ΣΗΜΕΙΩΣΕΙΣ ΔΙΑΤΑΞΕΩΝ ΦΑΣΜΑΤΟΣΚΟΠΙΑΣ

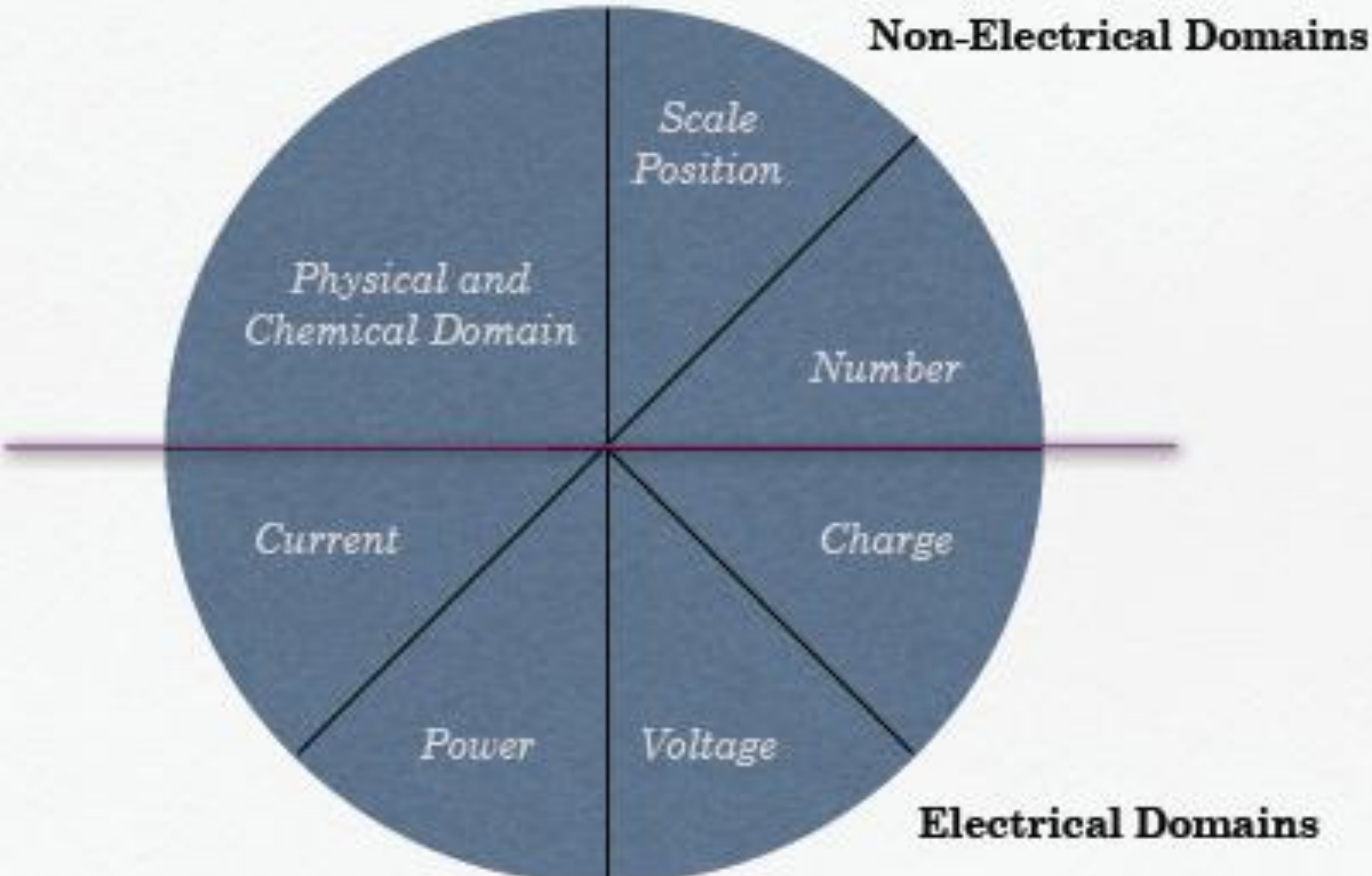
The Analysis Concept

- What is it?
- How much is there?
- How does it behave?

