Instrumental Considerations

Many of the limits of detection that are reported are for the **instrument** and not for the **complete method**. This may be because the instrument is the one thing that the analyst can control. One of the factors affecting instrumental response is **rise time** and **electronic noise**.

The **rise time** is a measure of the time it takes the instrument to move from 10% to 90% of the full signal. This is related to the frequency response of the instrument. Any signal generated by an instrument in response to some chemical measurement can be thought of as a voltage vs time plot. As an example consider the square wave. A reasonable square wave can be generated by summing a base frequency, f_1, sin wave with sin waves of decreasing amplitude and increasing frequency. The summed sin waves are odd number multiples of the base frequency in order to ensure that **constructive** interference leads to an increase in the voltage at the leading and falling edges of the sin wave with out causing an overall increase in the amplitude of the signal. Figure 15 shows the sin waves to be summed and indicates where constructive summation will occur. Figure 16 shows the various "square" waves obtained when an increasing number of frequencies are summed. Figure 17 is an expansion of Figure 16 at the leading edge of the square wave.

[21] $$V_t = \sum_1^n \frac{V_1}{n} \sin\left(2\pi t\left(nf_1\right)\right)\bigg|_{n=1,3,5,7,9,\ldots\ldots}$$

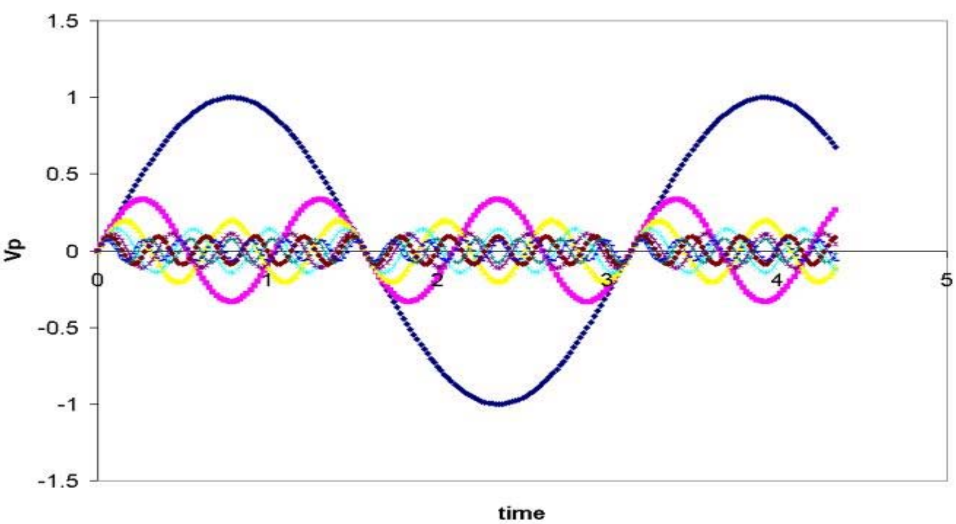

Figure 1 The sin waves shown in this figure represent a "base" frequency of amplitude 1, a frequency tripled wave of amplitude 1/3, a 5xbase frequency of amplitude 1/5 and so forth to 16xbase frequency. When these sin waves sum they will add in the region shown and will subtract or destructively sum in the region near the peak of the base frequency.

As shown in Figure 16 the rise time between 10 and 90% of the signal decreases as the summed frequencies increase from 1 (the base sin wave) to 17 where a reasonable approximation of a square wave appears. The rise time is expressed as:

[22]
$$t_r = \frac{1}{3\left(f_2 - f_1\right)} = \frac{1}{3\Delta f} \approx \frac{1}{3f_2}$$

where bandwidth)f is the difference between the high frequency at which amplitudes begins to roll off (f_2) and the low frequency at which the amplitude begins to fall (f_1). (See also Figure 20.) For modern **op amp** based instruments there is no low frequency roll off so that t_r is defined only by the high frequency roll off point.

