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Separating the Signal From the Noise

Chemistry in Context

“Laser” Detector



Optical methods of chemical analysis are being developed for the remote detection of explosives and drugs.

This van can detect TNT with a **Signal to Noise** ratio of 70 from a distance of 150 m.

What does Signal to Noise mean and how does it impact chemical analysis?

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CH 5 Homework

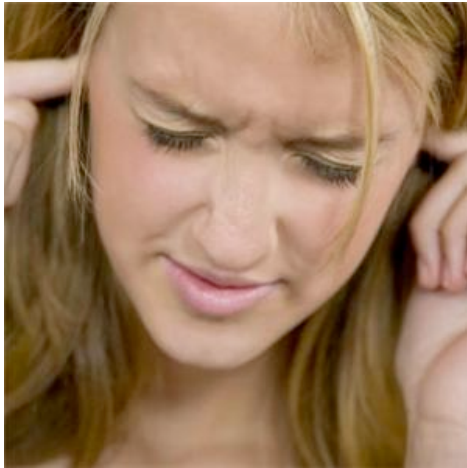
1. Name the types of noise that can be reduced by:
 - a) decreasing the temperature of the measurement
 - b) decreasing the bandwidth of the measurement
2. The following data were obtained for repetitive weighing of a 1.004g standard weight:

1.003	1.000	1.001
1.004	1.005	1.006
1.001	0.999	1.007

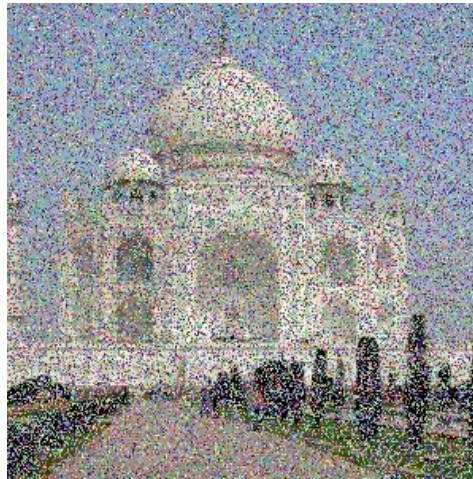
Assuming the noise is random, calculate the S/N for the balance.
How many measurements would have to be averaged to obtain a S/N of 500?

CH 5: Signal and Noise

Noise refers to random fluctuations observed whenever replicate measurements are made on signals that are monitored continuously.



Noise is derived from radio engineering, where unwanted signals literally produced audio static.



Example: Some pixels produced random colors, causing “noise”.



How can we deal with these random fluctuations to produce higher-quality data?

CH 5: Signal and Noise

When considering signal and noise, the important figure-of-merit is the signal to noise ratio:

