

Chapter 1

Read pp. 1-22

Problems 1,7,8,9 and 10

Analytical chemistry deals with methods for determining the chemical composition and quantity of matter (gas, liquid or solid): a measurement science.

Two types: classical (or so-called “wet” chemical methods) and instrumental methods.

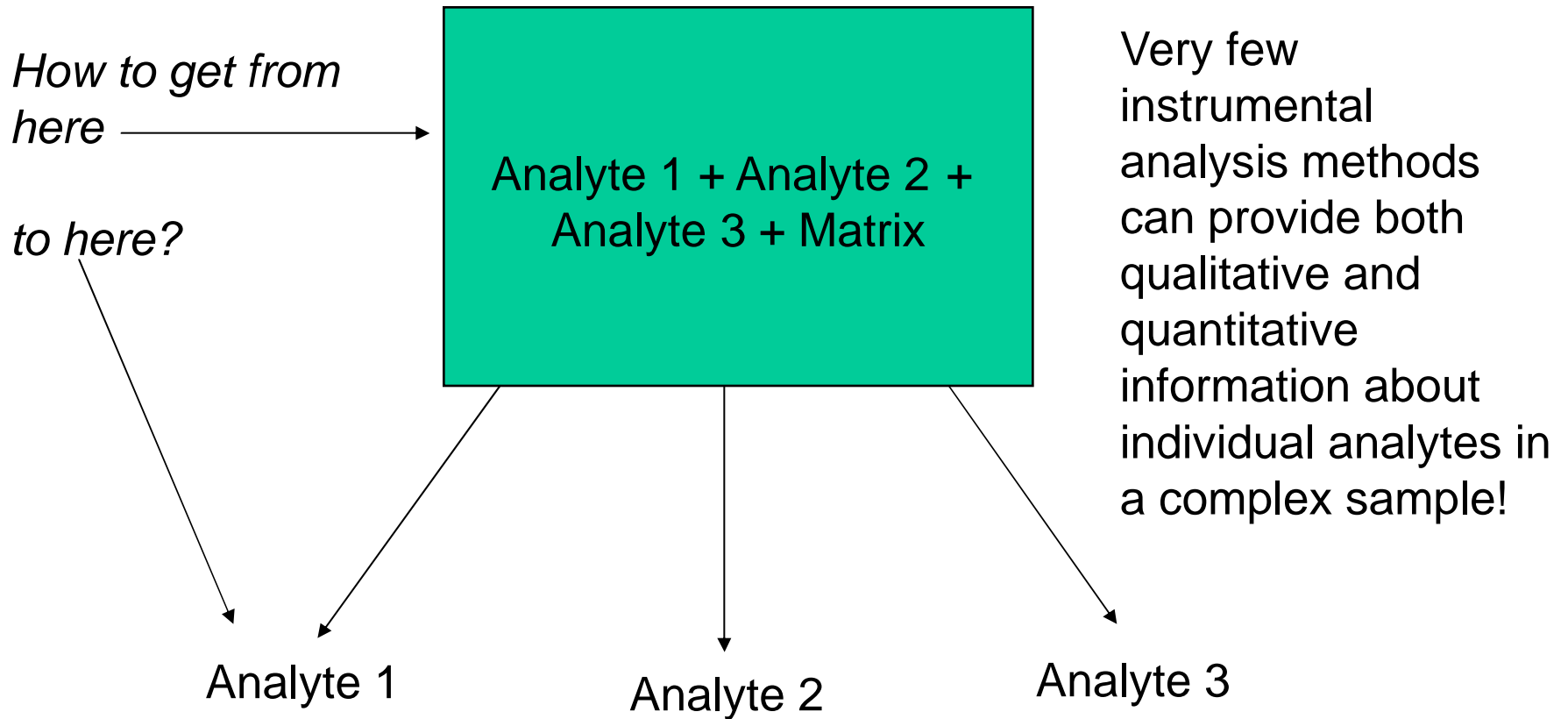
Qualitative analysis = information about the identity of atomic or molecular species. What is present in the sample?