In general, any time varying signal can be considered to be some summation of sin waves, expressed as a Fourier series:

[23]
$$f(x) = \int_0^{\infty} \left\{ A(\alpha)\cos\alpha x + B(\alpha)\sin\alpha x \right\} dx$$

where the amplitudes A(") and B(") are themselves integrals of sin waves. Figure 18 shows the amplitudes of the frequencies which sum to make a reasonable square wave. The plot shown is called a frequency domain plot and can be obtained by taking a Fourier Transform of the time varying data in equation 23

[24]
$$\Im\left\{ f(x) \right\} = F(x) = \int_{\infty}^{\infty} f(x) e^{-i\alpha x} dx$$

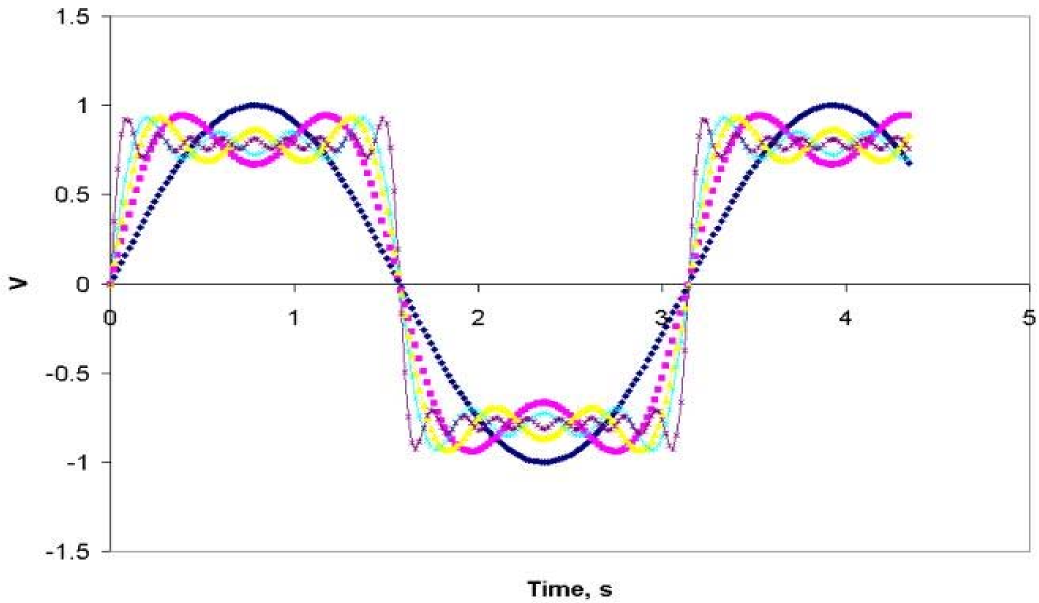

Figure 2 Plots of “square” waves obtained by summing multiple sin waves shown in fthe above figure. Note the ripple at the square wave that developes around the center of the base sin wave. The ripple decreases as more frequencies are summed.

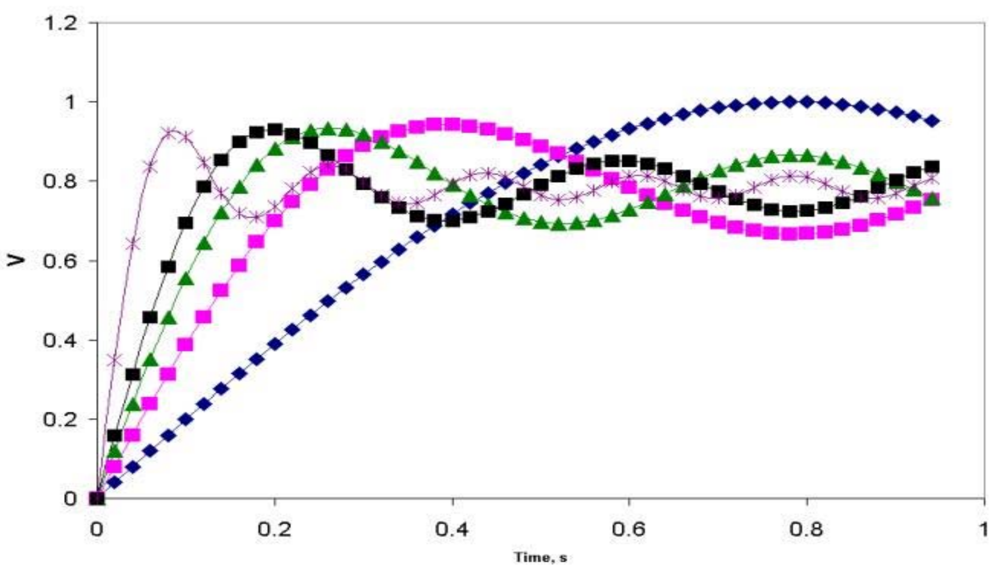

Figure 3 The “square” wave as a function of number of summed higher frequencies is plotted. As the number of higher order summed frequencies is added the time for the signal to rise from 10 to 90% of the full amount decreases.

