Topic Outline

IIIB2c. Spectral Analysis: Others

Differentiation

- Objectives
  - Accentuating Signals
  - Finding Peak Parameters
- Methodology
  - Via Software
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- Pros and Cons

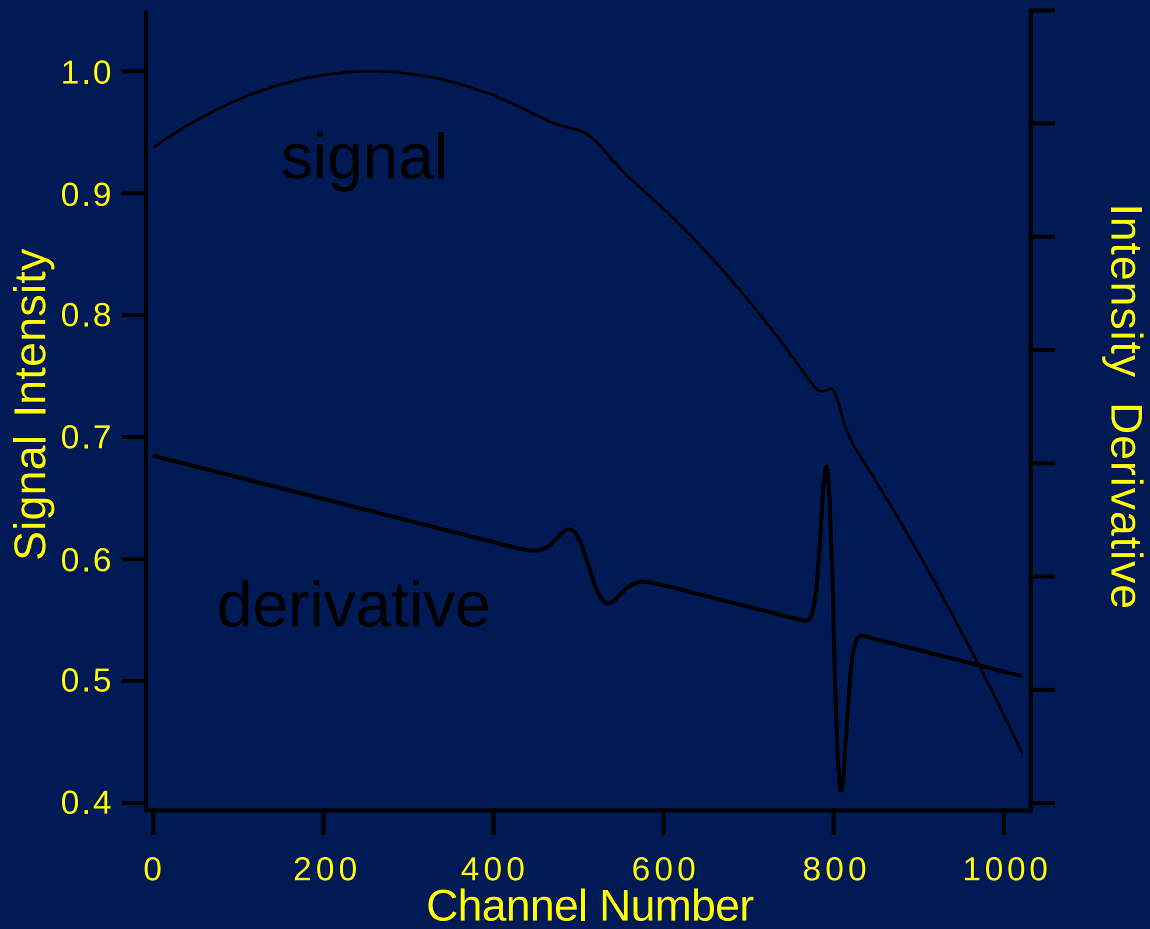
Deconvolution

- Objective
- Example
- Methodology
- Pros and Cons
- Practical Applications

Normalization

Accentuating Signals

One objective of differentiation is to accentuate small features on a broad background.



This is especially important for AES!