An Instrument

- Controls the applied probe
- Measures the system's response

Data Domains



Data Domain Conversion

- Analyst seeks to measure physical or chemical property of a system.
- Instrument creates an electrical signal to represent datum.
- Data proceeds through instrument; different transducers convert signal from one domain to another.
- Analysis of instrument behaviour: characterized as a sequence of data domain conversions, each analyzed separately.

Transducers

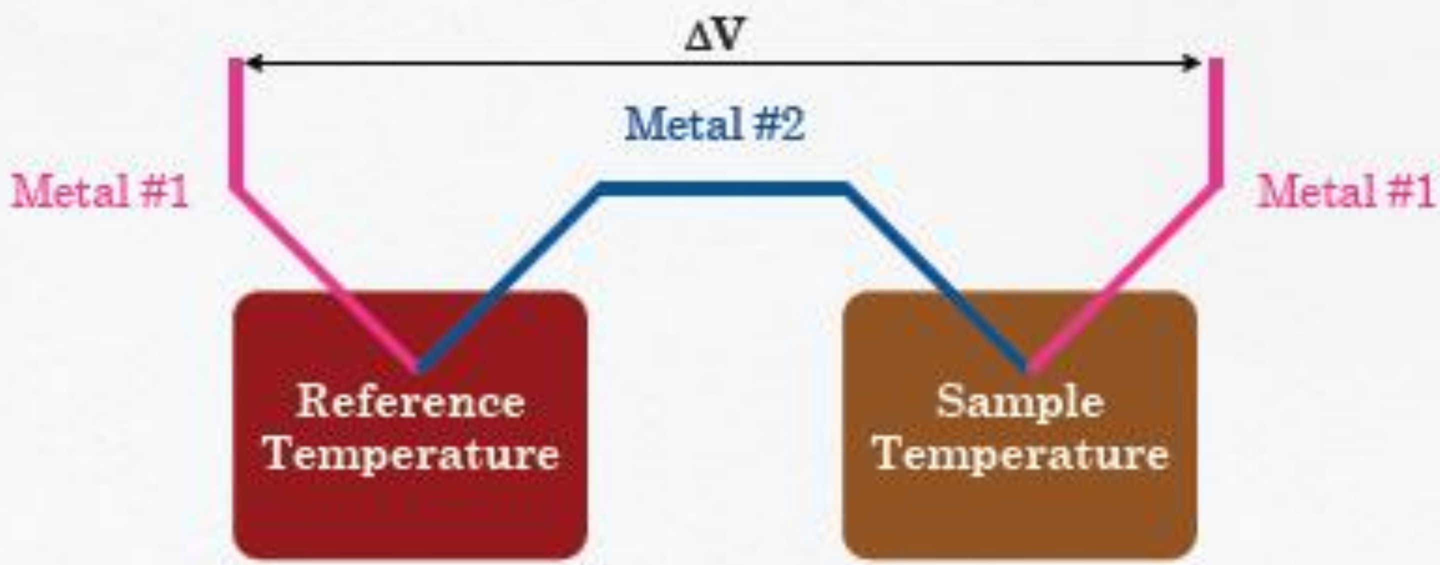
- Input Transducer: converts data from non-electrical to electrical domain.
- Output Transducer: converts data from electrical to non-electrical domain.

A thermocouple generates a specific voltage at a certain temperature. It is a temperature-to-voltage input transducer.

A stepper motor running a pen on a chart recorder moves the pen in response to a current flow. It is a current-to-position output transducer.

Example: The Thermocouple

- Temperature - to - Voltage transducer.
- Connect two dissimilar metals appropriately.
- Thermoelectric effect produces voltage difference which depends upon the temperature difference between the two junctions.