The Fourier Transform can be discretized as

[25] $$F(x) = \sum_{x=1}^{N} f(x)W^{nm}, m = 1,2,\ldots, N$$

Solution of N^2 multiplication operations are required which made it an undesirable application. However performing the operation as a matrix set of operations results in a fast Fourier transform (FFT) which can be used even within fairly simple computational packages including Excel.

This is very useful because an analog signal converted to a digital set of data within the computer can be manipulated by the FFT transform to derive a frequency spectrum of the signal. If the source of noise is known it can be removed from the frequency spectrum and the time domain signal reformed minus noise.

Not all instruments are capable of tracking higher frequency signals. In many cases an instrument may distort a square wave by rounding off the leading and falling edges. This is due to unintentional internal RC filtering of the analog components of the instrument.

Intentional filtering can be accomplished either computationally or by analog (electronic) circuits. Analog filtering is based on passing the electronic signal containing the signal and reducing signal of the blank or background discriminating against the two by the frequency at which the signal and background are found at.

A low pass circuit is shown in Figure 19. The output of the low pass circuit can be described by:

[26] $$\frac{V_o}{V_i} = \frac{1}{\sqrt{1 + (2\pi fRC)^2}}$$

where R is the magnitude of the resistor, C is the magnitude of the capacitor, and f is the frequency in Hertz of an ac signal. A plot of equation 26 is shown in Figure 20 as a **Bode** plot. When RC = 1/2**B**f the equation simplifies to:

[27] $$\frac{V_o}{V_i} = \frac{1}{\sqrt{1 + 1^2}} = \frac{1}{\sqrt{2}} = 0.707$$

This particular ratio of the output frequency to the input frequency is called the **cutoff frequency** and represents a way of ranking various RC circuits.

As an example we can consider the situation where the signal of interest arising from the chemical sample is of low frequency which during measurement picks up a high frequency noise (from an adjacent instrument) (Figure 21). Passing the acquired signal (signal plus noise) through a low pass filter results in recovery of the noise free sample signal.

The amplitude of the high frequency component often constitutes noise. This noise can be reduced by making use of equation 5, increasing the number of measurements. One

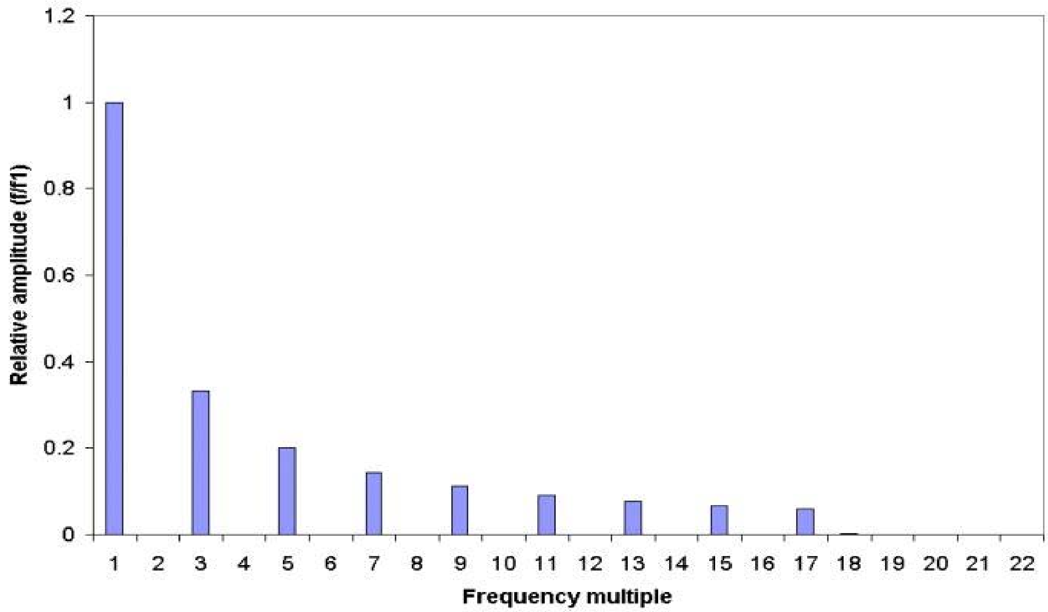

Figure 4 A fast Fourier transform of the square wave obtained by summing to the 17x base frequency is shown. The plot represents the amplitude of each frequency as a function of the frequency used in the summation. This FT was obtained using a simple spread sheet tool pack analysis.

