Introduction; Signals and Noise

Chem 221

Instrumental Analysis

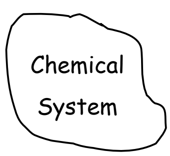
Spring 2005

What is Analytical Chemistry?

- "Analytical chemistry is what analytical chemists DO!"
- "The study of methods for determining the composition of substances."
- <u>Two areas:</u>
  1) ***Quali****tative* Analysis (*what?)*
  2) ***Quanti****tative* Analysis (*how much?)*

The Chemical System

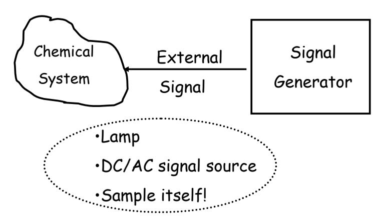
First, we need something to study:



- <u>Can be *anything:*</u>
  - Coal
  - Blood
  - Gas
  - Food
  - Reaction mixture

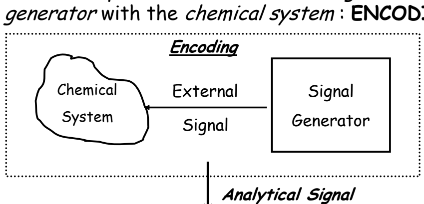
The Signal Generator

- Interacts with the *Chemical System* to produce an *Analytical Signal:*



The Analytical Signal

- Produced by the interaction of the *signal generator* with the *chemical system* : **ENCODING**



Analytical Signal
- EMR (optical spectroscopy)
- Electrons (echem, e^- spec)
- Chemical Species (separations)

Decoding the Analytical Signal

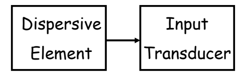
- How do we decipher the *chemical information* encoded in the *analytical signal* ?
- <u>**Four Steps:**</u>
  1. ***Disperse*** the analytical signal (selectivity)
  2. ***Convert*** to an *electrical* signal
  3. ***Process*** the electrical signal
  4. ***Output*** the resultant signal

Dispersive Element

- Enables the *selective* measurement of the analytical signal
- **Examples:**
  - ✓ *Monochromator* (optical spectroscopy)
  - ✓ *Magnetic Field* (mass spectrometry)
  - ✓ *Chromatographic Column* (separations)

Input Transducer

- Converts the *analytical signal* to an *electrical signal:*

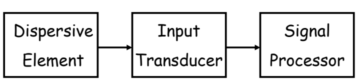


Examples:

- **·Photomultiplier tube (PMT)** (photons → electrons)
- **·Electrode** (chem potential → electrical potential)

Signal Processor

- *Buffers* input and output transducers (*impedance matching)*

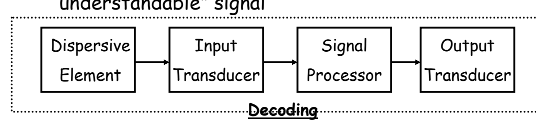


Examples:

- ·Amplification
- ·Current-to-voltage conversion
- ·AC-to-DC conversion
- ·Modulation/waveshaping
- ·ADC and/or DAC
- ·Math (log, FT, integration)

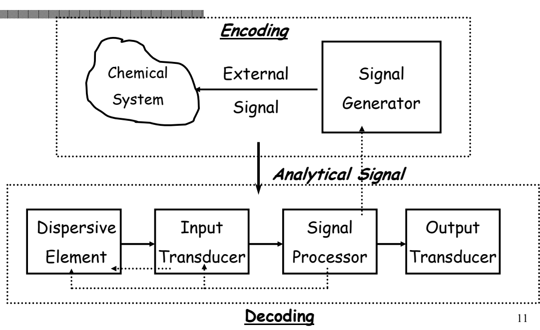
Output Transducer

- Converts electrical signal into a "human-understandable" signal

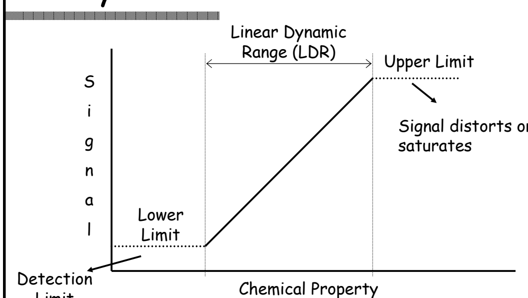


- ·Most often, a computer
- ·Also does much of the signal processing

The *General* Instrument



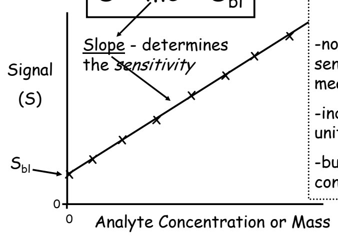
Quantitative Properties of Analytical Instrumentation



