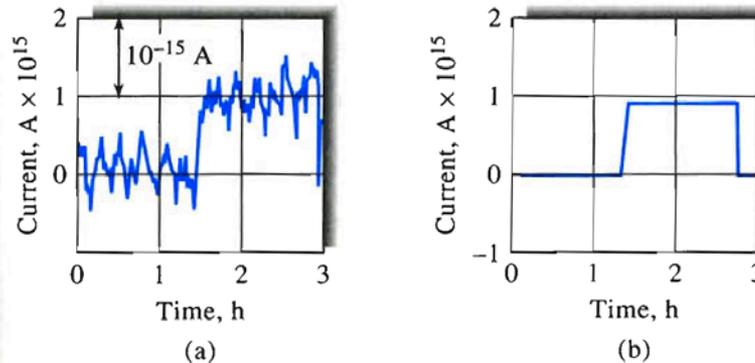


# Chapter 5 Signals and Noise

Read pp. 110 - 123

Impossible to detect a signal when the S/N becomes less than about 2.

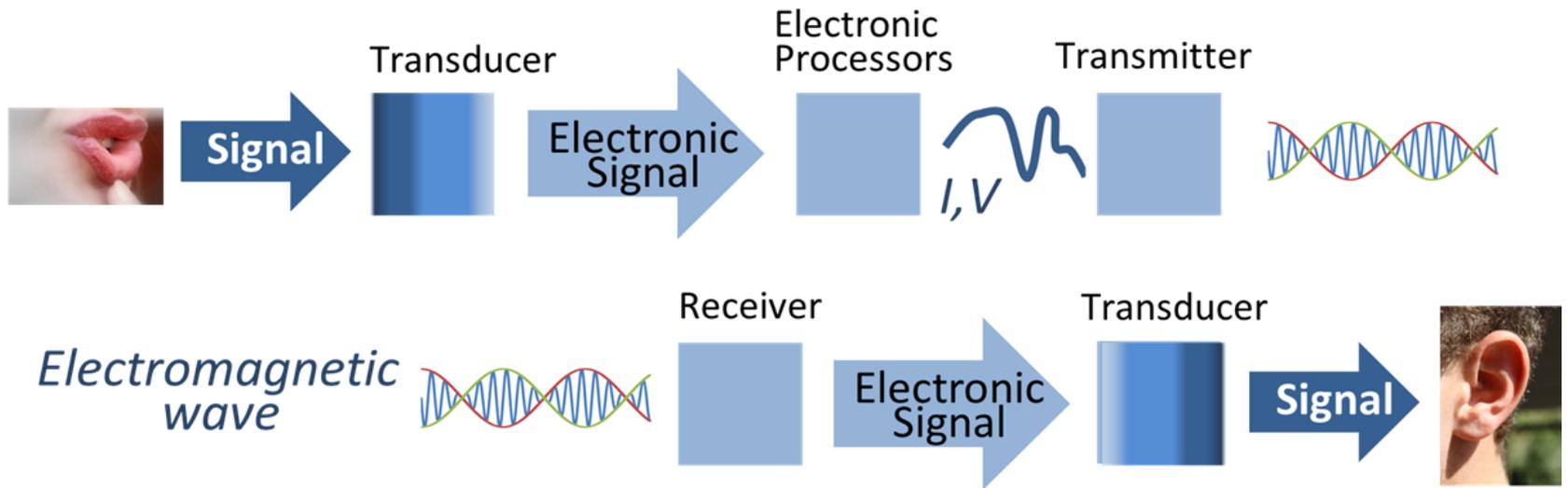


**FIGURE 5-1** Effect of noise on a current measurement: (a) experimental strip-chart recording of a  $0.9 \times 10^{-15}$  A direct current, (b) mean of the fluctuations. (Adapted from T. Coor, *J. Chem. Educ.*, **1968**, 45, A594. With permission.)

$$\frac{S}{N} = \frac{\text{mean}}{\text{Std. Deviation}} = \frac{\overline{X}}{s} = \frac{1}{\text{RSD}}$$

