CHEM*3440

Chemical Instrumentation

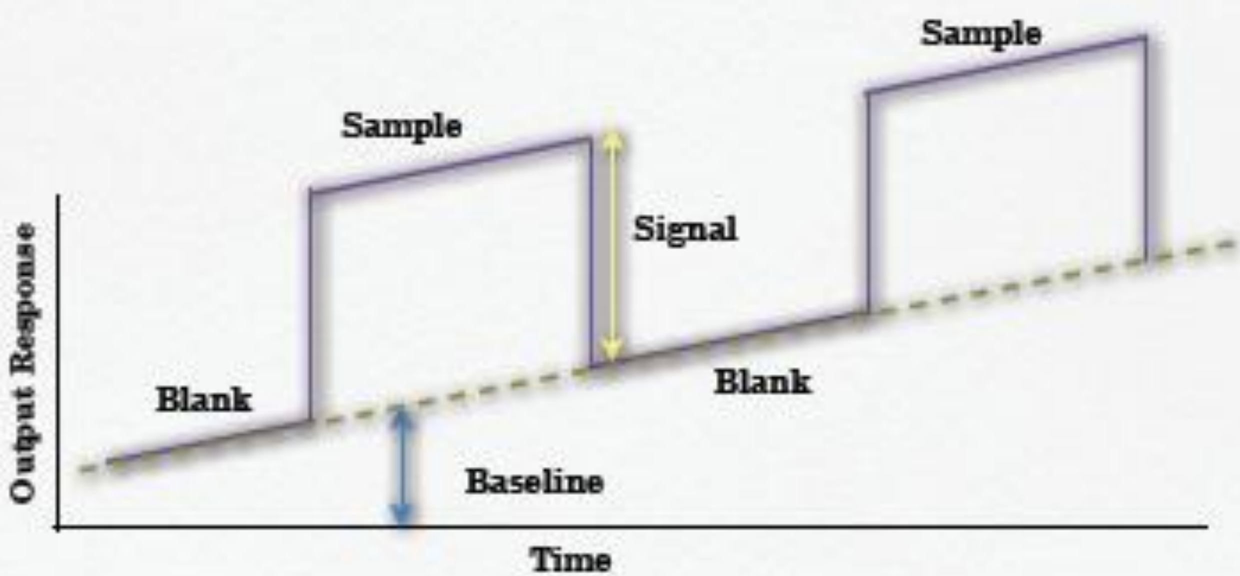
Topic 4

Signal *vs.* Noise

Drift

Ideally the baseline response is constant in time.

However, baseline changes slowly with time. This is called drift. Sometimes the drift is linear in time, but often it is more complex and difficult to predict.



Noise

Noise is a random(or almost random) time-dependent change in the instrument's output signal that is unrelated to the analyte response. These variations will tend to make the accurate measurement of sample, blank, and baseline response less certain.

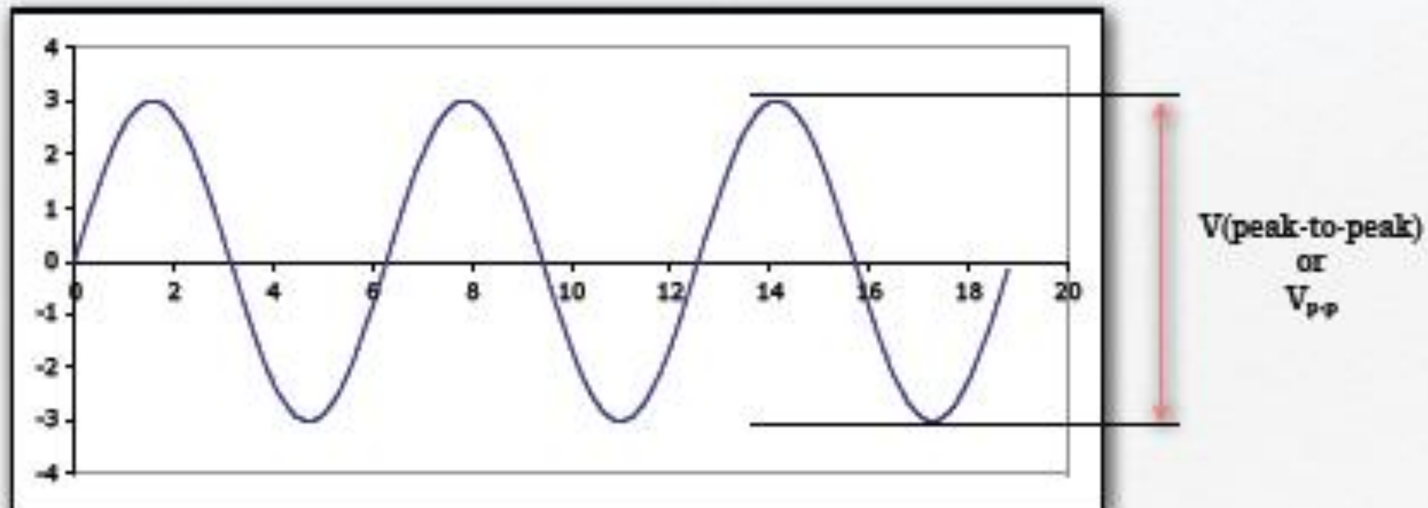
Noise can arise from many sources (to be discussed soon). The frequency of the noise response can span the entire spectrum.

We can treat noise as if it were a sine wave, or the sum of many (initie?) sine waves.

Measuring the intensity of the noise and comparing it to the signal is the key to determining the accuracy of a measurement and in specifying the smallest signal level one is able to measure (detection limit).

Peak-to-Peak Noise

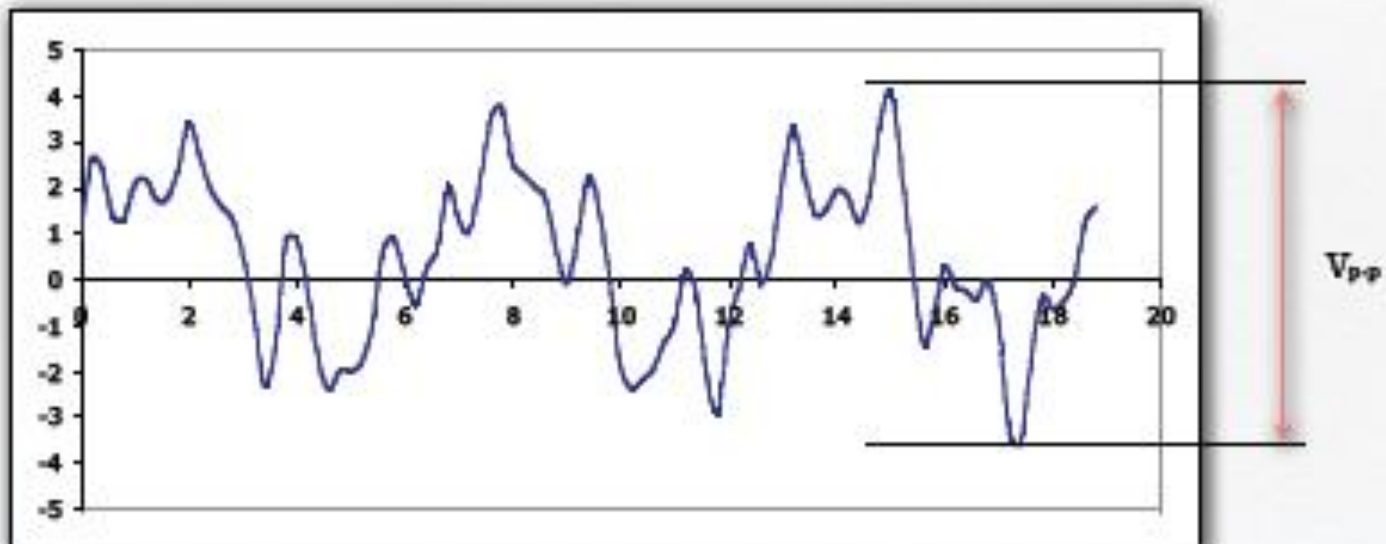
One measure of the amplitude of a sine wave is the peak-to-peak amplitude (twice the amplitude which appears in the defining equation for a sine wave).



