

Instrumental Analysis = non-classical!

Chapter 1

Introduction

Goals of Analytical Chemistry

- ❖ What is it?
 - Identification
 - Qualitative Analysis
- ❖ How much?
 - Quantitative Analysis

Instrumental Analysis in the 21st Century

- ❖ Better and Faster
- ❖ More Data (Images, simultaneous detections)
- ❖ Miniaturization
- ❖ Better data processing methods - Chemometrics

Instrumental Methods

TABLE 1-1 Chemical and Physical Properties Employed
in Instrumental Methods

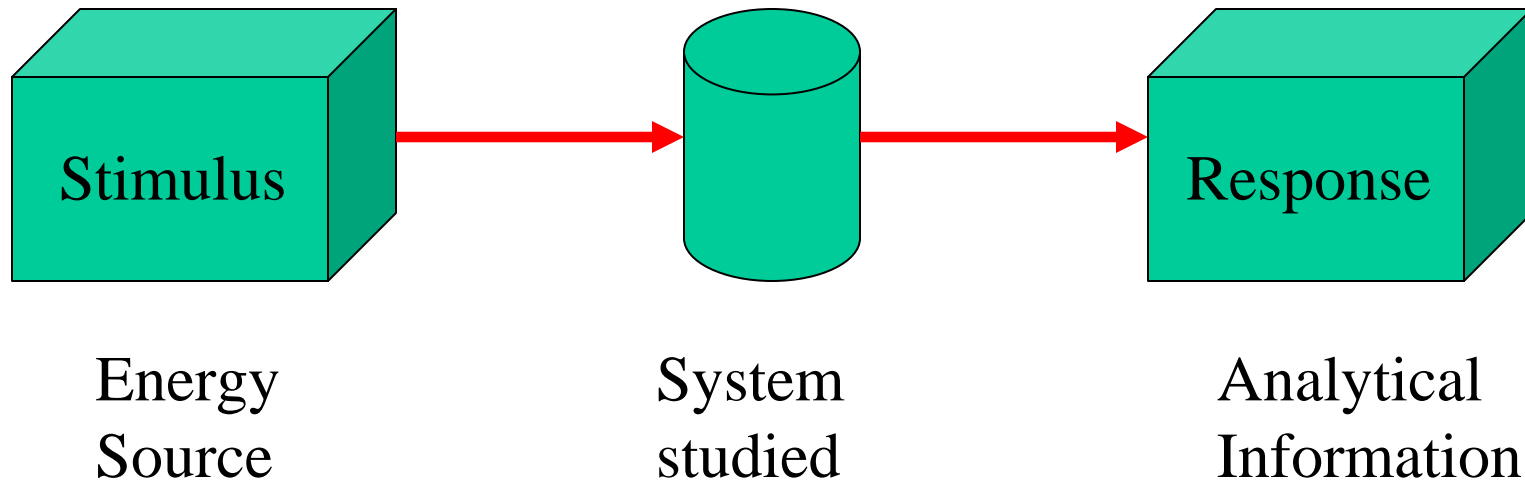
Characteristic Properties	Instrumental Methods
Emission of radiation	Emission spectroscopy (X-ray, UV, visible, electron, Auger); fluorescence, phosphorescence, and luminescence (X-ray, UV, and visible)
Absorption of radiation	Spectrophotometry and photometry (X-ray, UV, visible, IR); photoacoustic spectroscopy; nuclear magnetic resonance and electron spin resonance spectroscopy
Scattering of radiation	Turbidimetry; nephelometry; Raman spectroscopy
Refraction of radiation	Refractometry; interferometry
Diffraction of radiation	X-Ray and electron diffraction methods
Rotation of radiation	Polarimetry; optical rotary dispersion; circular dichroism
Electrical potential	Potentiometry; chronopotentiometry
Electrical charge	Coulometry
Electrical current	Amperometry; polarography
Electrical resistance	Conductometry
Mass	Gravimetry (quartz crystal microbalance)
Mass-to-charge ratio	Mass spectrometry
Rate of reaction	Kinetic methods
Thermal characteristics	Thermal gravimetry and titrimetry; differential scanning calorimetry; differential thermal analyses; thermal conductometric methods
Radioactivity	Activation and isotope dilution methods

