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

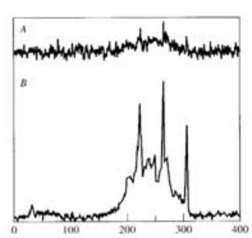


Figure 5-2 Effect of signal-to-noise ratio on the NMR spectrum of progesterone: A, S/N = 4.3; B, S/N = 43. (*Adapted from R. R. Ernst and W. A. Anderson, Rev. Sci. Inst., 1966 37, 101. With permission.*)

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

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

- Minimize by:

Instrumental Noise

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

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

- Minimize by:

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

- Minimize by:

Instrumental Noise

- **Environmental Noise**
  - many sources

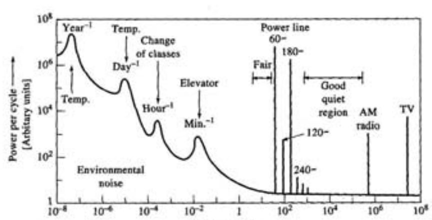


Figure 5-3 Some sources of environmental noise in a university laboratory. Note the frequency dependence and regions where various types of interference occur. *(From T. Coor, J. Chem. Educ., 1968, 45, A540. With permission.)*

- Minimize by:

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

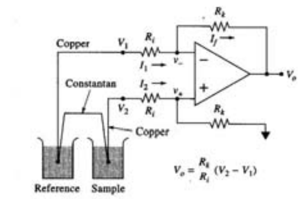
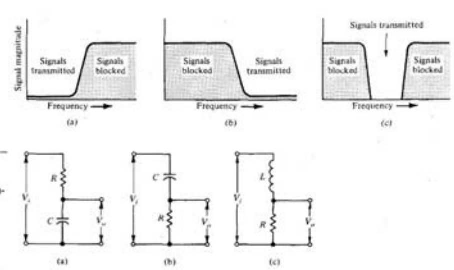


Figure 3-11 An operational amplifier difference amplifier measuring the output voltage of a pair of thermocouples.

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.
- **Lock-In Amplifiers:** Only “see” one frequency

Dealing with Noise: Software Methods

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

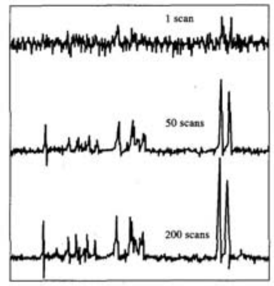


Figure 5-10 Effect of signal averaging. Note that the vertical scale is smaller as the number of scans increases. The signal-to-noise ratio is proportional to $\sqrt{n}$. Random fluctuations in the noise tend to cancel as the number of scans increases, but the signal accumulates; thus, *S/N* increases.

- 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

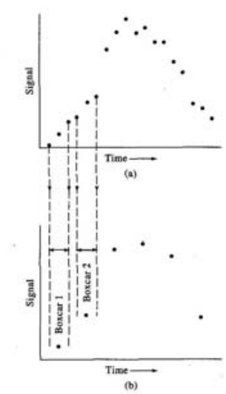


Figure 5-11 Effect of boxcar averaging: (a) original data, (b) data after boxcar averaging. *(Reprinted with permission from G. Dulaney, Anal. Chem., 1975, 47, 28A. Copyright 1975 American Chemical Society.)*

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.

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

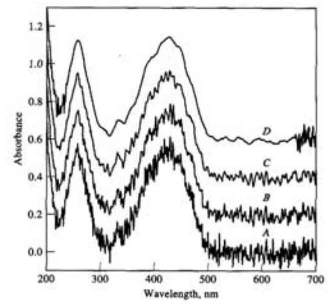


Figure 5-15 Effect of smoothing on a noisy absorption spectrum of tartrazine: *(A)* Raw spectrum, *(B)* quadratic 5-point smooth of the data in *A*, *(C)* fourth-degree 13-point smooth of the same data, *(D)* tenth-degree 77-point smooth of the data.