Noise is usually specified by measuring the peak-to-peak noise maximum found over a reasonable length of time ("reasonable" depends upon length of time needed to make a measurement).

p-p Noise 2

Even though the noise is clearly not a perfect sine wave, we know it can be decomposed into a sum of many sine waves and we can treat it mathematically as a sine wave.



Average Noise?

Another way of measuring the intensity of noise might be the average noise.

If noise were truly random, then $N_{average} = 0$. (Excursions above zero should balance excursions below zero over time).

If noise were not 0, then another signal must be present and we would need to account for it.

Therefore, average noise is NOT a useful measure.

Root-Mean-Square Noise

For average noise, it was the cancelling of the positive and negative excursions that made $N_{average}$ not a useful measure.

Squaring the signal makes everything positive. This can then be averaged meaningfully. Take the square root of the result to get back a value that can be related to the original signal. This is the RMS value of a signal.

For a perfect sine wave, we can calculate its rms value. A theoretical analysis gives us that

$$N_{RMS} = \frac{1}{2\sqrt{2}} N_{p-p}$$

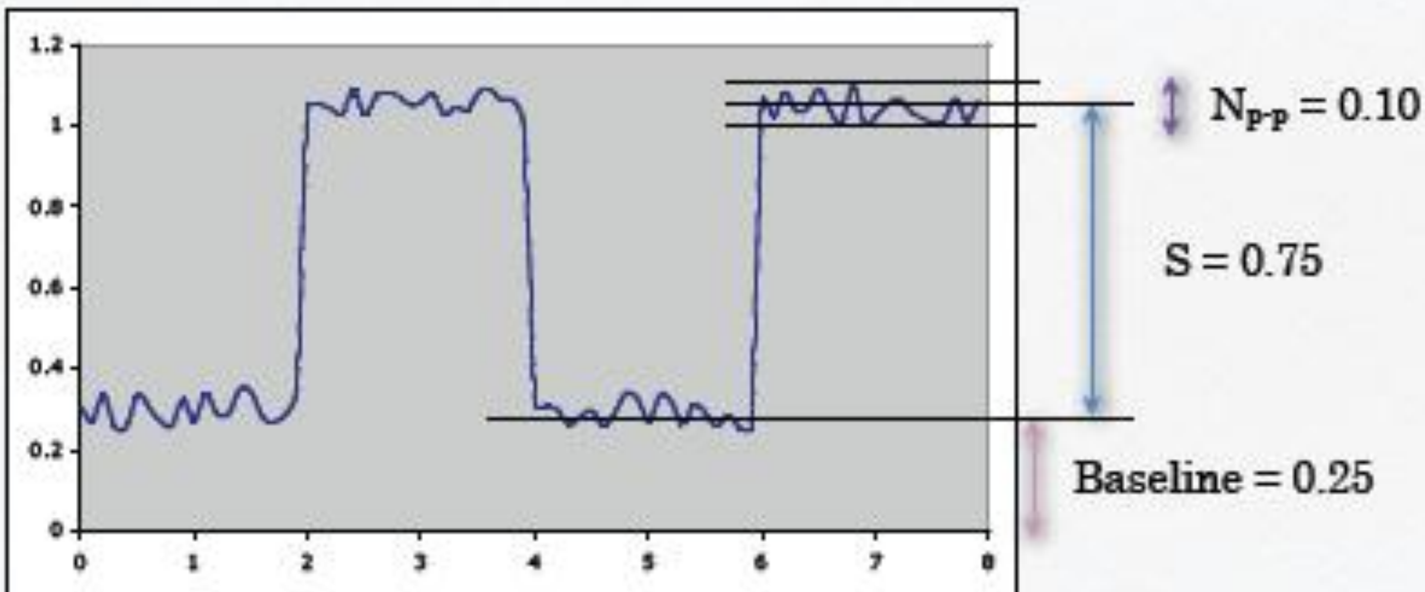
While peak-to-peak noise is easier to measure, rms noise is more meaningful. A quick estimate of the rms noise is

$$N_{RMS} = 0.35\ N_{p\text{-}p}$$

Signal-to-Noise Ratio

Total signal level nor total noise level determine an experiment's ability to accurately detect an analyte. rather it is the ratio of the two that is critical.

The S/N Ratio.

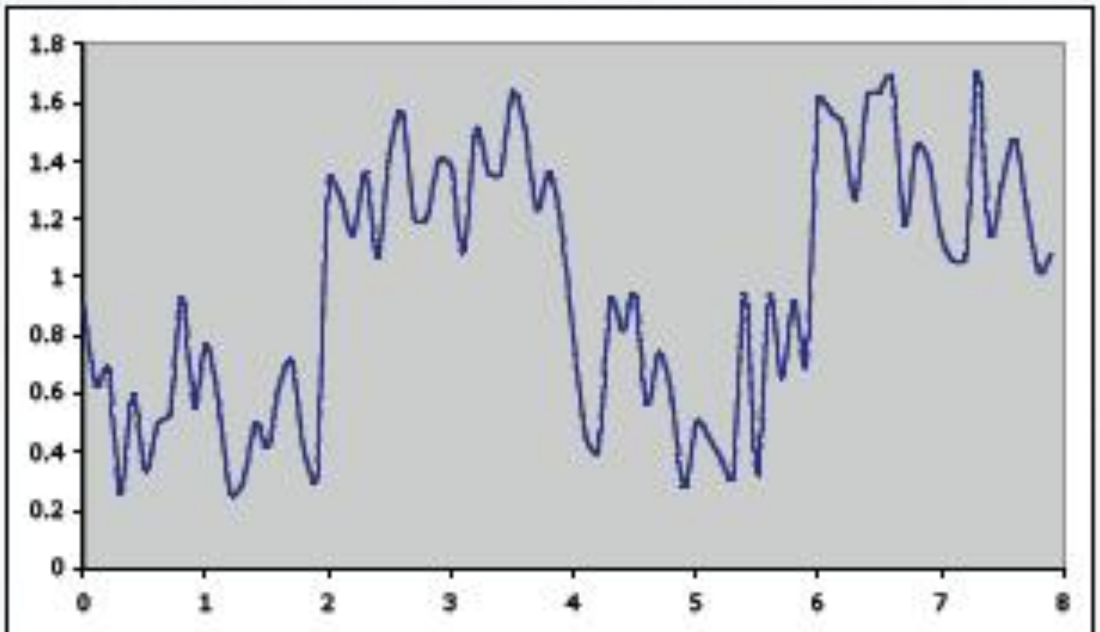


$N_{RMS} = 0.354\ N_{p\text{-}p} = 0.354 \times 0.10 = 0.035$

$S/N = 0.75/0.035 = 21.4$

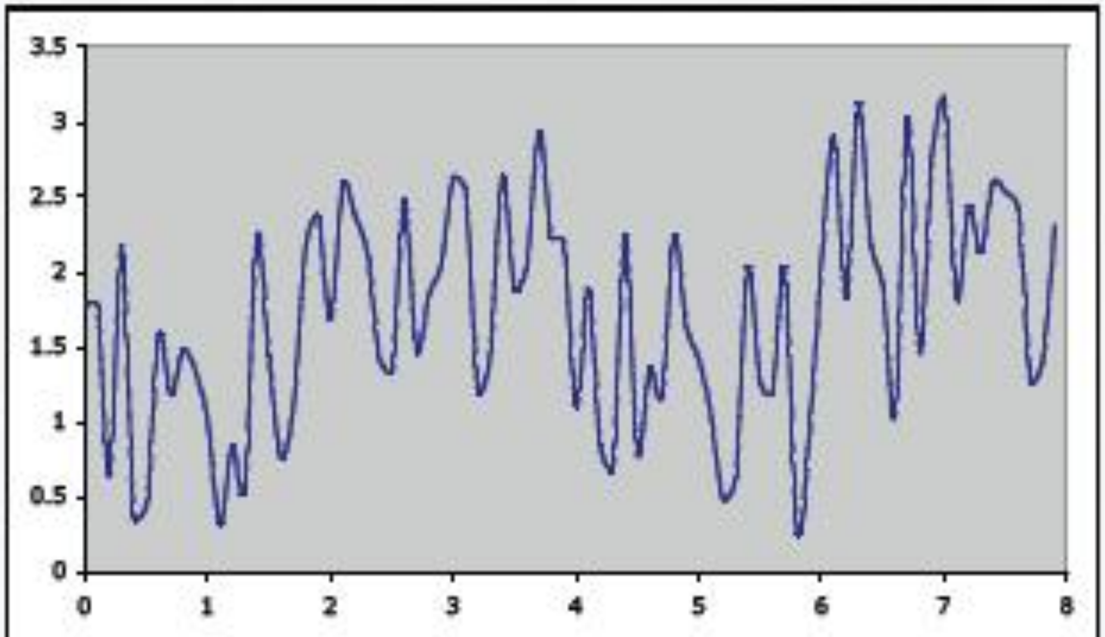
S/N 2

This is the same signal level as before and the same baseline. The noise is greater and the S/n = 3 in this case.



