84.314
Analytical Chemistry II
(Instrumental Analysis)

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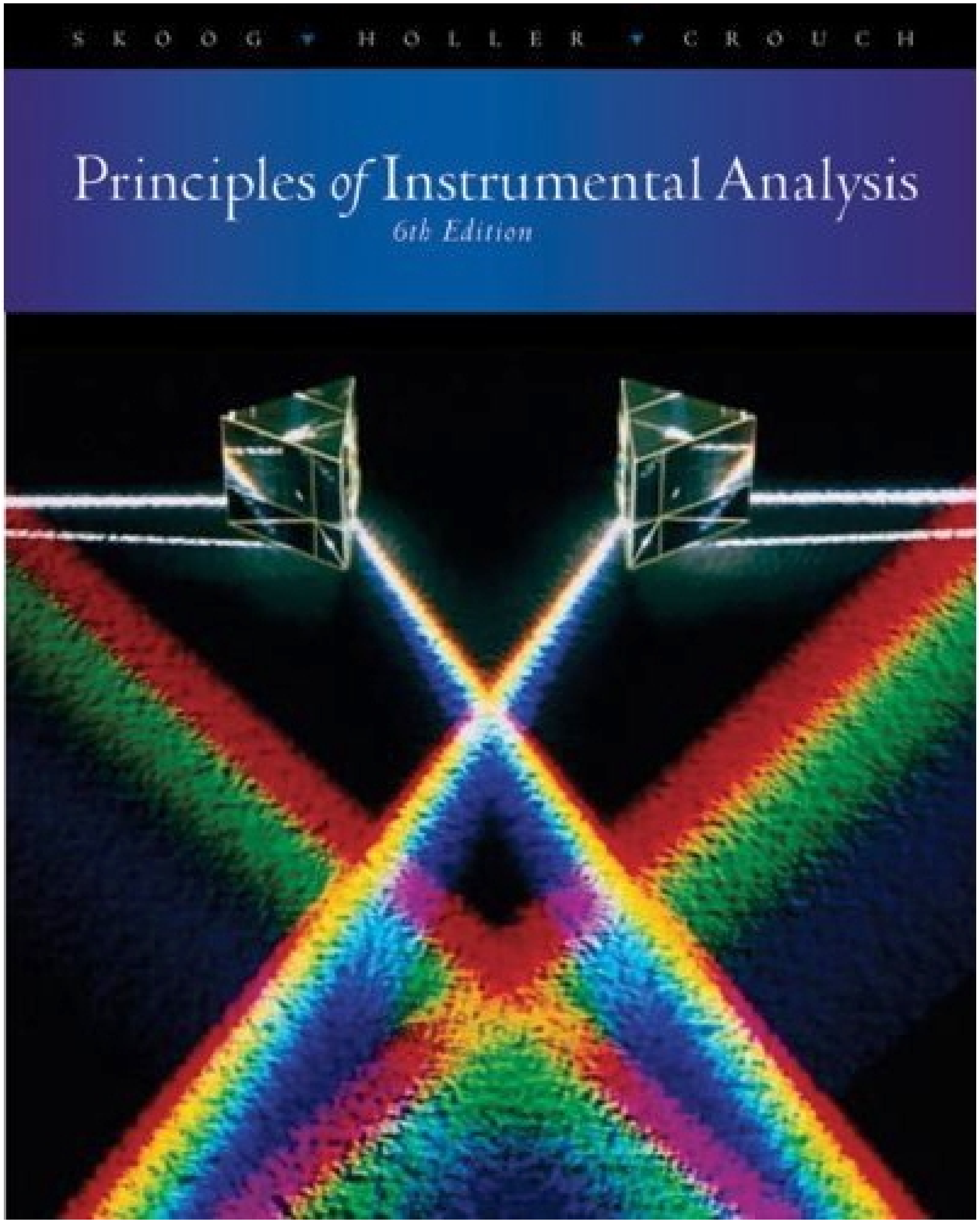


List Price $162

UML Bookstore $162

Internet as low as $85 ?

Fifth edition 1998

Sixth ed. just out 2007

Excellent reference book

Website

http://faculty.uml.edu/David_Ryan/84.314/

- Syllabus = course description
- Schedule
- Materials = Lecture Slides, Handouts, Scanned Chapters

Skoog – Chapter 1 Introduction

- Basics of Instrumental Analysis
  - Properties Employed in Instrumental Methods
  - Numerical Criteria
  - Figures of Merit

TABLE 1-1 Chemical and Physical Properties Employed in Instrumental Methods

Characteristic Properties	Instrumental Methods
Emission of radiation	Emission spectroscopy (X-ray, UV, visible, electron, Auger); fluorescence, phosphorescence, and luminescence (X-ray, UV, and visible)
Absorption of radiation	Spectrophotometry and photometry (X-ray, UV, visible, IR); photoacoustic spectroscopy; nuclear magnetic resonance and electron spin resonance spectroscopy
Scattering of radiation	Turbidimetry; nephelometry; Raman spectroscopy
Refraction of radiation	Refractometry; interferometry
Diffraction of radiation	X-Ray and electron diffraction methods
Rotation of radiation	Polarimetry; optical rotary dispersion; circular dichroism
Electrical potential	Potentiometry; chronopotentiometry
Electrical charge	Coulometry
Electrical current	Amperometry; polarography
Electrical resistance	Conductometry
Mass	Gravimetry (quartz crystal microbalance)
Mass-to-charge ratio	Mass spectrometry
Rate of reaction	Kinetic methods
Thermal characteristics	Thermal gravimetry and titrimetry; differential scanning colorimetry; differential thermal analyses; thermal conductometric methods
Radioactivity	Activation and isotope dilution methods

TABLE 1-3 Numerical Criteria for Selecting Analytical Methods

Criterion	Figure of Merit
1. Precision	Absolute standard deviation, relative standard deviation, coefficient of variation, variance
2. Bias	Absolute systematic error, relative systematic error
3. Sensitivity	Calibration sensitivity, analytical sensitivity
4. Detection limit (LOD)	Blank plus three times standard deviation of a blank
5. Concentration range	Concentration limit of quantitation (LOQ) to concentration limit of linearity (LOL)
6. Selectivity	Coefficient of selectivity

