.

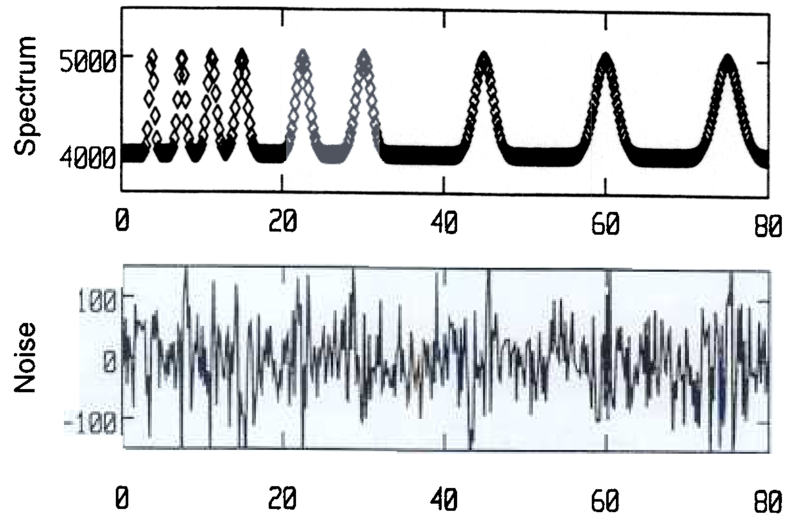


Figure 3: Specimen data for comparing the effects of smoothing procedures. Though it is impossible to do for real data, here we plot the true spectrum and the noise on that spectrum separately. This spectrum consists of nine peaks of increasing FWHM, so that the effects of smoothing can be compared. Here we have chosen an example of peaks with 1000 counts at their maxima, superposed on a constant background of 4000 counts. The noise, shown on the lower plot, is for the Poissonian statistics of electron detection.

of 4000 counts per channel. Before smoothing, the noiseless spectrum and the separately plotted noise are as shown in Fig. 3. Note however that the number of points one chooses in practice is very important, largely because it defines the width of a smoothing function in relation to the feature size of the spectrum you want smooth. So when you come to apply a Savitzky-Golay smoothing in practice, a sensible choice for the number of points in the smooth is essential. Figure 4 is a tableau showing the effect of Savitzky-Golay smoothing with four different choices for the number of points in the smooth. We can immediately make an number of useful observations from this tableau.

- for any given number of points in the smooth, the moving average method leads to more distortion than does the Savitzky-Golay quadratic / cubic, which in turn leads to more distortion than the Savitzky-Golay quartic/quintic.
- Whatever kind of smoothing is applied, sharper peaks suffer the greatest distortion.

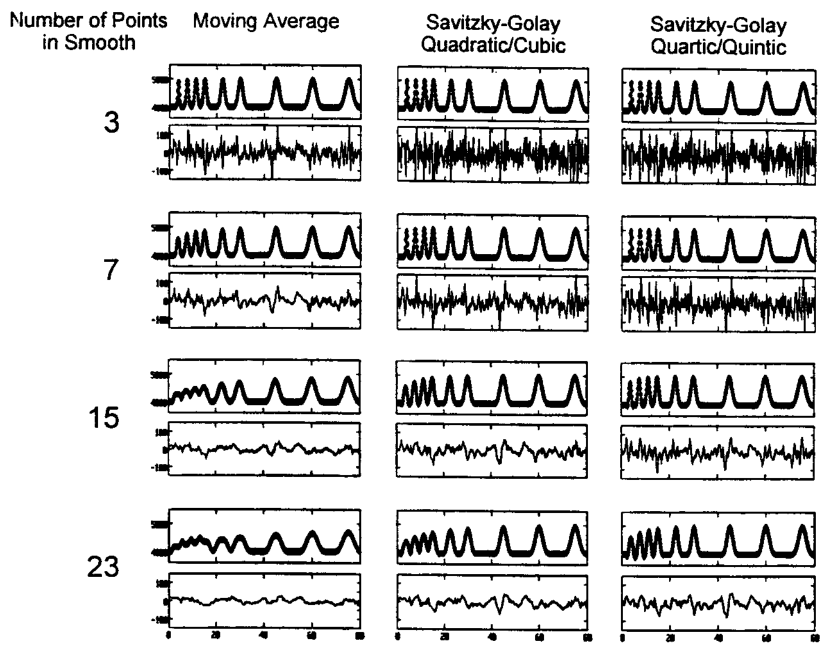


Figure 4: Tableau showing the effect of employing different numbers of points in the smooth, for three types of smoothing.