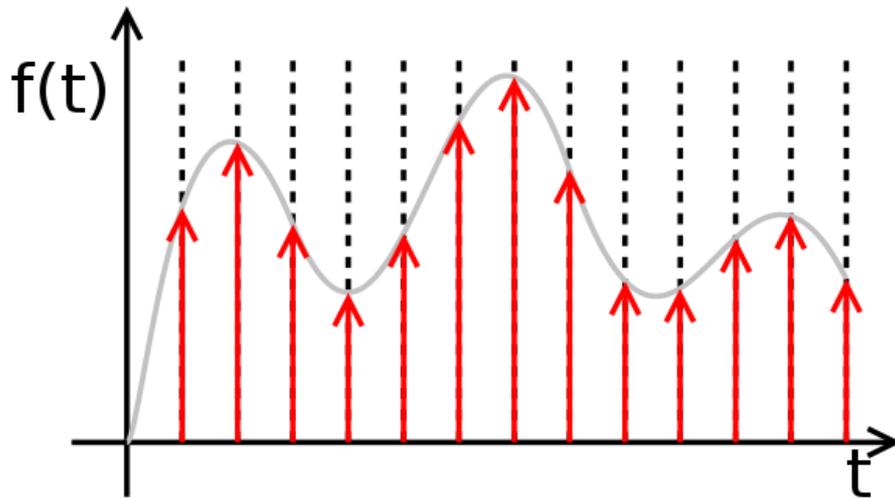
# Signal Transduction

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# Discrete Signal Processing and Sampling Theorem

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Sampling is the process of converting a signal (for example, a function of continuous time and/or space) into a numeric sequence (a function of discrete time and/or space).

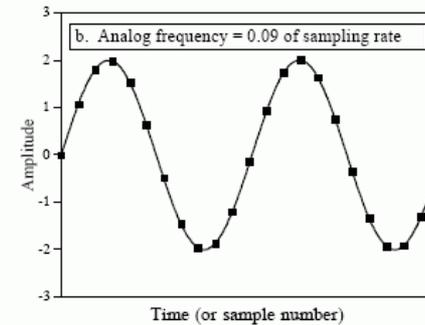
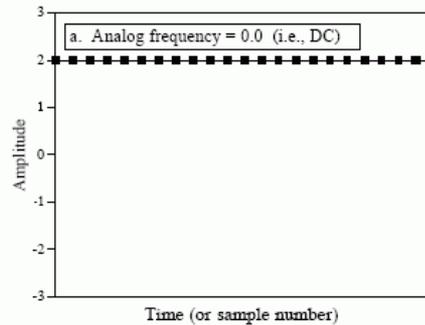
Nyquist sampling rate = sampling rate must be at least 2x greater than the highest frequency component in the complex signal.

For example, if the highest frequency component in a complex signal is 2000 Hz, then the minimum sampling rate must be 4000 Hz or 4000 pts/s ( $2.5 \times 10^{-4}$  s/pt)

**Complex signal sampled at discrete time points, for example collection of real signal by a computer.**

# Proper Sampling Frequency

Good sampling frequency



Poor sampling frequency  
"aliased signal"

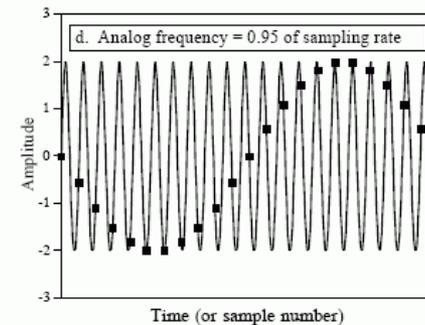
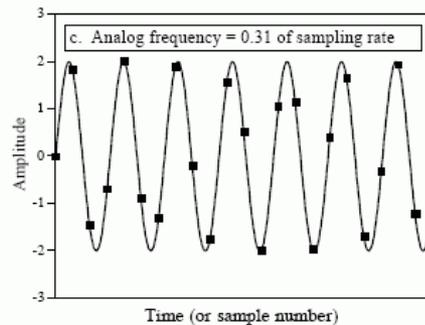
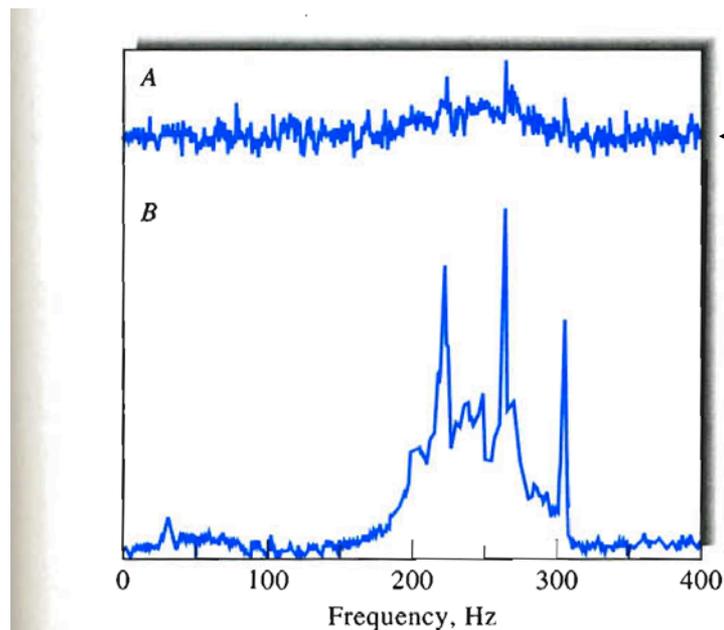