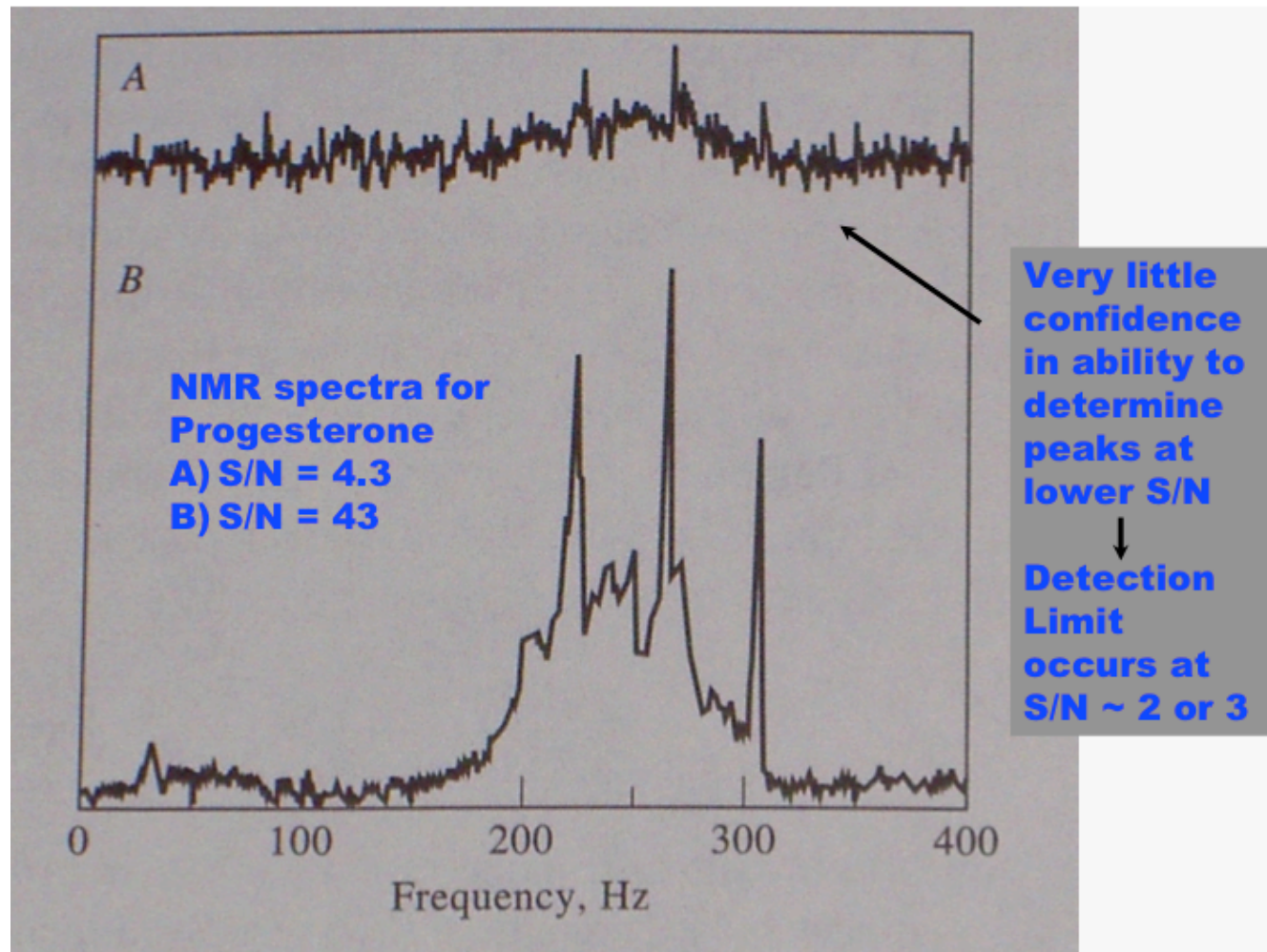
$$\frac{S}{N} = \frac{\text{mean}}{\text{Stdev}}$$

Note that this is the reciprocal of the relative stdev discussed earlier.

*Key Concept: As a general rule, it is impossible to detect a signal when the S/N ratio becomes less than 3.

Noise makes the assignment of signal amplitudes and positions less certain.

How many peaks can you pick out with any certainty?



Sources of Noise in Instrumental Analysis

Chemical

Due to uncontrolled variables that affect the chemistry of the system.

Temp fluctuations that change an equilibrium; humidity; light that causes a photochemical change, etc.

Instrumental

Due to fluctuations in electronic signals.

Sources of Noise in Instrumental Analysis

Instrumental Noise

Thermal or “Johnson” Noise

Caused by the thermal agitation of electrons or other charge carriers in electronic components such as conductive wires.

Random

Causes voltage fluctuations in the readout

“Root mean squared” (RMS) Noise (RMS is similar to stdev), but describes deviations in periodic signals.

$$\overline{v} = (4kTR\Delta f)^{1/2}$$

k = Boltzmann's constant

R = resistance in Ohms

Δf = frequency bandwidth of the electronics in Hz

Bandwidth

In communications, the difference between upper and lower frequencies in a contiguous set of frequencies. For example, bandwidth could be a frequency range over which electronic data are transmitted. Voice is transmitted over a bandwidth of 3 kHz, television images 6 kHz.

In instrumental analysis, the bandwidth is the data transfer rate, the amount of data that can be transferred in 1 sec.

The bandwidth is important because it is related both to the noise and rise time (or response time), t_r , of a measurement. The rise time defines how fast a measurement can be taken.

$$\Delta f = 1/(3t_r)$$

Rise time: time for a signal to change from 10% to 90% of the total change.

