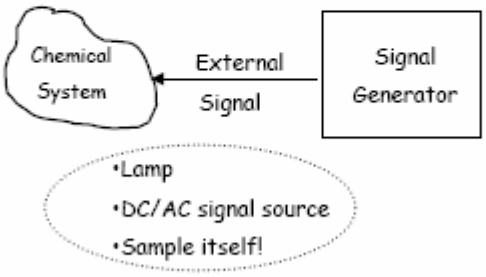
The Signal Generator

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



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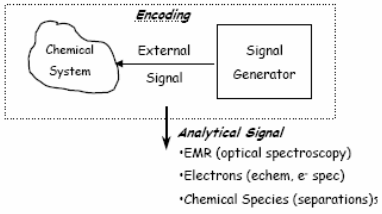
The Analytical Signal

- 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* ?

- **Four Steps:**
  1. ***Disperse*** the analytical signal (selectivity)
  2. ***Convert*** to an *electrical* signal
  3. ***Process*** the electrical signal
  4. ***Output*** the resultant signal

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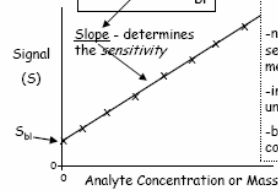
The Analytical Curve

$S = mC + S_{bl}$

Slope - determines the *sensitivity*



Analytical Sensitivity:

$\gamma = m/\sigma_s$

-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 **$S = 3\ \sigma_{blank}$**

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

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
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

Suppose that:
$\sigma_{blank} = 0.002$

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

So: $S_m = S_{blank} + S = 0.136 + 0.006 = 0.142$
(0.10 ppm Pb)

Noise

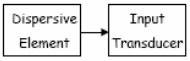
- **What is it?**
  -any "unwanted" part of the analytical signal
  -there is *always* some noise in a signal!
- **How can we *reduce* it?**
  Simple: -turn down the amplifier gain!
- **How can we *increase S/N?***
  Warning! There are *hidden costs* associated with S/N enhancement:
  -decreased resolution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

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:*

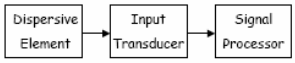


Examples:

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

Signal Processor

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

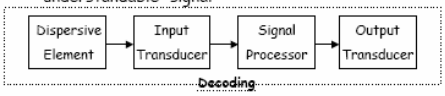


Examples:

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

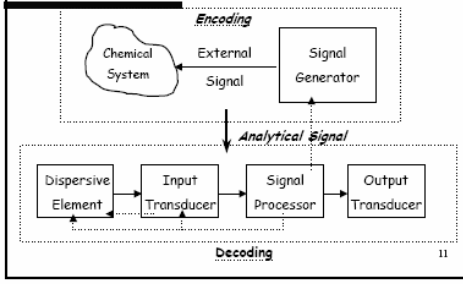
Output Transducer

- 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