84.314 Analytical Chemistry II (Instrumental Analysis)

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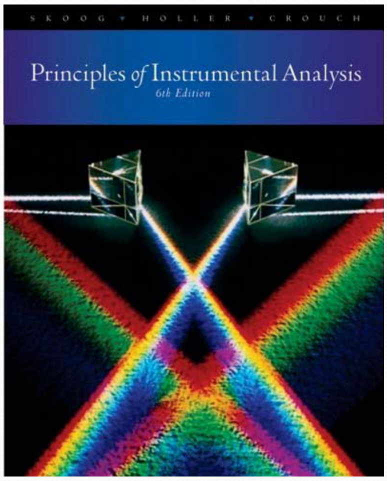


List Price $162
UML Bookstore $231?
Internet as low as $85 ?
Fifth edition 1998
Sixth ed. just out 2007
Excellent reference book

Website

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

- Syllabus = course description
- Schedule
- Materials = Lecture Slides, Handouts, Videos from last year

Skoog – Chapter 1 Introduction

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

Nobel Prizes

William H. **Bragg**	analysis of crystal structure by means of X-rays(physics)	1915
Francis W. **Aston**	for his discovery, by means of his mass spectrograph, of isotopes (Chemistry)	1922
Friderik **Pregl**	invention of the method of micro-analysis of organic substances (Chemistry)	1923
Arne **Tiselius**	his research on electrophoresis and adsorption analysis, especially for his discoveries concerning the complex nature of the serum proteins (Chemistry)	1948
Felix **Bloch** Edward M. **Purcell**	development of new methods for nuclear magnetic precision measurements and discoveries (Physics)	1952
Archer J P **Martin** Richard L M **Synge**	Invention of partition chromatography (Chemistry)	1952
Jaroslav **Heyrovsky**	discovery and development of the polarographic methods of analysis (Chemistry)	1959
Rosalyn **Yalow**	development of radioimmunoassays of peptide hormones (Physiology or Medicine)	1977
Kai M. **Siegbahn**	contribution to the development of high-resolution electron spectroscopy (physics)	1981
Gerd **Binnig** Heinrich **Rohrer**	design of the scanning tunneling microscope (physics)	1986

- Analytical Methods
  - Classical
    - Precipitation
    - Extraction
    - Distillation
      - Colors
      - Boiling or Melting Points
      - Solubilities
      - Odors
      - Optical
      - Gravimetric
      - Volumetric
  - Instrumental
    - Physical Properties
    - Conductivity
    - Electrode Potential
    - Light Absorption or Emission
    - Mass-to –Charge ratio
    - Fluorescence
    - Chromatographic
    - Electrophoretic

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

Instruments for Analysis

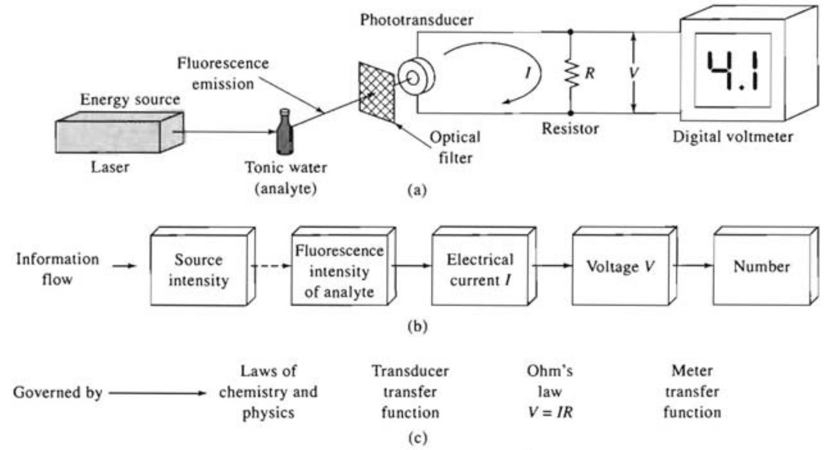


FIGURE 1-3 A block diagram of a fluorometer showing (a) a general diagram of the instrument, (b) a diagrammatic representation of the flow of information through various data domains in the instrument, and (c) the rules governing the data-domain transformations during the measurement process.