S/N 3

In this experiment, the S/N = 1 (noise is of the same intensity as the signal). Note how difficult it would be to make a reasonable measurement of signal under these conditions.



Decibel

Another way to measure S/N is the decibel (dB). It is defined in terms of the ratio of the power in the signal compared to the power in the noise.

$$\text{Power } S/N\,(decibels) = 10\log_{10}\frac{P_{\text{signal}}}{P_{\text{noise}}}$$

The definition is in terms of power, but we more readily measure current or voltage. The relationship between them is

$$P = \frac{V^2}{R} = I^2 R$$

Because of the quadratic relationship between P and I or V, the S/N ratio in decibels is given as

$$S/N\,(\text{dB}) = 10\log_{10}\frac{P_{\text{signal}}}{P_{\text{noise}}} = 20\log_{10}\frac{V_{\text{signal}}}{V_{\text{noise}}} = 20\log_{10}\frac{I_{\text{signal}}}{I_{\text{noise}}}$$

Sources of Electrical Noise

When sample is abundant, signal level is high, background is low, we hardly worry about noise. But at some point, every experiment needs to account for noise. When instruments are employed in the investigation, we need to consider noise arising from electrical activity. Electrical noise can be divided into four principal sources.

- Thermal Noise
- Shot Noise
- Flicker Noise
- Interference

Thermal Noise

Also known as ***White noise***, ***Johnson noise***, or ***Nyquist noise***.

Arises because the atoms of a solid state conductor are vibrating at all temperatures and they bump into conductors (electrons). This imposes a new, random motion on those conductors which generates noise.

$$V_{noise,rms} = \sqrt{4\, k_B\, T\, R\, B}$$

$V_{noise,\ rms}$ is the RMS voltage of the noise

k_B is Boltzmann's constant = 1.38×10^{-23} J K^{-1}

T is the temperature in kelvin (K)

R is the resistance in ohms

B is the bandwidth response of the instrument in Hz (s^{-1})

Thermal Noise Reduction by Cooling

A 10 kΩ resistor is used as a current-to-voltage converter. The voltage across it is amplified by an amplifier with a bandwidth of 15 kHz. What is the rms noise voltage at 20 ˚C? at liquid nitrogen temperature (77 K)? at liquid helium temperature (4.2 K)?

$$V_{noise,rms}(T = 298K) = \sqrt{4k_B TRB}$$

$$= \sqrt{4(1.38 \times 10^{-23})(298)(10^4)(1.5 \times 10^4)}$$

$$= \sqrt{2.43 \times 10^{-12}} = 1.56 \times 10^{-6}\,V = 1.56\,\mu V$$

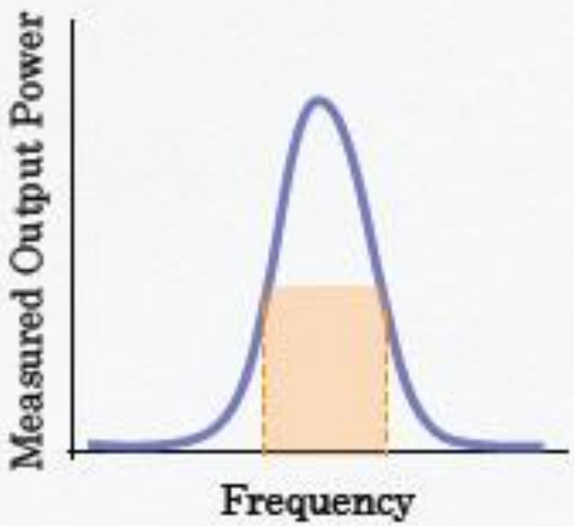
$$V_{noise,rms}(T = 77K) = 0.80\,V$$

$$V_{noise,rms}(T = 4.2K) = 0.19\,V$$

Cooling has dropped the noise originating in the resistor. We have (incorrectly) ignored noise in the amplifier itself.

Signal Bandwidth

Every instrument responds to rapid or slow signal changes differently. We specify the bandwidth or bandpass by referring to the range of frequencies over which it can effectively measure signals. Usually the bandwidth of an instrument can be adjusted by changing electronic filters.



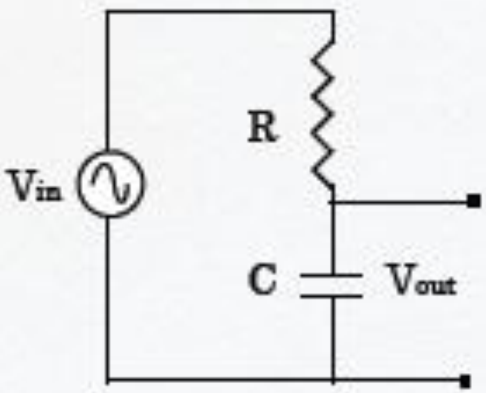
A simple RC circuit can act like a low pass filter (see next frame). It smoothes (or integrates) rapid changes. It allows slowly varying signals to pass unimpeded. The relationship between its time constant $\tau = RC$ and its bandwidth B is just

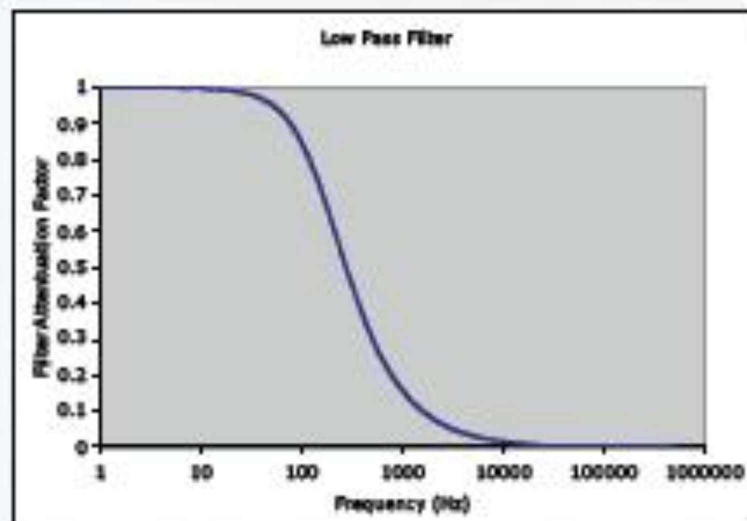
$B = 0.25\ \tau$

Other filters have different relationships.

Low Pass Filters

An RC circuit is one which has a resistor and a capacitor in series. When measuring the output voltage across the capacitor, the circuit behaves like a low pass filter. AC signals pass through the circuit unattenuated, while high frequency signals are dampened in intensity. Very high frequency signals are virtually eliminated.