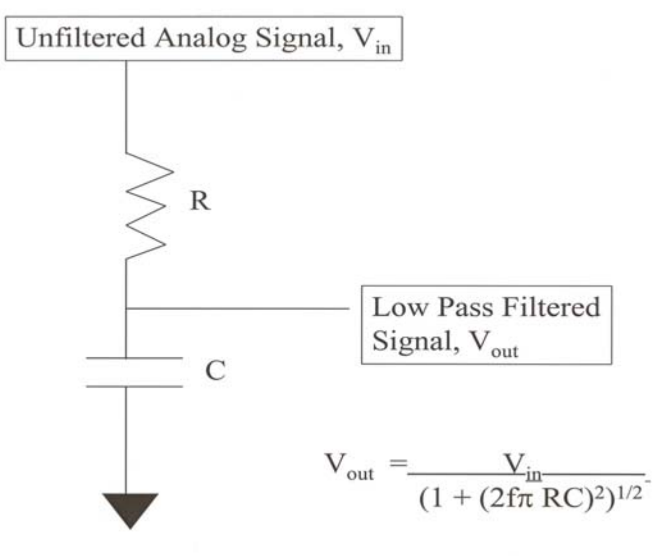

Figure 5 A low pass analog filter consits of a resistor in series with a capacitor tied to ground. The output voltage is sample between the resister and capacitor.

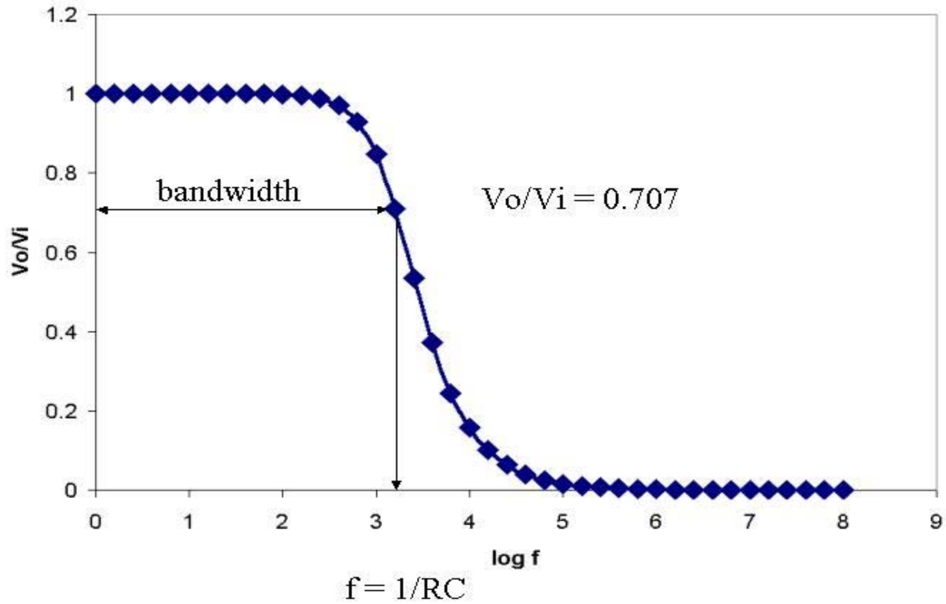

Figure 6 A Bode plot is a plot of signal attenuation vs frequency. The frequency at which the signal declines to 0.707 of its initial value is known as the cutoff frequency. It is also a rough estimate of f_2, the frequency used to characterize the bandwidth of an op amp based instrument.