Finding Peak Parameters

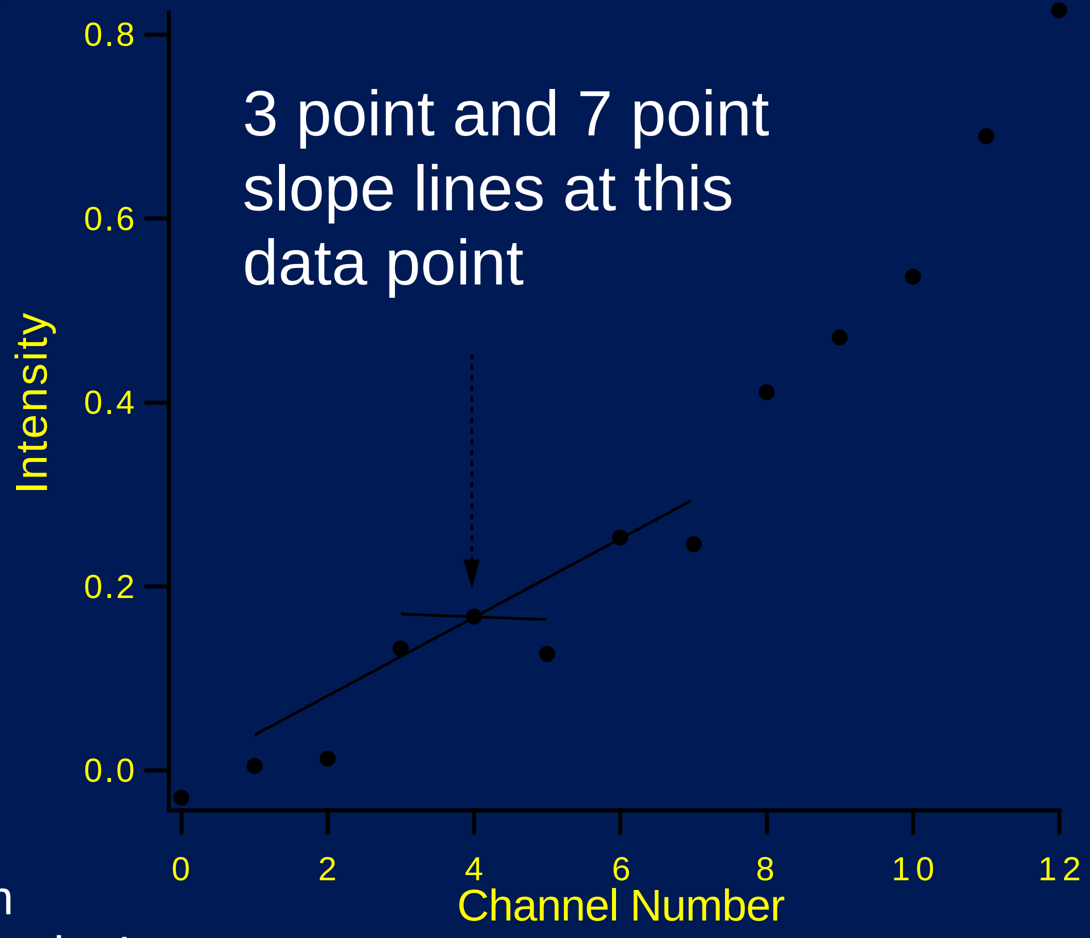
Differentiation can also be used to locate peak parameters more accurately.

this feature	appears as this here
Raw Signal	**Derivative Signals**
top of peak	curve crosses the baseline
overlapping peaks	inflection points

This is why first and second derivatives are often taken of infrared spectra.