- When the number of points in the smooth is large, and the peak is sharp, after smoothing the peak tends to look more like the smoothing function than a spectroscopic peak at all .
- In particular, for the two Savitzky-Golay smooths shown, the narrowest peaks can exhibit negative going wings.
- Whichever Savitzky-Golay smooth is chosen, similar levels of noise reduction lead to similar levels of peak distortion. One can see this by comparing the 15-point quadratic / cubic smooth and the 23-point quartic/quintic one. The noise level after each of these two smooths, and the distortion introduced by each smooth, is virtually identical. The 7-point moving average smooth causes similar distortion to the 15-point quadratic / cubic smooth and the 23-point quartic/quintic one, but leaves marginally more noise.

## 3.3 Choosing the right SG smooth

We can compare the "Trade-off" between remaining noise in the spectrum and peak distortion, both of which we wish to minimise. Figure 5 shows this trade-off curve for four different types of smoothing, including both Savitzky-Golay quadratic / cubic and quartic/quintic, for both Gaussian and Lorentzian peak shapes. The majority of peak shapes in electron spectroscopy fall somewhere between these two extremes. On can see in Fig. 5 that

- For a smoothing width to FWHM of up to about 0.2 Savitzky-Golay quadratic / cubic smoothing leads to virtually no distortion to either peak-height or peak width.
- For a smoothing width to FWHM of up to about 0.3 Savitzky-Golay quartic/quintic smoothing leads to virtually no distortion to either peak-height or peak width.
- Beyond this, the amount of distortion you are able to accept depends on your application. Sherwood suggests an upper-limit of 1.0 for this ratio for quadratic / cubic smoothing, and 1.7 for quartic/quintic smoothing. Both cause approximately 1.5% loss of peak height and less than 2.5% broadening of a Gaussian peak[7].

## 3.4 Conclusions about Savitzky-Golay Smoothing

Savitzky-Golay smoothing is the best general smoothing method available within a wide range of surface analysis software. It improves signal to noise without distorting peaks at all, *provided*

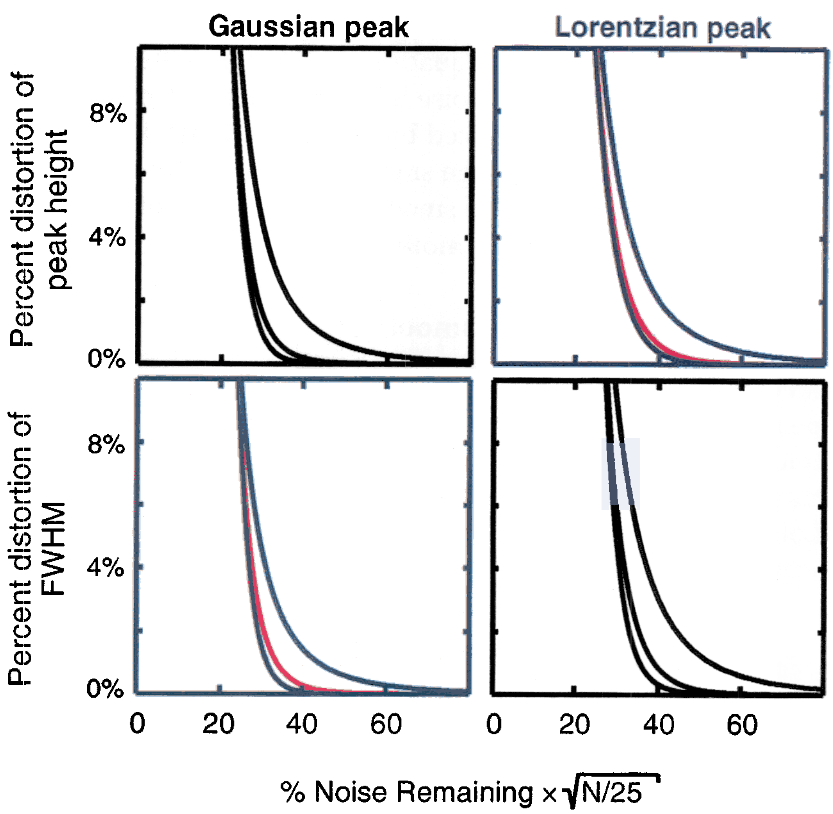


Figure 5: Trade-off curves for Gaussian peak-shapes, showing the distortion of peak height and FWHM for a range of noise reductions. The Savitsky-Golay functions give the best result for noise reduction and minimal distortion. $N$ is the number of channels within the FWHM of the peak (e.g. for a peak of FWHM 1.25eV acquired at channel separation 0.05eV, $N = 25$). Note that there is a clear point at which any attempt to gain better noise reduction leads to significant distortion.