Thermocouple con't 1

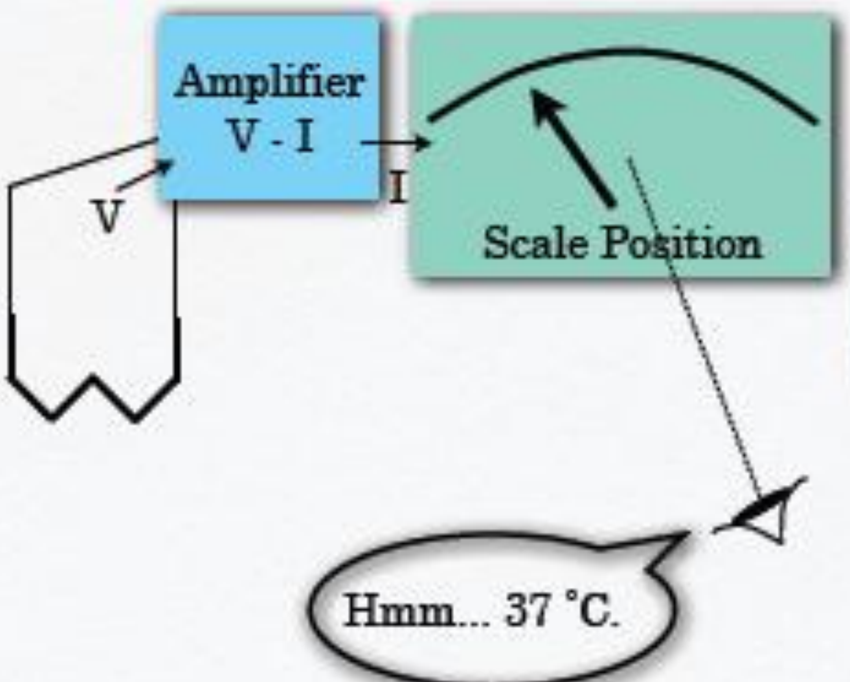
- Voltage depends on temperature difference (T_m - T_r). Relationship is called the transfer function.
- T_r is almost always 0 ˚C.
- Transfer is generally modeled as

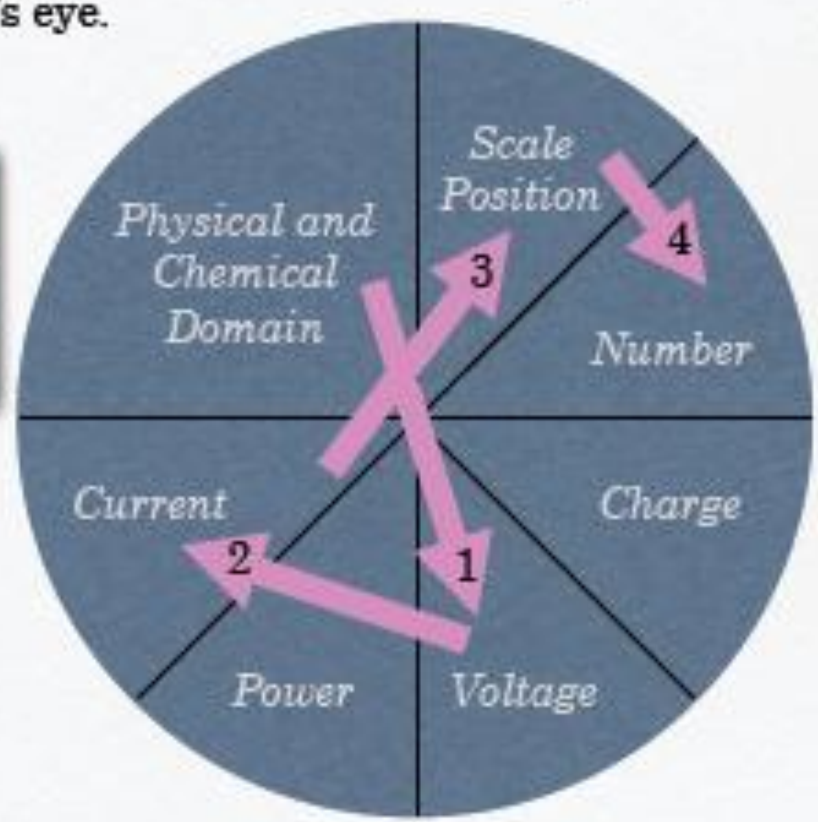
$$f(T_m - T_r) = A(T_m - T_r) + B(T_m - T_r)^2 + \frac{C}{(T_m - T_r)}$$

- B and C often ignored. Linear transfer function.
- Popular thermocouple called K-type (two metals are chromel and alumel). A = 4 x 10^{-5} V/˚C. (40 μV per degree Celsius).