Sources of Noise in Instrumental Analysis

Concept Test

The rise time of a measurement with a bandwidth of 0.033 kHz is:

(A) 10 sec

(B) 1 sec

(C) 10 msec

Sources of Noise in Instrumental Analysis

Concept Test

A faster measurement (shorter rise time) with lower RMS noise may be made by decreasing the bandwidth:

(A) True

(B) False

Decreasing the bandwidth decreases the noise but slows the rise time.

Sources of Noise in Instrumental Analysis

Concept Test

You are performing a measurement with an instrument that collects a data point every 1 sec ($\Delta f = 1$ Hz). You find that this data collection rate does not provide enough information so you change the settings to collect data every 1 μ s. The noise of the measurement will:

- (A) Increase by 1000-fold
- (B) Decrease by 10^6 -fold
- (C) Decrease by 1000-fold

Sources of Noise in Instrumental Analysis

Concept Test

You are performing a measurement with an instrument that collects a data point every 1 sec ($\Delta f = 1$ Hz). You find that this data collection rate does not provide enough information so you change the settings to collect data every 1 μ s. The noise of the measurement will:

Initially, data points were collected with a bandwidth of 1 Hz (1 pt/sec). The bandwidth was then changed to 1×10^6 pts/sec. $(10^6)^{1/2} = 1000$.

Sources of Noise in Instrumental Analysis

Concept Test

Many detection systems are cooled with liquid nitrogen.
Cooling a detector will:

(A) Increase the rise time

(B) Decrease the rise time

(C) Decrease the noise

$$v = (4kTR\Delta f)^{1/2}$$

Sources of Noise in Instrumental Analysis

Shot Noise

Occurs wherever electrons cross a junction: e.g., semiconductor interfaces.

Electrons can randomly cross the interface, causing unwanted currents.

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

Shot noise in a current is proportional to the average direct current signal I , the charge on an electron e , and the bandwidth. It can be minimized only by minimizing bandwidth.

For devices in series the voltage noise scales as:
 $(V_1^2 + V_2^2 + \dots)^{1/2}$

Sources of Noise in Instrumental Analysis

Environmental Noise

Arises from the surroundings because each conductor in an instrument is a potential antenna capable of picking up EM radiation from the environment and converting it into an electrical signal. TV, radio, elevator, daily temp cycles, vibrations, and power lines are all sources of noise.

Concept Te\$t

You are running an instrument in a CU lab and notice that your signal has noise spikes that repeat every ~50 min, but only during the day on weekdays. Which of the following is the most likely source of the noise?