TABLE 1-4 Other Characteristics to Be Considered in Method Choice

1. Speed
2. Ease and convenience
3. Skill required of operator
4. Cost and availability of equipment
5. Per-sample cost

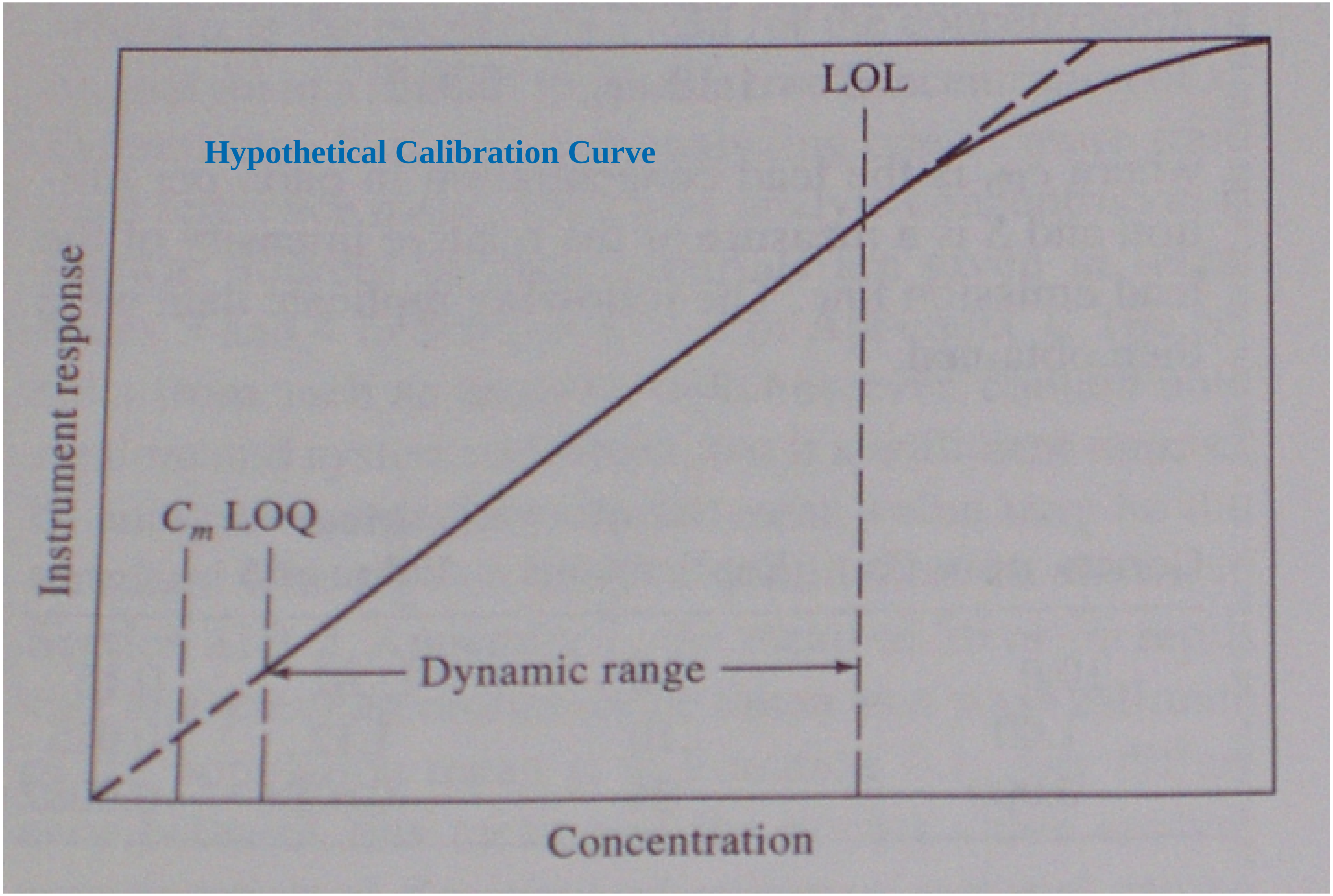
TABLE 1-5 Figures of Merit for Precision of Analytical Methods

Terms	Definition*
Absolute standard deviation, s	$s = \sqrt{\frac{\sum_{i=1}^{N}(x_i - \bar{x})^2}{N-1}}$
Relative standard deviation (RSD)	$\mathrm{RSD} = \frac{s}{\bar{x}}$
Standard deviation of the mean, s_m	$s_m = s/\sqrt{N}$
Coefficient of variation, CV	$\mathrm{CV} = \frac{s}{\bar{x}} \times 100\%$
Variance	s^2

*x_i = numerical value of the ith measurement.

$\bar{x}$ = mean of N measurements = $\frac{\sum_{i=1}^{N} x_i}{N}$

Hypothetical Calibration Curve



Skip the following chapters

- Chapter 2 – Electrical Components and Circuits
- Chapter 3 – Operational Amplifiers in Chemical Instrumentation
- Chapter 4 – Digital Electronics and Microcomputers

Skoog – Chapter 5 Signals and Noise

- Signal to Noise Ratio

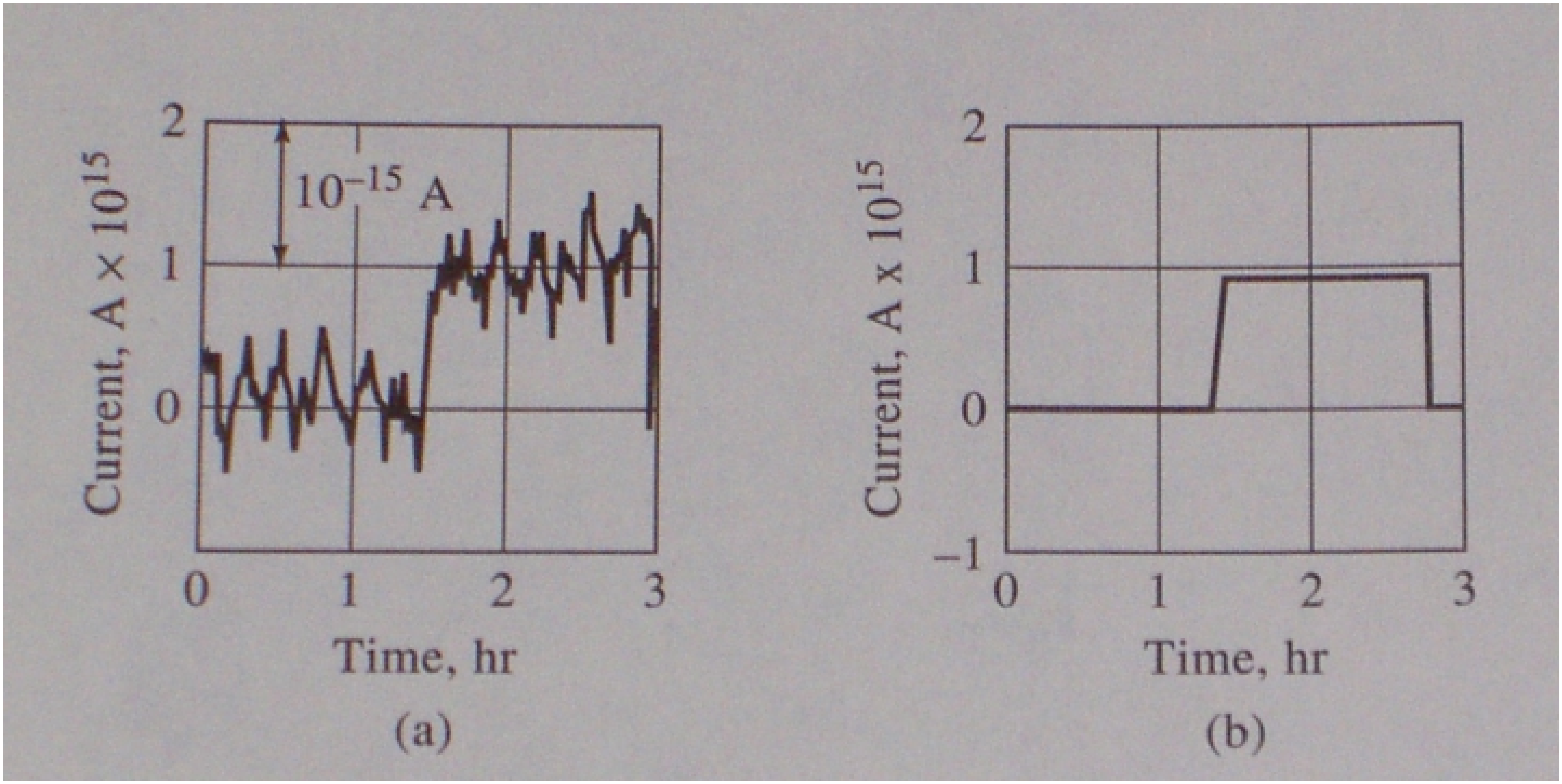
All instrumental measurements involve a signal