Instrumental Methods

TABLE 1-1 Chemical and Physical Properties Employed in Instrumental Methods

Characteristic Properties	Instrumental Methods
Emission of radiation	Emission spectroscopy (X-ray, UV, visible, electron, Auger); fluorescence, phosphorescence, and luminescence (X-ray, UV, and visible)
Absorption of radiation	Spectrophotometry and photometry (X-ray, UV, visible, IR); photoacoustic spectroscopy; nuclear magnetic resonance and electron spin resonance spectroscopy
Scattering of radiation	Turbidimetry; nephelometry; Raman spectroscopy
Refraction of radiation	Refractometry; interferometry
Diffraction of radiation	X-Ray and electron diffraction methods
Rotation of radiation	Polarimetry; optical rotary dispersion; circular dichroism
Electrical potential	Potentiometry; chronopotentiometry
Electrical charge	Coulometry
Electrical current	Amperometry; polarography
Electrical resistance	Conductometry
Mass	Gravimetry (quartz crystal microbalance)
Mass-to-charge ratio	Mass spectrometry
Rate of reaction	Kinetic methods
Thermal characteristics	Thermal gravimetry and titrimetry; differential scanning calorimetry; differential thermal analyses; thermal conductometric methods
Radioactivity	Activation and isotope dilution methods