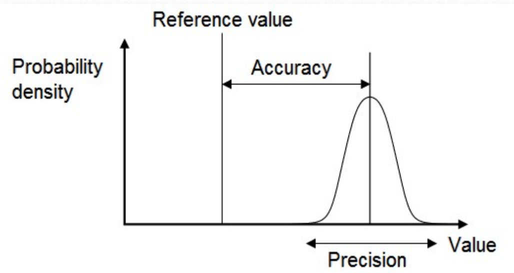
Performance Characteristics Of Instruments

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	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

Precision

- The precision of a measurement system, also called reproducibility or repeatability, is the degree to which repeated measurements under unchanged conditions show the same results.



accuracy of a measurement system is the degree of closeness of measurements of aquantity to its actual (true) value.

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)	$\text{RSD} = \frac{s}{\bar{x}}$
Standard deviation of the mean, s_m	$s_m = s/\sqrt{N}$
Coefficient of variation, CV	$\text{CV} = \frac{s}{\bar{x}} \times 100\%$
Variance	s^2

*x_i = numerical value of the ith measurement.

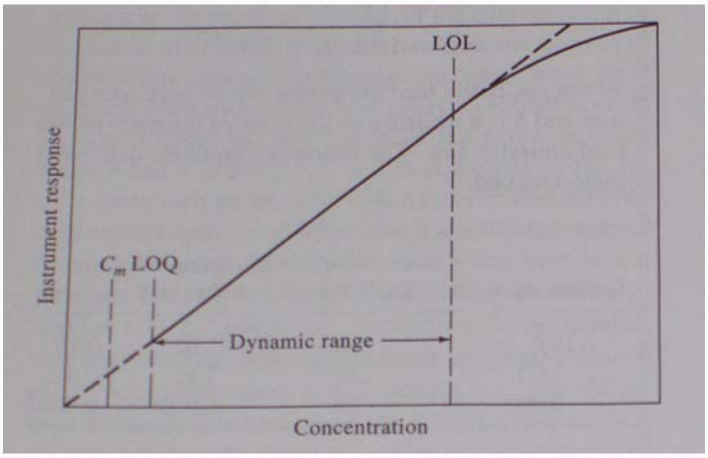
$\bar{x}$ = mean of N measurements = $\frac{\sum_{i=1}^{N} x_i}{N}$

- **Bias**
- Bias provides a measure of the systematic, or determinate, error of an analytical method.
- $\Delta = \mu - \tau$
- Where μ is the population mean for the concentration of an analyte
- τ is the true value

- **Sensitivity**
- Sensitivity of a method or instrument is a measure of its ability to discriminate between small differences.
- Two factors limit sensitivity
  - The slope of calibration curve
  - Reproducibility or precision of the measuring device
  - $S = mc + S_{bl}$

  - **Detection limit**
  - Minimum concentration or mass of analyte can be detected at a known confidence level
  - $Sm = S_{bl} + ks_{bl}$
- Usually, k = 3

Dynamic range



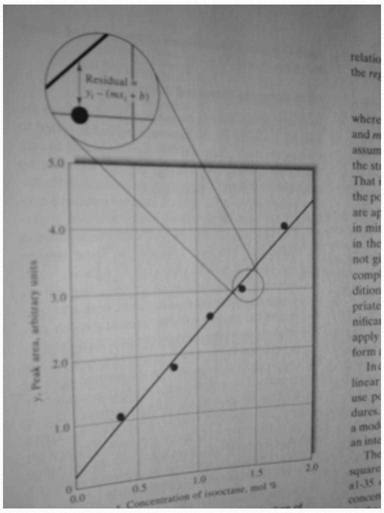
- LOQ limit of quantitation
- LOL limit of linearity
- Dynamic range should be at least a few orders of magnitude

Selectivity

- Selectivity refers to the degree to which the method is free from interference by other species in sample

Calibration of instrumental method

- Calibration determines the relationship between analytical response and analytical concentration.
- 1. external-standard calibration
  - No interference effects
  - Obtain response signal as a function of known analyte concentration



