January 20, 2012

- Thanks for the emails – still waiting for some . . .
- **REMINDER:** 1st problem set/reading assignments are posted!
- **Office Hours:** will be posted by Monday

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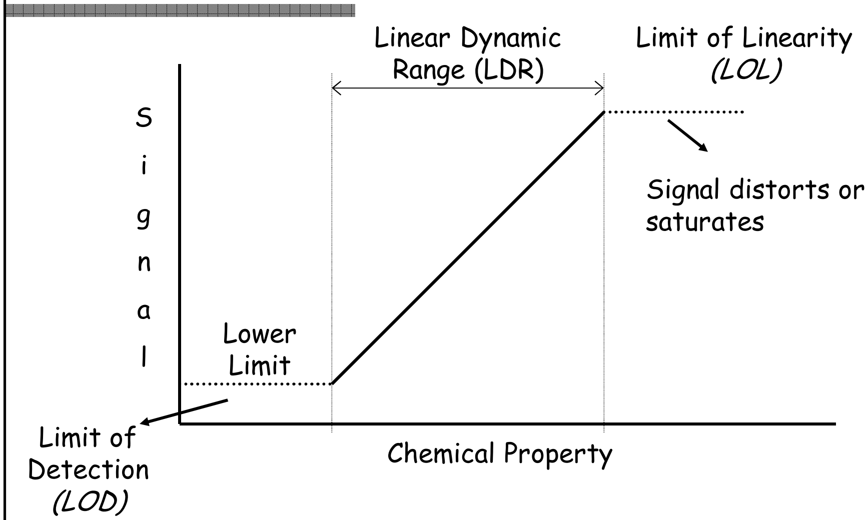
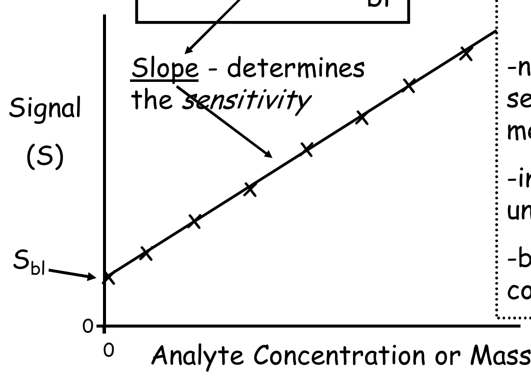
Quantitative Properties of Analytical Instrumentation



2

The Analytical Curve

$S = mC + S_{bl}$



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

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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?

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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 σ_{blank}**

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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.

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Back to our example

Concentration	Signal	NET Signal
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0.010 ppm	0.137	0.001

Suppose that:

σ_{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)

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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!

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Calculating S/N

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

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

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