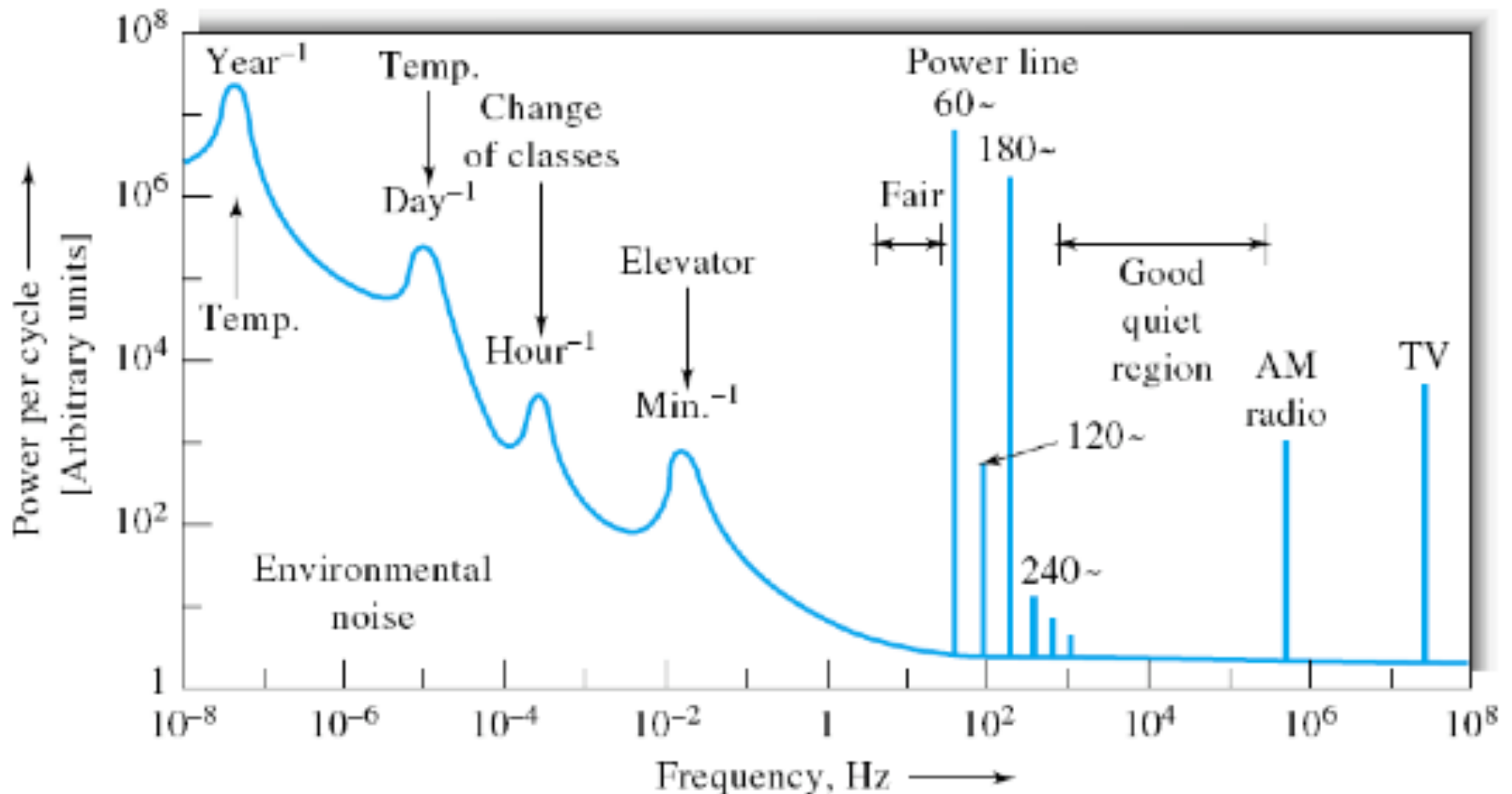
(A) Power lines

(B) The radio in your lab

(C) Student traffic outside your lab

(D) The elevator

Sources of Noise in Instrumental Analysis



Signal-To-Noise Enhancement

Many methods are available for reducing noise and amplifying signal.

Grounding and Shielding

Environmental noise can often be reduced by shielding, grounding, and minimizing the length of conductors.

Signal Averaging

Modulation

Low frequency fluctuations in signals can often cause noise. Modulating the signal can decrease this type of noise.