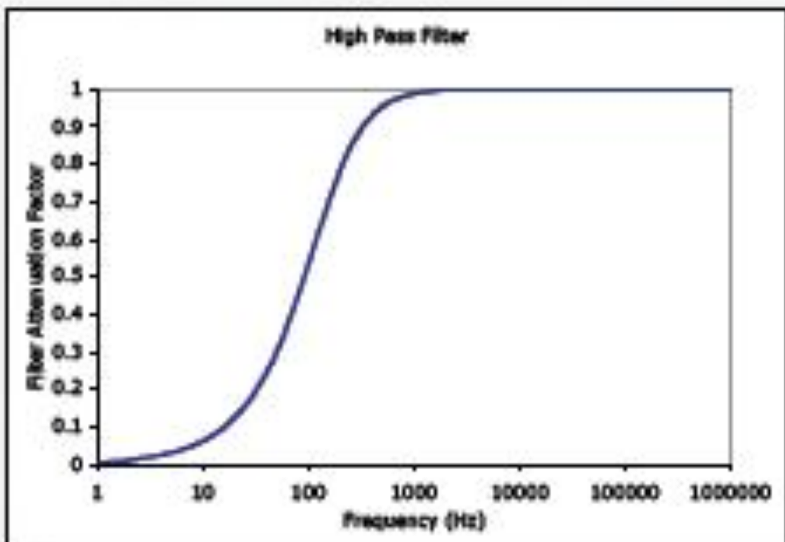


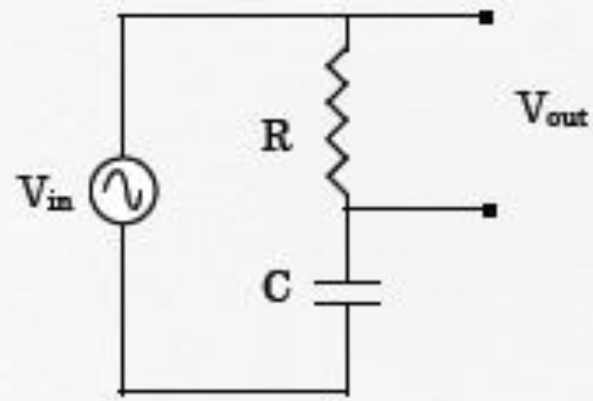


$$\frac{V_{out}}{V_{in}} = \frac{X_C}{\sqrt{R^2 + X_C^2}}$$

High Pass Filters

The same RC circuit can function as a high pass filter (allow high frequency signals to pass while rejecting low frequency ones. The only alteration is to take the output voltage from across the resistor, rather than the capacitor.





$$\frac{V_{out}}{V_{in}} = \frac{R}{\sqrt{R^2 + X_C^2}}$$

Band Pass Filters

Many more complex filters can be designed and the frequency response can be very complex. A simple combination of a high pass and a low pass filter can be used to produce a band pass filter.

$R_1 = 70\ k\Omega$

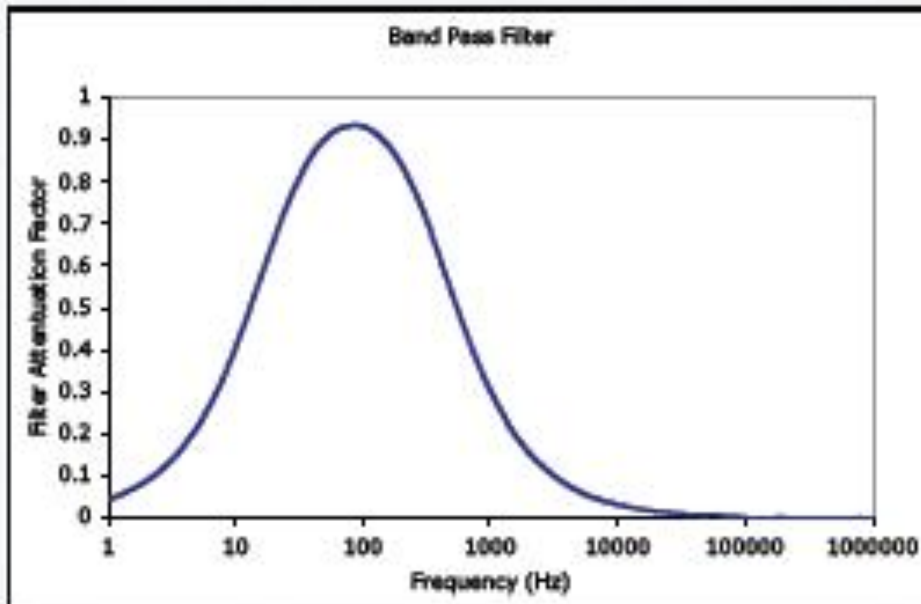
$C_1 = 100\ nF$

$F_1 = 23\ Hz$

$R_2 = 5\ k\Omega$

$C_2 = 100\ nF$

$F_2 = 318\ Hz$



Thermal Noise Reduction by Bandwidth

Reconstider the 10kΩ resistor being used as the current-to-voltage converter. Pass the signal through a noiseless RC circuit (impossible, since the R in this new circuit will introduce noise, but lets pretend, O.K.?) which has a time constant τ of 0.1 s. What is the expected rms noise from this filtered signal?

$$B = 1/(4\ \tau) = 1/(4 \times 0.1\ s) = 2.5\ s^{-1}$$

$$V_{noise,rms}\left(T = 298K, B = 2.5s^{-1}\right)$$

$$= \sqrt{4\left(1.38 \times 10^{-23}\right)(298)\left(10^{4}\right)(2.5)}$$

$$= 2.0 \times 10^{-8}\ V = 20\ nV$$

Noise reduction be filtering was greater than by cooling alone. The consequence, however, is that we are limited to the speed with which we can make a measurement and hence the rates of processes we can monitor.

Shot Noise

Also known as ***quantum noise*** or ***Schottky noise***.

Arises because charge and energy are quantized. Electrons and photons leave sources and arrive at detectors as quanta; while the average flow rate may be constant, at a given instant there are more quanta arriving than at another instant. There is a slight fluctuation because of the quantum nature of things.

$$I_{noise,rms} = \sqrt{2qI_{dc}B}$$

q is the electron charge = 1.602×10^{-19} C

I_{dc} is the DC current flowing across the measurement interface

B is again the measurement bandwidth

Shot Noise Reduction by Bandwidth

What is the shot noise present in a 1 amp DC current looking in a 15 kHz bandwidth? What is it when the bandwidth is reduced to 2.5 Hz?

$$\mathrm{I}_{noise,rms}(B = 15k\mathrm{Hz})$$

$$= \sqrt{2(1.602 \times 10^{-19})(1)(1.5 \times 10^{4})}$$

$$= 6.9 \times 10^{-8}\,\mathrm{A} = 69\,n\mathrm{A}$$

$$\mathrm{I}_{noise,rms}(B = 2.5\mathrm{Hz}) = 8.9 \times 10^{-10}\,\mathrm{A} = 890\,p\mathrm{A}$$

Again, a lower noise level is achieved but at the expense of only being able to measure slow enough processes.

Flicker Noise

Also known as ***1/f noise*** or ***pink noise***.

Origins are uncertain. Depends upon material, design, nature of contacts, etc. Flicker noise is determined for every measurement device. it is recognized by its 1/f dependence. Most important at low frequencies (from DC to ~200 Hz).

Long term drift in all instruments comes from flicker noise.

Measurements taken above 1 kHz can usually neglect flicker noise.

A narrow bandwidth makes flicker noise seem constant over that bandwidth and so it is indistinguishable from white noise.

Signal Modulation

Flicker noise, because of its 1/f behaviour, is particularly unforgiving when attempting to amplify a DC signal. This is remedied by modulating the signal to a higher frequency, then amplifying the signal, and then demodulating it.

Noise with a frequency characteristic different from that for the modulation-demodulation process is average to zero.

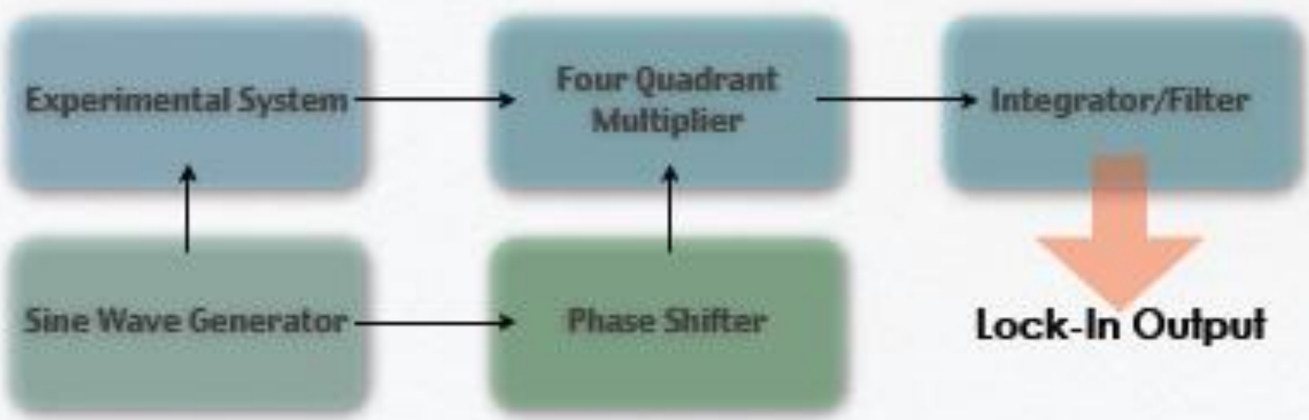
An older technique to accomplish was the chopper amplifier.