FIGURE 3-3

Illustration of proper and improper sampling. A continuous signal is sampled *properly* if the samples contain all the information needed to recreate the original waveform. Figures (a), (b), and (c) illustrate *proper sampling* of three sinusoidal waves. This is certainly not obvious, since the samples in (c) do not even appear to capture the shape of the waveform. Nevertheless, each of these continuous signals forms a unique one-to-one pair with its pattern of samples. This guarantees that reconstruction can take place. In (d), the frequency of the analog sine wave is greater than the Nyquist frequency (one-half of the sampling rate). This results in *aliasing*, where the frequency of the sampled data is different from the frequency of the continuous signal. Since aliasing has corrupted the information, the original signal cannot be reconstructed from the samples.

# Effect of S/N Ratio on Measurement Quality



Only a couple of the peaks can be recognized and measured with certainty.

**FIGURE 5-2** Effect of signal-to-noise ratio on the NMR spectrum of progesterone: A,  $S/N = 4.3$ ; B,  $S/N = 43$ . (Adapted from R. R. Ernst and W. A. Anderson, *Rev. Sci. Inst.*, **1966**, 37, 101. With permission.)

**Signal** carries the information about the analyte, while the **noise** is made up of extraneous information that is unwanted because it degrades accuracy and precision of the measurement.

# Types of Noise

- *Chemical* – arises from some uncontrollable variables such as fluctuations in temperature or pressure, changes in relative humidity, reaction with oxygen, etc.
- *Instrumental* – associated with components in the instrument (e.g., source, input transducer, the output transducer, and all signal processing elements).
  - *Thermal or Johnson Noise*
  - *Shot Noise*
  - *Flicker Noise*
  - *Environmental Noise*

# Instrumental Noise

*Thermal or Johnson Noise* →  $V_{\text{rms}} = (4kTR\Delta f)^{1/2}$

$k = 1.38 \times 10^{-23}$  J/K     $T =$  temperature (K)     $R =$  ohms

Thermal agitation of electrons across resistive and capacitive components in circuits. Voltage fluctuations.

$$\Delta f (\text{bandwidth}) = 1/3t_r$$

$t_r$  = response time – time required for output to increase from 10-90% of final value.

What is the effect on thermal noise of decreasing the response time of an instrument from 1 s to 1  $\mu$ s?