The Analytical Curve

$S = mC + S_{bl}$

Slope - determines the *sensitivity*



Analytical Sensitivity:

$\gamma = \mathbf{m}/\sigma_s$

-normalizes the sensitivity based on the measurement precision

-independent of signal units or gain

-but, can also vary with concentration or mass

Detectability

- **Bottom Line Question:**
  Is the Analytical Signal distinguishable from the Blank?
- Example: **Pb analysis**

Concentration	Signal	NET Signal
0 ppm (blank)	0.136	0.000
10. ppm	0.721	0.585
1.0 ppm	0.195	0.059
0.10 ppm	0.142	0.006
0.010 ppm	0.137	0.001

We need to know the *uncertainty* of the measurements.

Std Deviation (σ) *(NOISE)*

Which of these are detectable?

Defining the Detection Limit

- We use the *Signal-to-Noise Ratio* (S/N) as the defining figure of merit.
- Most commonly accepted definition:

  The detection limit is the concentration of analyte needed to produce a **S/N = 3**

- Where: S = signal due to analyte
  N = σ_{blank}

Signal different from blank at about 89% confidence level

So, Det. Limit occurs when $\mathbf{S = 3\ \sigma_{blank}}$

Finding the Detection Limit

- BUT: recall that the signal that is measured *includes* the blank (S_{blank}), so we define:

  S_m = signal *measured* at the det. Limit

So: $$\frac{S_m - S_{blank}}{\sigma_{blank}} = 3$$

REMEMBER: It is not the *magnitude* of the blank (S_{blank}) that limits detection -- rather, it is the ***fluctuation*** or ***uncertainty*** of the blank (σ_{blank}) that limits detectability.

Back to our example

Concentration	Signal	NET Signal
0 ppm (blank)	0.136	0.000
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1.0 ppm	0.195	0.059
0.10 ppm	0.142	0.006
0.010 ppm	0.137	0.001

Suppose that:

$\sigma_{blank} = 0.002$

$S = 3\ \sigma_{blank} = 3\ (0.002) = 0.006$

So: $S_m = S_{blank} + S = 0.136 + 0.006 = \mathbf{0.142}$

(0.10 ppm Pb)

Noise

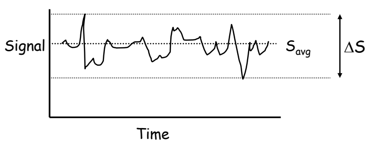
- **What is it?**
  -any "unwanted" part of the analytical signal
  -there is *always* some noise in a signal!
- **How can we *reduce* it?**
  Simple: -turn down the amplifier gain!
- **How can we *increase S/N?***
  Warning! There are *hidden costs* associated with S/N enhancement:
  -decreased resolution (selectivity)
  -increased measurement time
  -NEW sources of noise!

Calculating S/N

- <u>For a set of data (replicate measurements):</u>

$$S/N = S_{avg} / \sigma_s = (RSD)^{-1}$$

- <u>For a temporally-varying signal:</u>



$\Delta S \approx 5\sigma = 5N$

<u>So</u>: $N \approx \Delta S/5$

<u>Thus:</u>

$S/N \approx 5S_{avg}/\Delta S$

Noise Sources

- We'll characterize by their *frequency response*

1. **<u>White Noise</u>** - *amplitude invariant with respect to frequency*

Two types:

- **<u>Johnson (Thermal) Noise</u>**

-voltage fluctuations due to random e^- motion in resistive devices

$$V_{rms} = (4\,k\,T\,R\,\Delta f)^{1/2}$$

Boltzmann's Constant; Absolute Temp; Resistance; Frequency Bandwidth

More White Noise

- **<u>Shot Noise</u>**

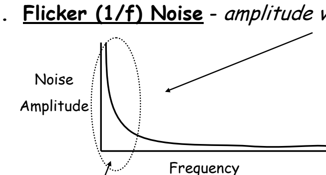
-current fluctuations due to random motion of e^- across a junction

$$i_{rms} = (2\,i_{avg}\,e\,\Delta f)^{1/2}$$

Average Current; Charge on an electron; Frequency Bandwidth

More Noise

2. **<u>Flicker (1/f) Noise</u>** - *amplitude varies with 1/f*



Most significant at low (<100 Hz) frequencies

<u>What is it?</u>

-drift

-*low freq.* signal fluctuations

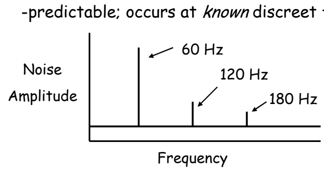
Still More Noise!