Calibration of instrumental method

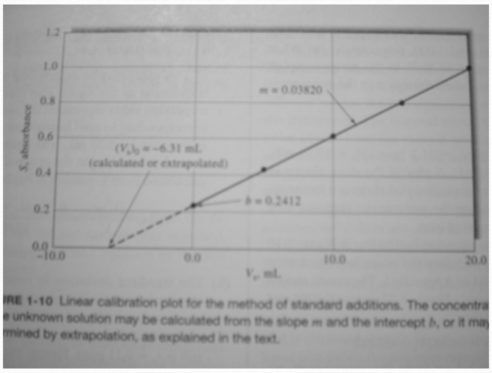
- 2. Standard- additional methods

- Adding one or more increments of standard solution to sample aliquots
- $Sx = K1\ Cx$
- $S_T = K1\ (Cx + Cs)$

$Cx = CsSx\ /(S_T - Sx)$

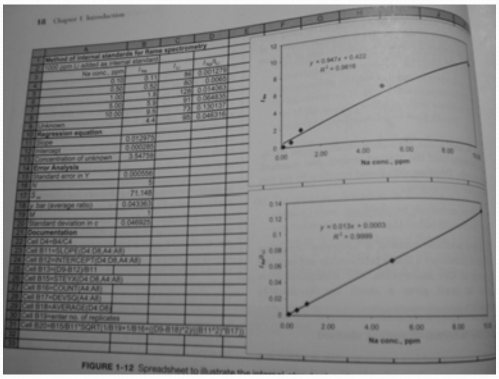
When $S_T = 0$

- $Cx = -Cs$



Calibration of instrumental method

- 3. internal-standard method
- Add a constant amount of substance to all samples, blanks, and calibration standard.
- Plot ratio of analyte signal and internal-standard as a function of analyte concentration.