1 Hz to  $10^6$  Hz so there would be an increase in the noise by  $(10^6/1)^{1/2}$  or 1000-fold.

# Instrumental Noise

*Shot Noise* →  $i_{\text{rms}} = (2Ie\Delta f)^{1/2}$

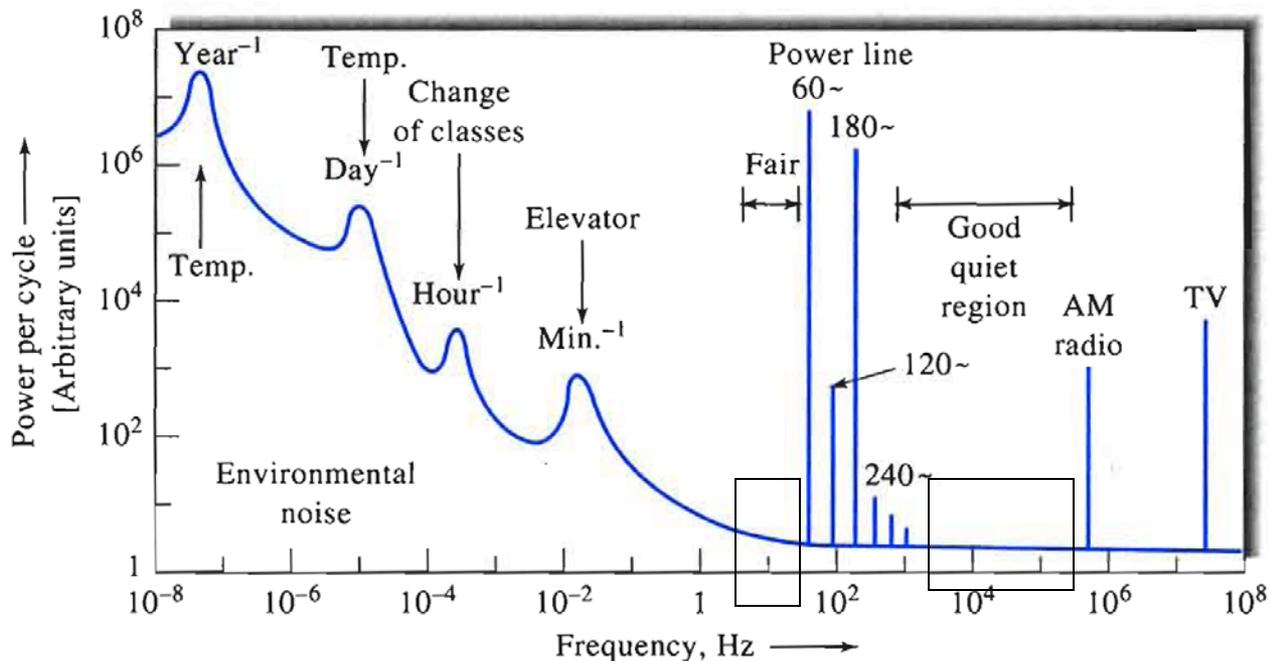
I = mean dc current (A)    e =  $1.60 \times 10^{-19}$  C

Encountered whenever electrons or other charged particles cross a junction, like that which exists in a photodetector.

*Flicker Noise* → magnitude  $\propto 1/f$  (one-over-f) noise

Sources are not totally understood but ubiquitously present at  $< 100$  Hz. Long-term drift.

# Instrumental Noise - *Environmental*



**FIGURE 5-3** Some sources of environmental noise in a university laboratory. Note the frequency dependence and regions where various types of interference occur. (From T. Coor, *J. Chem. Educ.*, **1968**, 45, A540. With permission.)

# Hardware Devices for Noise Reduction

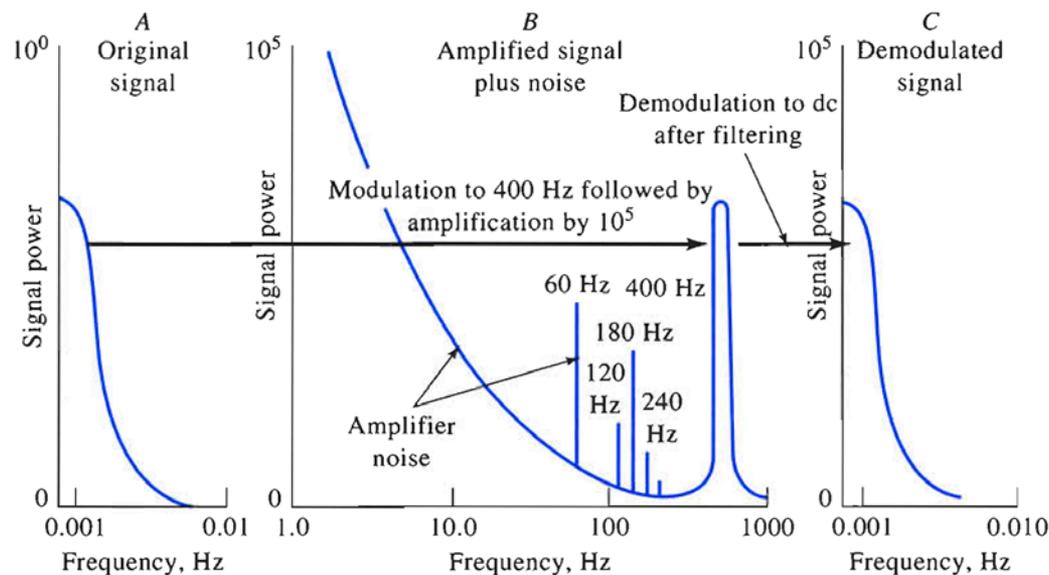
*Grounding and Shielding* → Making sure all circuits have the same common earth ground; surrounding a circuit or instrument with a conducting material that is attached to earth ground; and reducing the lengths of conducting wires.

Noise pick-up and possible amplification by the instrument circuit can be minimized.