Unfortunately all signals have noise present

Sometimes the noise is large

Sometimes it is so small you can't see it

Current measurements
(a) with noise,
(b) with noise averaged out



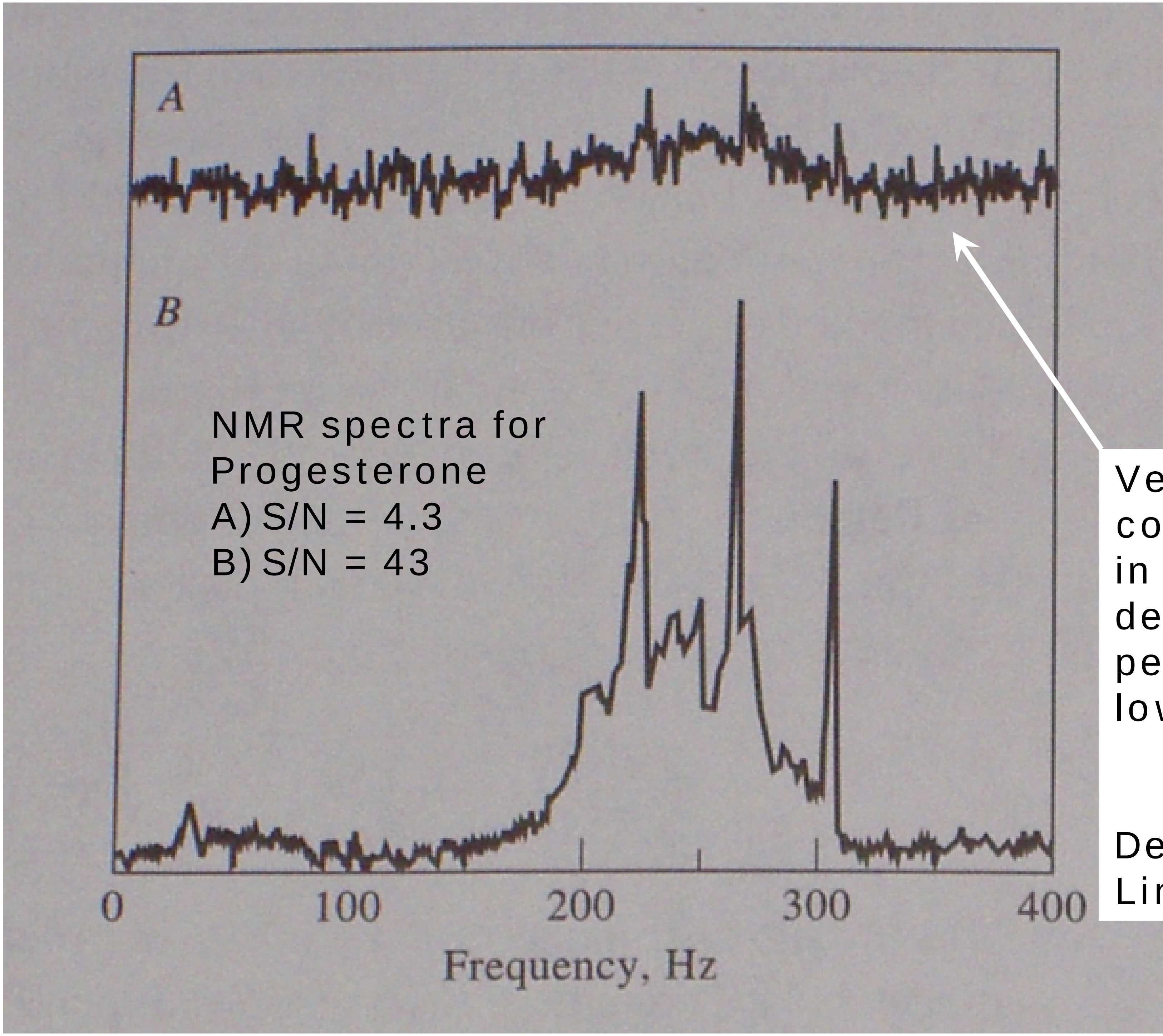
Noise is often constant and independent of signal

Signal to Noise Ratio (S/N)

- Parameter describing quality of data
- Often referred to as “figure of merit”

$$\frac{S}{N} = \frac{\text{mean of signal}}{\text{standard deviation}} = \frac{x}{s} = \frac{1}{RSD}$$

RSD = relative standard deviation



NMR spectra for Progesterone

A) S/N = 4.3

B) S/N = 43

Very little confidence in ability to determine peaks at lower S/N

Detection Limit

Sources of Noise

- Chemical noise – temp, pressure, humidity, etc. fluctuations = uncontrolled variables
- Instrumental noise – noise from instrumental components
  - Thermal noise (Johnson noise) – thermal motion of electrons in load resistor

$$v_{rms} = \sqrt{4\ k\ T\ R\ \Delta f}$$

Thermal noise

$$v_{rms} = \sqrt{4\ k\ T\ R\ \Delta f}$$

v_{rms} = root mean square noise voltage

k = Boltzmann constant 1.38×10^{-23} J/K

T = temperature

R = resistance

Δf = frequency bandwidth of noise

Instrumental noise

- Shot noise – movement of electrons across a junction

$$i_{rms} = \sqrt{2\ i\ e\ \Delta f}$$

i_{rms} = root-mean square current fluctuation

i = average current

e = charge on electron

Δf = frequency bandwidth

- Instrumental noise
  - Flicker noise – any noise that is inversely proportional to signal