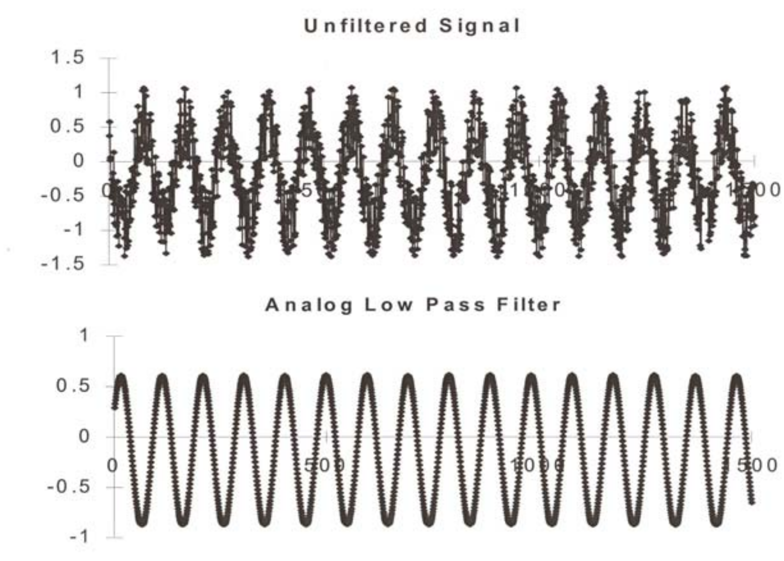

Figure 7 A noisy voltage vs time signal (upper trace) when passed through a low pass filter can be enhanced as shown in the lower trace. The low pass filter attenuates the amplitude of the high frequency components while passing the low frequency component unattenuated.

way to do this is to sum a waveforms obtained. In order to do this the **phase angle** of the "identical" waveforms to be summed must be considered. Sin waves can be identical in amplitude, V_p, and in frequency, f, and differ in their offset or phase angle, **1** (Figure 22):

[21] $$V_i = V_p \sin(2\pi f + \theta_i)$$

When sin waves with identical **1** are summed the effect is to increase the amplitude of the sin wave. This effect is termed **constructive interference**. When sin waves are 180^o out of phase the effect is to sum the amplitude to zero, an effect termed **destructive interference** (Figures 23-25).

Because noise is random, it can be thought of as incoherent, therefore destructive interference is likely to occur on summation. The signal, on the other hand, is coherent, and therefore sums constructively, thus increasing it's amplitude. As repetitive waveforms are summed the result is to increase the relative amplitude of the signal compared to the noise. S/N increases (Figure 26). The difficulty of this form of filtering is that it requires absolute precision in initiating the waveforms. If the waveforms of the base signal are at all out of phase they will **destructively** sum and the signal is lost (Figure 27) or greatly distorted.

The second way of enhancing the signal (decrease the standard deviation of the signal) is to perform a **boxcar** filter. Here we assume that over a short time range of the waveform the signal magnitude has not changed greatly and that variation in the measured signal is due to a high frequency random perturbation (noise). By summing several of the "noise" points destructive interference will result in a loss of the high frequency noise. The summed points are averaged to
give the estimated value for the signal, with a decreased contribution from the noise. The boxcar can be of any particular size (3 points, 5 points, 10 points) just so long as the length of the box is small enough that the assumption that the signal is not varying is valid. One problem with boxcar filtering is that data is lost at the front and rear end of the waveform, and that the number of data points is reduced by the averaging process (Figure 28). In a moving (sliding) boxcar, the data is treated as a string of points arranged in order of acquisition. For a five-point boxcar we start with the first five points (original data points 1-5, Figure 28), average the value of those points and store as point number 3. The boxcar is slid to the next five points (original data points 2-6), averaged and stored as point number four. This process is followed sequentially with the last five points (n-5 to n) averaged and stored as the n-2 point. Filtering efficiency increase with the size of the box and the number of points averaged (Figure 28).

The coupling of such electronic and digital filtration to an increased sampling has lowered the magnitude of the blank, lowered the standard deviation of the blank, thus lowering the limit of detection (equation 12). A concrete example of this is the drop in the limit of detection for lead from 0.5 ppm in the 1920 to 1 ppt in the 1990s, or by nearly 5 orders of magnitude.

Acquiring the "Physical" Sample

To estimate the randomness of, for example, lead in a soil, the physical sampling of the soil must be randomized and of sufficiently large number of individual "grabs" that a normalized