*Difference Amplifiers* → Analyte signal and reference signals are fed into the inputs of an operational amplifier in a scaler-type configuration. Common mode noise rejection.

$$V_o = \frac{R_k}{R_i} (V_2 - V_1)$$

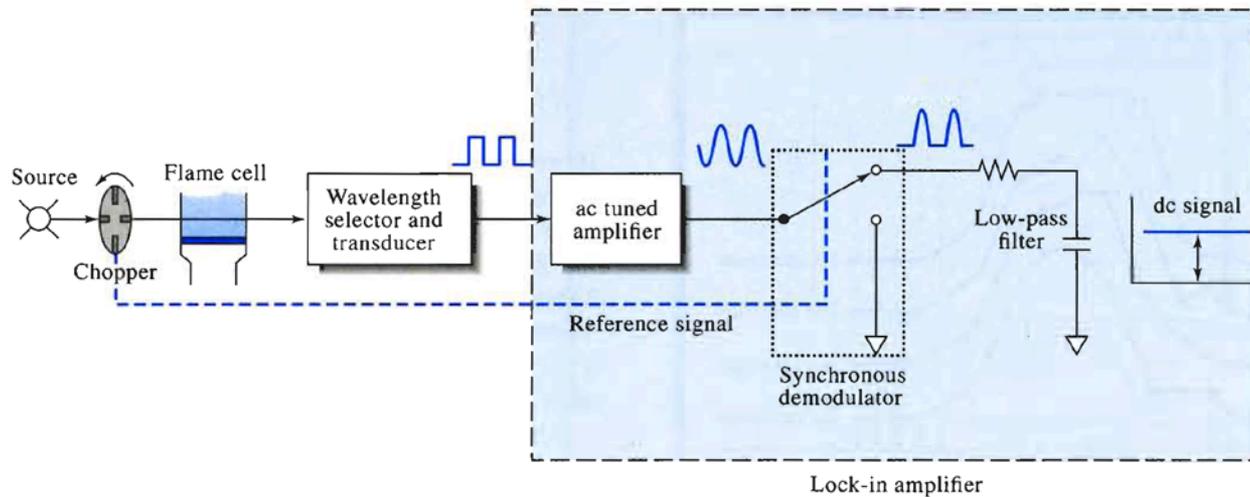
# Hardware Devices for Noise Reduction



**FIGURE 5-6** Amplification of a modulated dc signal. (Adapted from T. Coor, *J. Chem. Educ.*, 1968, 45, A540. With permission.)

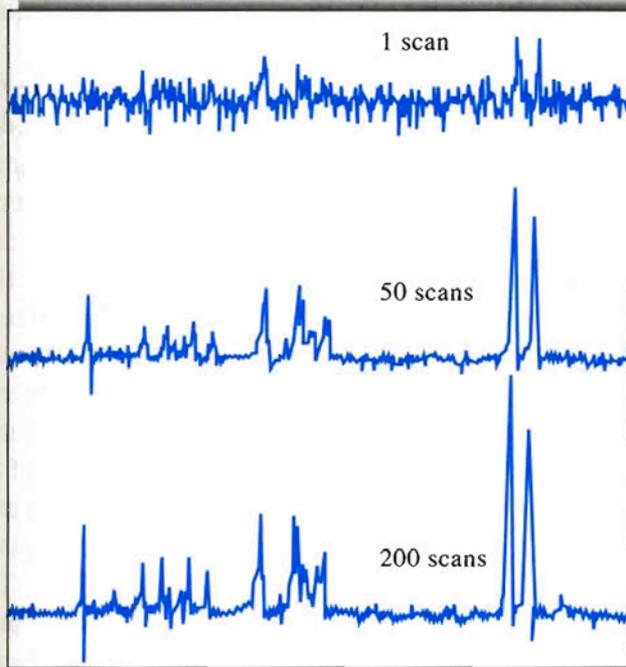
Modulate signal to a frequency region that is more noise free! Must first modulate the signal by adding it to a carrier frequency, and the demodulate it after measurement to remove the carrier frequency.

# Common Example of Signal Modulation



**FIGURE 5-8** Lock-in amplifier for atomic absorption spectrometric measurements. The chopper converts the source beam to an on-off signal that passes through the flame cell where absorption occurs. After wavelength selection and transduction to an electrical signal, the ac square-wave input to the lock-in amplifier is amplified and converted to a sinusoidal signal by the tuned amplifier. The synchronous demodulator is phase-locked to the ac signal and provides a half-wave rectification of the signal. The low-pass filter converts the demodulated signal to a dc signal for measurement.