- Sensible choice of number of points to smooth
- Peaks are well approximated by a polynomial

# 4 Gaussian Smoothing

Gaussian smoothing can be seen as an intermediary between simple moving average smoothing (ie by a top hat function) and Savitzky-Golay smoothing. Intuitively one feels that any successful smoothing method should weight central points strongly and peripheral points weakly. This leads one to any of a large number of bell-shaped functions, of which a Gaussian is simply the most well known. There is no fundamental reason why Gaussian should give the best possible performance in this role. Instead, the justification for using it comes from its simplicity and the fact that it will mimic the effect of a large number of instrumental broadening processes[11]. The Central Limit Theorem[12] from statistics tells us that whatever the shape of these individual instrumental broadening functions, a large number of them taken together will give the instrument as a whole and Gaussian resolution function. Therefore Gaussian smoothing has an almost pedagogic purpose in that the effect is to mimic instrument with poorer energy resolution. If one is aiming for the best possible noise reduction with least peak distortion then Savitzky-Golay smoothing will always be superior the correct width of smooth is chosen.

Thus, for Gaussian Smoothing we can conclude;

- Improves signal to noise but always at the expense of some peak broadening
- Easy to visualise, because Gaussian smoothing is similar to decreasing the energy resolution of an instrument.
- Gaussian smoothing can make some kinds of quantitative analysis more precise by degrading data from different instruments to remove the systematic effect of their different energy resolutions.

# 5 Other Smoothing and Filtering Methods

## 5.1 Exponential filtering

This is largely of historical interest, being the simplest smoothing method to impliment electronically by means of a simple "low-pass" RC filter. There are still a few cases where this filtering is of interest to the AES spectroscopist - for example when acquiring direct spectra using beam-blanking and lock-in amplifier, followed by an adjustable electronic RC filter. As a method of smoothing previously-acquired spectra however, it has been shown[9] to be to be inferior to the Savitzky-Golay smoothing methods in all conceivable spectroscopic applications, and is best avoided when developing software for smoothing.

## 5.2 Smoothing by taking the Moving Average

This is sometimes known as a "top-hat" smooth, because the convolutional smoothing function is square and resembles a top-hat in cross-section. This is very simple to program, but causes more distortion to the peak than Savitzky-Golay smoothing for any given noise-reduction factor, as can be seen in Fig. 5. Savitzky-Golay smoothing, with the right choice of number of points in the smooth, can often achieve the same levels of noise reduction with little or no peak distortion.

If one has a spectrum with a narrow channel separation (perhaps 0.05eV or 0.1eV) and facilities for other types of smoothing are not available, then a three-point moving-average smooth will reduce the noise by a useful 42% without causing unacceptable distortion to spectra acquired in the range of resolution 0.25 to 1eV which are typically used.

## 5.3 Wiener Filtering

Sometimes known as "optimal" filtering, this is performed in Fourier space, though it can equally well be viewed in real space as another type of convolutional smooth. XPS applications of frequency domain smoothing (and deconvolution) have been discussed by Wertheim[13].

When using any method with the word "optimal" in its title one must take care to understand what is being optimised. Wiener filtering is mathematically equivalent to a smooth which attempts to minimise the difference between smoothed spectrum and true spectrum in the least-squares sense[10]. This difference comprises two sources; noise and the distortion due to smoothing.

This is fine for some purposes, and if implimented using Fast Fourier Transform (FFT) algorithms[10] Wiener Filtering will be very fast. However, usually one would rather optimise other aspects of a smoothed spectrum, for example minimising the broadening of peak shapes at the expence of reducing the spectrum noise a little less; Savitzky-Golay smoothing achieves this very effectively with the right choice of number of points in the smooth. Note that is clear in Fig. 5 that any smoothing greater than the optimal choice for the Savitzky-Golay functions leads to strong distortion for very small gains in noise reduction.

The effect of Wiener filtering in practice is very similar to a Savitzky-Golay smooth using more points than recommended above. The result is a spectrum in which noise has been very effectively surpressed, though at the expense of some energy resolution which could have been retained with the right Savitzky-Golay smooth. Nevertheless, if easily available Wiener Filtering can be a very useful and powerful smoothing method.