Homework: P23 1-10

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

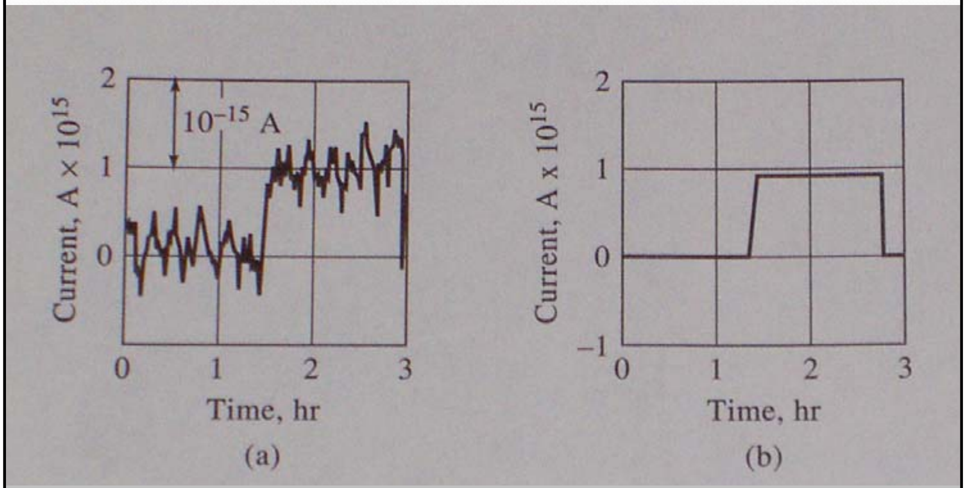
Sometimes the noise is large

Sometimes it is so small you can't see it

Noise is constant and independent, small signal large noise

S/N is very important

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



Noise is often constant and independent of signal

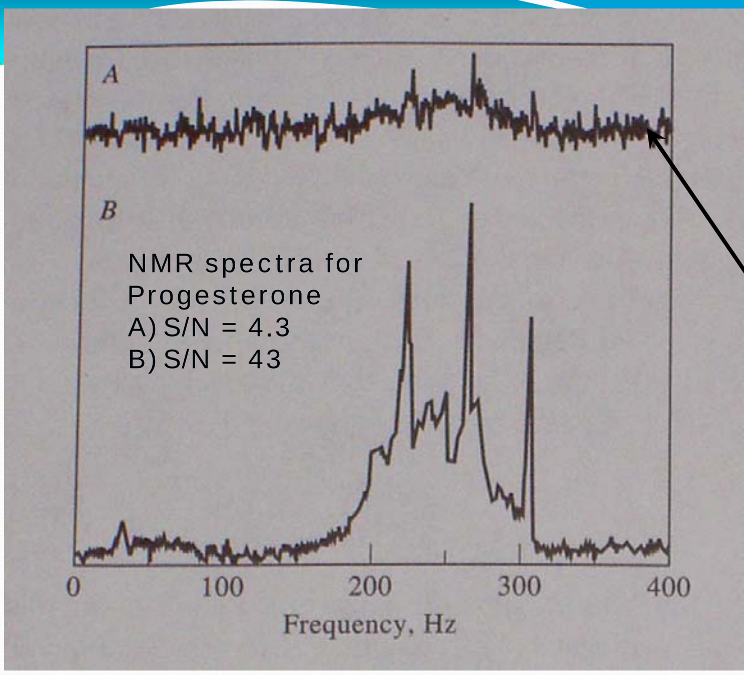
Signal to Noise Ratio (S/N)

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

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

RSD = relative standard deviation

Impossible to detect a signal when S/N less than 2 or 3



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
  - Voltage fluctuation

$$v_{rms} = \sqrt{4\,k\,T\,R\,\Delta f} \qquad \Delta f = 1/3t_r$$

Narrow bandwidth to decrease noise, but instrument will be slower

- Instrumental noise
  - 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

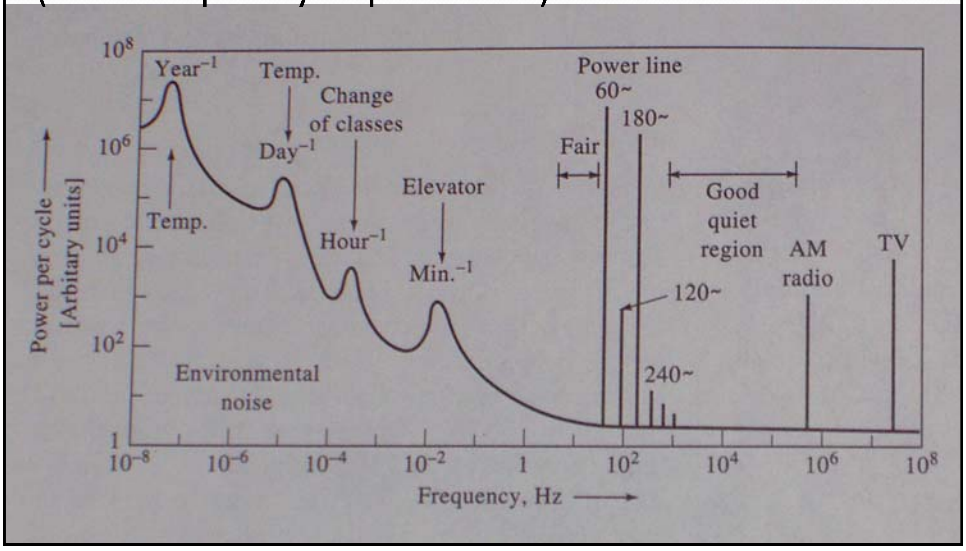
- Flicker noise – any noise that is inversely proportional to signal

