Chemistry 4631

Instrumental Analysis

Lecture Noise

Optical Instruments

Instrumental Noise

Uncertainties in the measurement of transmission and concentration give measurable standard deviations.

Where does this uncertainty in measurement come from?

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Noise

% error in a signal becomes larger as the signal becomes smaller.

Signal-to-noise (S/N) = mean/std. dev.

General rule S/N > 3 to consider as reliable data

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Chemical Noise

Typically from changes in variables (not part of the measured data) during the experiment,

i.e. changes in pressure, T, humidity; vibrations; outside light or electronic signals (environmental); changes in atmosphere; etc…

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Environmental Noise

Components in the instrument can act like an antenna to pick up electromagnetic energy in the environment and convert it to an electrical signal.

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Environmental Noise

Can reduce by shielding, grounding, or destructive interference.

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Instrumental Noise

Electrical or mechanical noise associated with a component in the instrument.

Sources:

- $s_T = k_1$
- $s_T = k_2 (T^2 + T)^{1/2}$
- $s_T = k_3 T$

(s_T – standard deviation of transmittance measurement)

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Instrumental Noise

Thermal or Johnson noise

$s_T = k_1$

Encountered with less expensive equipment and readouts with limited resolution.

Random noise.

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Instrumental Noise

$$s_T = k_1$$

Also for IR equipment, due to Johnson noise (thermal noise) in the detector.

Johnson noise is caused by thermal agitation of electrons or carriers in resistors, capacitors, transducers, etc.. This creates voltage fluctuations.

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Instrumental Noise

$$s_T = k_1$$

How to minimize?

-keep instrument cool

-reduce frequency or response time in circuits, i.e. the slower the response to a signal, the lower the thermal noise

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Instrumental Noise

$$s_T = k_2 \, (T^2 + T)^{½}$$

Limits precision of high quality instruments.

Due to shot noise (random noise)

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Instrumental Noise

$$s_T = k_2 (T^2 + T)^{1/2}$$

Shot noise

When electrons or charge particles cross a junction such as at pn interfaces or movement of electrons from a cathode to an anode in a PMT.

Can minimize by slowing the response of the circuit.

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Instrumental Noise

$$s_T = k_3 T$$

From a slow drift in radiant output of the source called source flicker noise (or 1/f noise).

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Instrumental Noise

$$s_T = k_3 T$$

Flicker noise is inversely proportional to the frequency of the signal.

Becomes significant at frequencies below 100 Hz.

Shows up as long-term drift.

Minimized by good voltage power supplies or a split beam arrangement.

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TABLE 13-3 Types and Sources of Uncertainties in Transmittance Measurements

Category	Characterized by[a]	Typical Sources	Likely To Be Important In
Case I	$s_T = k_1$	Limited readout resolution	Inexpensive photometers and spectrophotometers having small meters or digital displays
		Heat detector Johnson noise	IR and near-IR spectrophotometers and photometers
		Dark current and amplifier noise	Regions where source intensity and detector sensitivity are low
Case II	$s_T = k_2\sqrt{T^2 + T}$	Photon detector shot noise	High-quality UV-visible spectrophotometers
Case III	$s_T = k_3T$	Cell positioning uncertainties	High-quality UV-visible and IR spectrophotometers
		Source flicker	Inexpensive photometers and spectrophotometers

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Noise Reduction

Electronics can be designed to address noise problems.

Filters – used to exclude unwanted bandwidths. Filters can be designed to exclude:

-high frequencies (since those can carry noise) LPF (low pass filter)

-low frequencies HPF (high pass filter)

-unwanted noise or frequencies around a narrow bandwidth (band stop or notch filter) or the inverse the signal is contained in a narrow frequency BPF (band pass filter)

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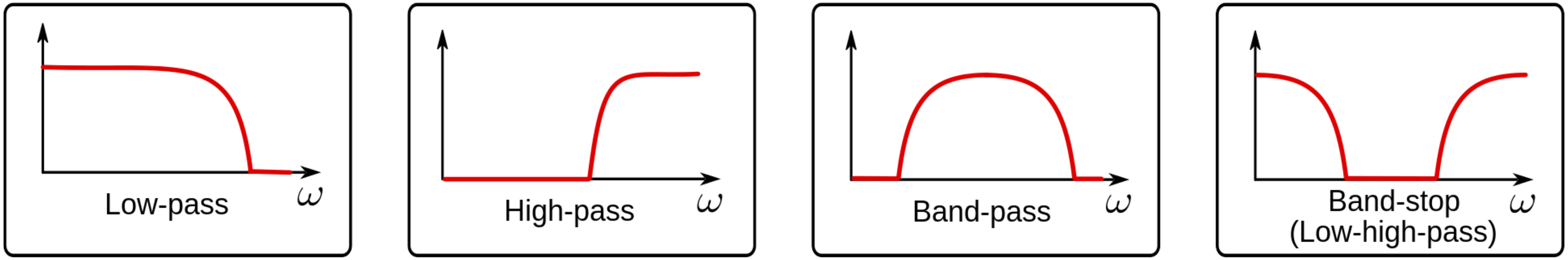
Noise Reduction

Electronics can be designed to address noise problems.