### 5.4 Multiple-pass smoothing

For convolution functions which have no negative-going regions (for example moving average smoothing, or Gaussian smoothing) multiple repeat smooths can be shown to rapidly approach the effect of a single pass by a Gaussian smoothing function. This is a consequence of the Central Limit Theorem[12], which is of fundamental importance in classical statistics[12]. Therefore multiple passes of such convolution functions are rather pointless, compared to a single pass by a gaussian smoothing function whose width has been chosen correctly

This is not neccessarily the case for other convolving functions, such as the Savitzky-Golay smoothing functions[14]. Multiple passes of these functions do not[3] tend to the effect of a single pass by a gaussian, but instead become more closely equivatent to fitting higher and higher order polynomials. We have seen that, when viewed in terms of noise reduction for a given acceptable level of distortion, there is little to choose between quadratic / cubic and quartic/quintic smooths. It is unlikely that the higher order polynomial fitting implied by multiple Savitzky-Golay smooths would deliver significantly better results.

## 6 Conclusion

We have seen that the most generally useful kind of smoothing is the Savitzky-Golay type. Considerations of noise reduction vs. distortion of the peak lead us to suggest maximum smoothing widths of 1.0 and 1.7 of the peak FWHM for Savitzky-Golay quadratic / cubic and quartic/quintic smoothing respectively. Since in XPS many peaks have a width of 1eV and since high resolution data are recorded at 0.1eV intervals, a useful choice is a 9 point quadratic / cubic Savitzky-Golay smooth. For spectra acquired at 0.05eV intervals, a useful choice is a 17 point quartic/quintic Savitzky-Golay smooth.

Gaussian smoothing has some useful special applications, especially where one needs to reduce a set of data are acquired on several instruments to a common, low, energy resolution.

Very occasionally simple moving average smoothing may be useful when neither of the two above methods are available. Wiener filtering is fast, and in terms of its effect on the spectrum, will always have a virtually identical counterpart from the set of Savitzky-Golay filters.

# 7 Acknowledgements

This work was carried out under the Valid Analytical Measurement programme of the UK Department of Trade and Industry.

# References

[1] P. Gans, *Data Fitting in the Chemical Sciences*. Chichester, UK: John Wiley, 1992.

[2] A. W. Bowman and A. Azzalini, *Applied Smoothing Techniques for Data Analysis*, vol. 18 of *Oxford Statistical Science Series*. Oxford, UK: Oxford University Press, 1997.

[3] M. P. Seah, W. A. Dench, B. Gale, and T. E. Groves, "Towards a single recommended optimal convolutional smoothing algorithm for electron and other spectroscopies," *J. of Phys. E: Sci. Instrum.*, vol. 21, pp. 351–363, 1988.

[4] A. Savitzsky and M. J. E. Golay *Anal. Chem.*, vol. 36, p. 1627, 1964.

[5] J. Steinier, Y. Termonia, and J. Deltour *Anal. Chem.*, vol. 44, p. 1906, 1972.

[6] P. G. Guest, *Numerical Methods of Curve Fitting*. Cambridge, UK: Cambridge University Press, 1961.

[7] M. P. Seah and W. A. Dench, "Smoothing and signal-to-noise ratio of peaks in electron spectroscopy," *Journal of Electron Spectroscopy*, vol. 48, pp. 43–54, 1989.

[8] M. U. A. Bromba and H. Ziegler, "Application hints for savitzky-golay digital smoothing filters," *Anal. Chem.*, vol. 53, pp. 1583–1586, 1981.

[9] H. Ziegler, "Properties of digital smoothing polynomial (DISPO) filters," *App. Spectrosc.*, vol. 35, pp. 88–92, 1981.

[10] W. H. Press, B. P. Flannery, S. A. Teukolsky, and W. T. Vetterling, *Numerical Recipes*. Cambridge: Cambridge University Press, 1986.

[11] S. Evans and A. G. Hiorns, "Convolution smoothing algorithms in electron spectroscopy," *Surf. Interface Anal.*, vol. 8, pp. 71–74, 1986.

[12] M. G. Bulmer, *Principles of Statistics*. New York: Dover, 1979.

[13] G. K. Wertheim, "Deconvolution and smoothing: Applications in ESCA," *J. Elec. Spectrosc.*, vol. 6, pp. 239–251, 1975.

[14] A. Proctor and P. M. A. Sherwood, "Smoothing of digital x-ray photoelectron spectra by an extended sliding least-squares approach," *Anal. Chem.*, vol. 52, pp. 2315–2321, 1980.