Thermocouple con't 2

An instrument is created when the voltage of the thermocouple transducer is amplified and turned into a current which drives a meter dial to report the temperature as viewed by the analyst's eye.



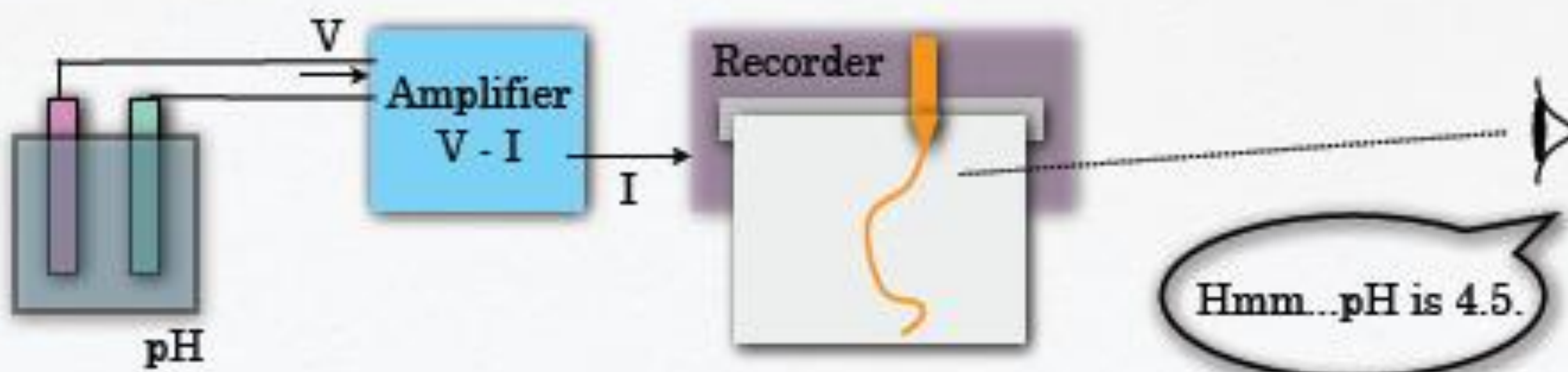


Convolution of Transfer Functions

- Each transducer has its own transfer function. The thermocouple has an almost linear function that relates output voltage for an input temperature: $V = f(T)$.
- The amplifier produces an output current for a given input voltage. $I = g(V)$. This is convolved to give $I = g(f(T))$.
- The meter needle will deflect a certain amount, depending upon the magnitude of the current. This is a new transfer function: $D = h(I)$ which gives the overall convolution to be $D = h(g(f(T)))$.
- In principle, the reading of the meter can depend upon the individual; a short person and a tall person may read the meter differently because of different parallax. The final number then is $N = k(D) = k(h(g(f(T))))$.

Example: pH Meter

- An instrument that can be used to record the hydrogen ion activity (pH) of a solution.
- First transducer is a pair of electrodes, one at a fixed pH; they produce a voltage difference.
- This is amplified and turned into a current.
- This current drives a pen displacement motor on a chart recorder, giving a record of pH as a function of chart position which is related to time.