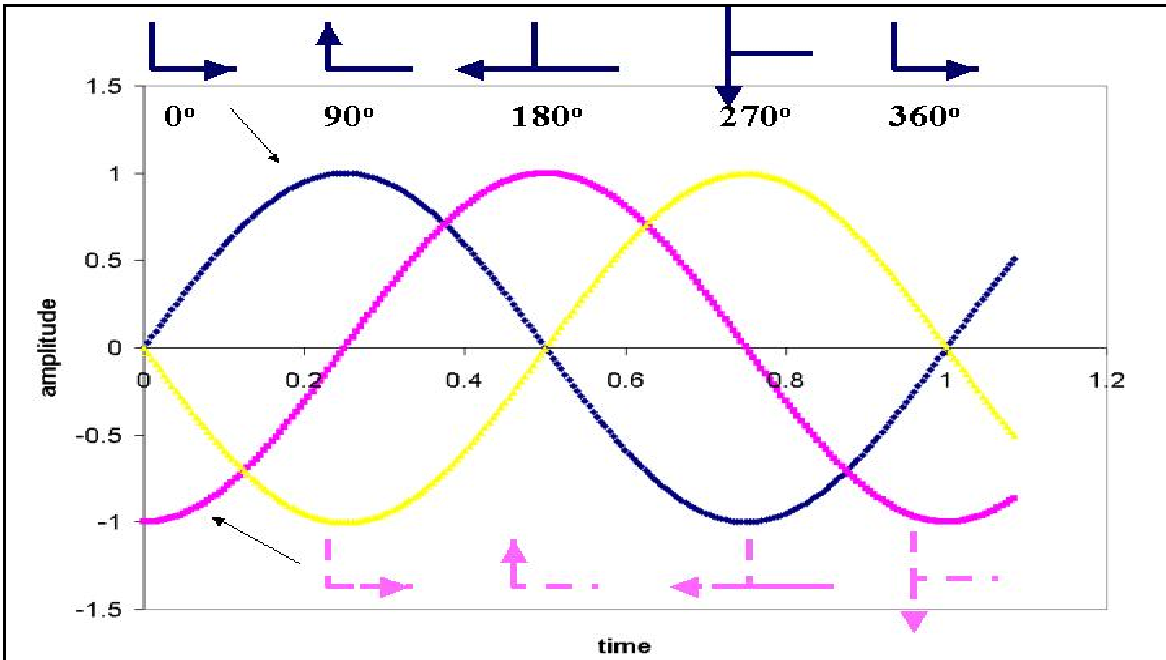

Figure 8 Sin waves of identical amplitude and frequency can differ by their point of initiation, or phase angle. In this figure one sin wave is captured beginning at o° and a second begins 90° out of phase. The third wave form is 180° out of phase.

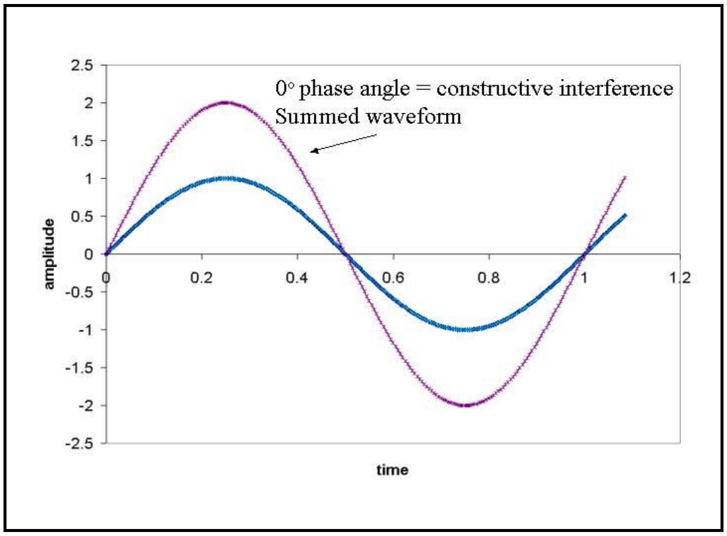

Figure 10: Waveforms in phase sum constructively to increase the amplitude.

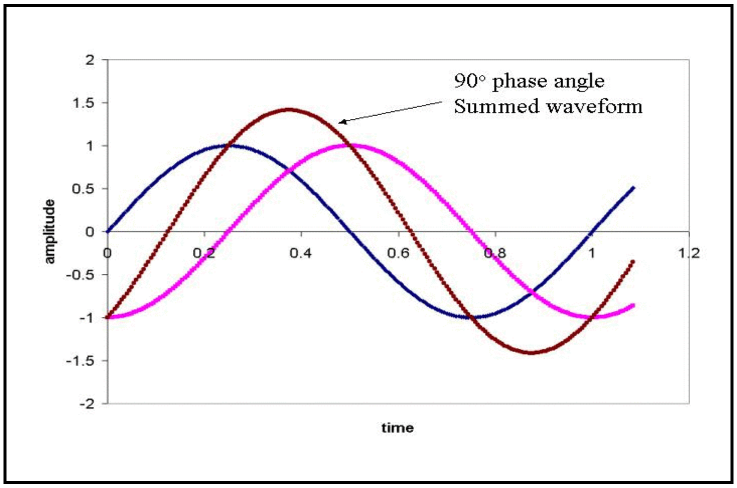

Figure 9: Waveforms that are 90° out of phase sum both constructively and destructively.