# Ensemble Signal Averaging



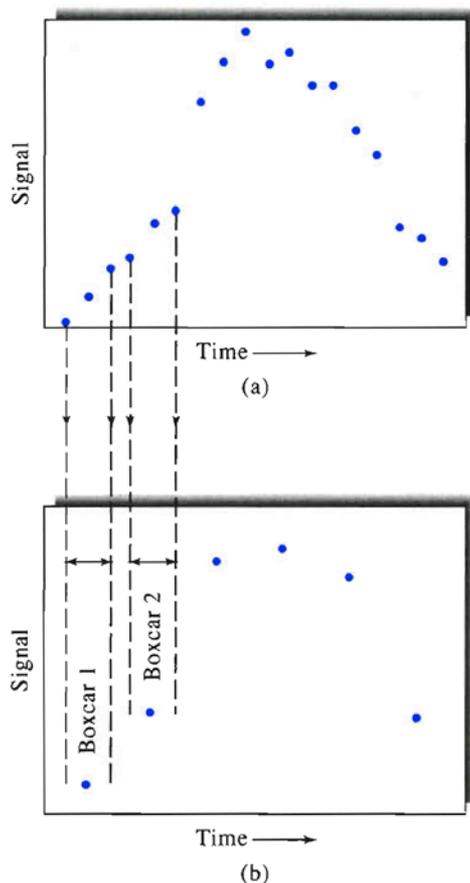
$$\left( \frac{S}{N} \right)_n = (n)^{1/2} \left( \frac{S}{N} \right)_i$$

← Factor ~7 improvement

← Factor ~14 improvement

**FIGURE 5-10** Effect of signal averaging. Note that the vertical scale is smaller as the number of scans increases. The signal-to-noise ratio is proportional to  $\sqrt{n}$ . Random fluctuations in the signal tend to cancel as the number of scans increases, but the signal itself accumulates. Thus, the  $S/N$  increases with an increasing number of scans.

# Boxcar Averaging



**FIGURE 5-11** Effect of boxcar averaging: (a) original data, (b) data after boxcar averaging. (From G. Dulaney, *Anal. Chem.*, **1975**, *47*, 27A. Figure 2, p. 27A. Copyright 1978 American Chemical Society.)

Useful for smoothing irregularities and enhancing the S/N assuming that irregularities are the result of noise.

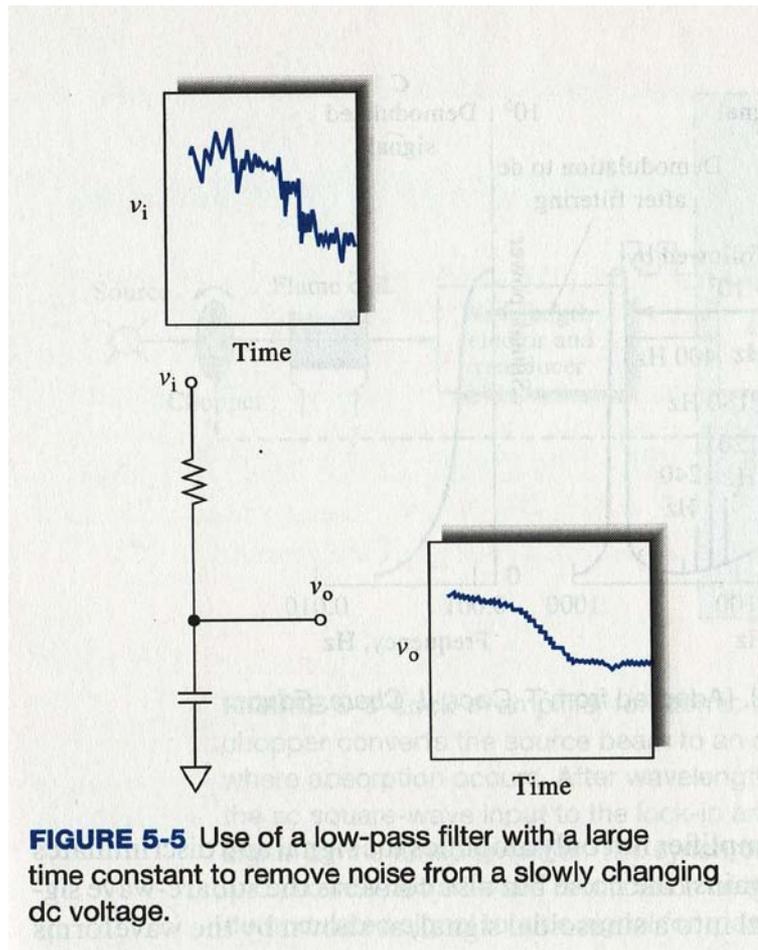
Assumption that the analytical signal varies more slowly in time than the noise components.