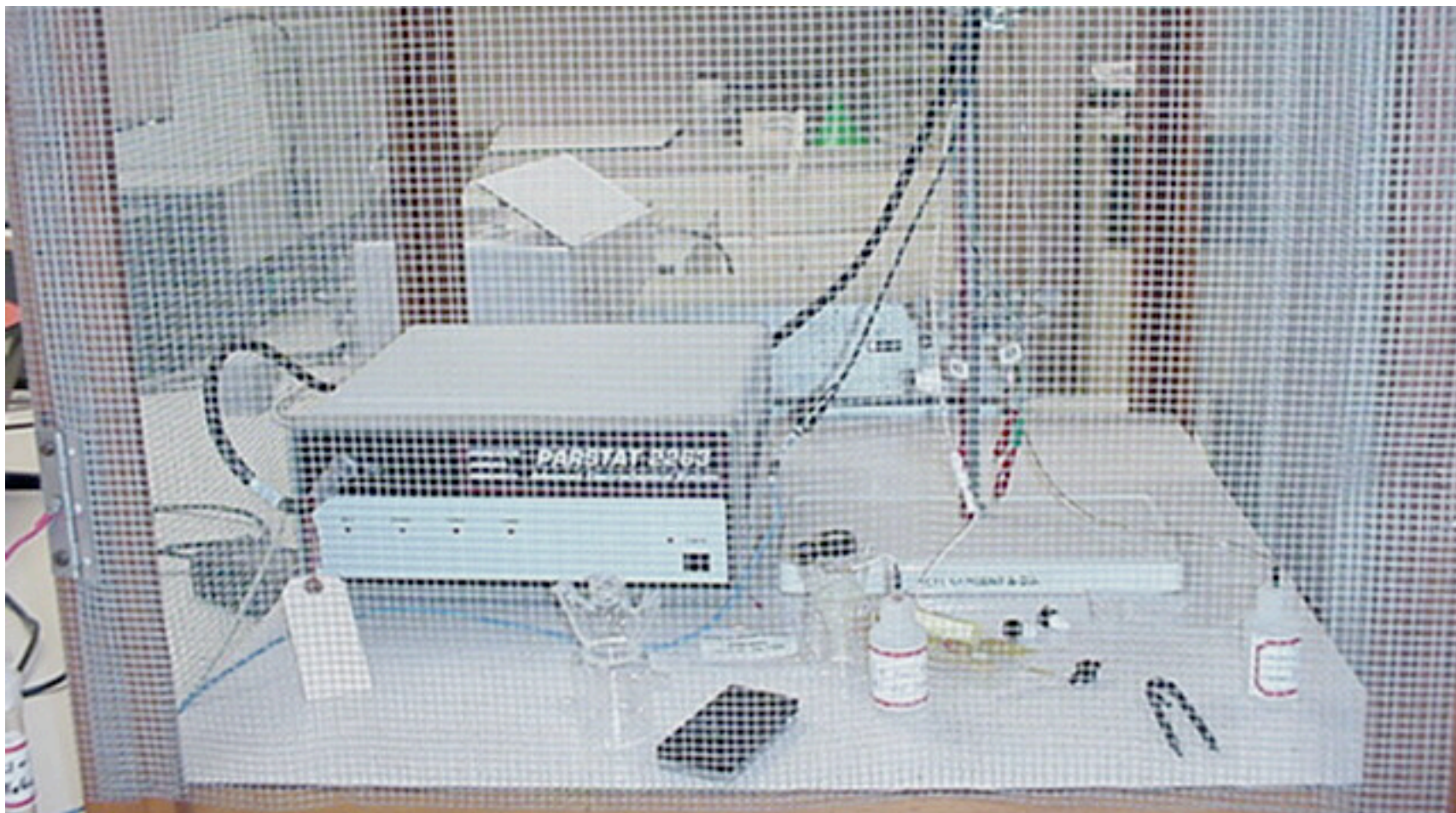
Signal-To-Noise Enhancement

Shielding: The Faraday Cage (from Michael Faraday, who also discovered benzene and invented the Bunsen burner)