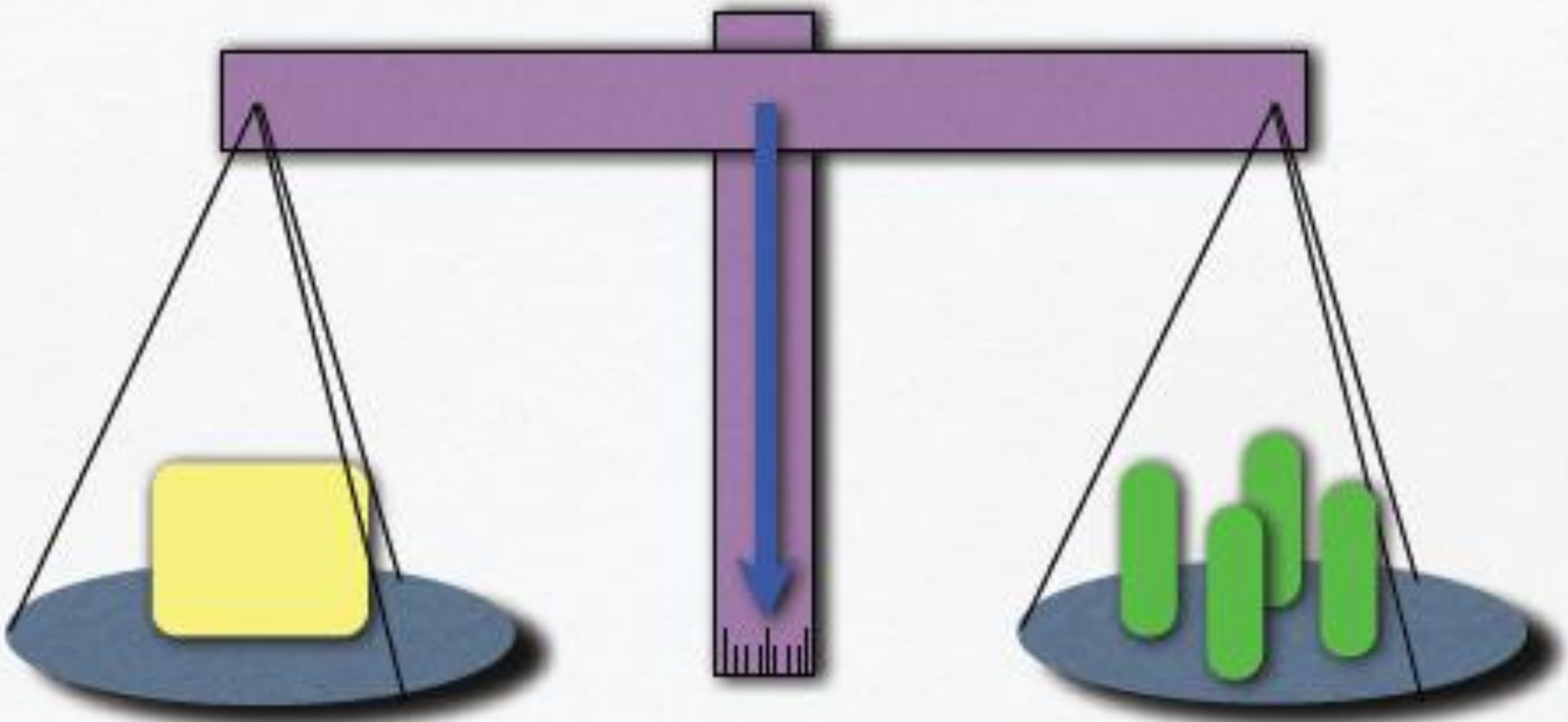


Reference Standards

- All measurement devices consist of
  - a difference detector
  - a reference standard

$$Signal = Q_{meas} - Q_{ref}$$

Example: Double Pan Balance



Unknown mass to be measured.

Difference Detector

System for adjusting a collection of standard masses.

Balance con’t 1

- Null Detector: Add reference masses until needle points to zero.
- Sensitivity: The size of the smallest reference mass.
- Precision: Also dictated by smallest mass.
- Accuracy: Masses are correctly calibrated, not worn or dirty. Balance pivots without resistance.
- Comparator: The magnitude of difference in null detector is not considered; only sign is needed to know which way to adjust masses.

Balance con't 2

- Top Loading Balance / Analytical Balance: Calibrated weights almost achieve null condition. Residual error is calibrated.
- Electronic Balance: Sometimes an electromagnet is used to push against the mass. CUrrent necessary to produce a null condition relates to mass. Or, strain gauge can be used to measure very small deflections. Again, must be calibrated for local gravity field.
- Bathroom Scales: Manufacturer calibrates the springs at the factory. Measure weight by markings on off-null detector.