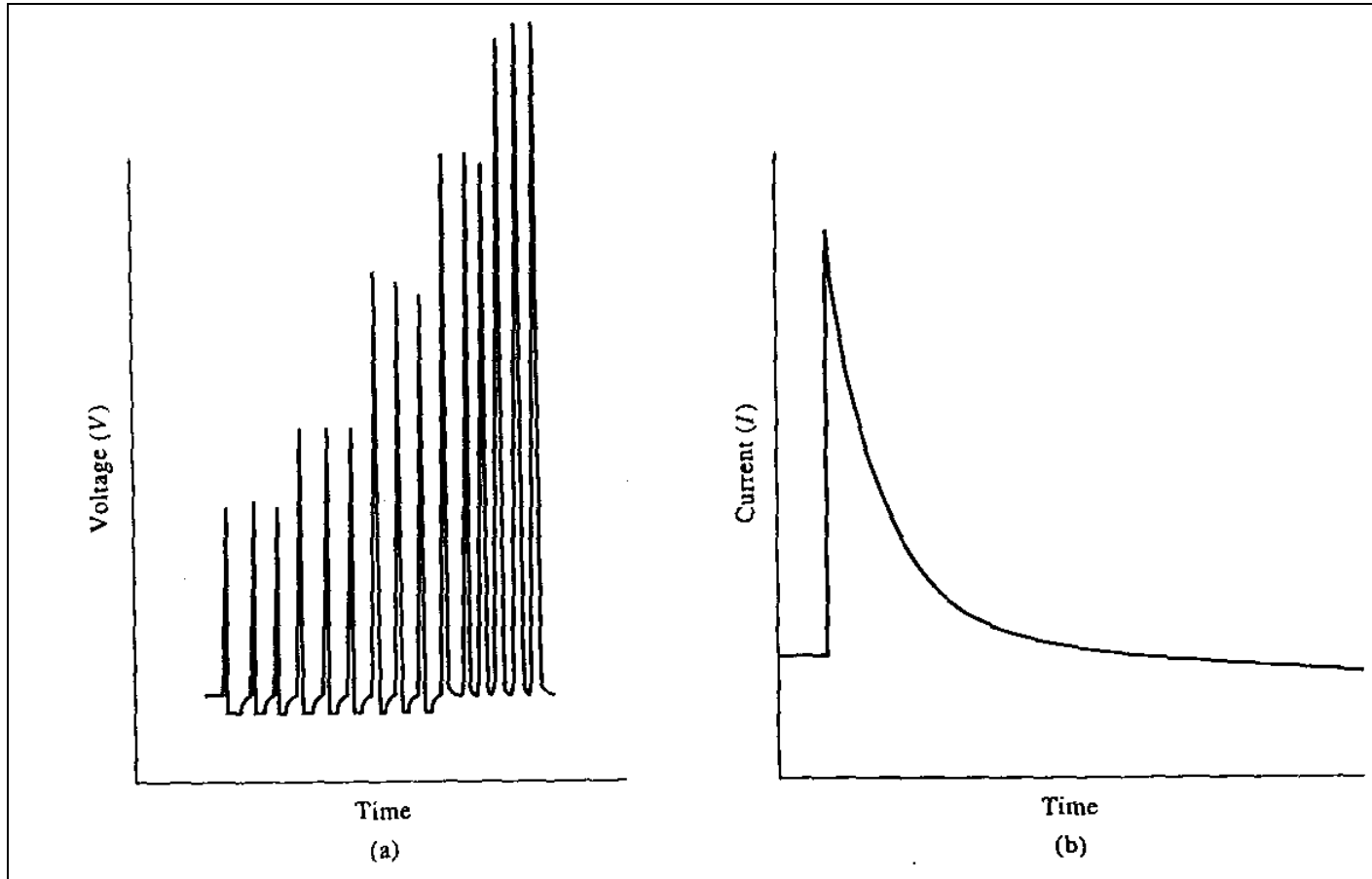
Analytical Instruments



Analytical Signals

- ❖ Data Domain – information encoded
- ❖ Non-electrical Domains (scale, number, chemical)
- ❖ Electrical Domains – (volts, current, charge)
- ❖ Analog Domains – continuous quantities (volts, current)
- ❖ Time Domains– (pulses, slopes)
- ❖ Digital Domains – (Off/On or Hi/Lo)