    1/f

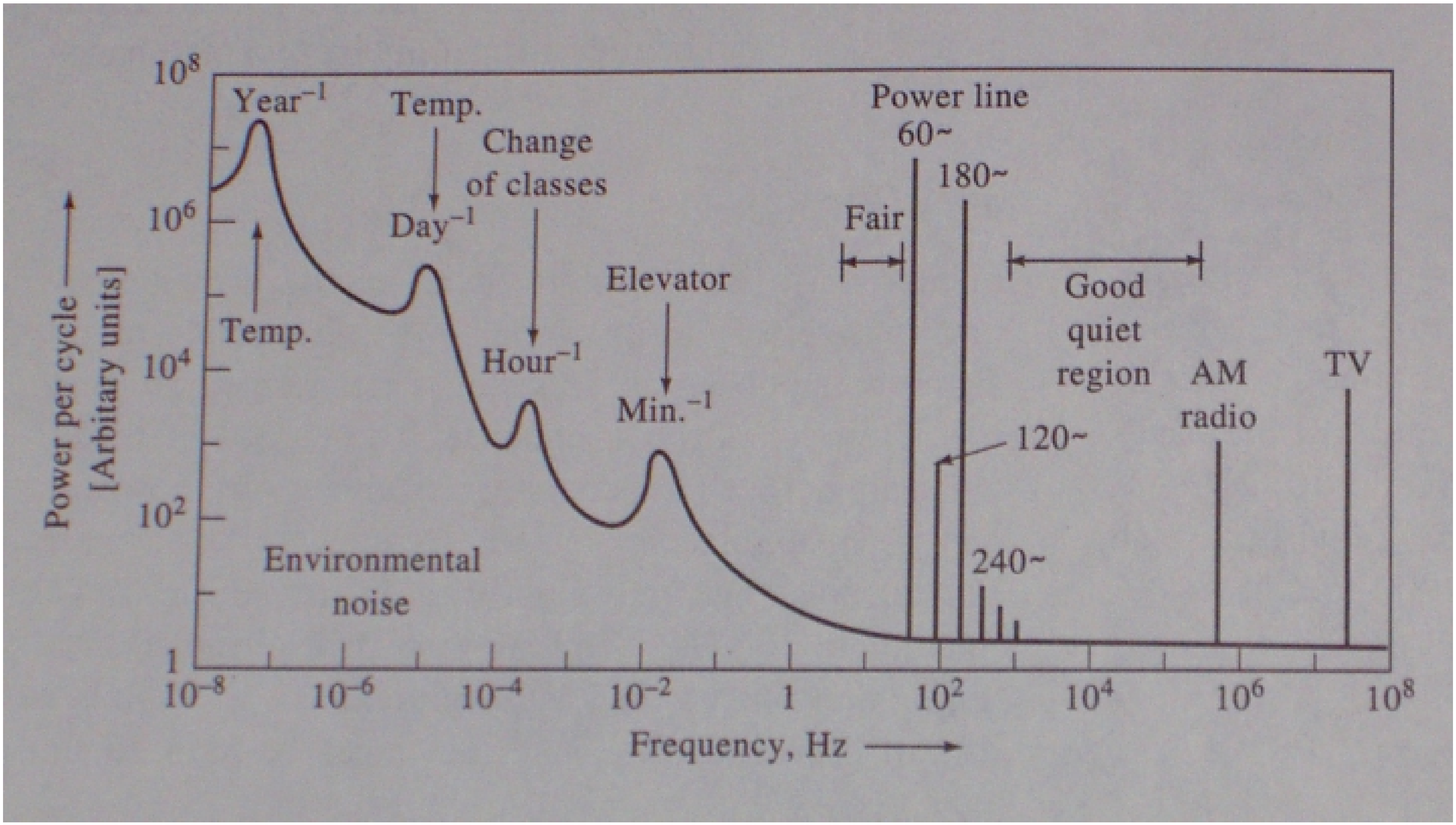
  Significant at low frequency (<100 Hz)
  - Environmental noise – composite of many noise sources

    e.g. any electrical device gives off EM (electromagnetic radiation)

    ELF radiation = health controversy

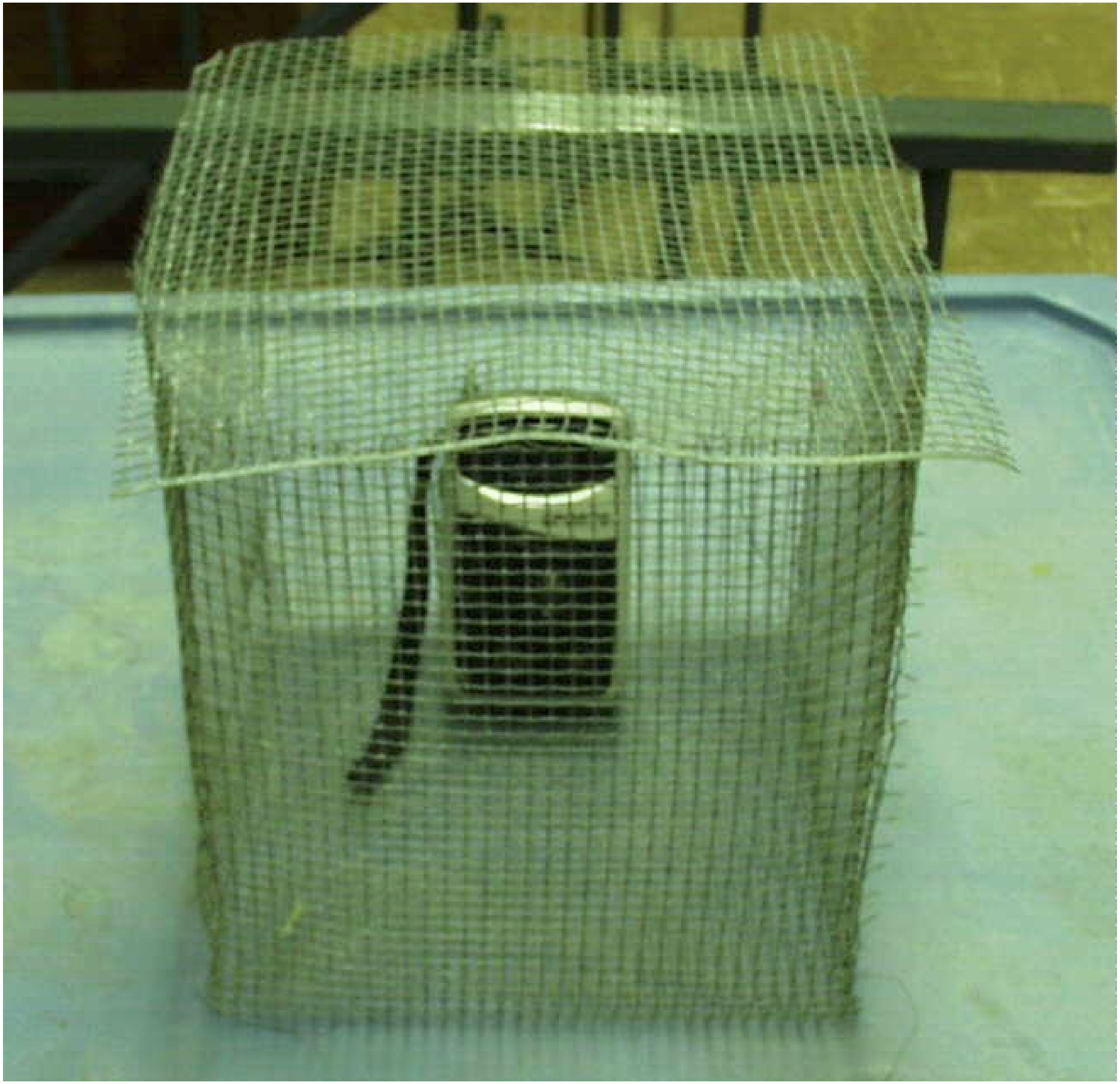
    instruments may pick up signals

Environmental noise sources (note frequency dependence)