Quantitative analysis = numerical information as to the relative amount (e.g., concentration of atomic or molecular species in a sample. How much is present in the sample?

- Classical methods include solubility tests, odors, optical activity, melting points, etc.
- Distillation, extraction and precipitation often used in classical methods to separate the analyte from the complex sample.
- Instrumental methods involve studying the physical and or chemical properties of analytes. Conductivity, electrode potential, light absorption or emission, mass-to-charge ratio are properties often probed.
- Highly efficient chromatographic (HPLC, GC) and electrophoretic methods used for analyte separation in modern day measurements prior to analyte detection.

Analyte + Matrix = Complex Sample

Complex Sample



Separation of sample components followed by **detection** is usually necessary!

Overall Process of an Instrumental Measurement

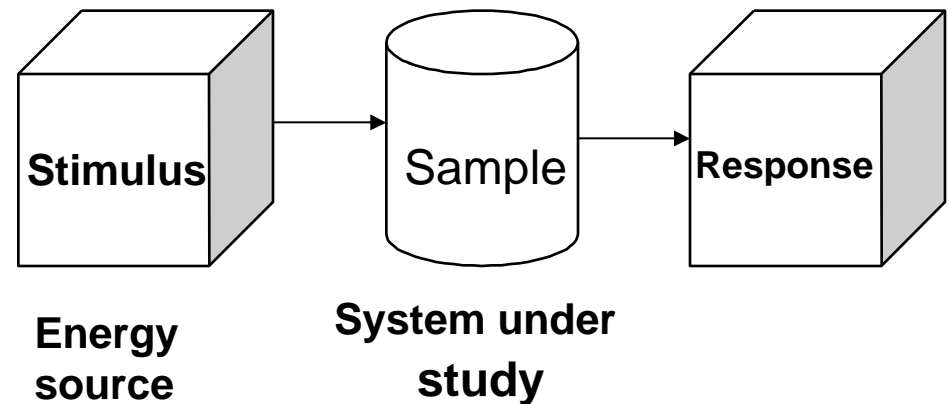
Absorption and emission of radiation ($h\nu$). [Ultraviolet/ visible and fluorescence spectroscopy of molecules, and atomic absorption and emission]

Vibrations of molecules.
[Infrared spectroscopy]

Electrical potential and current. [electrochemistry]

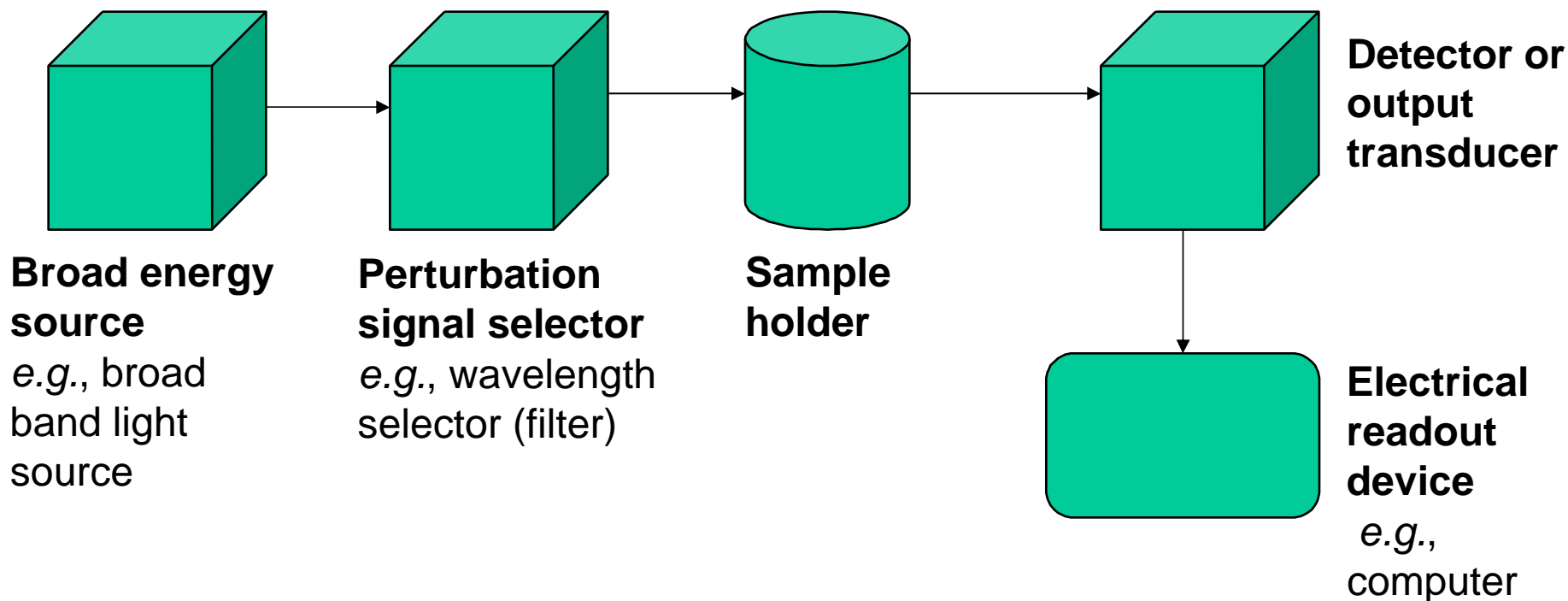
Mass-to-charge ratio. [mass spectrometry]