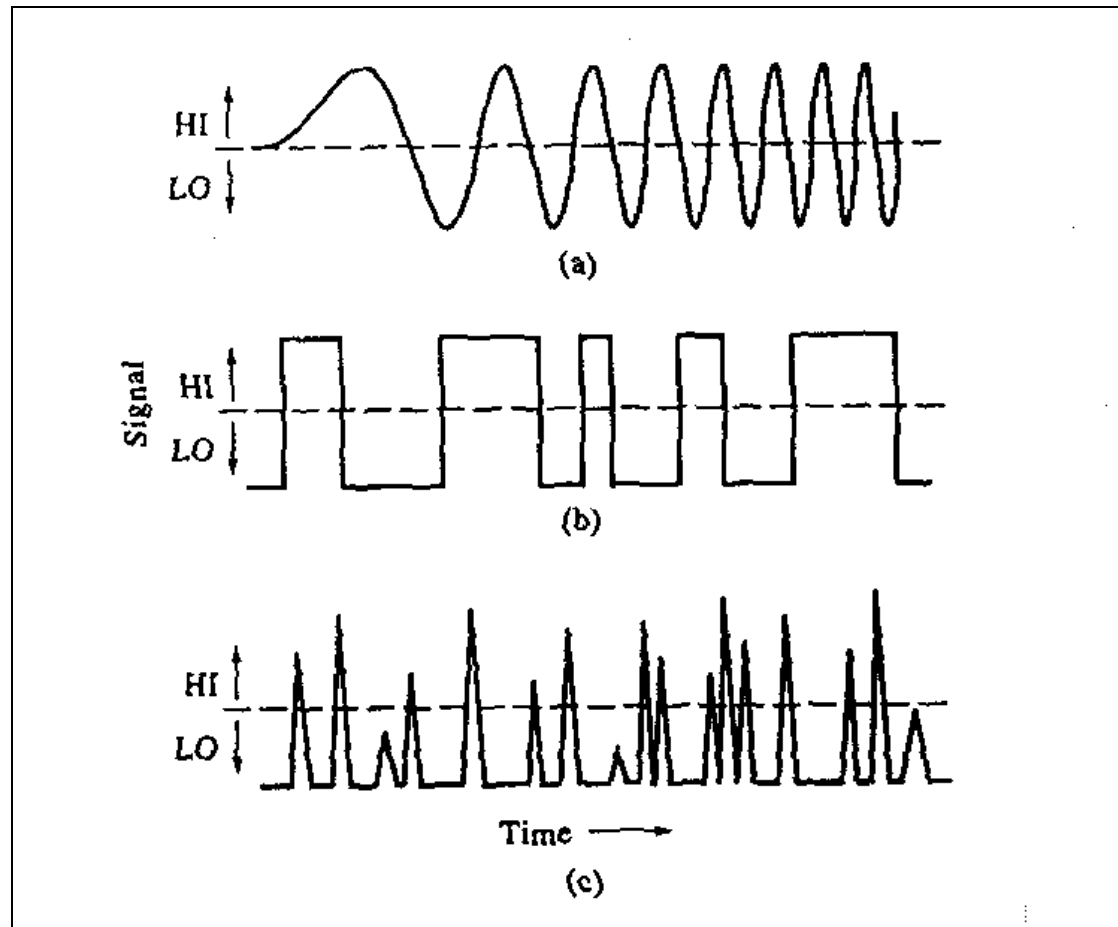
Time Domains



Pulses

Slope/shape

Time => Digital Domains



Continuous → Hi/Lo

Instrumental Components

TABLE 1-2 Some Examples of Instrument Components

Instrument	Energy Source (stimulus)	Analytical Information	Input Transducer	Data Domain of Transduced Information	Information Processor	Readout
Photometer	Tungsten lamp, glass filter	Attenuated light beam	Photocell	Electrical current	Meter scale	Current meter
Atomic emission spectrometer	Flame	UV or visible radiation	Photomultiplier tube	Electrical potential	Amplifier, demodulator, monochromator chopper	Chart recorder
Coulometer	DC source	Cell current	Electrodes	Electrical current	Amplifier	Chart recorder
pH meter	Sample/glass electrode	Hydrogen ion activity	Glass-calomel electrodes	Electrical potential	Amplifier, digitizer	Digital unit
X-Ray powder diffractometer	X-Ray tube, sample	Diffracted radiation	Photographic film	Latent image	Chemical developer	Black images on film
Color comparator	Sunlight	Color	Eye	Optic nerve signal	Brain	Visual color response

