Signals and Noise

- **Noise** limits detectability of every instrumental method

- Present in every instrumental method! Cannot be completely removed.

- Best we can do is understand contributions of noise and try to minimize noise.
  - Enhance Signal
  - Reduce Noise
  - Modify Instrumental Method

- Always trying to maximize the signal to noise ratio.
  - Relates magnitude of noise to magnitude of signal.

Signal to Noise Ratio

- Analytical signal is a combination of three components:
  - chemical information
  - background
  - Noise
    - p-p vs. rms noise

- For a dc signal,

S/N = mean / standard dev.

= x/s

Where; s is the standard deviation of the measured signal strength and x is the mean of the measurement .

- x/s is the reciprocal of the relative standard deviation (RSD)

S/N=1/RSD

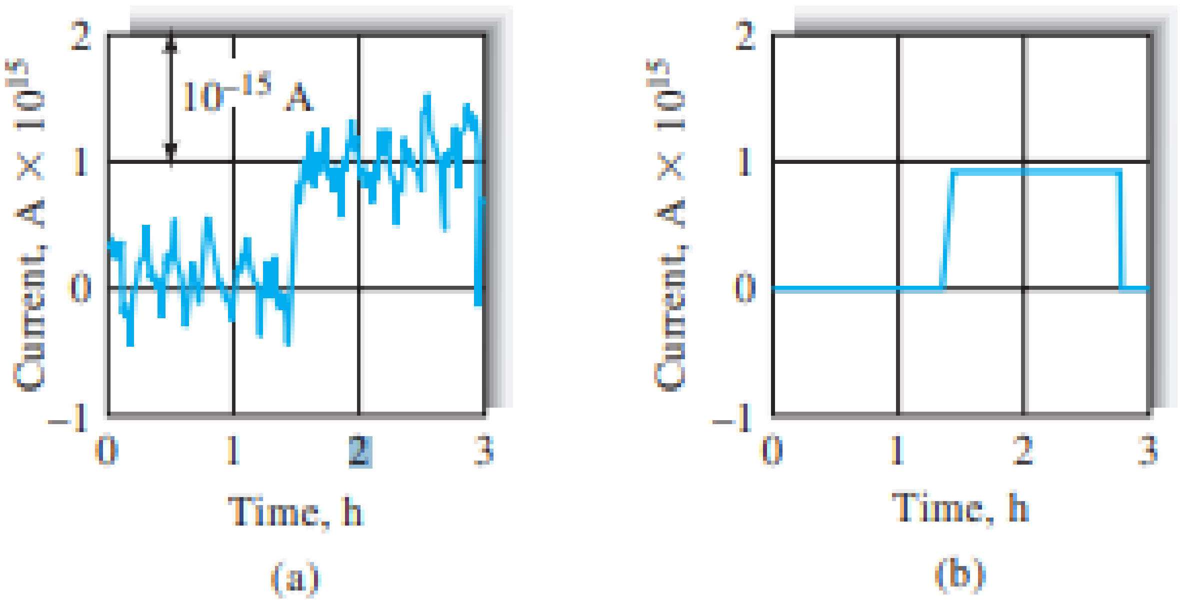


FIGURE 5-1 Effect of noise on a current measurement: (a) experimental strip-chart recording of a 0.9×10^{-15} A direct current, (b) mean of the fluctuations. (Adapted from T. Coor, *J. Chem. Educ.*, **1968**, 45, A583. With permission.)

- the standard deviation can be estimated easily at a 99% confidence level by dividing the difference between the maximum and the minimum signal by five.
- Here, we assume that the excursions from the mean are random and can thus be treated by the methods of statistics.
- it is seen in Appendix 1, that 99% of the data under the normal error curve lie within ±2.5σ of the mean.

- Thus, we can say with 99% certainty that the difference between the maximum and minimum encompasses 5 σ
- One fifth of the difference is then a good estimate of the standard deviation.