In practice, 2-50 points are averaged to generate a final point.

Must be careful not to adulterate the *real* signal.

# Hardware Devices for Noise Reduction

## Low-Pass Analog Filter



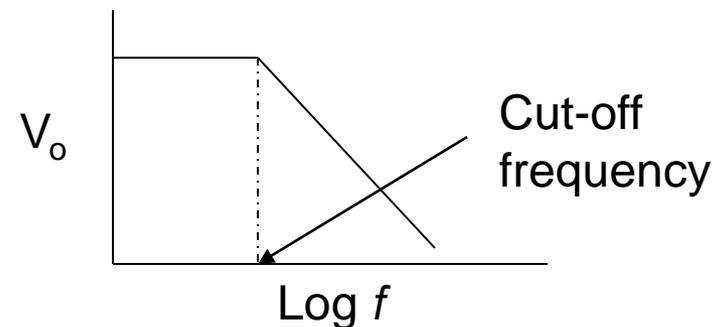
$$Q = C V$$

$$X_C = 1/(2\pi f C)$$

$$R \cdot C = \text{seconds}$$

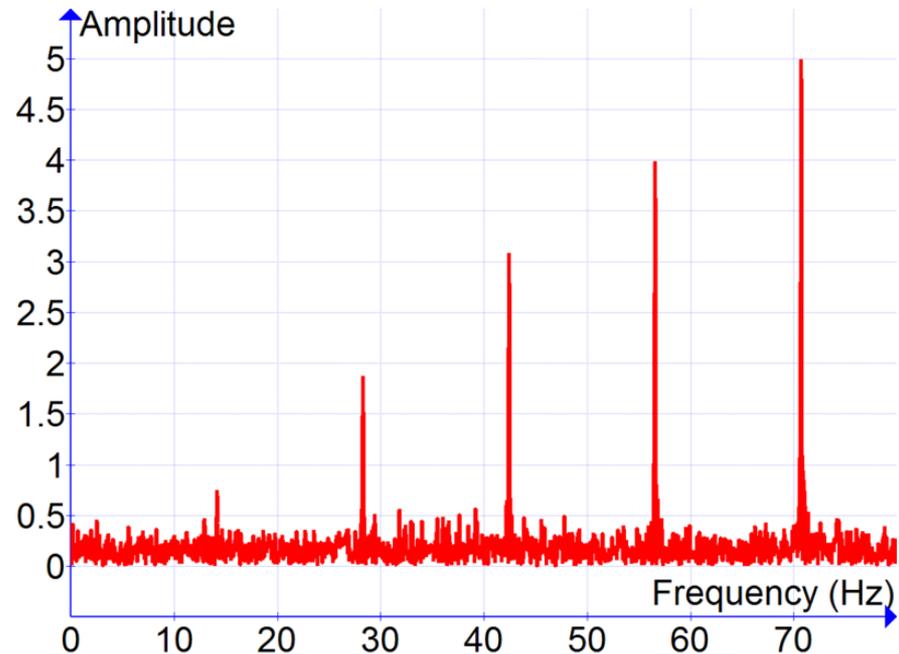
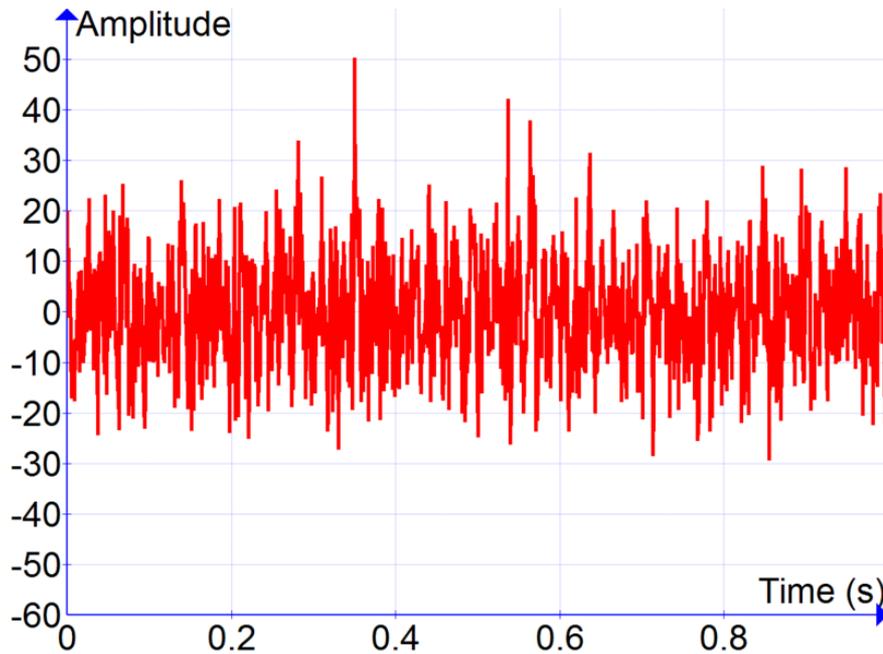
$$1 \mu\text{F} \cdot 1000 \text{ ohm} = 1 \times 10^{-3} \text{ s}$$