Signal Domains

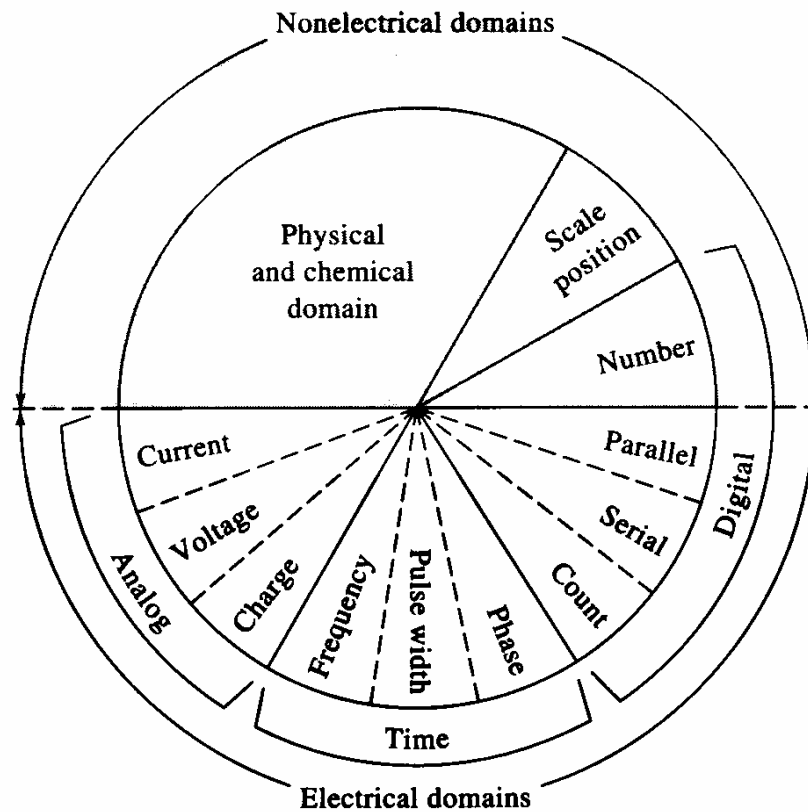
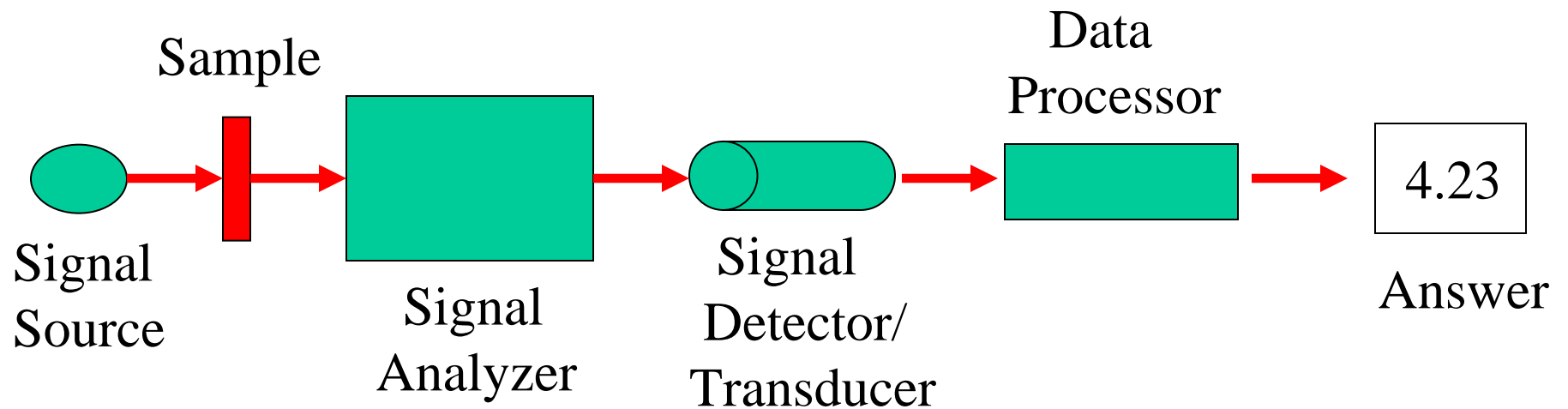


Figure 1-2 Data domains map. The upper (shaded) half of the map comprises nonelectrical domains. The bottom half is made up of electrical domains. Note that the digital domain spans both electrical and nonelectrical domains.