Problem now dealt with almost universally with a Lock-In Amplifier.

Lock-In Amplifier

Modern solution to the flicker noise problem. Can recover useful signal even when S/N < 1. Key components are

- a sine wave reference signal that also perturbs the system under investigation.
- a phase sensitive detector, including a four-quadrant multiplier and phase shifter.



LIA 2 - Perturb the System

The experimental design challenge is to control the expeirment so that the relevant system properties are modulated at the desired frequency.

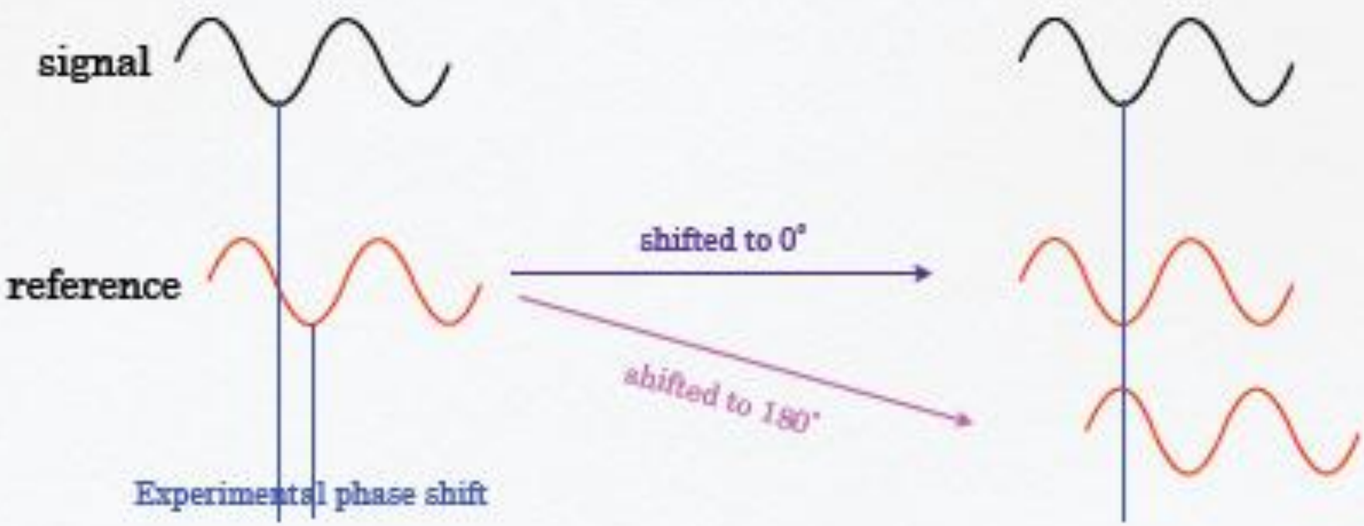
Light Spectroscopy: uses a ***chopper wheel***.

Electron Spectroscopy: modulate the ***bias potential***.

Electrochemical Experiment: modulate the ***cell potential.***

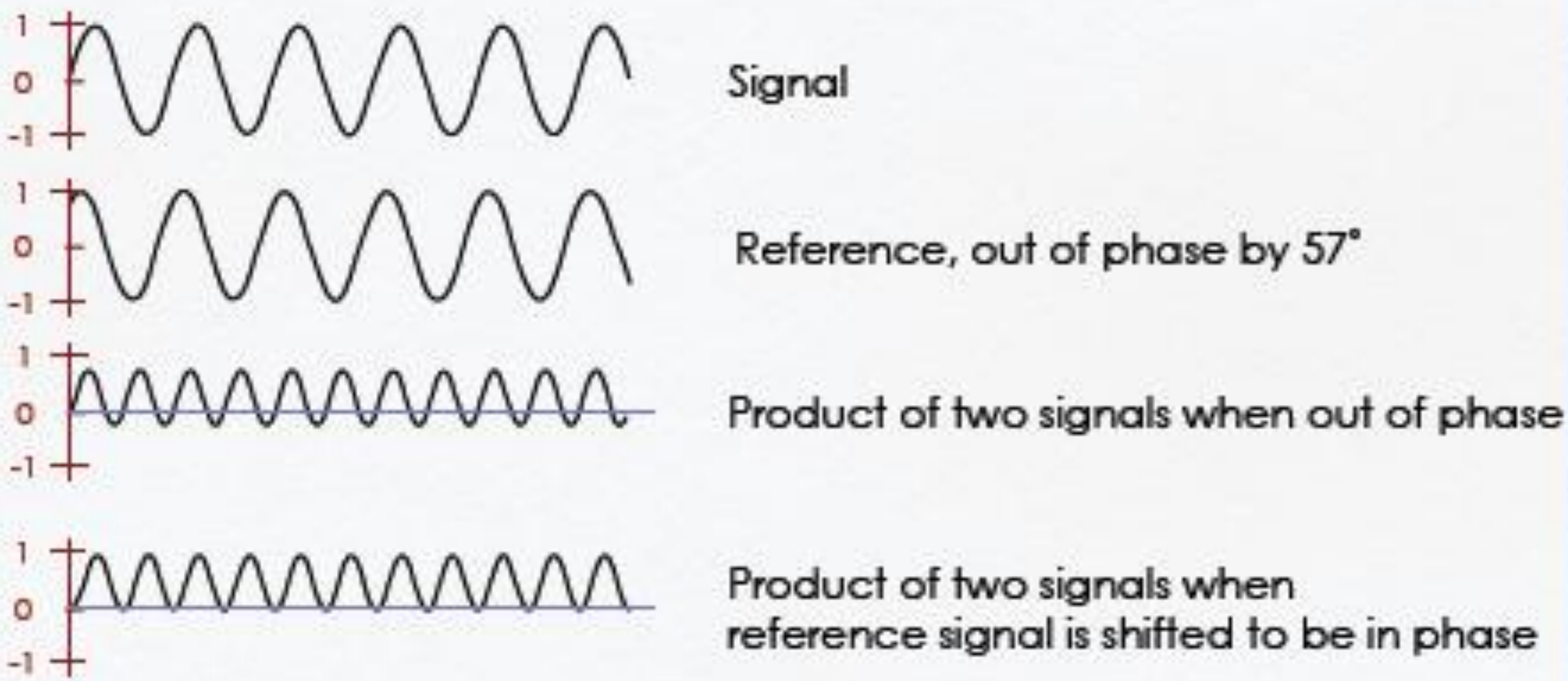
LIA 3 - Phase Shifter

The system's response is modulated at the same frequency as the reference signal, but different response rates mean that they arrive at the four quadrant multiplier phase shifted with respect to each other. A phase shifting circuit brings the reference signal back in phase with the experimental signal.



LIA 4 - Four Quadrant Multiplier

The two waveforms - the signal and the phase-shifted reference - are multiplied together, point-by-point.



LIA 5 - Integrator, Time Constant

The product waveform is fed into another circuit. A low pass filter, or better yet, an integrator, averages the waveform over several periods to provide a DC output signal. The magnitude is a maximum when the phase shift is either 0˚ or 180˚.

Out-of-phase Average = 0.27

Note that the fraction of the waveform below zero subtracts from the portion above zero, making the average smaller.

In-phase Average = 0.50

This is what happens when the signal and reference are of the identical frequency, but with a varying phase relationship.