Separation science. [Gas chromatography, high performance liquid chromatography and electrophoretic methods]



Basic Design of an Instrument for Chemical Analysis

e.g., light absorption by a molecule



Data Domains

An instrument is a communication device between the “chemical system” and the user (usually some electrical signal).

- **Chemical system** = intensity of light, density, pressure, size, chemical composition, etc.
- **Analog signals** = electrical signals discrete or continuous in amplitude (current, voltage or charge).
- **Time Domain Signals** = frequency, pulse width, phase information stored in time domain.
(Susceptible to electrical noise)
- **Digital signals** = two-level scheme to represent electrical signals (Hi-Lo).

Defining the Problem

- What accuracy is required?
- How much sample is available?
- What is the concentration range of the analyte?
- What components of the sample will cause interference (matrix effect)?
- What are the physical and chemical properties of the sample?
- How many samples are to be analyzed?
- What information is desired – qualitative or quantitative?

Performance Characteristics –Analytical Figures of Merit

- **Precision** – absolute standard deviation, relative standard deviation or coefficient of variance (measure of the reproducibility of a measurement).
- **Bias** – absolute systematic error or relative systematic error (measure of the accuracy of a measurement).
- **Sensitivity** – calibration or analytical sensitivity (response magnitude change with concentration change).
- **Detection limit** – minimum amount detectable with a certain level of confidence.
- **Linear dynamic range** – concentration range over which a linearly changing instrumental response is observed.
- **Selectivity** – measure of how selective the instrumental response for one analyte is over another.

1. Precision (reproducibility)

$$s = \sqrt{\frac{\sum_{i=1}^N (X_i - \bar{X})^2}{N - 1}}$$

(absolute standard deviation)

X_i = value for each measurement

\bar{X} = mean or average of all measurements

N = number of measurements

$$RSD = \frac{s}{\bar{X}}$$

(relative standard deviation)

$$CV = \frac{s}{\bar{X}} \cdot 100\%$$

(coefficient of variance)

