CHEM*3440
Chemical Instrumentation

Topic 1
Concept of the Instrument

The Analysis Concept
- What is it?
- How much is there?
- How does it behave?

Sample for Analysis
Electrons, photons, atoms, molecules, ions, heat, ...

Probe
Heat, ions, molecules, atoms, photons, electrons, ...

An Instrument
- Controls the applied probe
- Measures the system’s response

Instrument
- Encodes Data
- Transformation

The Physical and Chemical Domain
The Analyst’s Domain

Data Domains
- Non-Electrical Domains
- Electrical Domains
- Physical and Chemical Domain
- Number
- Current
- Charge
- Scale Position
- Voltage
- Power
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.

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

- B and C often ignored. Linear transfer function.
- Popular thermocouple called K-type (two metals are chromel and alumel). \( A = 4 \times 10^{-5} \text{ V/˚C} \). (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

\[ \text{Signal} = Q_{\text{meas}} - Q_{\text{ref}} \]
**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
- 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

Sensitivity

Selectivity

Detection Limit

Quantitation Limit

Linearity Limit

Dynamic Range
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.

\[ S_{\text{total}} = R a_i + R \sum k_{ij} a_j \]

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?

\[ S_{\text{det}} = S_{\text{blank}} + k s_{\text{blank}} \]

Minimum distinguishable analytical signal  Mean signal of blank  Standard deviation of blank

Usually taken to be 3.

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**.

High Sensitivity  High Precision = High Sensitivity

Low Sensitivity  Low Precision = Low Sensitivity
**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?”

\[ S_{\text{quant}} = S_{\text{blank}} + k s_{\text{blank}} \]

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.