Via Software

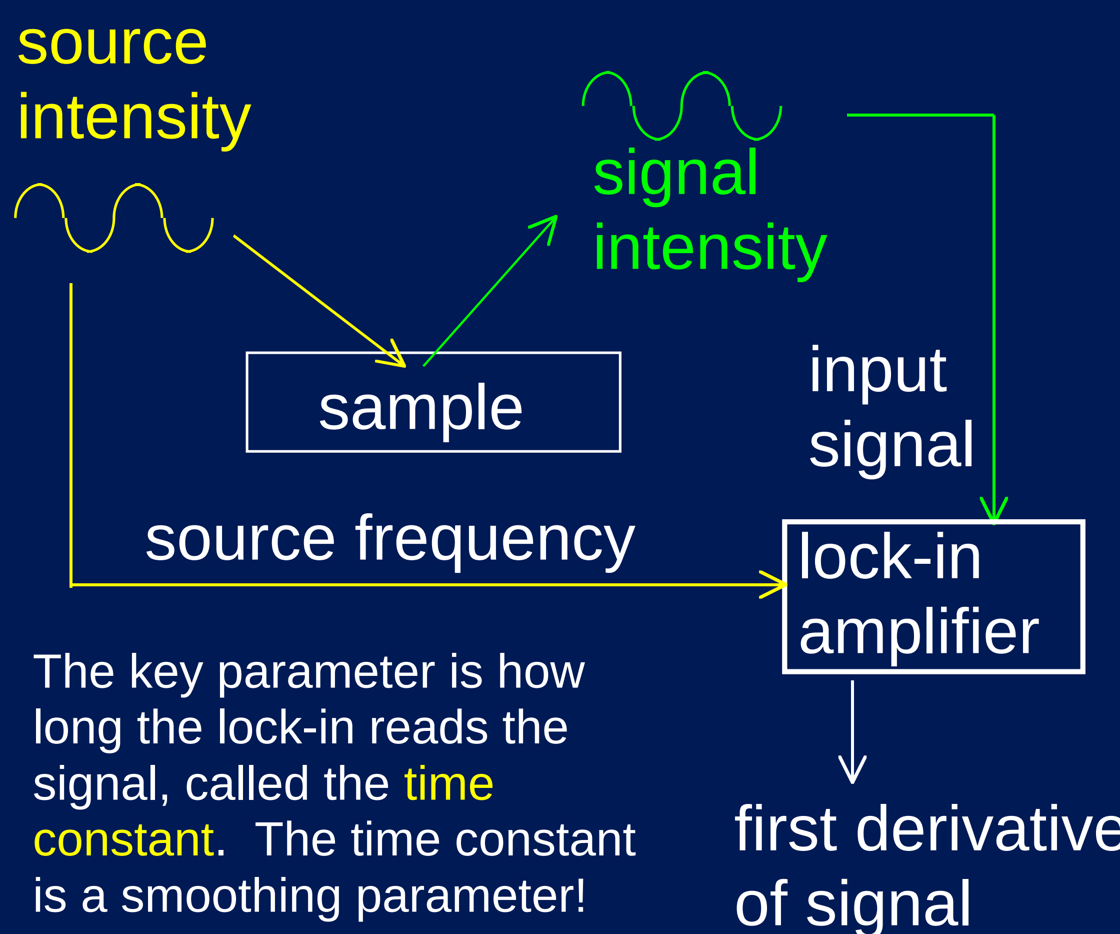
The slope of the best fit line is determined at a given point over a range of points in the spectrum.



This is equivalent to an n-point smoothing operation!

Via Hardware

A sinusoidally varying signal is applied to the source in order to vary the intensity of the event. Locking in to the signal at the frequency of the source gives the first derivative of the true signal.



The key parameter is how long the lock-in reads the signal, called the time constant. The time constant is a smoothing parameter!

Pros and Cons

Pros

Differentiation can be used to show small features on broad backgrounds.

Cons

Whether it is done via software or hardware, differentiation is equivalent to an n-point smoothing operation with all of the associated effects on peak parameters.