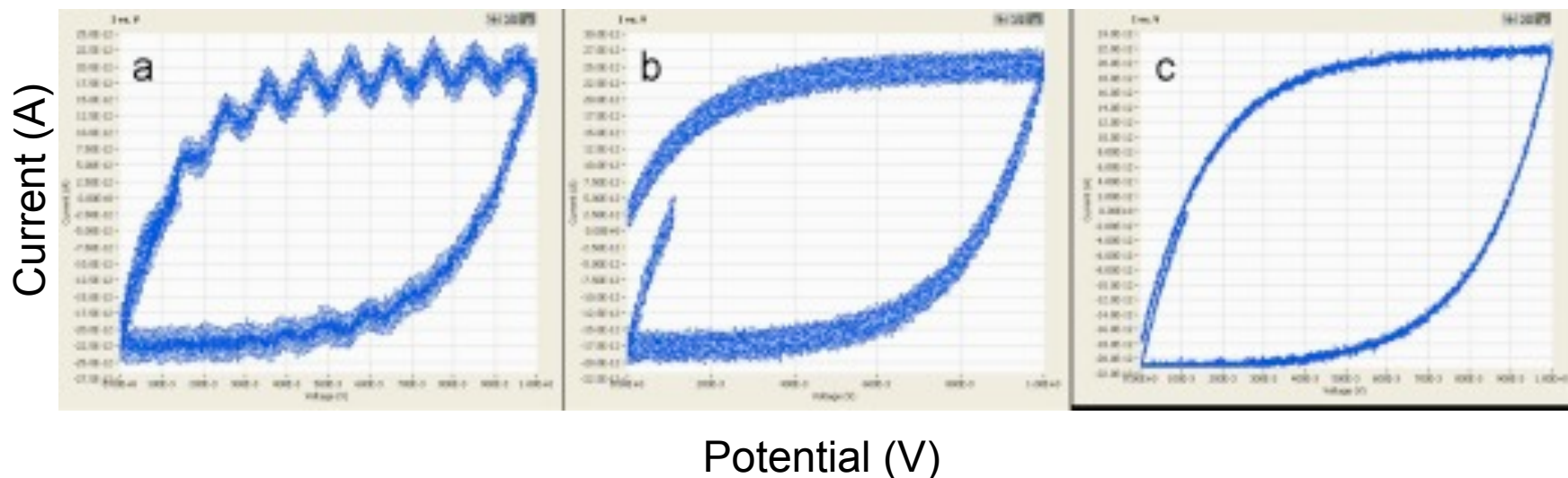
Signal-To-Noise Enhancement

Shielding: The Faraday Cage-Very common in electrochemistry, and on microwave oven doors.



Signal-To-Noise Enhancement

Shielding: The Faraday Cage

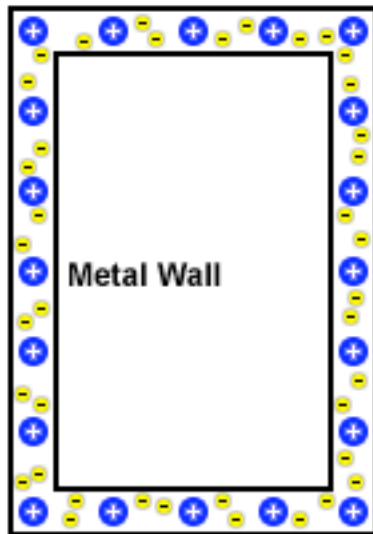


These are called cyclic voltammograms. They are measurements of current vs. potential, although you need not worry about this now. Notice the noise reduction in going from a to c. Data in a were collected outside of a Faraday cage. Data in b were collected inside a Faraday cage that was not grounded to the potentiostat. C was in a cage and grounded.

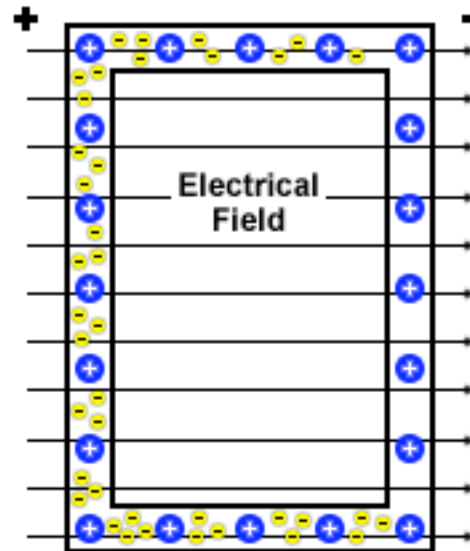
Signal-To-Noise Enhancement

Shielding: The Faraday Cage

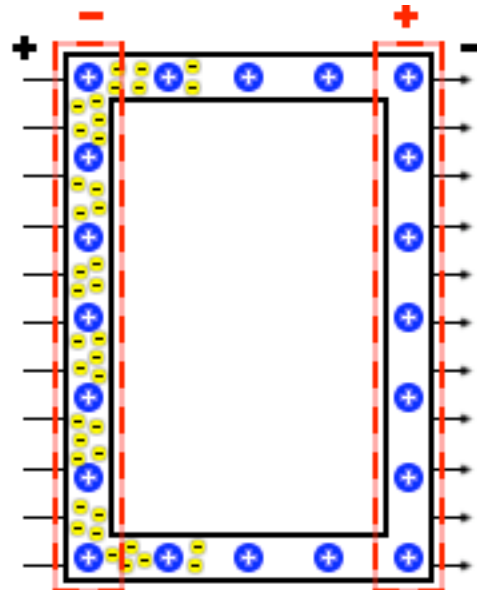
Works because charge in a conductor always resides on the surface (Gauss's Law). An electric field causes the electrons in a metal to redistribute in a way that cancels the field. Thus, an alternating EM field outside the cage never penetrates inside the cage, it is shielded by the charge of the metal cage.