LIA 6 - Other Frequency Signals

Noise occurs at all frequencies, but anything which is at a frequency other than the reference frequency will average out to zero, once sufficient periods have been included in the integration period

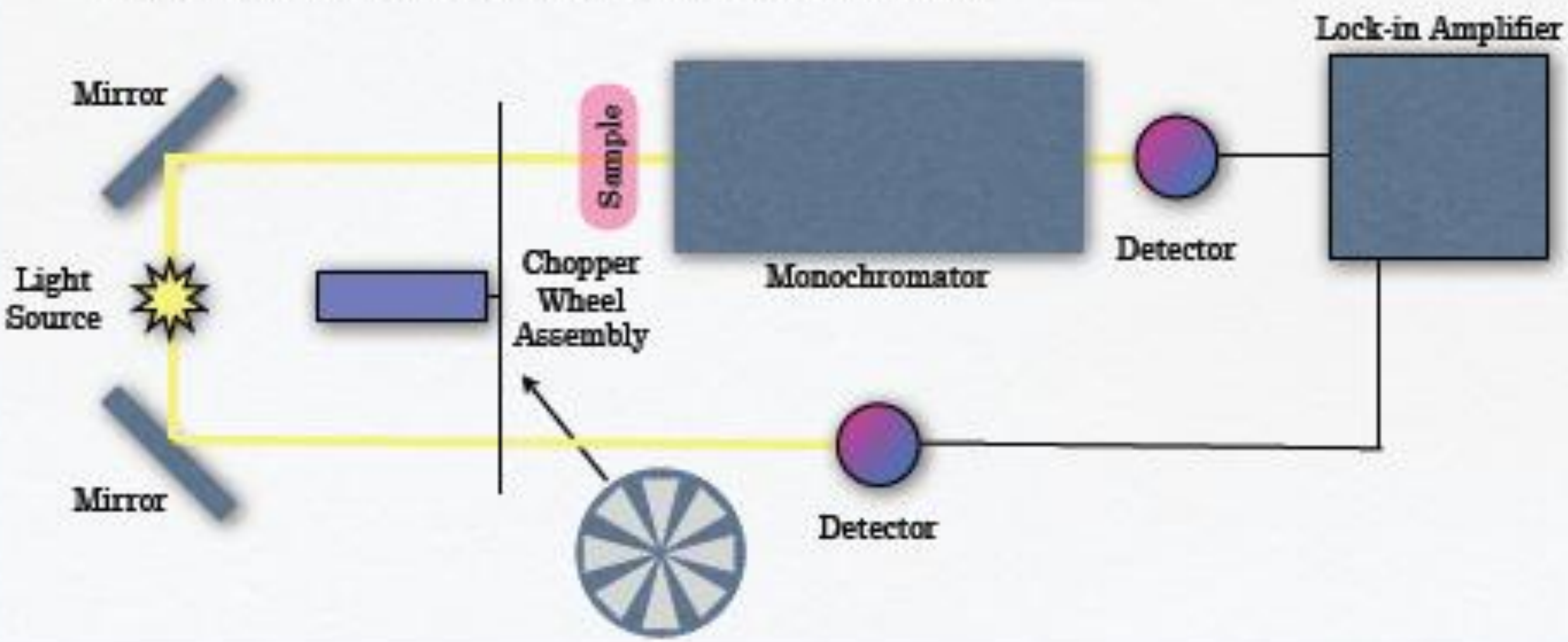
Reference

Signal at frequency 1.75 times higher than reference frequency

Product of both waveforms:
Average signal = 0.01

Optical Spectroscopy Example

Optical spectroscopy can take advantage of the lock-in technique. using mirrors, a light source directs its emissions down ttwo channels. each is chopped by a rotating mechanical blade (much like a fan), producing a square wave modulation. These modulated beams produce the signal and reference that enters the four quadrant multiplier.



Interference

Also known as ***environmental noise*** or ***electrical pickup***.

Broadcasting electric and magnetic fields.

- Lines noise and harmonics (60 Hz, 120 Hz, 180 Hz, etc.)
- Electrical devices (elevators, air conditioners, motors)
- Broadcasting stations (radio, T.V.)

Microphonics (mechanical vibrations coupled capacitively)

Remediate by shielding, eliminate ground loops, rigidly secure all cables and detectors, isolate from temperature variations, compensate for magnetic fields, etc.

Difference Amplifiers

Soon we will discuss amplifiers. One configuration amplifies the **difference** between two inputs. If one signal is a reference, then any low frequency flicker noise (drift) or any interference noise (line interference at 60 Hz) appears common to both channels. Since the amplifier only is sensitive to the difference between the two, this noise is effectively eliminated.

Common Mode Rejection Ratio (CMRR) is a measure of how well an amplifier can reject common mode signals. It is defined as the ratio of the difference gain ($A_{difference}$) to the common mode gain (A_{common}).

The larger the value of CMRR, the better the amplifier. Values as high as 10^6 with signal amplifications of 10^3 are readily achievable.

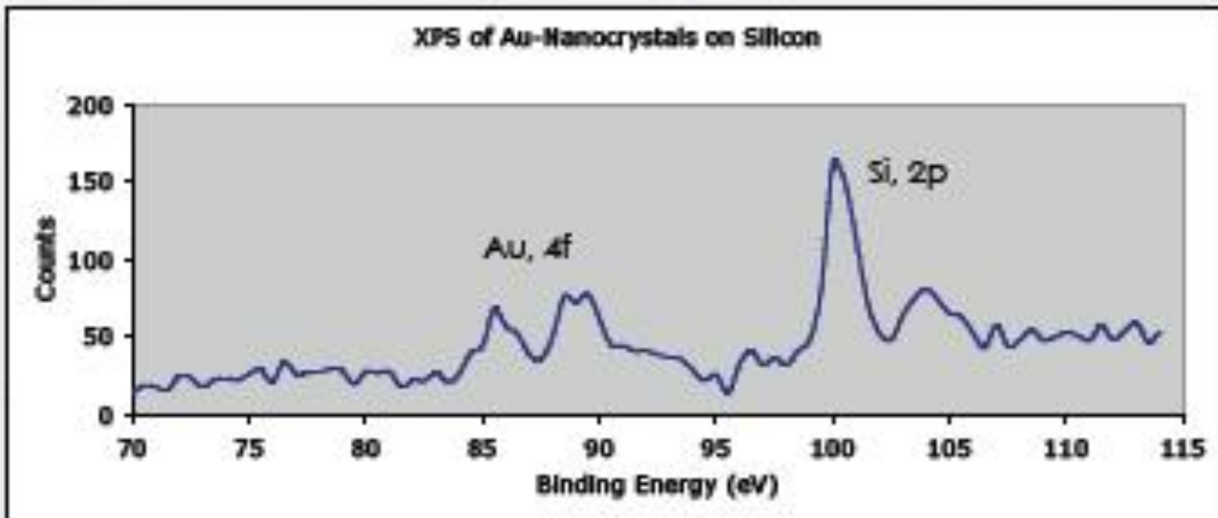
Software Methods

Computers have dramatically changed the way in which we deal with noise. Many of these mathematical techniques can help to “pull the signal out of the noise”.

- Software smoothing or “digital low pass filtering”.
- Ensemble averaging
- Fourier Transform Filtering

Software Low Pass Filtering

An X-ray Photoelectron spectrum (XPS) of AU nanocrystals attached to a silicon surface by 3-mercaptopropyltrimethoxysilane.