  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

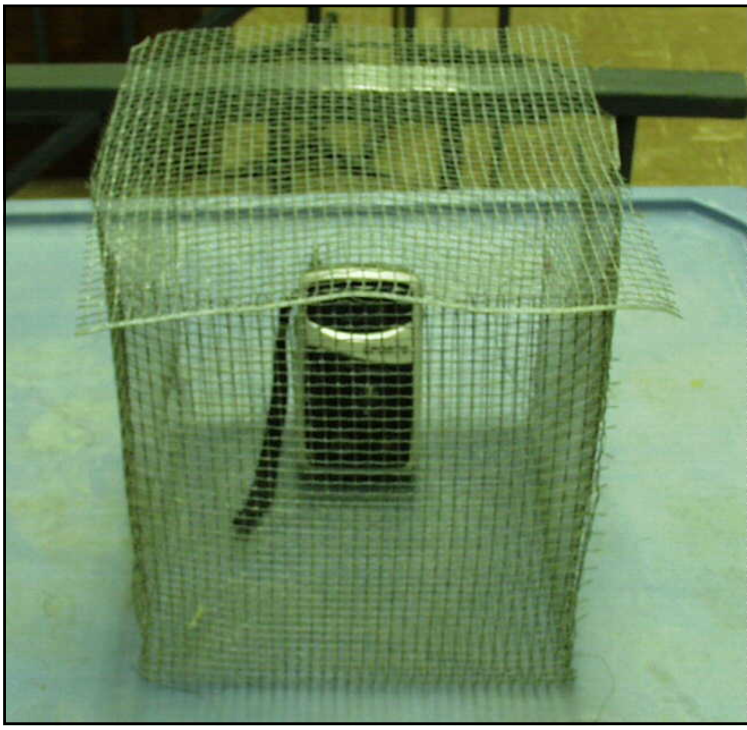
Environmental noise sources (note frequency dependence)



Improving S/N

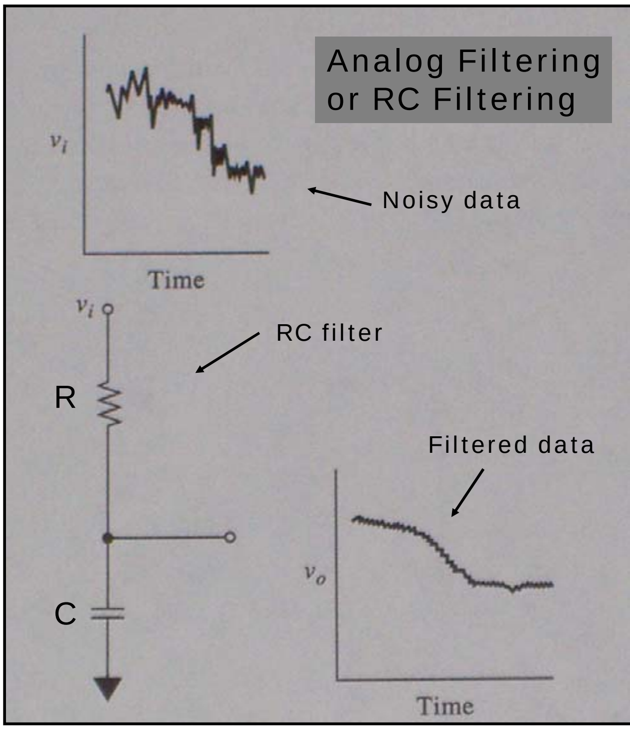
hardware & software

- 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

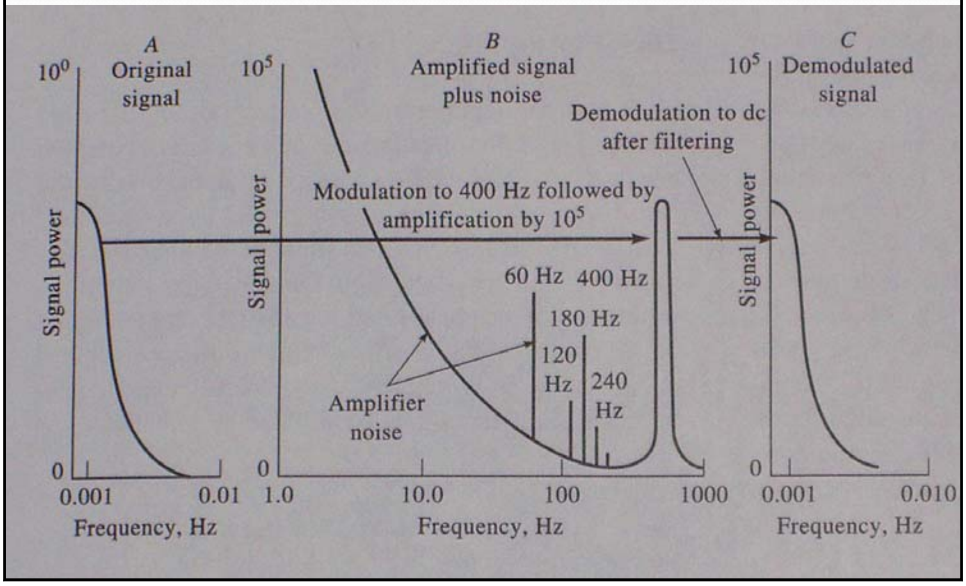


Primitive Faraday Cage for shielding instruments from EM Radiation – must be grounded