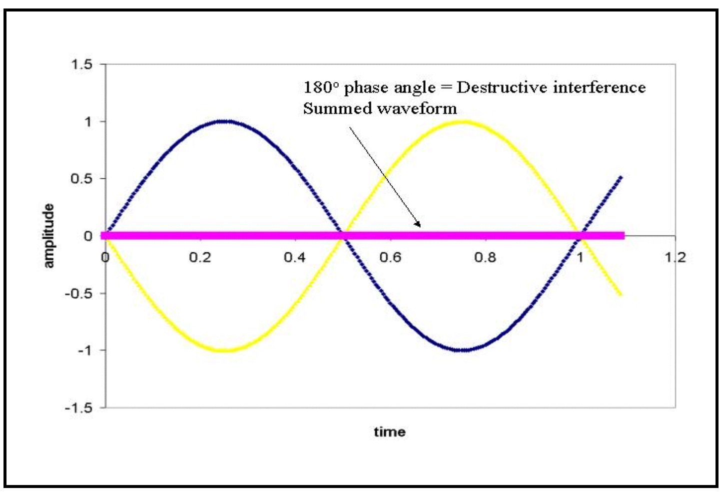

Figure 11 Waveforms that are 180 ° out of phase will sum destructively.

error curve associated with sampling the soil can be approximated. That is, the reliability of the estimate of lead in the soil goes up with the number of samples taken.

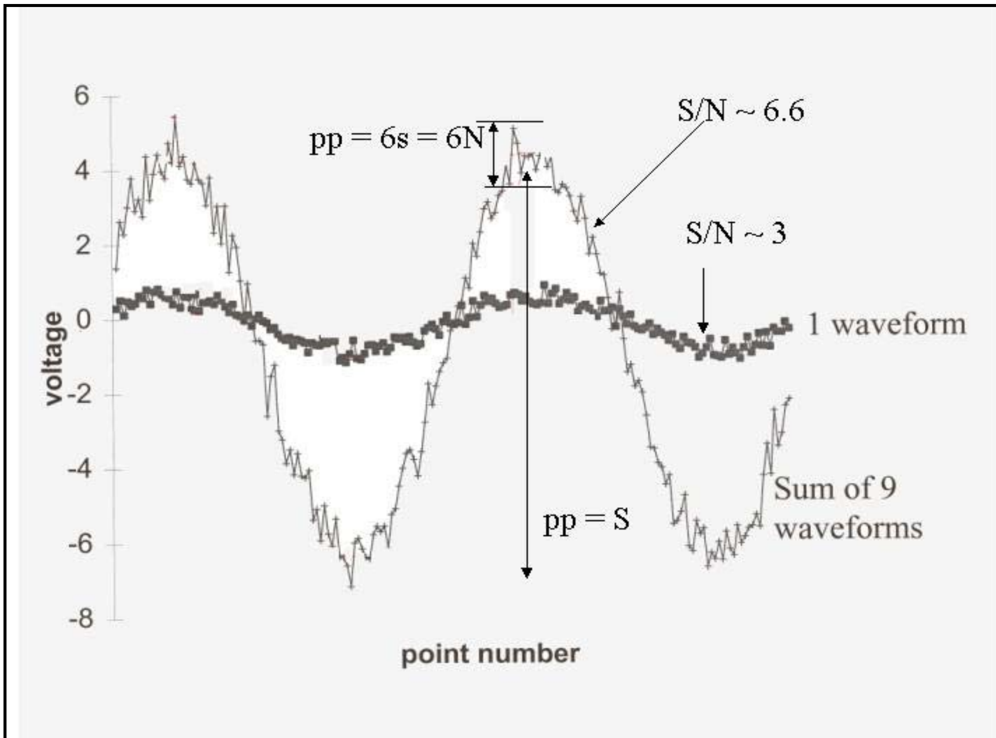

Figure 12 Summing a series of captured signals will increase the S/N if the noise component is random due to destructive interference of the noise component and constructive interference of the underlying signal.