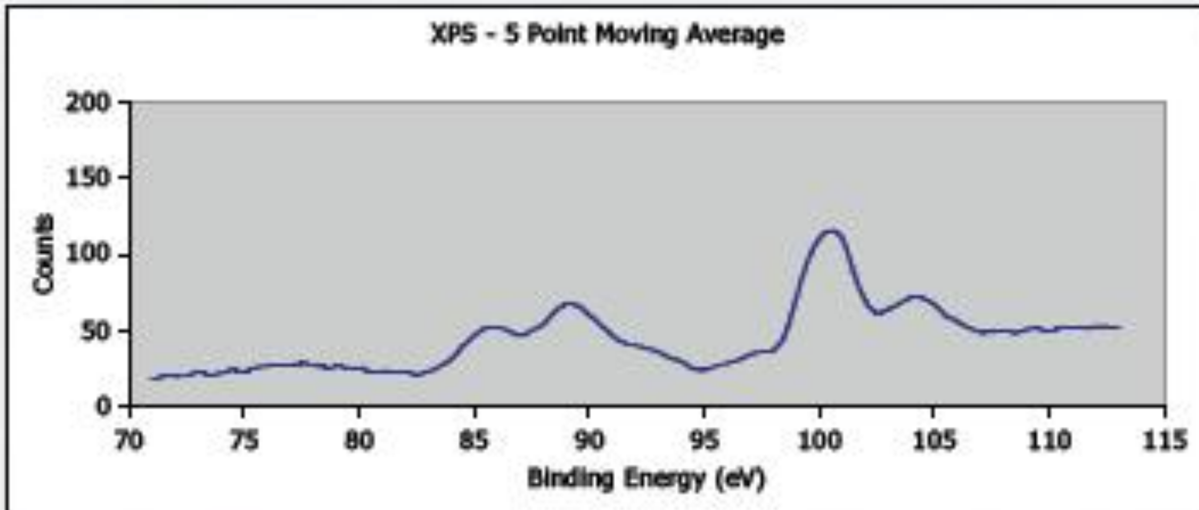


1 scan; 0.5 eV step size

S/N = 29 for the Si peak at 100 eV.

SLPF 2

A 5 point moving average to smooth the data.

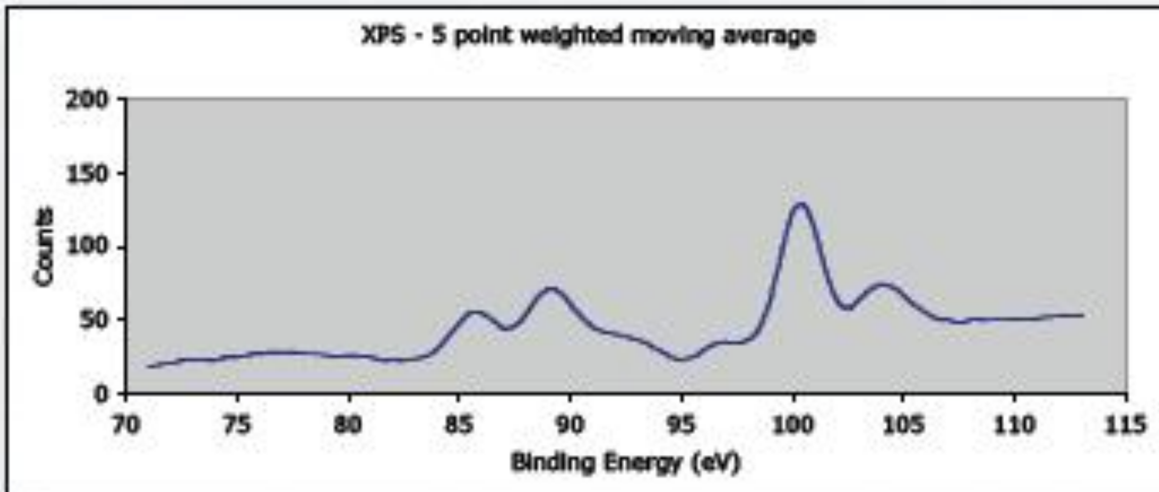


Noise is decreased but so is peak amplitude.

S/N = 53 for the Si peak at 100 eV.

SLPF 3

A weighted 5 point moving average: weighting factors are 1:2:3:2:1

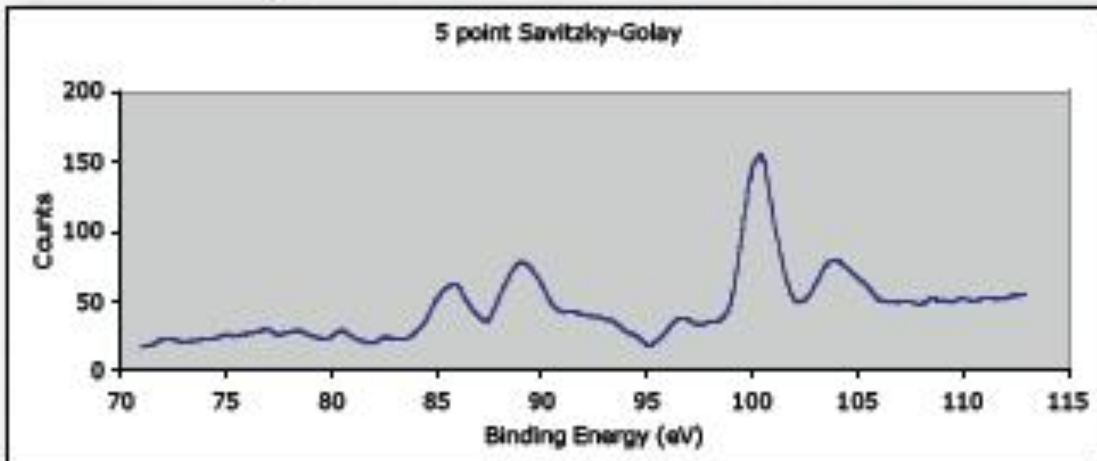


Noise is decreased but so is peak amplitude. However it is not so much as for the non-weighted smoothing.

S/N = 57 for the Si peak at 100 eV.

SLPF 4

A 5 point weighted moving average using Savitzky-Golay weighting factors for a quadratic fit. They are -3:12:17:12:-3



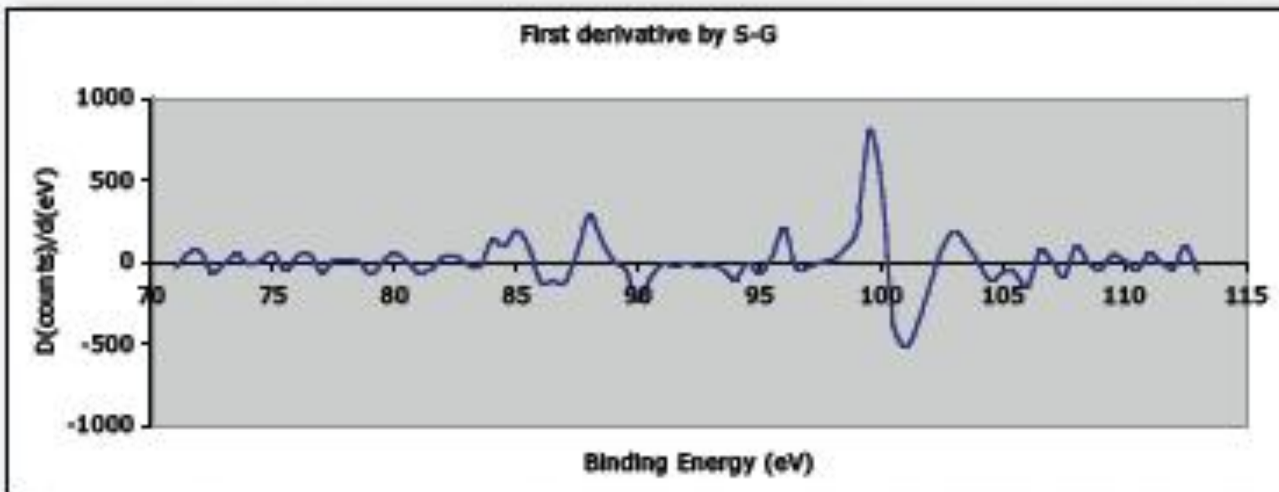
Best noise reduction without compromising peak intensity.

S/N = 81 for the Si peak at 100 eV.