Signal

- Signal: derived from the output of the difference detector.
- Background or Baseline: non-zero output even when there is no difference at the inputs.
- Drift: background varies slowly with time.

The analytical signal is the difference between the output amplitude and the expected baseline at the same moment in time.

Noise

- Unwanted periodic, random, or almost random time-dependent changes in the output signal.
- Measured in the same units as signal.
- Two common measures of noise are:
  - Peak-to-Peak
  - Root-Mean-Square (RMS)

Signal-to-Noise Ratio

- Measure the difference between the output and background.
- Blurred by the presence of noise.
- Measurability of quantity must account for both signal level and noise level.

Can report RMS S/N or peak-to-peak S/N. RMS most useful. For a set of discrete measurements, the S/N can be defined as the ratio of the mean to the standard deviation.

Performance Characteristic

Describes a general property of an analytical technique that permits comparisons so a user can evaluate its applicability in a given situation.

Precision *Accuracy*

Sensitivity *Selectivity*

Detection Limit *Quantitation Limit* *Linearity Limit*

Dynamic Range

Precision

- Mutual agreement of replicate measurements.
- Variation arises from random errors.
- Standard Deviation and Variance are most common measures of precision.
  - Repeatability: agreement between replicate measures taken by same analyst on same instrument on the same day. How good is the analyst?
  - Reproducibility: agreement between replicate measures taken by various analysts and various instruments over a long time. How robust is the technique?

Accuracy

- A measure of how close the measured response is to the true value of the quantity.
  - Instrumental: something is wrong with the instrument (batteries low, temperature effects, etc.)
  - Analyst: judgment errors, reading meter from wrong angle, lack of careful technique.
  - Method: the method itself is inherently inaccurate, non-ideal chemical behaviour, slow reactions, contaminants, instability of reagents. Use guaranteed standards.

Selectivity

- Each analysis looks for a signal that comes from a specific analyte.
- However, signal always has a contribution from everything present in the sample.
- Need to minimize contributions from other species or know their contribution from their selectivity coefficient.

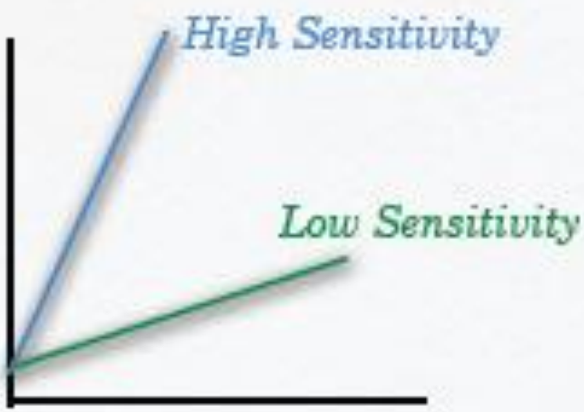
$$S_{total} = R\,a_i + R\sum k_{ij}\,a_j$$

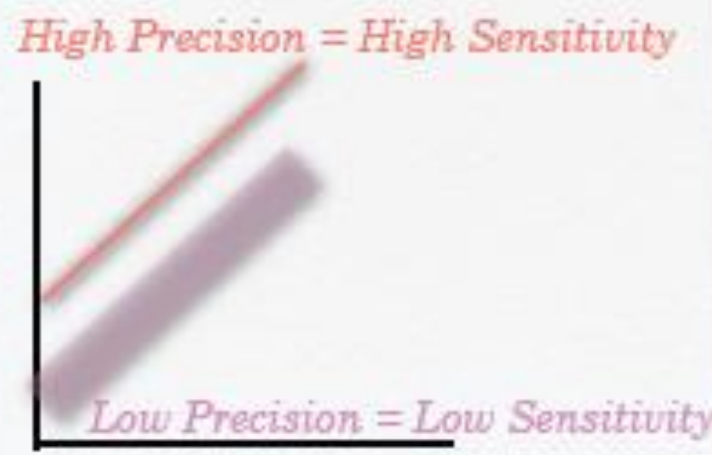
Signal of analyte

Signal of all other species interfering with i.

