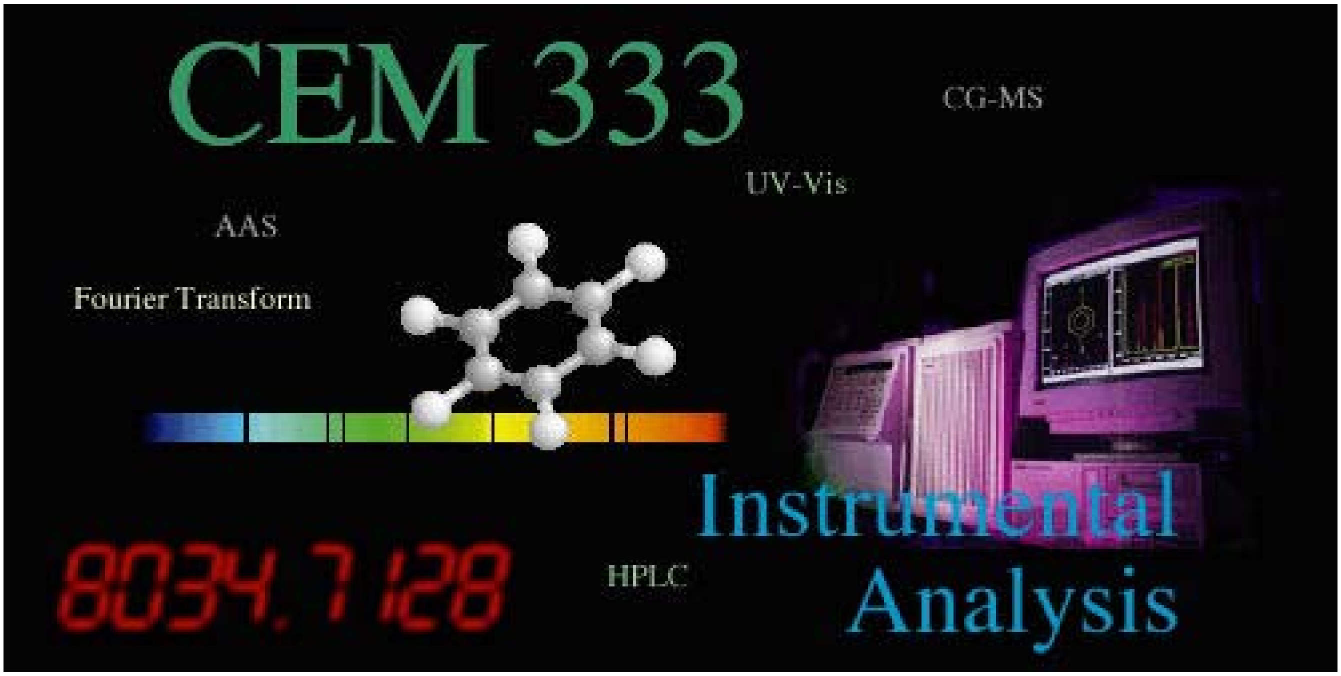
CEM 333

Instrumental Analysis



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Lectures: Tuesday, Thursday 9:00-9:50 am Room 136

Office Hours: Tuesdays 10:00-11:00 am

Course Objectives

Teach fundamentals of instrumental analysis

Lecture: Discuss theory and background for

(1) chemical/physical property measured

(2) origin of chemical/physical property

(3) instrument design and nature of response

(4) signal processing and relationship between readout to property measured

Laboratory: Provides hands-on experience in

(1) relating lecture material to practical analysis

(2) design and operation of a real instrument

(3) measurements on range of instruments

(4) example analyses to illustrate value of technique

Introduction (Chapter 1)

Classification of Analytical Methods

Qualitative instrumental analysis is that measured property indicates *presence* of analyte in matrix

Quantitative instrumental analysis is that magnitude of measured property is proportional to *concentration* of analyte in matrix

Species of interest

All constituents including analyte.
Matrix-analyte =concomitants

Often need pretreatment - chemical extraction, distillation, separation, precipitation

(A) Classical:

Qualitative - identification by color, indicators, boiling points, odors

Quantitative - mass or volume (e.g. gravimetric, volumetric)

(B) Instrumental:

Qualitative - chromatography, electrophoresis and identification by measuring physical property (e.g. spectroscopy, electrode potential)

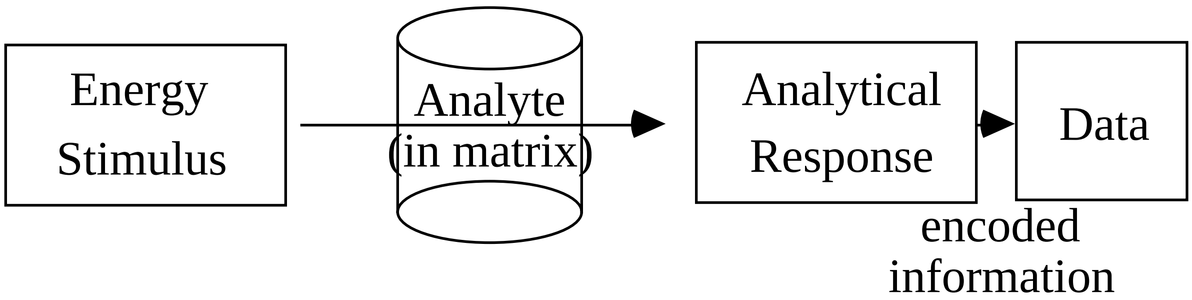
Quantitative - measuring property and determining relationship to concentration (e.g. spectrophotometry, mass spectrometry)

Often, same instrumental method used for qualitative and quantitative analysis

Types of Instrumental Methods:

Property	**Example Method**
Radiation emission	Emission spectroscopy - fluorescence, phosphorescence, luminescence
Radiation absorption	Absorption spectroscopy - spectrophotometry, photometry, nuclear magnetic resonance, electron spin resonance
Radiation scattering	Turbidity, Raman
Radiation refraction	Refractometry, interferometry
Radiation diffraction	X-ray, electron
Radiation rotation	Polarimetry, circular dichroism
Electrical potential	Potentiometry
Electrical charge	Coulometry
Electrical current	Voltammetry - amperometry, polarography
Electrical resistance	Conductometry
Mass	Gravimetry
Mass-to-charge ratio	Mass spectrometry
Rate of reaction	Stopped flow, flow injection analysis
Thermal	Thermal gravimetry, calorimetry
Radioactivity	Activation, isotope dilution

(Often combined with chromatographic or electrophoretic methods)



<u>Example:</u>

Spectrophotometry

> Instrument: spectrophotometer
> Stimulus: monochromatic light energy
> Analytical response: light absorption
> Transducer: photocell
> Data: electrical current
> Data processor: current meter
> Readout: meter scale

<u>Data Domains:</u> way of encoding analytical response in electrical or non-electrical signals.

Interdomain conversions transform information from one domain to another.

$$\text{Light Intensity} \xrightarrow{\text{Photocell}} \text{Current} \xrightarrow{\text{Current Meter}} \text{Scale}$$

Detector (general): device that indicates change in environment

Transducer (specific): device that converts non-electrical to electrical data

Sensor (specific): device that converts chemical to electrical data

Non-Electrical Domains	Electrical Domains
Physical *(light intensity, color)*	Current
Chemical *(pH)*	Voltage
Scale Position *(length)*	Charge
Number *(objects)*	Frequency
	Pulse width
	Phase
	Count
	Serial
	Parallel