$$\bar{X} = \frac{\sum_{i=1}^N X_i}{N} \quad (\text{mean or average})$$

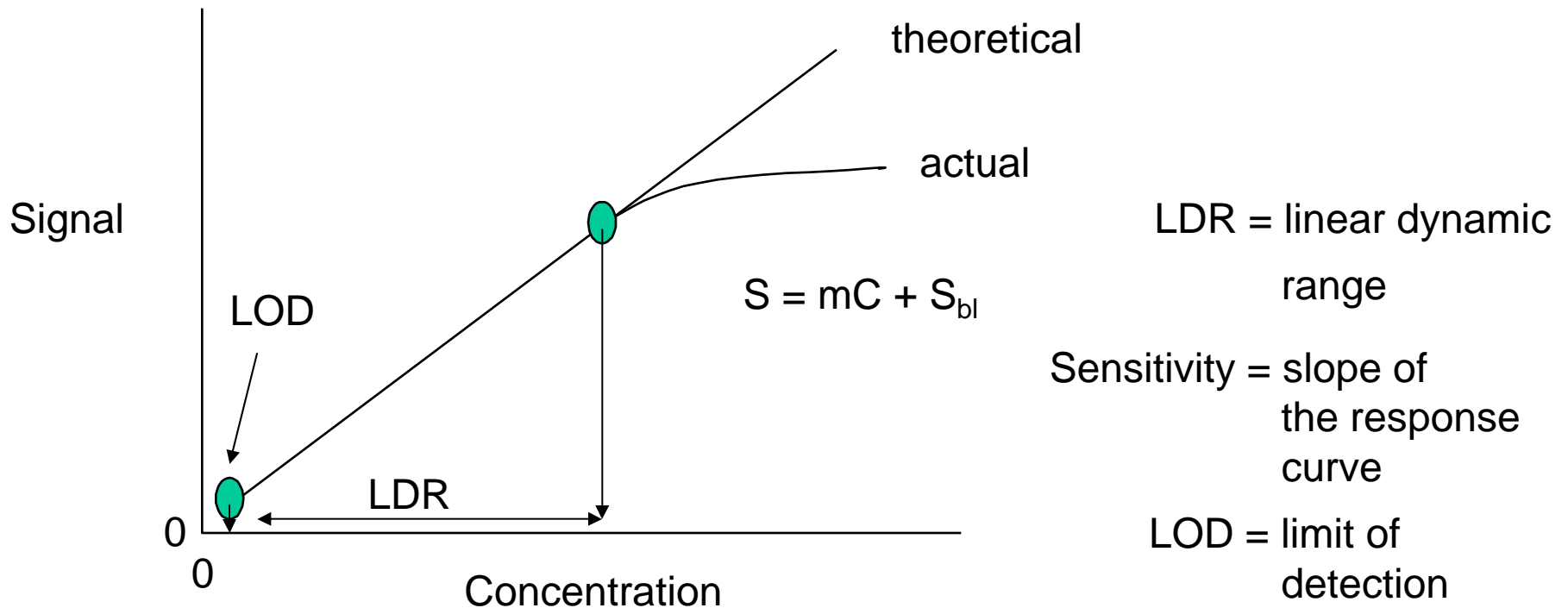
2. Bias (accuracy)

$$\text{bias} = \mu - x_t$$

μ = mean concentration of the sample

x_t = true concentration of a sample (a reference)

3. Sensitivity, Linear Dynamic Range and Limit of Detection



LOD = minimum concentration detectable for a given signal-to-noise ratio.

$$S_m = \bar{S}_{bl} + ks_{bl} \quad \begin{array}{l} \text{LOQ} \rightarrow k = 10 \\ \text{LOD} \rightarrow k = 3 \end{array}$$

LOD = magnitude of the analytical signal
magnitude of fluctuations in
the background

$$C_m = \frac{S_m - \bar{S}_{bl}}{m}$$

Every measurement is characterized by a signal for analyte and a background signal for the blank.

4. Selectivity

$$S = m_a C_a + m_b C_b + m_c C_c + S_{bl}$$

All instrumental methods require **calibration** and **validation**!

How does one relate an analytical signal, provided by an instrument, to the actual concentration of the analyte present in the sample??

Instrument Signal \longrightarrow Analyte Concentration

1. **Calibration Curves** (known concentrations of analyte prepared accurately in a controlled matrix).
2. **Standard Addition** (adding an increment of a standard to the sample solution – *spiking*. Particularly useful when matrix effects are significant).
3. **Internal Standard** (substance added in a constant amount to all samples, blanks and standards).