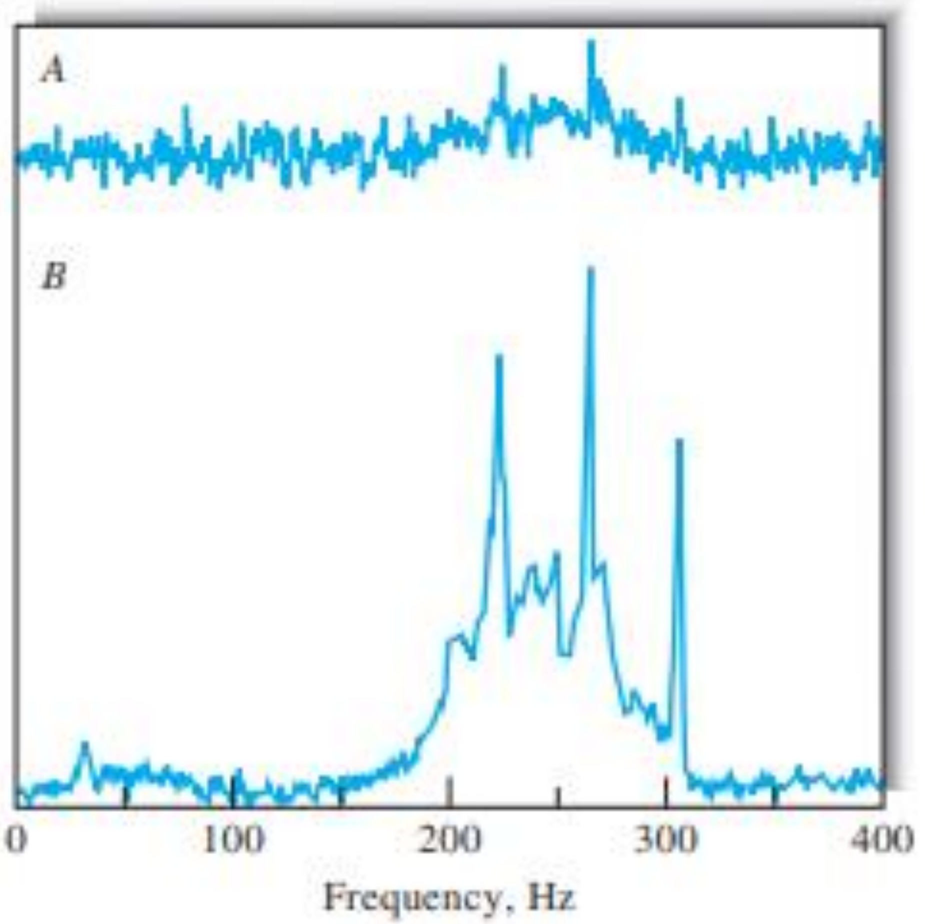


FIGURE 5-2 Effect of signal-to-noise ratio on the NMR spectrum of progesterone: *A*, *S/N* = 4.3; *B*, *S/N* = 43. (Adapted from R. R. Ernst and W. A. Anderson, *Rev. Sci. Inst.*, **1966**, *37*, 93, **DOI:** 10.1063/1.1719961. With permission.)

- As a general rule, it becomes impossible to detect a signal when the signal-to-noise ratio becomes less than about 2 or 3.
- Figure 5-2 illustrates this rule. The upper plot is a nuclear magnetic resonance (NMR) spectrum for progesterone with a signal-to-noise ratio of about 4.3.
- In the lower plot the ratio is 43. At the smaller signal-to-noise ratio, only a few of the several peaks can be recognized with certainty

Noise Sources

- Chemical Noise
  - Result of chemical or physical properties of the sample.
  - Degradation, photoreactivity, temperature and pressure effects, etc.
  - Minimization requires that you understand your sample!
- Instrumental Noise
  - Inherent in electrical devices
  - Four main types
    - thermal noise
    - shot noise
    - flicker noise
    - environmental noise

Instrumental Noise

- **Thermal Noise**
  - Johnson, Resistance
  - Result of random thermal motion of electrons
  - Magnitude of thermal noise based on thermodynamics

$$v_{rms} = \sqrt{4kTR\,\Delta f}$$

V is the average voltage due to thermal noise,
k is the Boltzmann constant,
T is the absolute temperature.
R is the resistance of the electronic device, and
f is the bandwidth of measurement frequencies

- Minimize by:

- Thermal noise is caused by the thermal agitation of electrons or other charge carriers in resistors, capacitors, radiation transducers, electrochemical cells, and other resistive elements in an instrument.
- This agitation of charged particles is random and periodically creates charge inhomogeneities, which in turn create voltage fluctuations that then appear in the readout as noise.
- It is important to note that thermal noise is present even in the absence of current in a resistive element and disappears only at absolute zero.