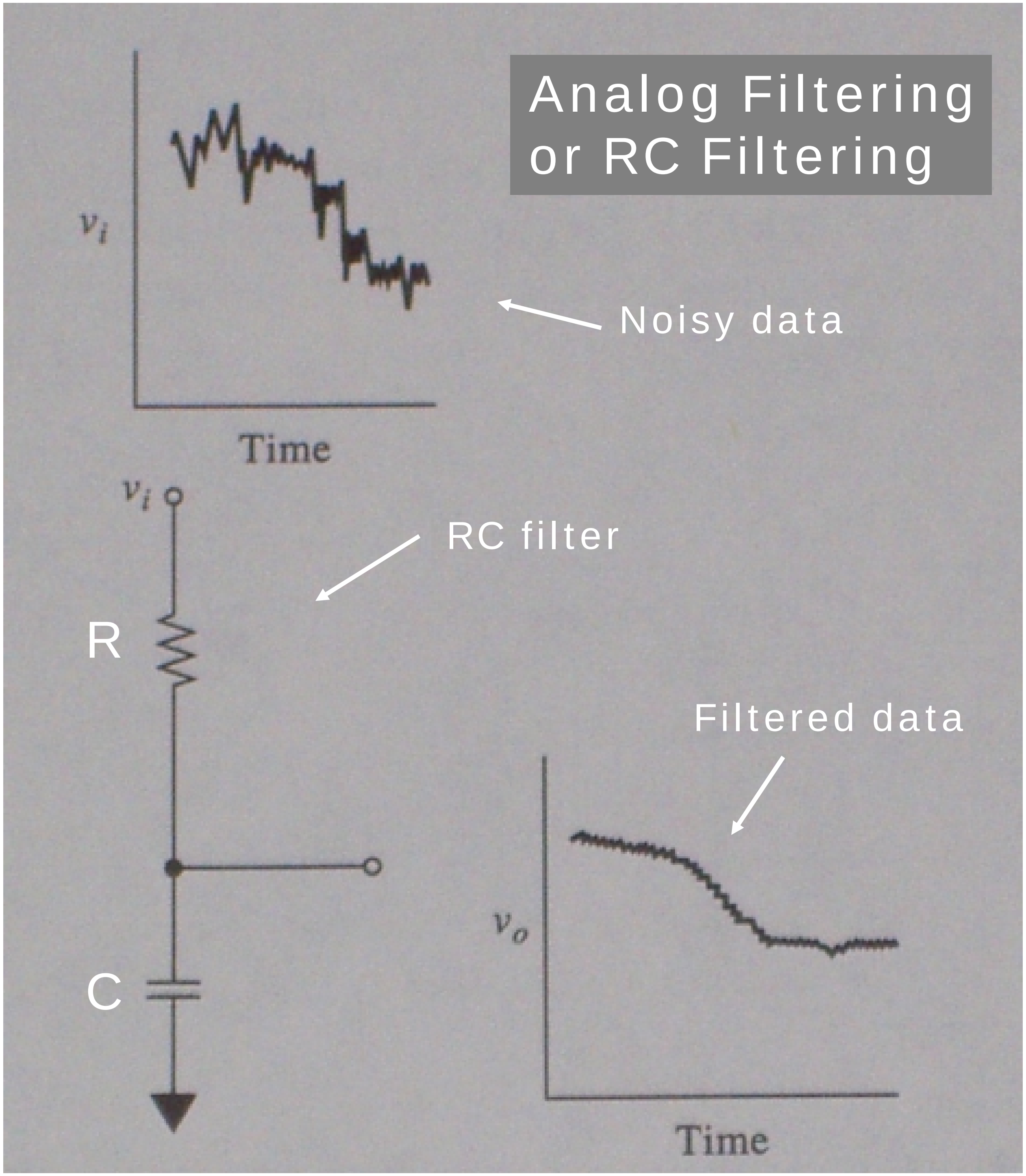


Improving S/N
hardware & software

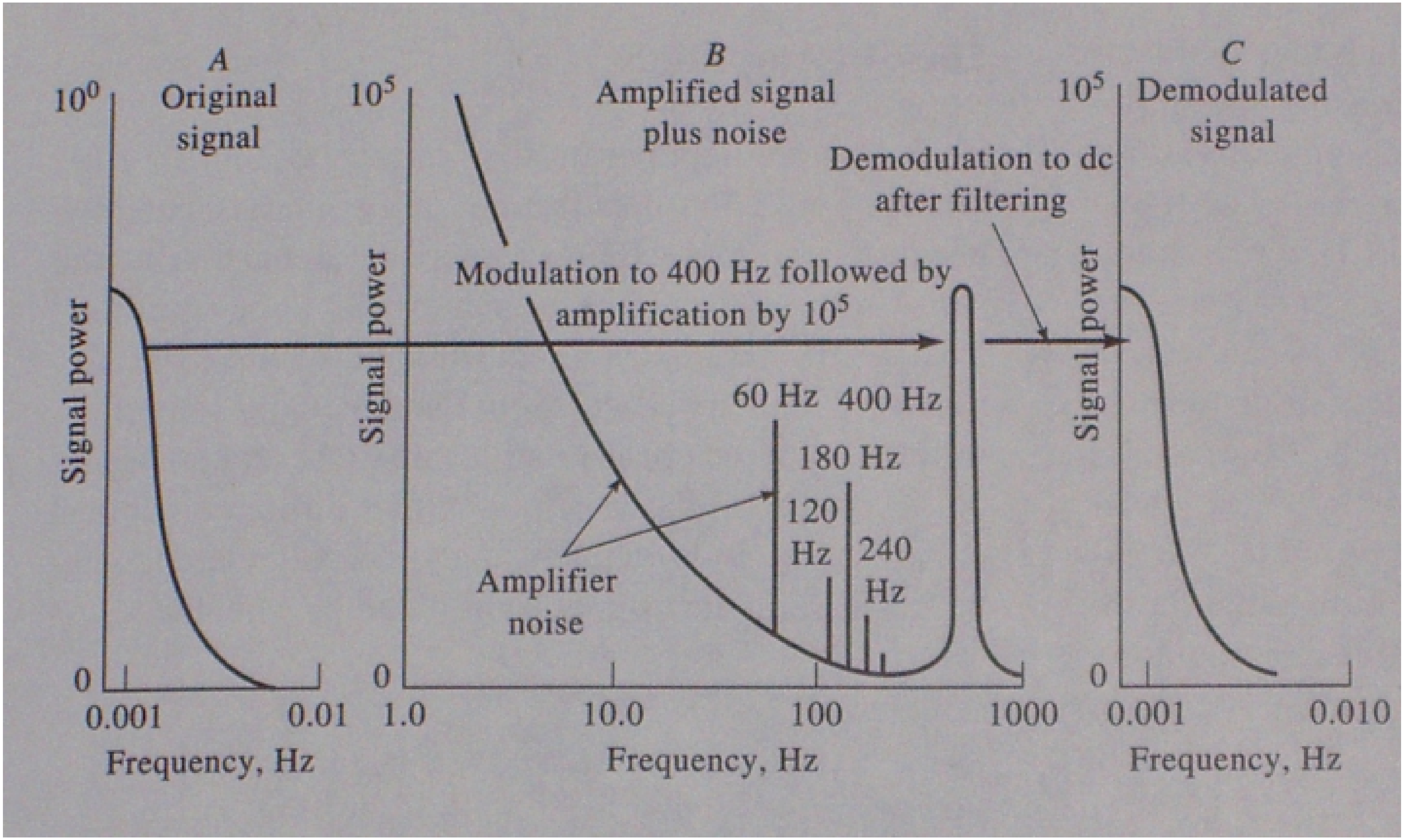
- Hardware
  - Grounding & shielding – Faraday cage
  - Analog filtering – RC filtering
  - Modulation – convert DC signal to high frequency AC then demodulate
  - Signal chopping – rotating wheel to differentiate e.g. IR source from heat
  - Lock-in amplifiers