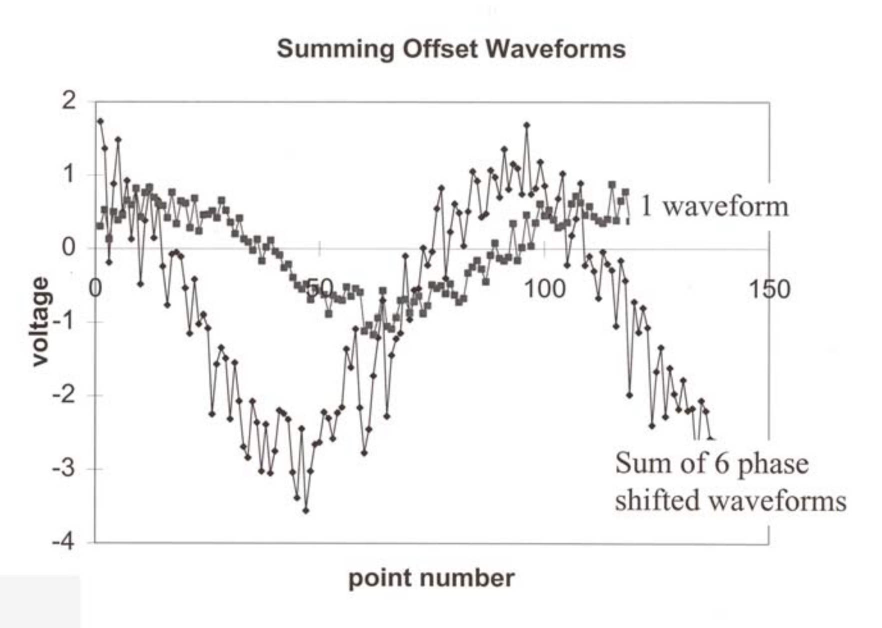

Figure 13 Summing offset or out of phase or incoherent waveforms distorts the signal.

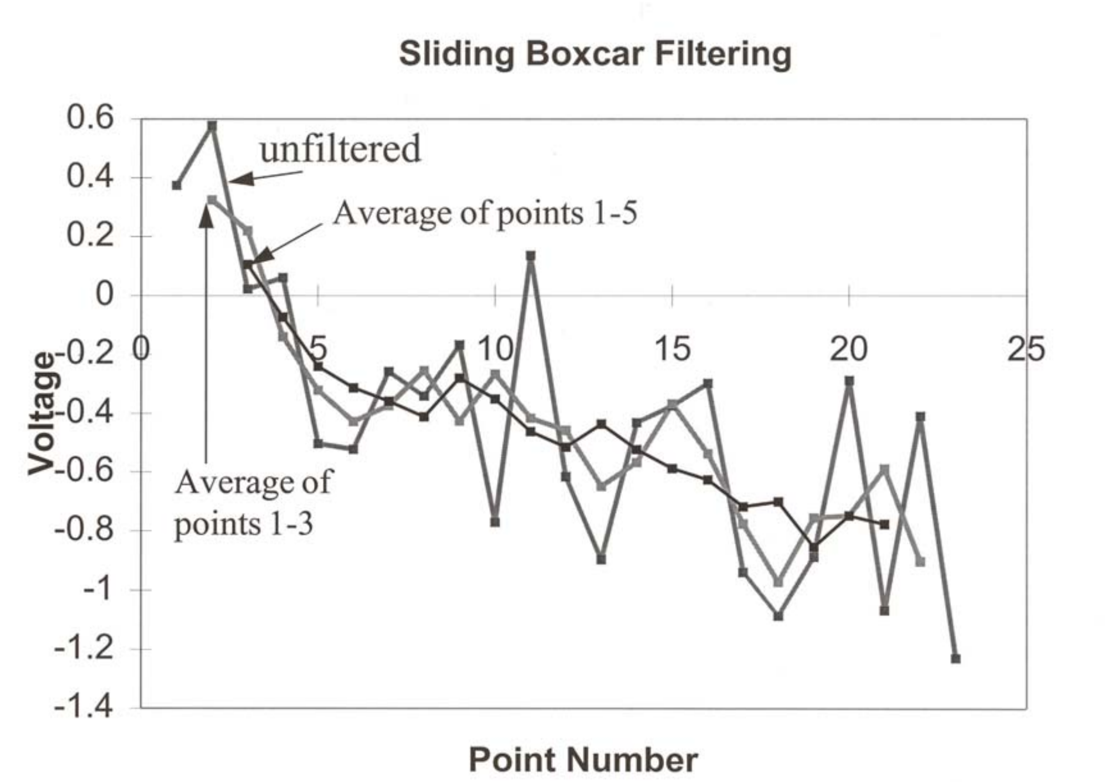

Figure 14 Voltage vs time (or point number) for an unfiltered signal and for signals filtered by boxcar averaging 3 and 5 points. The larger the number of points in the box , the more the "noise" component decreases. The data string shortens as con be observed by the loss of points at the beginning and end of the data string.