Instrumental Noise

- **Shot Noise**
  - collection of random, quantized events

$$i_{rms} = \sqrt{2Ie\Delta f}$$

- Minimize by:

- Shot noise refers to the random fluctuations of the electric current in an electrical conductor, which are caused by the fact that the current is carried by discrete charges (electrons).
- The strength of this noise increases for growing magnitude of the average current flowing through the conductor. Shot noise is to be distinguished from current fluctuations in equilibrium, which happen without any applied voltage and without any average current flowing. These equilibrium current fluctuations are known as Johnson-Nyquist noise.

- **Flicker Noise**
  - related to signal frequency
  - $V \propto 1/f$

- Minimize by:

- Flicker noise
- Its magnitude is inversely proportional to frequency of signal
- Can be significant at frequencies lower than 100 Hz
- Causes long term drift in the amplifiers, meters, and galvanometers
- Can be reduced significantly by using wire-wound or metallic film resistors rather than composition type

Instrumental Noise

- **Environmental Noise**

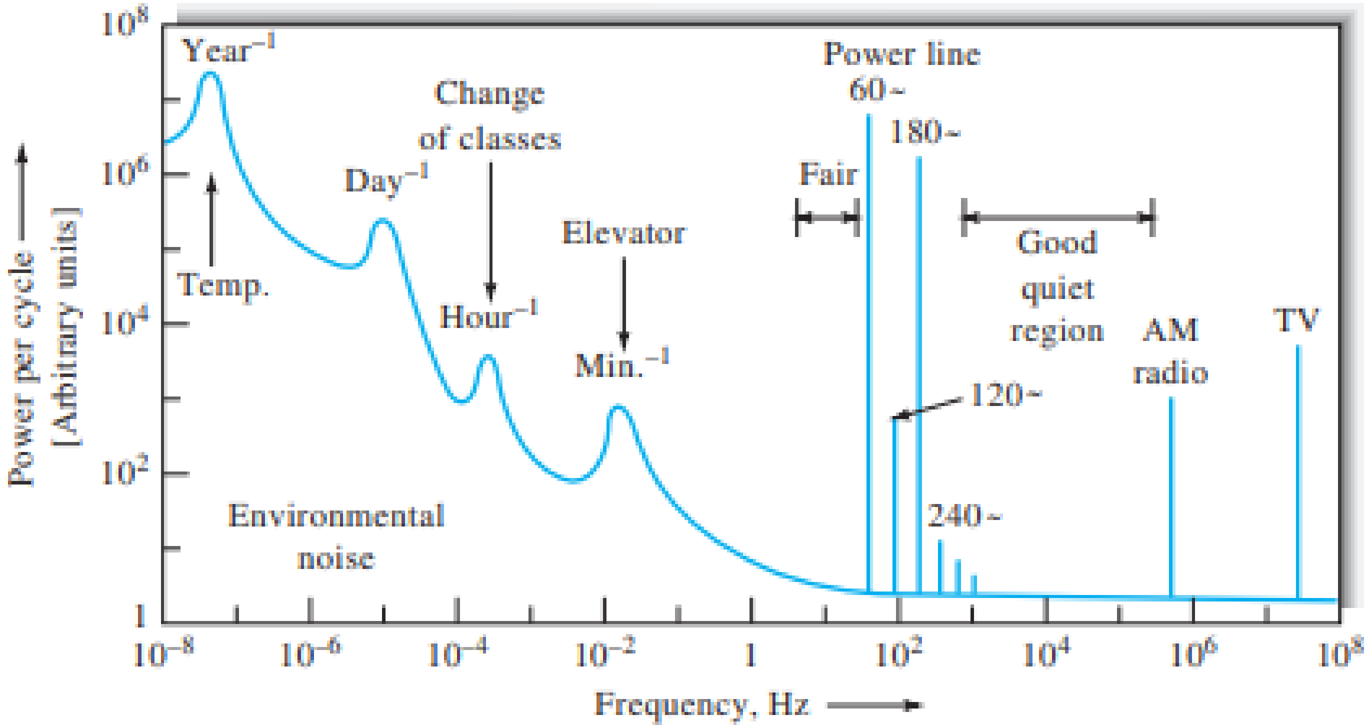


FIGURE 5-3 Some sources of environmental noise in a university laboratory. Note the frequency dependence and regions where various types of interference occur. (From T. Coor, *J. Chem. Educ.*, **1968**, *45*, A583. With permission.)