Analog Filtering or RC Filtering

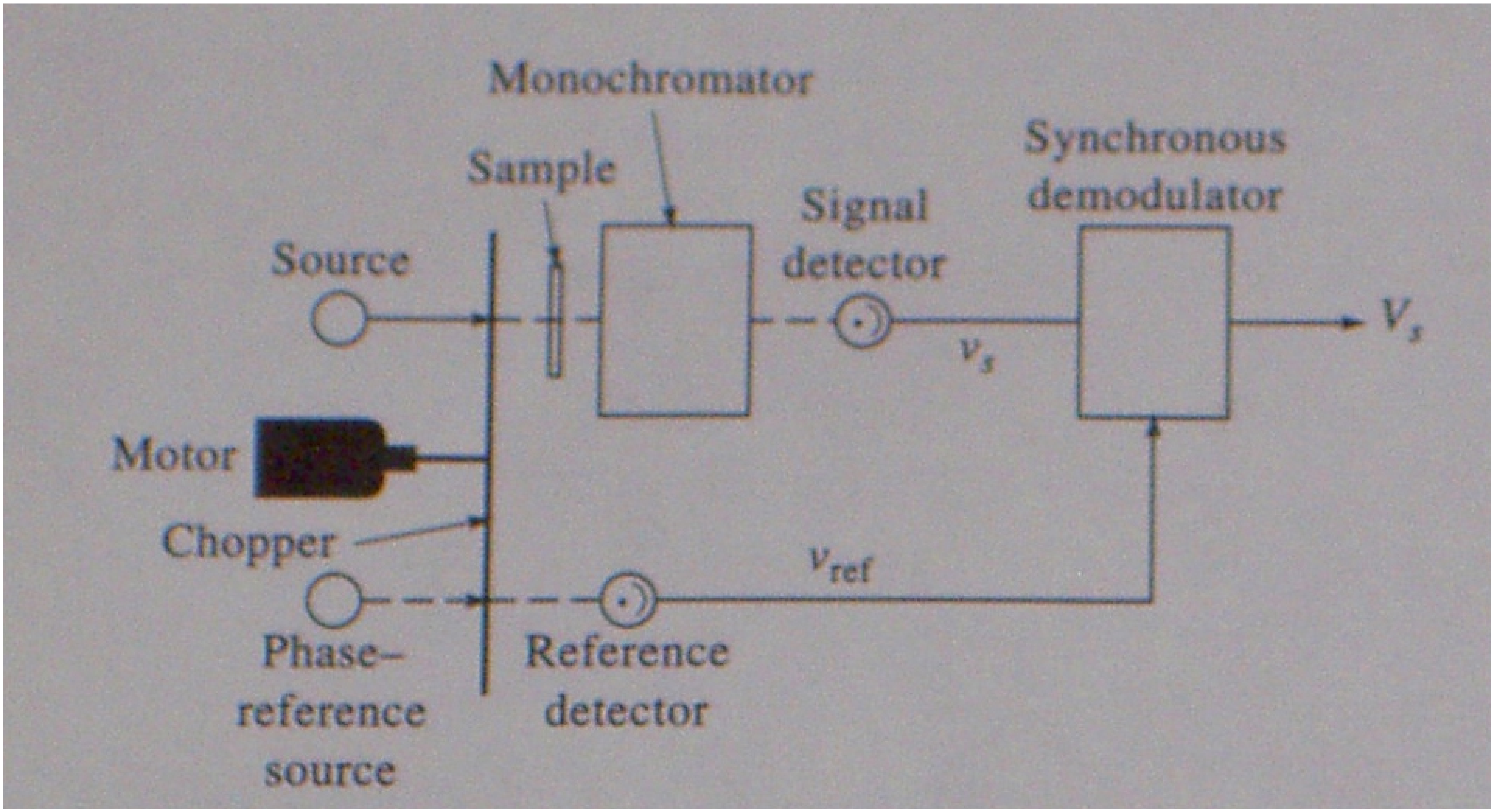


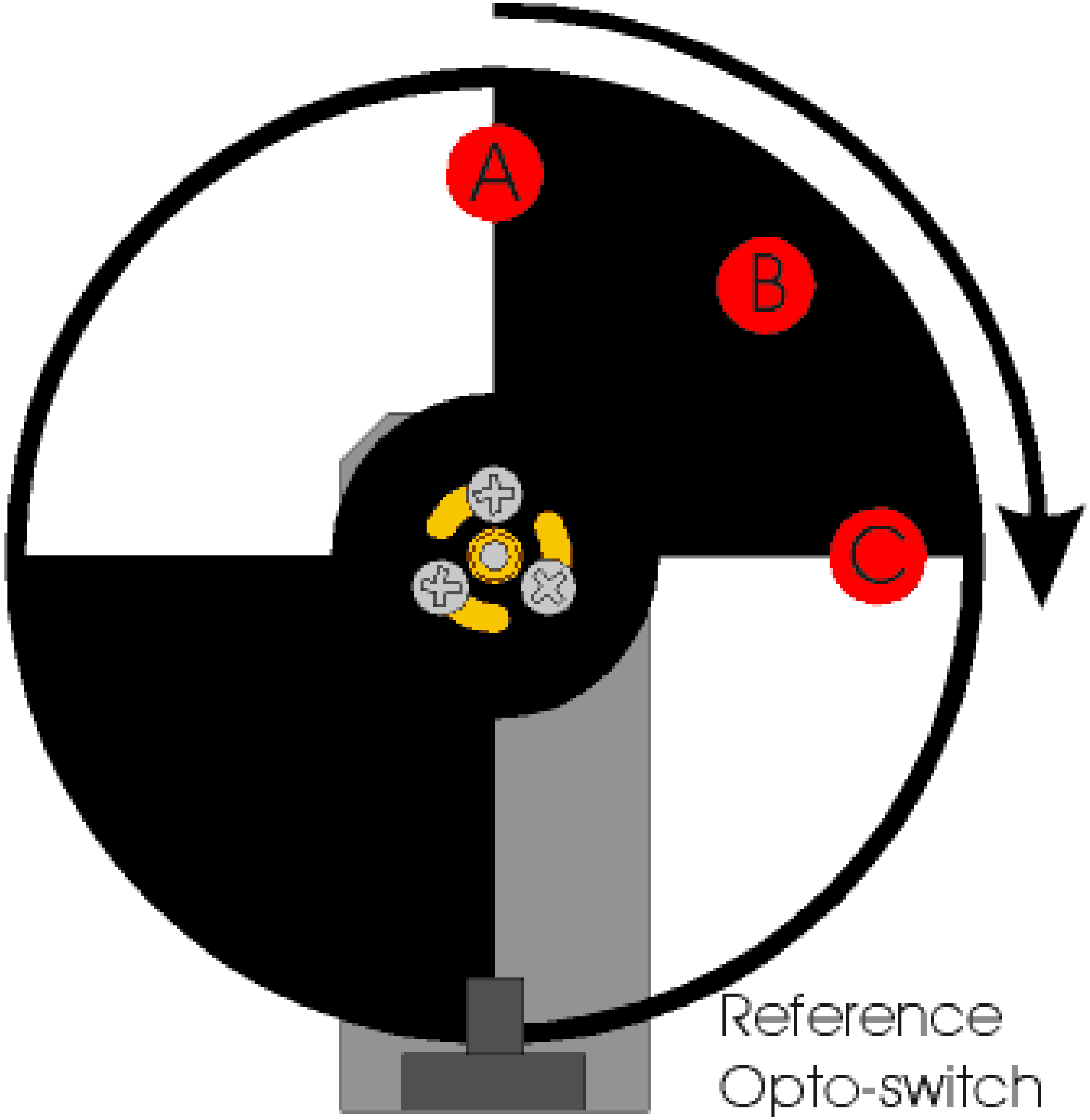
Modulation



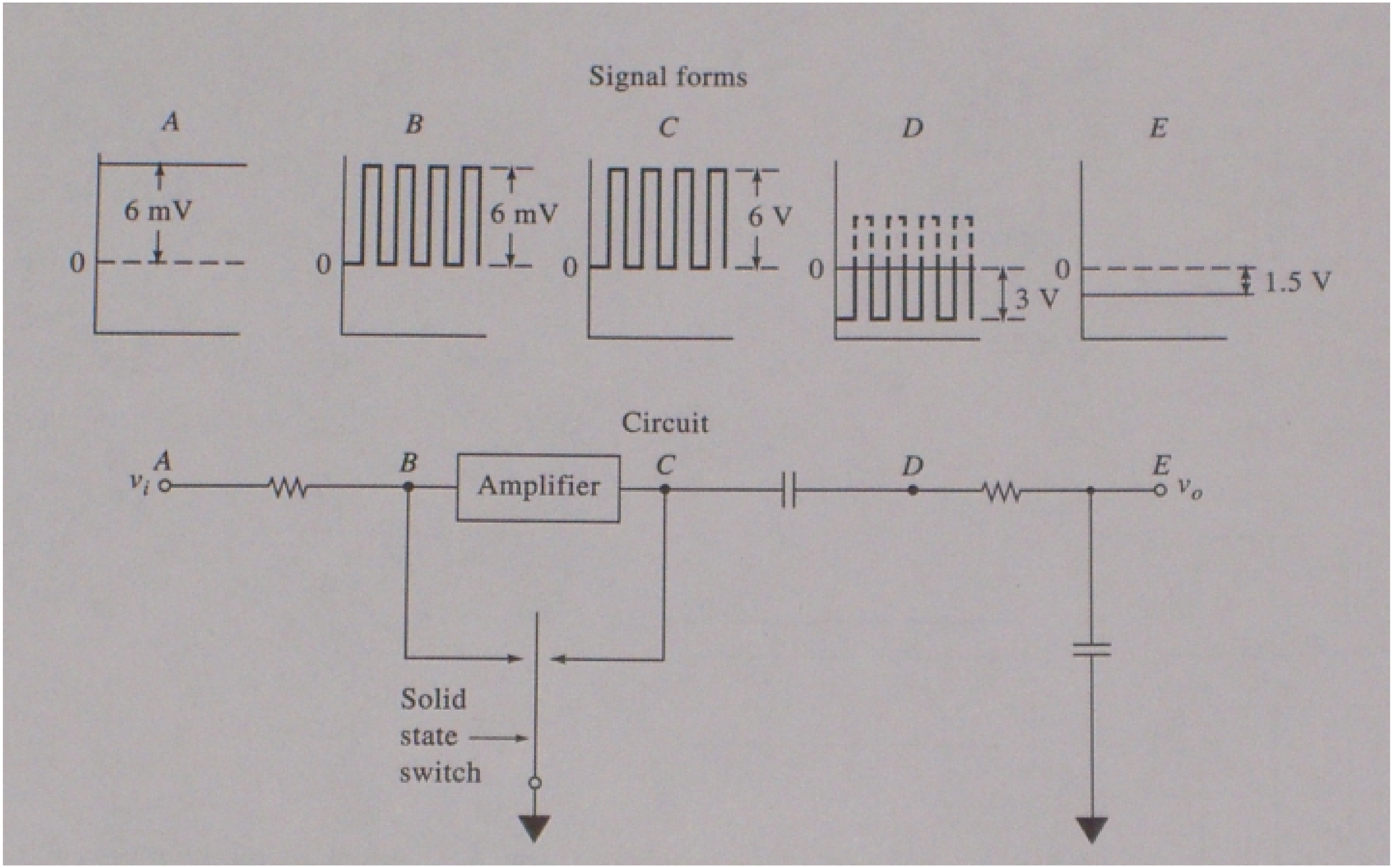
A
Original signal
10^0
Signal power
0
0.001
0.01
Frequency, Hz
B
Amplified signal plus noise
10^5
Signal power
Modulation to 400 Hz followed by amplification by 10^5
60 Hz
400 Hz
180 Hz
120 Hz
240 Hz
Amplifier noise
0
1.0
10.0
100
1000
Frequency, Hz
Demodulation to dc after filtering
C
Demodulated signal
10^5
Signal power
0
0.001
0.010
Frequency, Hz