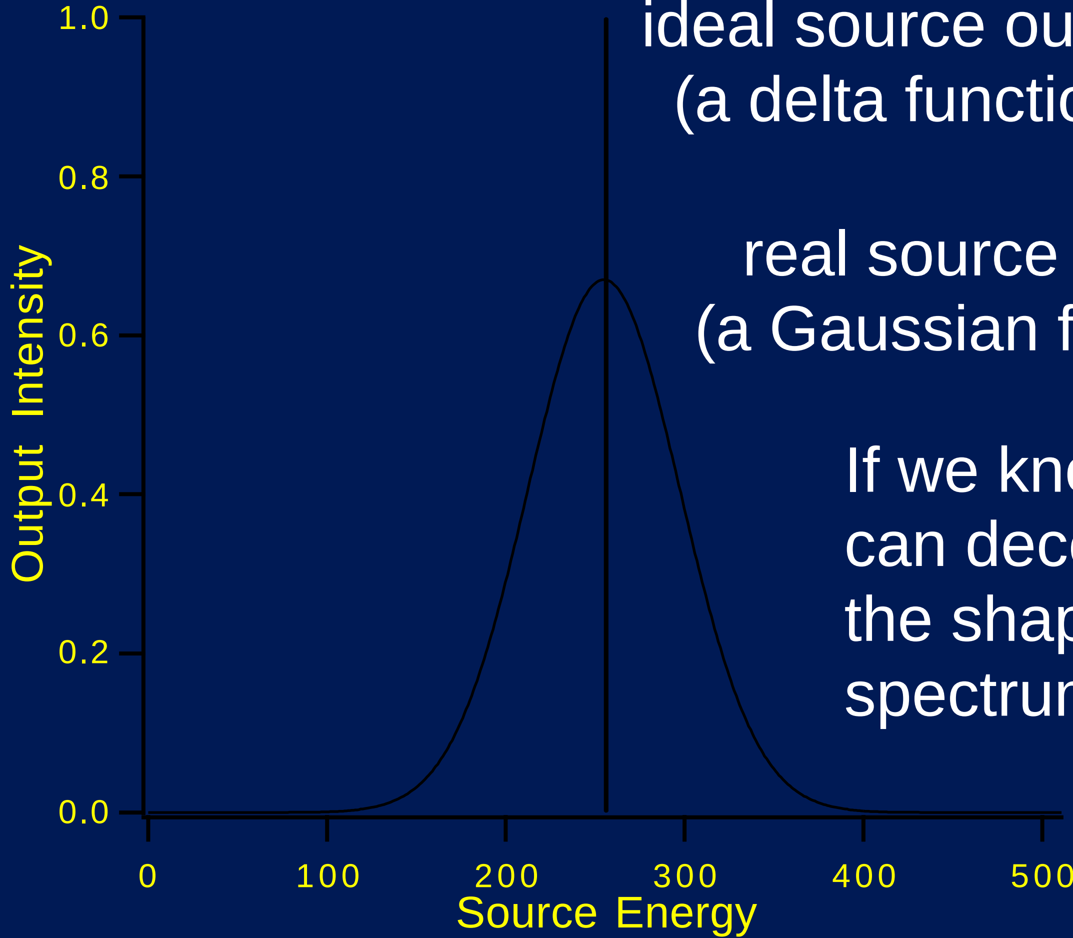
Objective

The source is NOT monochromatic in energy. It puts out a distribution of energies in its beam to the sample. The distribution of source energies is called the source lineshape.

All signals do NOT reach the dectector with equal probability. How the signals are distorted by the analyzer before they reach the dectector depends on the transmission function of the system.

Deconvolution is used to remove “blurring” effects of the source and analyzer in order to obtain the true peak shape due to an event.

Example



ideal source output
(a delta function)

real source output
(a Gaussian function)

If we know this shape, we can deconvolve it from the shape of peaks in the spectrum!

Methodology

Real Space

Deconvolution in real space involves iterative methods that depend on initial guesses about the shape of the distoration.

Deconvolution with Applications in Spectroscopy, P. A. Jansson (Academic Press, Orlando) 1984.

Fourier Space

Convolution in real space is mathematically equivalent to multiplication in Fourier space. Deconvolution is therefore equivalent to division by the Fourier coefficient of the blurring function.

In practice, deconvolution is typically done via software in real space using iterative routines.

Pros and Cons

Pros

Deconvolution can remove blurring effects.

Cons

The shape of the blurring distribution must be known accurately.

Excessively noisy data will become excessively distorted during deconvolution, so the S/N ratio in the raw spectrum must be as high as possible.

Using too many iterations during deconvolution will distort the resulting spectrum beyond the “true” spectrum, therefore one must watch the process carefully after each step.

Practical Applications

XPS source lineshapes were once a limiting factor in determining peak shapes accurately. The lineshapes have been deconvolved from spectra with success in the past. Today, many XPS systems use a monochromatized source, so that that removing source lineshapes is not needed.

No analyzer is perfect. Those who require a very high degree of precision in quantitiative XPS (and AES) may determine the transmission function of their system and deconvolve it from the spectrum.

Normalization

Spectra can be normalized in one of two ways.

Height Normalization

The spectrum is rescaled in order to set the maximum and minimum signals to unity and zero, respectively.

Area Normalization

The spectrum is rescaled in order to set the area under a peak (or spectral feature) to a defined value.

This has importance utility when comparing two spectra (via subtraction or other methods).