- Environmental noise is due to a composite of noises from different sources in the environment surrounding the instrument.
- Much environmental noise occurs because each conductor in an instrument is potentially an antenna capable of picking up electromagnetic radiation and converting it to an electrical signal.
- There are numerous sources of electromagnetic radiation in the environment including ac power lines, radio and TV stations, gasoline engine ignition systems, arcing switches, brushes in electrical motors, lightening, and ionospheric disturbances.

Dealing with Noise: Hardware Methods

- Grounding: Be sure that "common" is really common to all circuits
- Shielding: Surround susceptible components with a conducting "shield" that is connected to ground
- Op-Amp circuitry: Difference and Instrumentation amplifiers.
  - Reject "common mode" noise

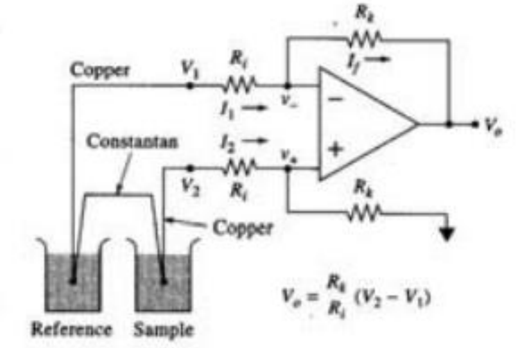


Figure 3-11 An operational amplifier difference amplifier measuring the output voltage of a pair of thermocouples.

Dealing with Noise: Hardware Methods

- **Filters:** Simple RC circuits. Selection of output voltage and time constant determines action of filter.

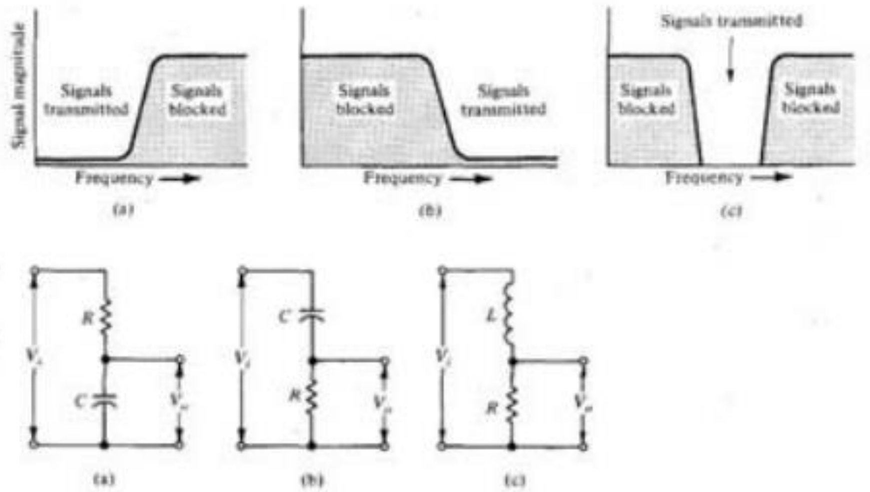


FIGURE 2.6
Passive filters: (a) low-pass RC filters, (b) high-pass LC filter, and (c) low-pass LR filter.

- **Modulation:** Deliberately cause signal to occur at a single frequency.