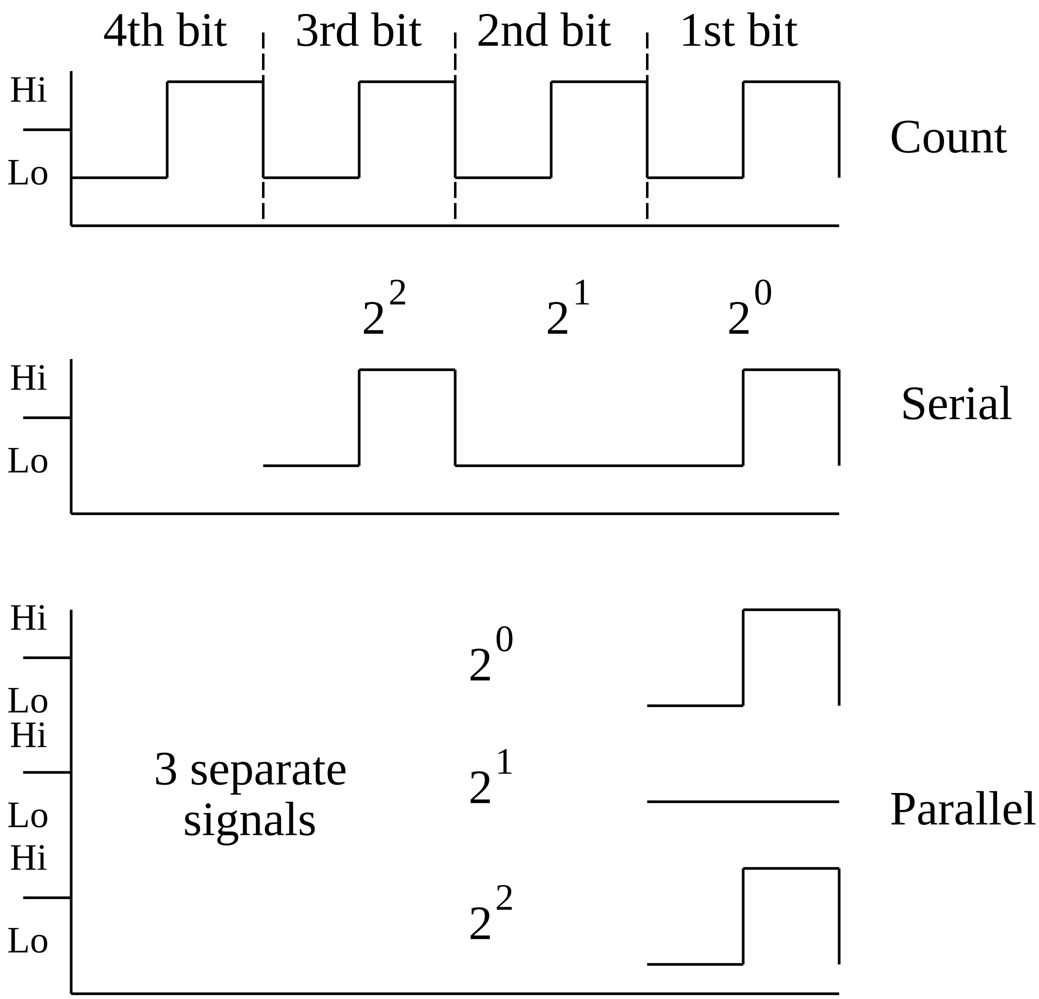
Time - vary with time (frequency, phase, pulse width)

Analog - continuously variable magnitude (current, voltage, charge)

Digital - discrete values (count, serial, parallel, number*)

<u>Digital Binary Data</u>

Advantages (1) easy to store (2) not susceptible to noise



$2^0=1$, $2^1=2$, $2^2=4$…

Performance Characteristics: Figures of Merit

How to choose an analytical method? How good is measurement?

How reproducible? - Precision

How close to true value? - Accuracy/Bias

How small a difference can be measured? - Sensitivity

What range of amounts? - Dynamic Range

How much interference? - Selectivity

Precision - Indeterminate or random errors

Absolute standard deviation: $s = \sqrt{\dfrac{\sum_{i-0}^{i=N} (x_i - \bar{x})^2}{N-1}}$

Variance: s^2

Relative standard deviation: $RSD = \dfrac{s}{\bar{x}}$

Standard deviation of mean: $s_m = \dfrac{s}{\sqrt{N}}$

Accuracy - Determinate errors (operator, method, instrumental)

Bias: $\text{bias} = \bar{x} - x_{true}$

Sensitivity

Calibration sensitivity: $$\begin{aligned} S &= \frac{dSignal}{dc} c + Signal_{blank} \\ &= mc + Signal_{blank} \end{aligned}$$

(larger slope of calibration curve m, more sensitive measurement)

Detection Limit

Signal must be bigger than random noise of blank

Minimum signal: $Signal_{min} = Av.\ Signal_{blank} + ks_{blank}$

From statistics k=3 or more (at 95% confidence level)

Dynamic Range

At detection limit we can say confidently analyte is present but cannot perform reliable quantitation

Level of quantitation (LOQ): k=10

Limit of linearity (LOL): when signal is no longer proportional to concentration

Dynamic range: $\dfrac{\text{LOL}}{\text{LOQ}}$ $\quad 10^2 \text{ to} > 10^6$

Selectivity:

No analytical method is completely free from interference by concomitants. Best method is more *sensitive* to analyte than interfering species (interferent).