3. **<u>Environmental Noise</u>**

Two types:

- <u>Interference Noise</u>

-predictable; occurs at *known* discreet frequencies



<u>Example:</u>
AC "hum" from power-line

More Environmental Noise

- **<u>Impulse Noise</u>**

-erratic and unpredictable

-*difficult to find source*

-motors

-solar flares

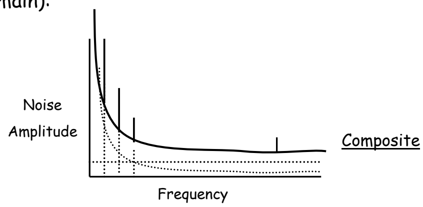
-computers

-temperature variations

-difficult to correct!

Composite Noise Spectrum

- In order to understand S/N enhancement, need to look at ALL noise sources together (in frequency domain):



Strategies for Increasing S/N

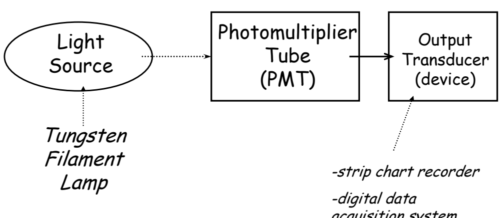
- White Noise: *reduce* Δf, temp, resistance, i_{avg}
- Flicker Noise: *make measurements at frequencies >100 Hz*

BUT:

- Signal: -often at or near dc (low freq.)
  - -often directly proportional to resistance
  - -often directly proportional to current
  - -often measured with transducers having very LARGE Δf

Hypothetical Instrument

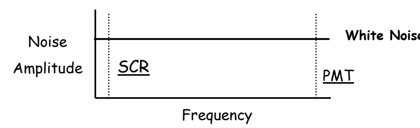
- Let's explore the signal and noise behavior of a simple light measurement instrument:



Reducing Δf

- Look at *frequency response* of instrument components:

PMT: 10^7 Hz
SCR: 10^0 Hz
DDA: 10^0 - 10^7 Hz (variable)



S/N Enhancement: Impact of Δf

- Output device/transducer limts Δf:

$$\frac{S/N\ (\Delta f = 10^0)}{S/N\ (\Delta f = 10^7)} \approx 10^3$$

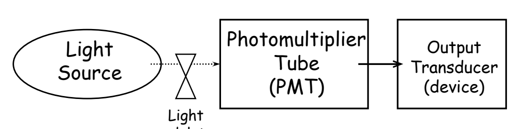
- Δf can be easily adjusted using a *low-pass* frequency filter
- BUT: remember that Δf also affects ability to measure the signal (at f_o); $f_o > 0$

So, object is to keep Δf to a *minimum*, **without reducing the SIGNAL**

Reducing 1/f Noise

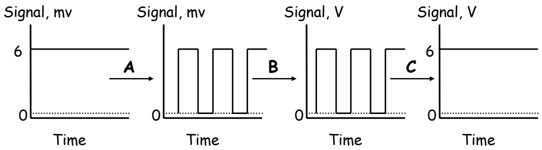
- We need to *move* $\mathbf{f_o}$ to >100 Hz . . . ***HOW?***

→ **MODULATE** the source
-analytical signal "encoded" at a freq. where 1/f noise is negligible



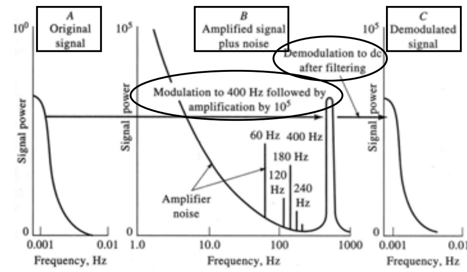
Tuned Amplification: *Chopper Amplifiers*

- If we *amplify* the signal **at the modulation frequency**, then we can also *increase the signal* while we *reduce the noise:*



A: *modulate* **B**: *amplify* **C**: *demodulate*

Chopper Amplifiers: In the Frequency Domain



Lock-In Amplification

- Tuned (chopper) amplification is limited by stability of f_o reference

  -this limits the effective Δf to about 1 Hz

- *Lock-in* amplification tunes the amplifier to *both* f_o as well as the **phase** of the signal

  -results in an effective reduction of Δf to about 0.01 Hz

Signal Averaging

- Need a *repeatable* signal (time domain method)
- Sum digitally-stored replicate signals
- How does this improve S/N?