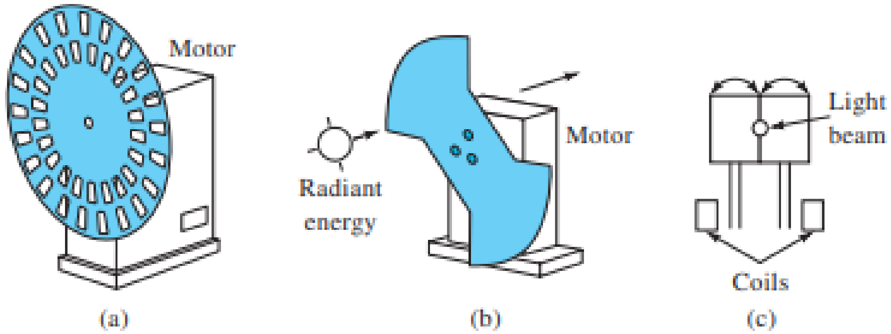


FIGURE 5-7 Mechanical choppers for modulating a light beam: (a) rotating disk chopper, (b) rotating vane chopper, (c) oscillating tuning fork design where rotational oscillation of a vane causes periodic interruptions of a light beam.

- **Lock-In Amplifiers:** Only "see" one frequency

Permit recovery of signals even when S/N is unity or less. Generally requires a reference signal at same frequency and phase (must have fixed phase relationship) as signal to be amplified

Dealing with Noise: Software Methods

- Signal averaging
  - collect several data sets (n)
  - add sets together and divide by n

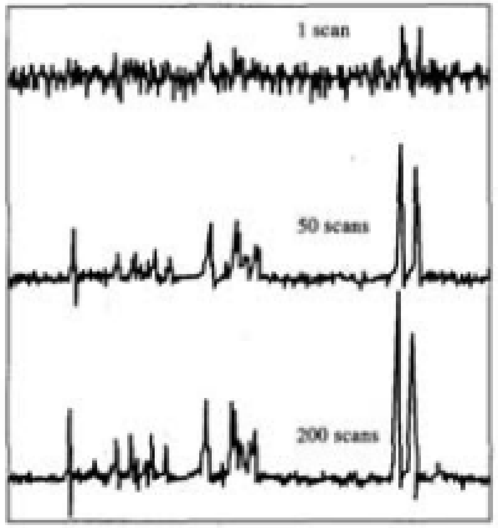


Figure 5-10 Effect of signal averaging. Note that the vertical scale is smaller as the number of scans increases. The signal-to-noise ratio is proportional to $\sqrt{n}$. Random fluctuations in the noise tend to cancel as the number of scans increases, but the signal accumulates; thus, *S/N* increases.

- S/N improvement:

$$\text{rms noise} = \sqrt{\frac{\sum_{i=1}^{n}(S_x - S_i)^2}{n}}$$

$$\frac{S}{N} = \frac{S_x}{\sqrt{\frac{\sum_{i=1}^{n}(S_x - S_i)^2}{n}}}$$

Dealing with Noise: Software Methods

- Sampling considerations
  - stable signal
  - adequate sampling frequency

- Boxcar Averaging
  - average adjacent data points in a single scan
  - sampling rate must be sufficiently high to minimize distortion in analytical signal