A. Savitzky and M.J.E. Golay, Anal. Chem. 1964, 36, 1627.

SLPF 5

The Savitzky-Golay technique can be extended to many more process by choosing the right weighting factors. Differentiation of a waveform can be done; here is the first derivative of our waveform using the weighting factors 1:-8:0:8:-1



Ensemble Averaging

Text

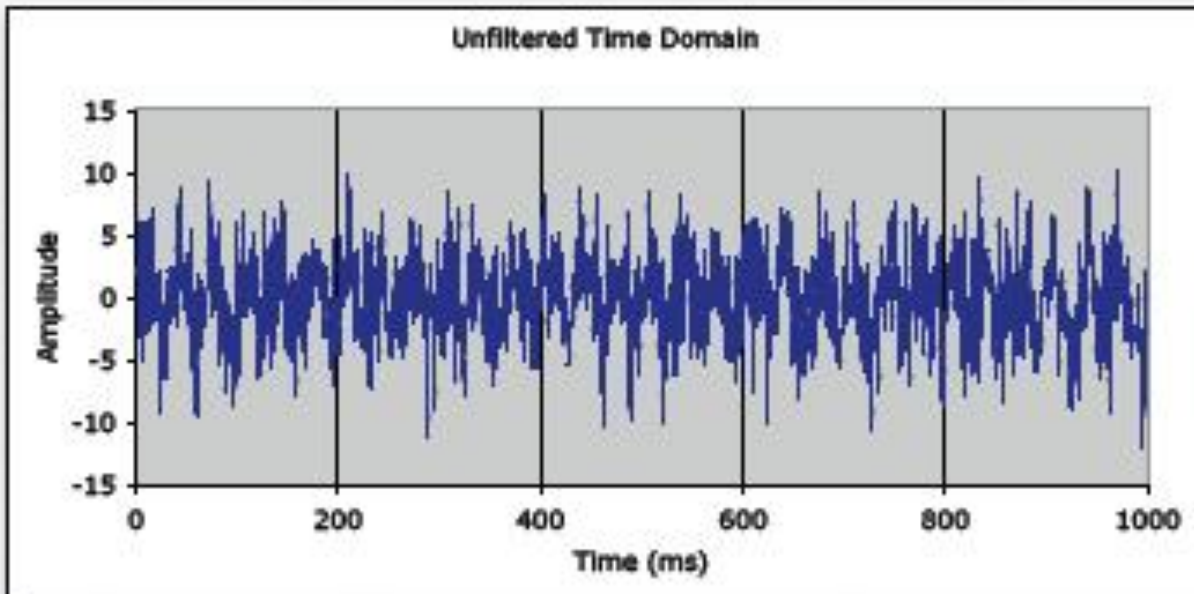
Fourier Smoothing

A Fourier transform can decompose a spectrum into the many sinusoidal contributions that make it up. Noise is generally high frequency; drift is low frequency; environmental noise is of specific, narrow frequencies. With a Fourier transform, the selective removal of offending frequency components, followed by an inverse Fourier transform, can significantly improve a spectrum's appearance.

A Fourier Transform takes data that is encoded in the time domain and converts it to data that is in the frequency domain and *vice versa*.

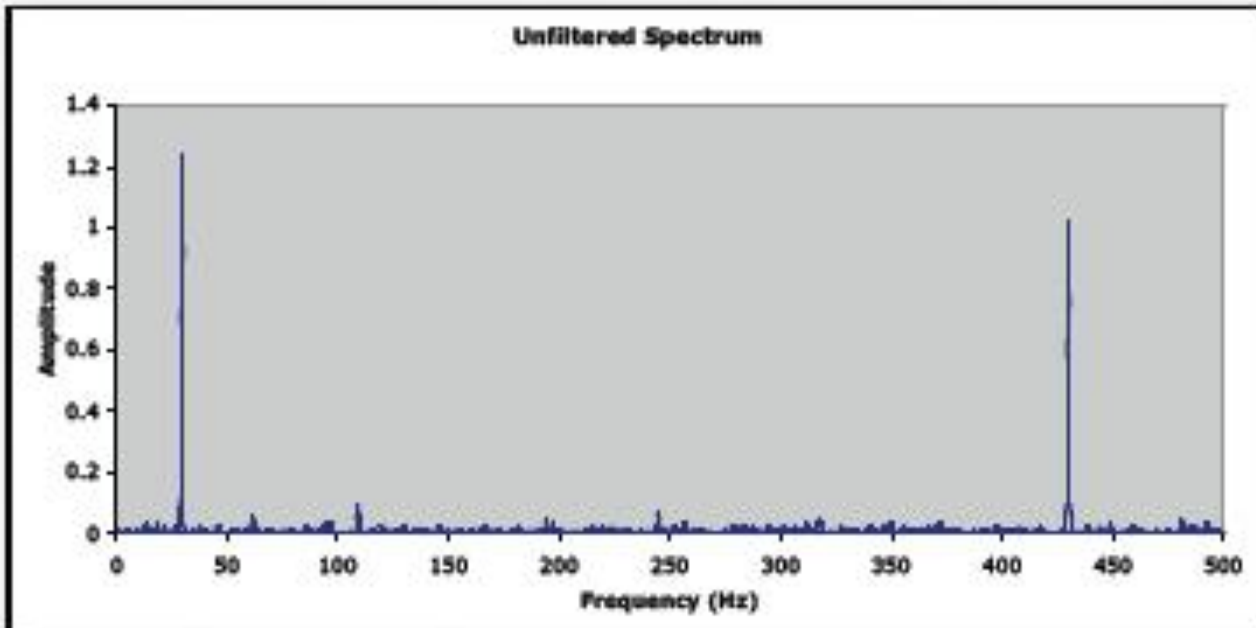
Time Domain Signal with Noise and Interference

This is a 30 Hz sine wave which is contaminated by a much higher frequency interference signal and with broad spectrum white noise.



Unfiltered Frequency Spectrum

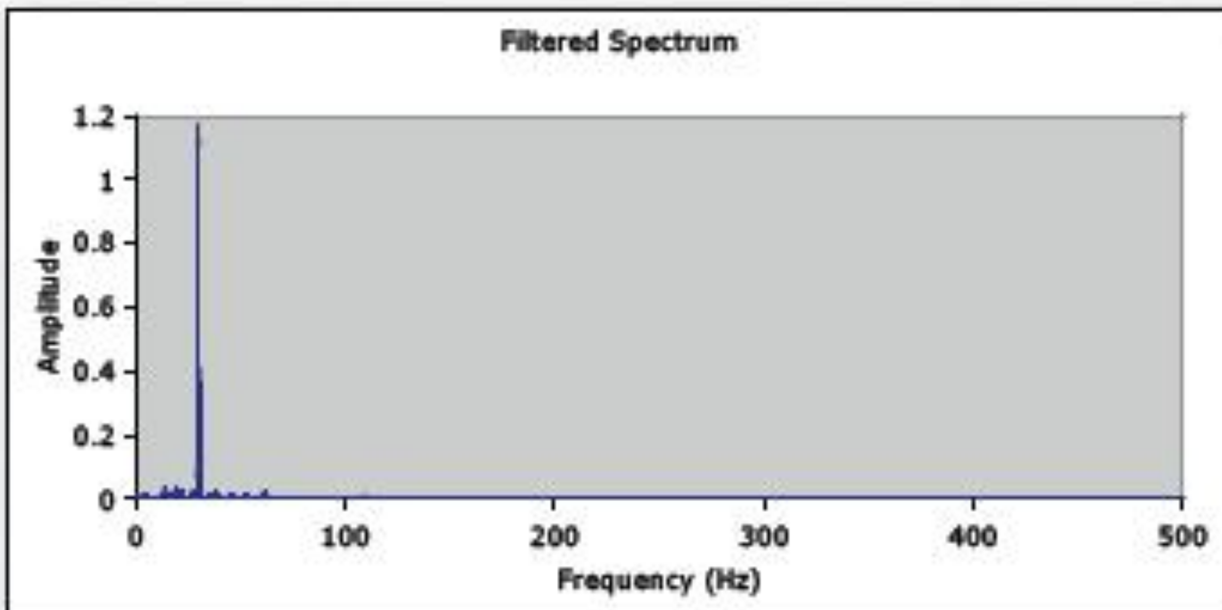
A Fourier transform of the time domain provides a spectral decomposition of the frequency components, revealing the interfering signal (at 480 Hz) and the white noise.



Filtered Frequency Spectrum

We multiply the spectrum with a box-like function, but with an exponential decay to higher frequencies. This preserves unchanged all frequency components below 100 Hz while attenuating higher frequency with an exponentially increasing efficiency as the frequency increases.

The inset is the full range of the spectrum amplified to reveal the details of how the signal drops off at higher frequencies from filtering.



Filtered Time Domain

An inverse Fourier transform takes the filtered spectrum and produces the filtered time domain data. It is not perfectly clean yet because of the white noise present within the selected filter bandwidth of 100 Hz.