Filters



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Noise Reduction

Software methods can be used to minimize noise.

For example:

- ensemble averaging – adding signals from successive runs. To double S/N take 4x # of points.

- boxcar averaging – digital method to smooth out noise. Assumes average of several points is better representation than any signal point. Take between 2 – 50 points and average together to replace a point. Disadvantages – lose some detail, does not work for rapidly changing signals.

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Instrumental Noise

Software methods can be used to minimize noise.

For example:

- Fourier transform
    - -acquire data in time domain (as a function of time),
    - -do FT to change to frequency domain (signal is usually low frequency – changes slowly and noise changes quickly – has high frequency),
    - -keep only the low frequency components, zero out high frequency, inverse FT to get back data.

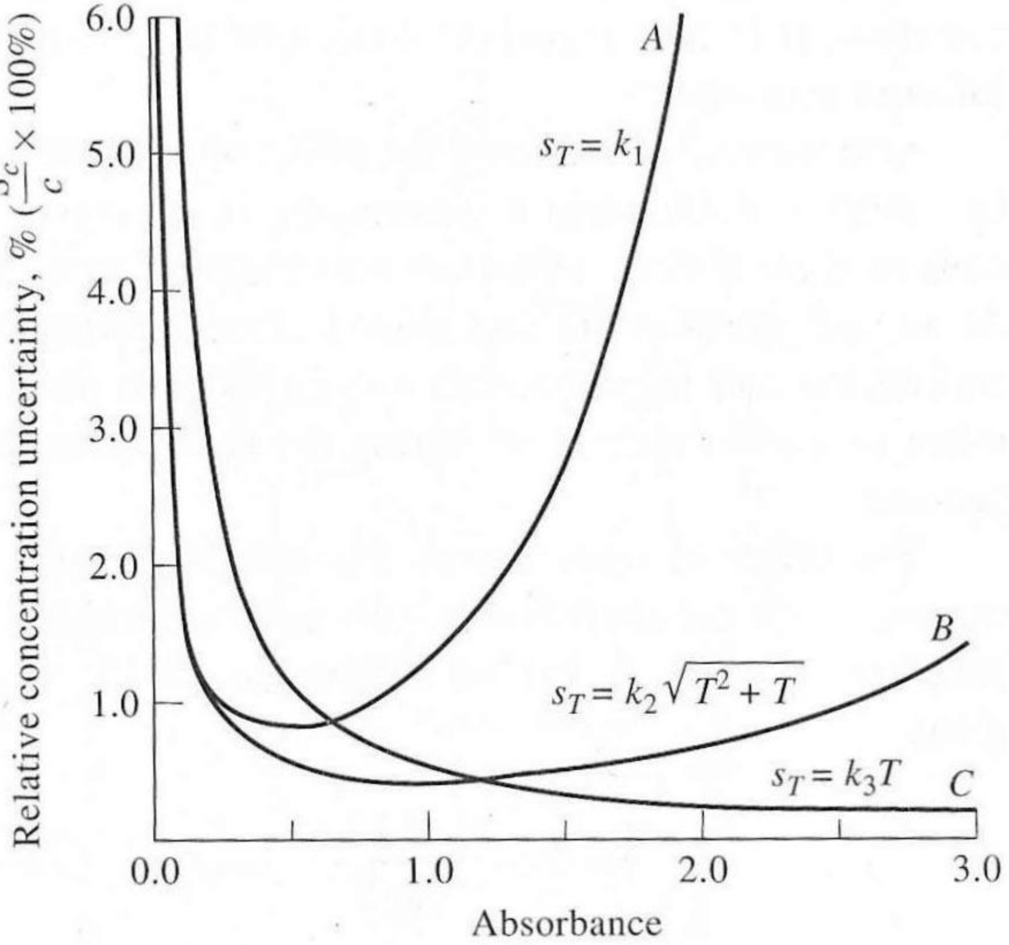

Figure 13-7 Relative concentration uncertainties arising from various categories of instrumental noise: *A*, Case I; *B*, Case II; *C*, Case III. The data are taken from Table 13-4.

Assignment