or  
1000 Hz



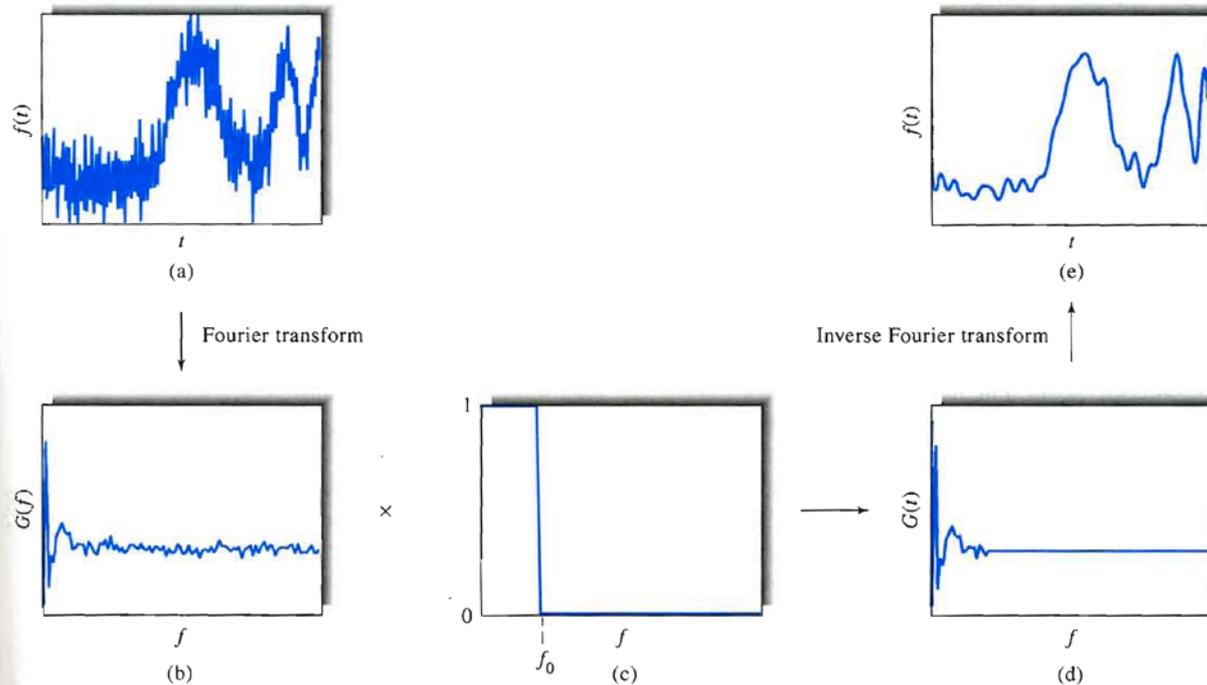
# Signals and Noise

**Fourier Transformation - Complex time domain into frequency components**



**Signal on the left has no useful information. FT process can identify noise frequencies and remove them, thereby making the analytical signal more visible.**

# Digital Filtering - Fourier Transformation



**FIGURE 5-12** Digital filtering with the Fourier transform: (a) noisy spectral peak, (b) the frequency-domain spectrum of part (a) resulting from the Fourier transformation, (c) low-pass digital-filter function, (d) product of part (b) and part (c), (e) the inverse Fourier transform of part (d) with most of the high-frequency noise removed.