  Signal: increases *linearly* with number (n) of replicate signals

  Noise: increases as $(n)^{1/2}$

  So, **S/N** increases as $\mathbf{(n)}^{1/2}$

Signal Averaging: Example

- Suppose we wish to *mass* a **10-mg** object on an analytical balance (σ *= 0.1 mg*)

For a single (n =1) measurement:
S = 10. mg, N = 0.1 mg → **S/N** = ***100***

For n = 4:
S = *n x 10. mg* = 4 x 10. mg = *40. mg*
N = $\sigma_T = (n(\sigma)^2)^{1/2} = (4(0.1)^2)^{1/2} = 2(0.1) = 0.2$ *mg*
S/N = 40./0.2 = ***200***

For n = 16: **S/N** = ***400***

Signal Averaging: General

- In general, we can say:

$$(S/N)_n = (n)^{1/2}\,(S/N)_{n=1}$$

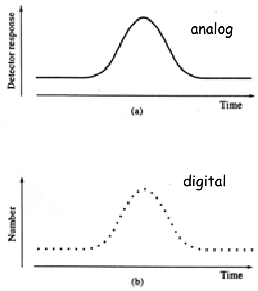
•Diminishing returns:

Suppose, it takes 1 second per measurement?

S/N	n	Time
3	1	1 sec
6	4	4 sec
30	100	100 sec
300	10,000	2.8 ***hours***
3000	1,000,000	11.6 ***days***

More Signal Averaging

- **Signal must be digitized . . .** *How?*
- **Digitization frequency?**
  - *-Nyquist Theorem*
- **Precision of digitization?**
  - *- how many bits?*
  - 8-bit = 2^8 = *256* (0.4 %)
  - 12-bit = 2^{12} = *4096* (0.02 %)

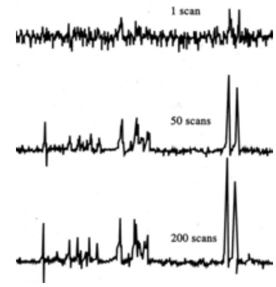


Signal Averaging a Spectrum

•*Get same S/N enhancement:*

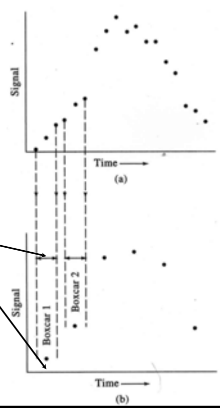
-incr. with $n^{1/2}$

•Need good *synchronization* for each replicate scan



Boxcar Averaging

- **Just a *single-channel* signal averager:**
  - -select a single *delay time*
  - -integrate signal over selected *time gate*
  - -average signal for *n-replicates*
  - *-repeat at new delay time*
- **Gives S/N incr. with $n^{1/2}$ for *each data point***

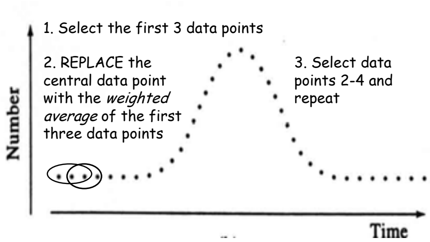


Digital Filtering

- ***Can manipulate digitized signals to improve S/N***
  - -can do this ***after*** data collection
  - -don't need a repetitive signal
- **Two methods we'll consider:**
  - -*Savitsky-Golay Smoothing* (time domain)
  - -*Fourier Filtering* (frequency domain)

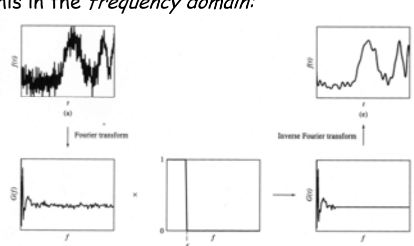
Savitsky-Golay Smoothing

- A *weighted moving average* applied to a series of data. **EXAMPLE: *3-point smooth***



Fourier Filter/Smooth

- We would have greater *control* if we were to do this in the *frequency domain:*



Beware!

- <u>It is easy to *smooth/filter* **signal** as well as noise</u>
  -overlay original and processed waveforms
  -make sure that result is not ***distorted***

- <u>Need high point density</u>
  -trade-off between *resolution* and <u>noise</u>
  (high point density = greater Δf)

  -trade-off between *resolution* and **time**
  (lotsa data points = incr. storage and processing time)