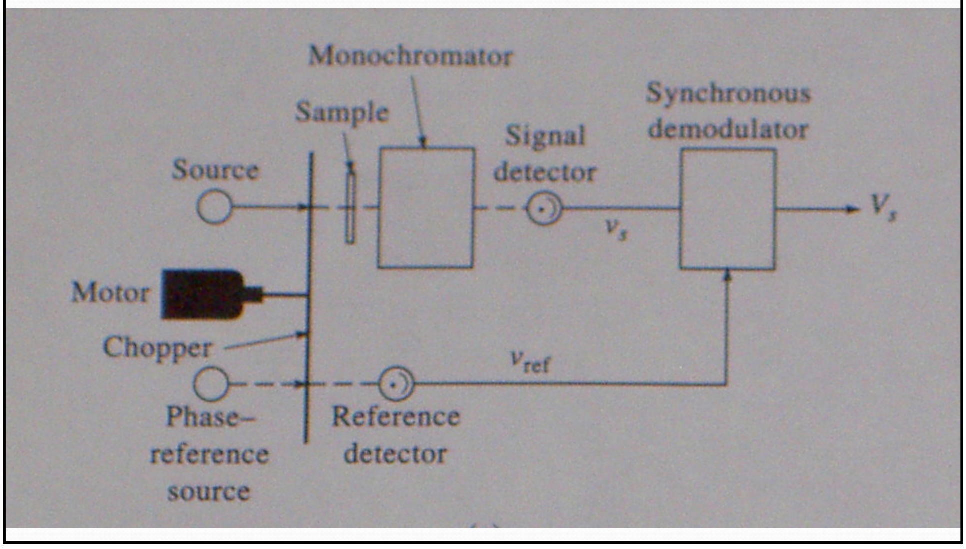
Analog Filtering or RC Filtering

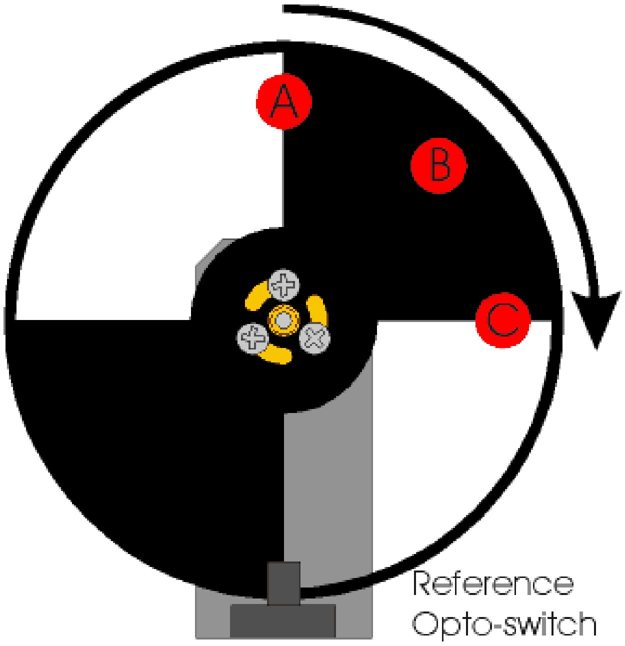


Modulation

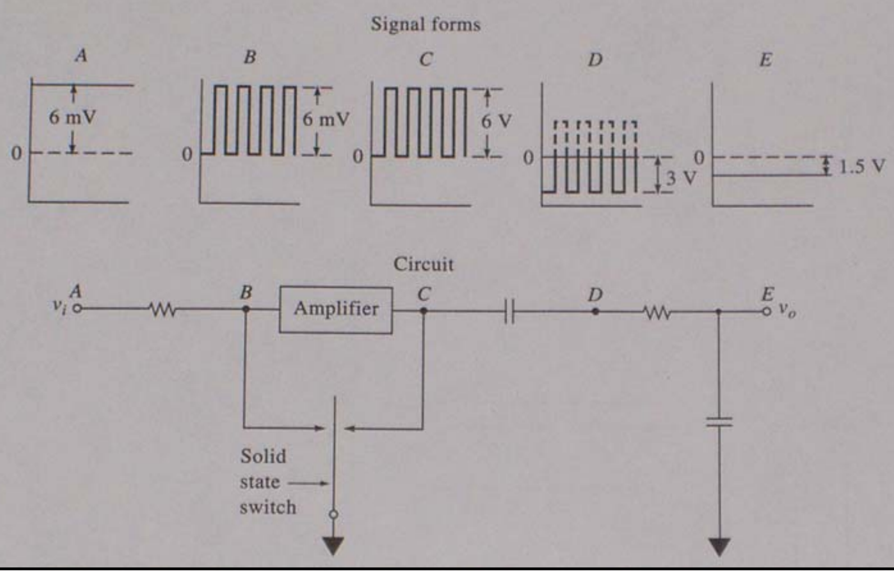


Signal chopping in an IR spectrophotometer