Matrix with species A&B: $\text{Signal} = m_A c_A + m_B c_B + \text{Signal}_{\text{blank}}$

Selectivity coefficient: $k_{B,A} = \dfrac{m_B}{m_A}$

k's vary between 0 (no selectivity) and large number (very selective).

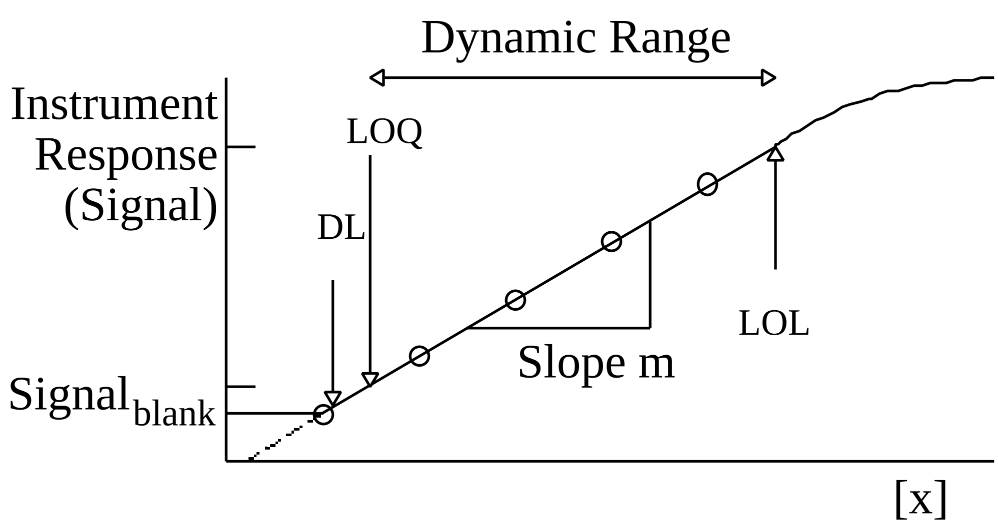
Calibration methods

Basis of *quantitative* analysis is magnitude of measured property is proportional to *concentration* of analyte

$$\text{Signal} \propto [x] \quad \text{or} \quad \text{Signal} = m[x] + \text{Signal}_{\text{blank}}$$

$$[x] = \frac{\text{Signal} - \text{Signal}_{\text{blank}}}{m}$$

Calibration curves (working or analytical curves)



Example (if time):

Analyte Concentration (ppm*)	Absorbance
0.0 (blank)	0.05
0.9	0.15
2.0	0.24
3.1	0.33
4.1	0.42

*ppm=1 μg per L

Define Variance and Covariance:

$$S_{xx} = \frac{\sum(x_i - \bar{x})^2}{N-1} \qquad S_{xy} = \frac{\sum(x_i - \bar{x})(y_i - \bar{y})}{N-1}$$

$$\bar{x} = 2.02 \qquad \bar{y} = 0.238$$

$$S_{xx} = \frac{\left(2.02^2 + 1.12^2 + 0.02^2 + 1.08^2 + 2.08^2\right)}{4} = \frac{10.828}{4} = 2.707$$

$$S_{xy} = \frac{(-2.02 \times -0.188) + (-1.12 \times -0.088) + (-0.02 \times 0.002) + \ldots}{4}$$

$$= \frac{0.9562}{4} = 0.23905$$

Slope: $m = \frac{S_{xy}}{Sx} = \frac{0.23905}{2.707} = 0.0883$

$$b = \bar{y} - m\bar{x}$$

Intercept: $= 0.238 - (0.0883 \times 2.02)$

$$= 0.0596$$

Calibration expression is

Absorbance=0.0883[Analyte (ppm)]+0.0596