Signal chopping in an IR spectrophotometer



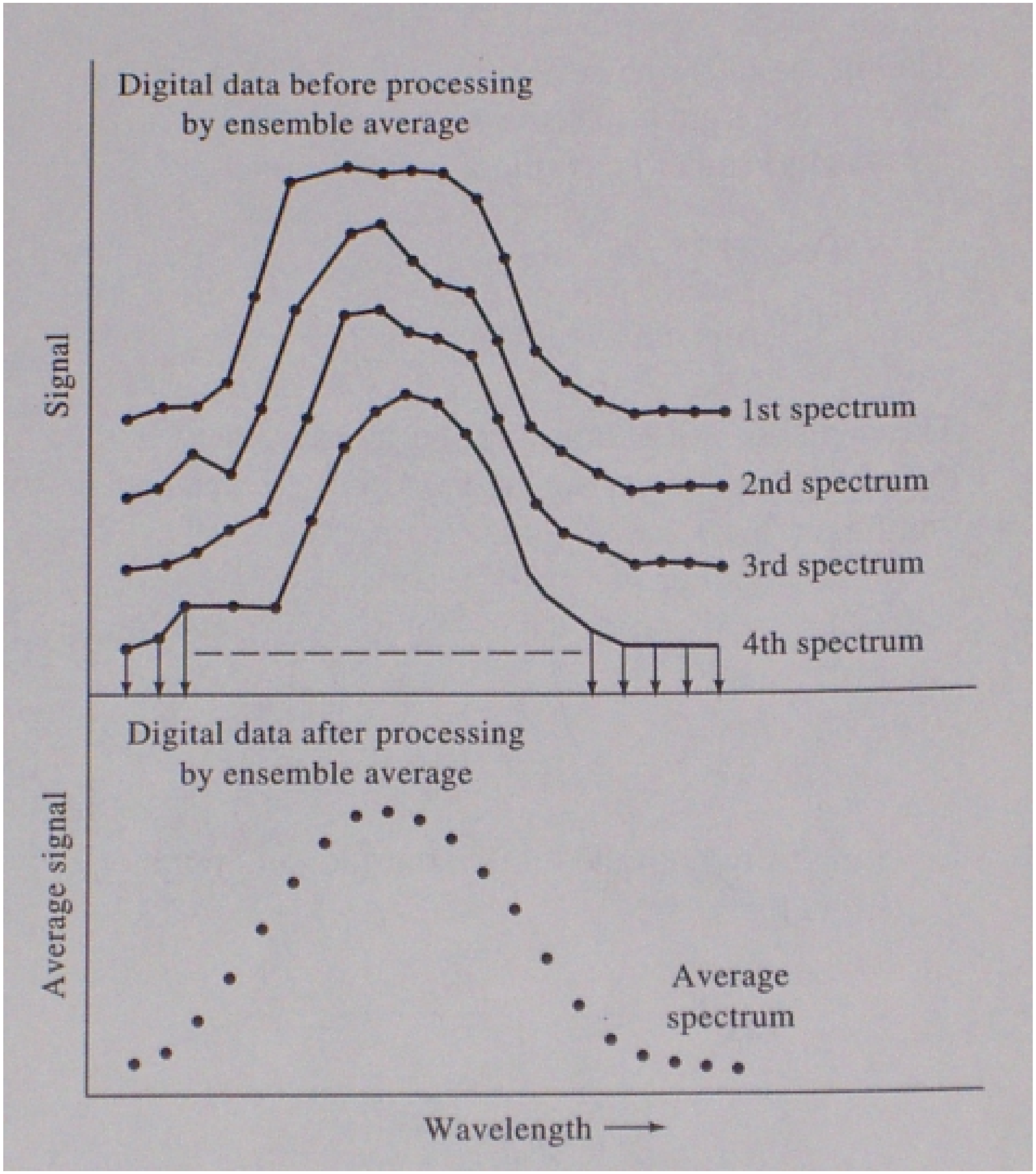

A
B
C
Reference
Opto-switch

Chopper amplifier

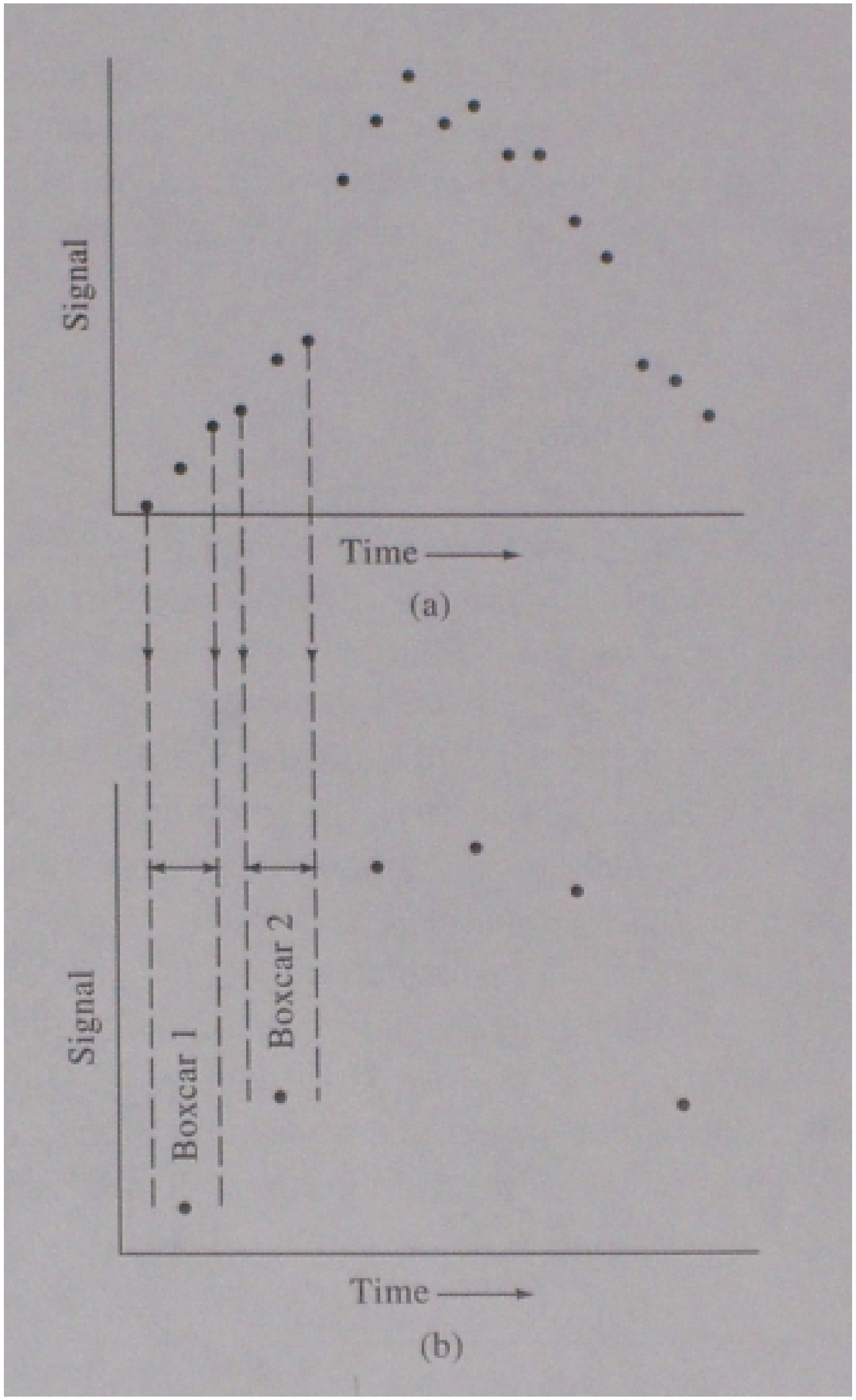


Improving S/N
hardware & software

- Software
  - Ensemble averaging – adding spectra
  - Boxcar averaging –
  - Digital filtering – moving window, sliding average
  - Correlation methods



Ensemble averaging i.e. adding or averaging signal



Boxcar averaging