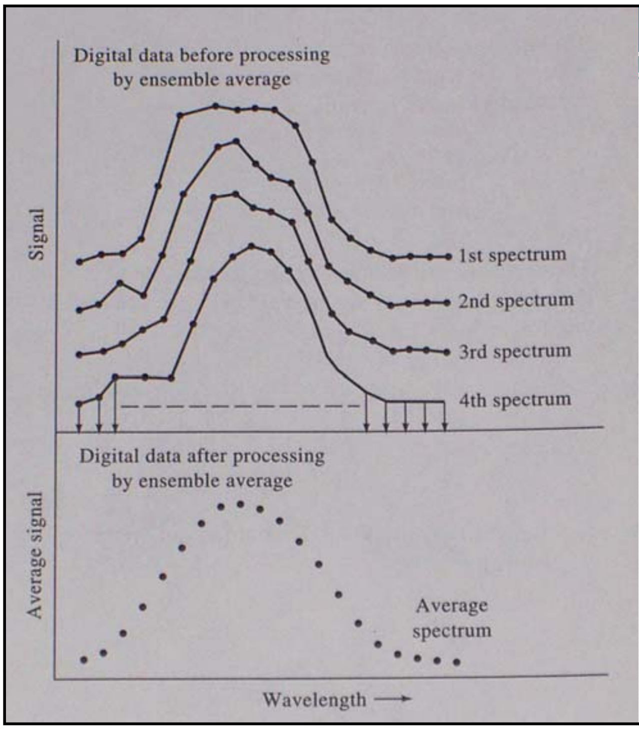


Chopper amplifier

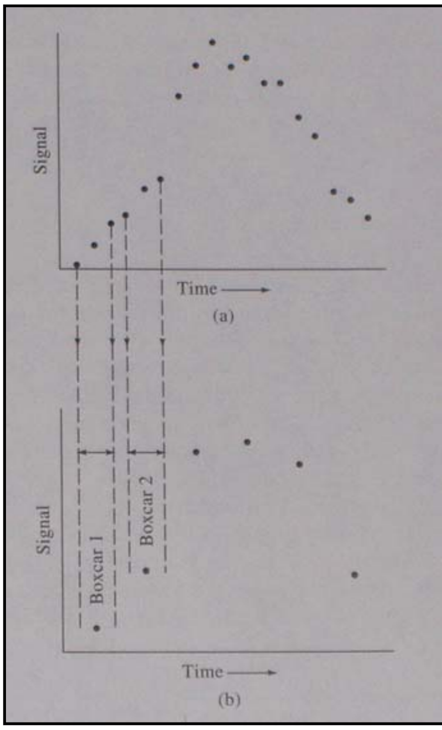


Improving S/N
hardware & software

- 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