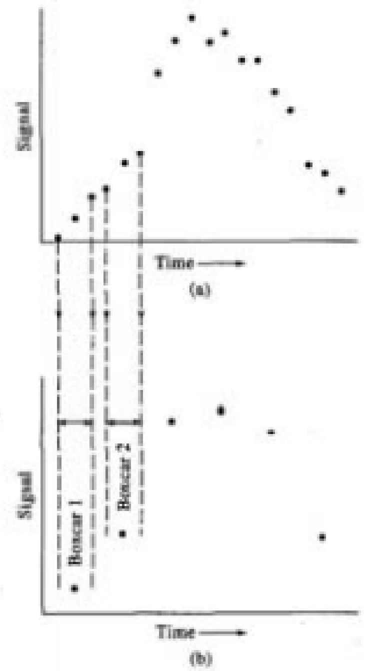
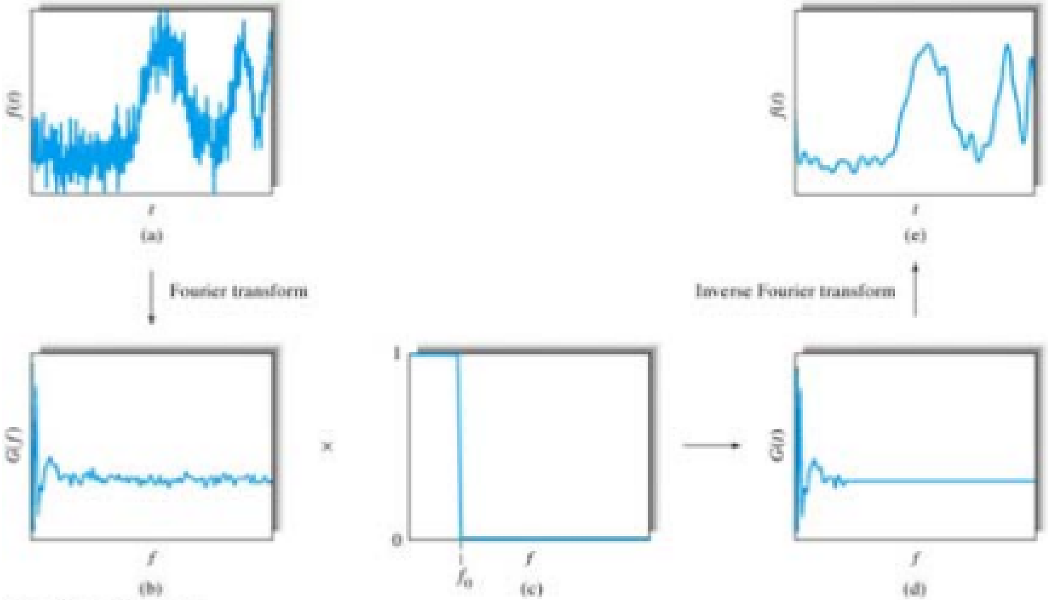


Figure 5-11 Effect of boxcar averaging: (a) original data, (b) data after boxcar averaging. *(Reprinted with permission from G. Dulaney, Anal. Chem., 1975, 47, 28A. Copyright 1975 American Chemical Society.)*

Dealing with Noise: Software Methods

- Digital Filters and Smoothing
  - Fourier Transform: allows discrimination against specific frequencies
  - Time domain signal is converted to frequency domain, filtered, then converted back.



Dealing with Noise: Software Methods

- Smoothing
  - Least-squares polynomial analysis
  - Often suffers from less distortion than boxcar averaging
  - Savitzky-Golay smoothing

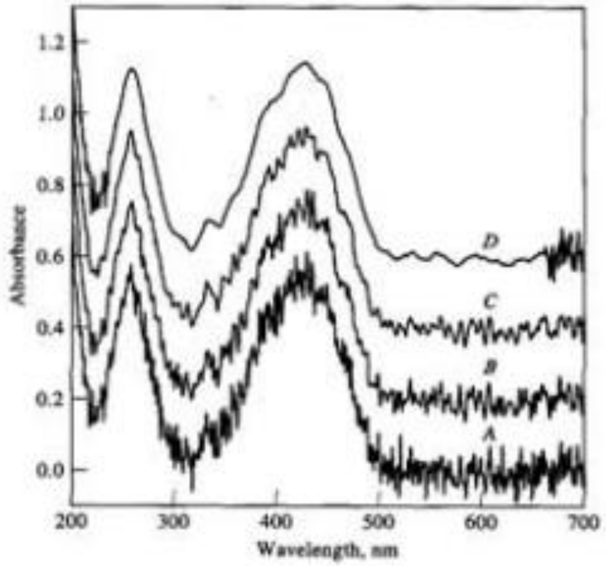


Figure 5-15 Effect of smoothing on a noisy absorption spectrum of tartrazine: *(A)* Raw spectrum, *(B)* quadratic 5-point smooth of the data in *A*, *(C)* fourth-degree 13-point smooth of the same data, *(D)* tenth-degree 77-point smooth of the data.