Sensitivity

- Technique's ability to detect changes in the signal property.
    - Slope of response curve.
    - Precision of Measurement.





Detection Limit

- The smallest amount of analyte that can be reliably detected.
- Depends upon signal-to-noise ratio.
- Analysis signal must be larger than the blank signal. How much larger?

$$S_{det} = S_{blank} + k\ s_{blank}$$

Minimum distinguishable analytical signal

Mean signal of blank

Standard deviation of blank

Usually taken to be 3.

Quantitation Limit

- Detection limit answers the question “Is the analyte present or not?”
- Quantitation requires a larger signal-to-noise level. Answers question “How much of the analyte is present?”

$$S_{quant} = S_{blank} + k\, s_{blank}$$

Minimum distinguishable analytical signal

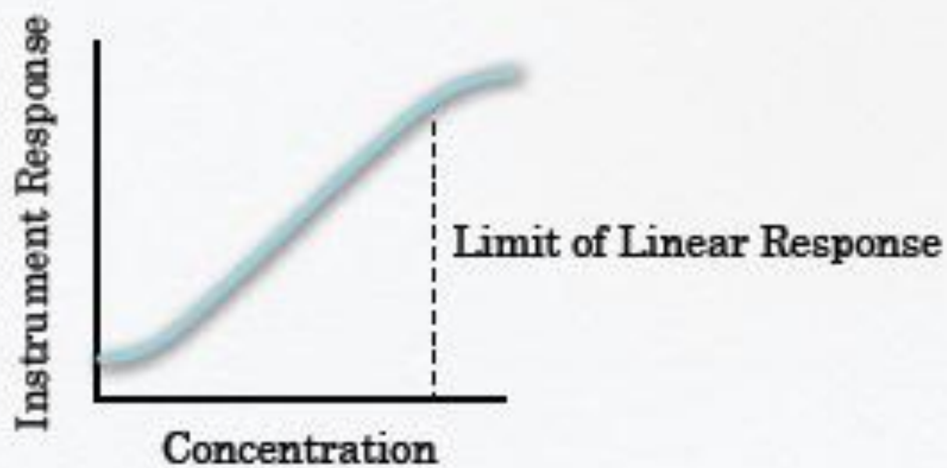
Mean signal of blank

Standard deviation of blank

Usually taken to be 10.

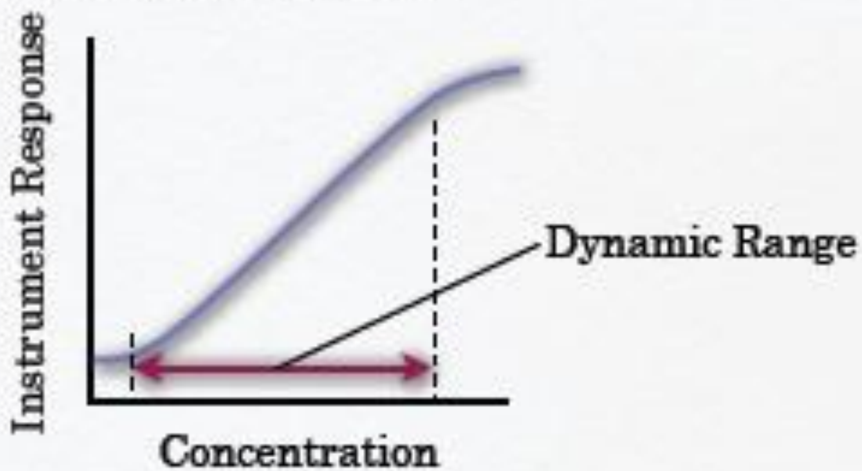
Linearity Limit

At the other end, as analyte concentration increases, every detector finally stops responding linearly. (Amplifier cannot produce a larger output, the balance arm bends or breaks, etc.)



Dynamic Range

The range of concentration between the limit of quantitation and the linearity limit; the range over which the technique is useful.



Worthwhile technique must have dynamic range of at least two orders of magnitude. Some techniques have 5 or six orders of magnitude.