Faraday Cage in the absence of an electrical field.



The charged particles in the wall of the Faraday cage respond to an applied electrical field.



Electrical fields generated inside the wall cancel out the applied field, neutralizing the interior of the cage.

Signal-To-Noise Enhancement

Software Methods

Ensemble Averaging

Successive sets of data are collected and the mean is computed point-by-point. The effect on signal/noise is:

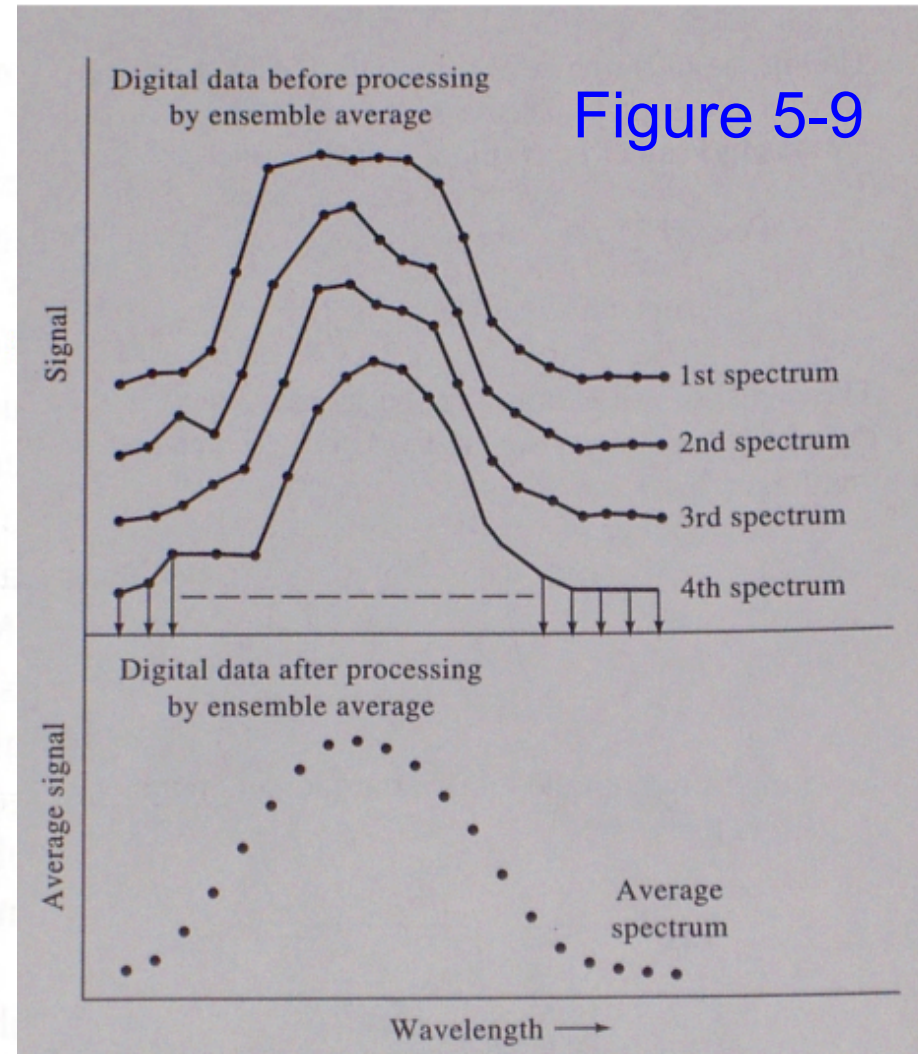
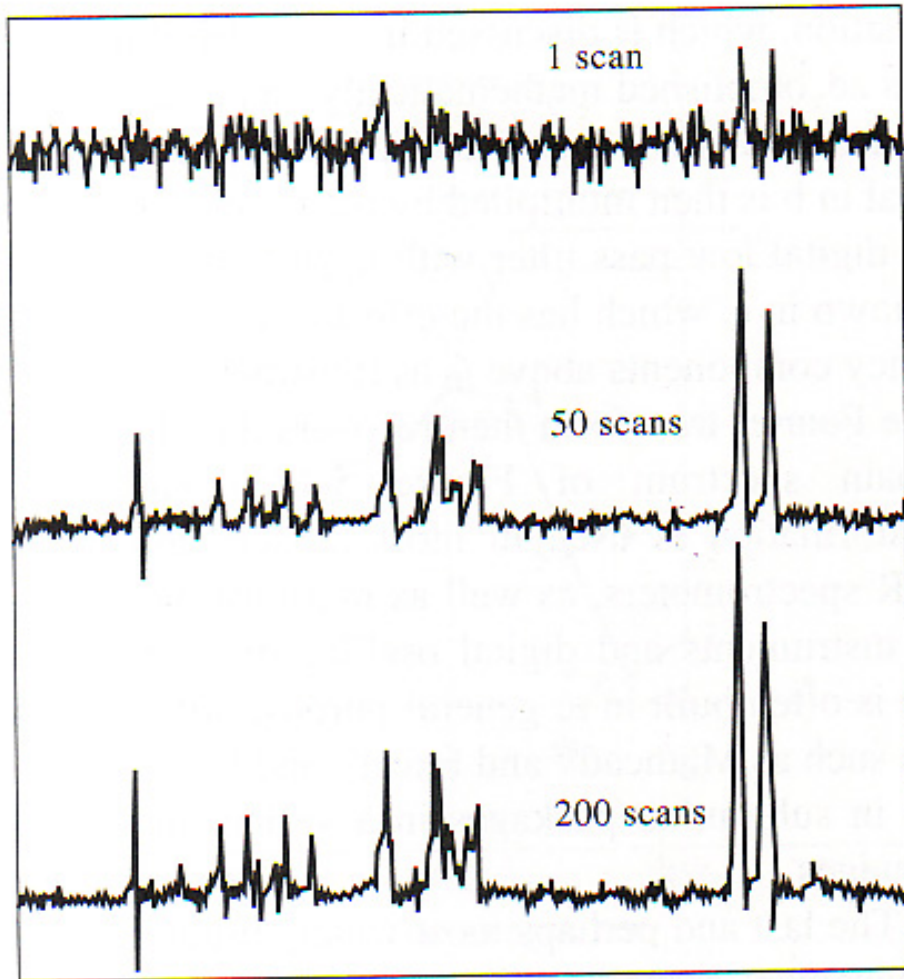
$$\left(\frac{S}{N} \right) = n^{1/2} \frac{S_i}{N_i}$$

S_i and N_i are the signal and noise for the first data set.

Signal to noise increase with the square root of the number of measurements averaged.

Works because random fluctuations in signal tend to cancel each other out as the signal is summed.

Signal-To-Noise Enhancement



Concept Te\$t

The following 8 data points were obtained for a voltage measurement in mV:

1.37, 1.84, 1.35, 1.47, 1.10, 1.73, 1.54, 1.08

What is S_i/N_i ?

(Remember S = mean, N = STDev, and $SNR = n^{1/2}SNR_i$, where SNR means Signal to Noise Ratio.)

(A) 1.89

(B) 3.50

(C) 8.72

(D) 16.05

$S = \text{mean} = 1.44$

$N = \text{STDev} = 0.27$

$SNR \text{ of 8 data pts} = 5.33$

$SNR = n^{1/2}(SNR_i)$

$SNR_i = 5.33/2.83$

$SNR_i = 1.89$

Concept Test

The following 8 data points were obtained for a voltage measurement in mV.

1.37, 1.84, 1.35, 1.47, 1.10, 1.73, 1.54, 1.08

How many total measurements would be needed to increase the S/N to 10?

(A) 4

$$\text{SNR} = n^{1/2}(\text{SNR}_i)$$

$$10 = n^{1/2}(1.89)$$

(B) 18

$$n = 27.99 = 28$$

(C) 28

(D) 56