Instrument Components



Fluorometer Components

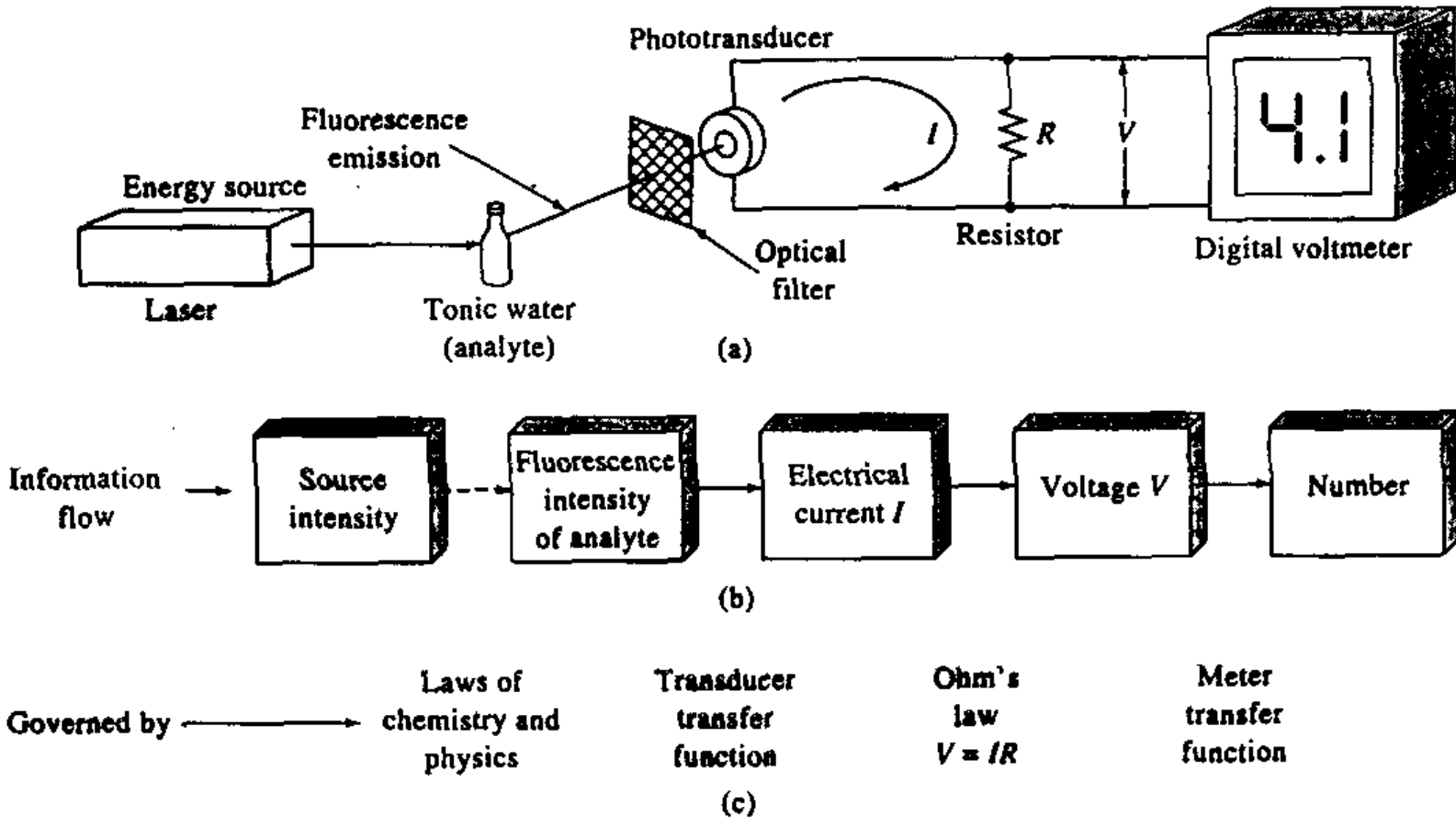


Figure 1-3 A block diagram of a fluorometer showing (a) a general diagram of the instrument,

Selecting an Analytical Method

- ❖ Required Accuracy
- ❖ Amount of sample
- ❖ Concentration range(s) of analyte(s)
- ❖ Possible interferences
- ❖ Chemical and physical properties of matrix
- ❖ Number of samples

Desirable Characteristics for an Analytical Method

- ❖ Speed
- ❖ Ease and Convenience
- ❖ Skill required of operator
- ❖ Cost and availability of equipment
- ❖ Per-samples cost

Numerical Criteria for Selecting an Analytical Method

❖ Precision

- Absolute standard deviation
- Relative standard deviation
- Coefficient of variation
- Variance

❖ Bias

- Absolute systematic error
- Relative systematic error

❖ Sensitivity

- Calibration
- Analytical

❖ Detection Limit

- Blank plus three times Std. Dev. of blank

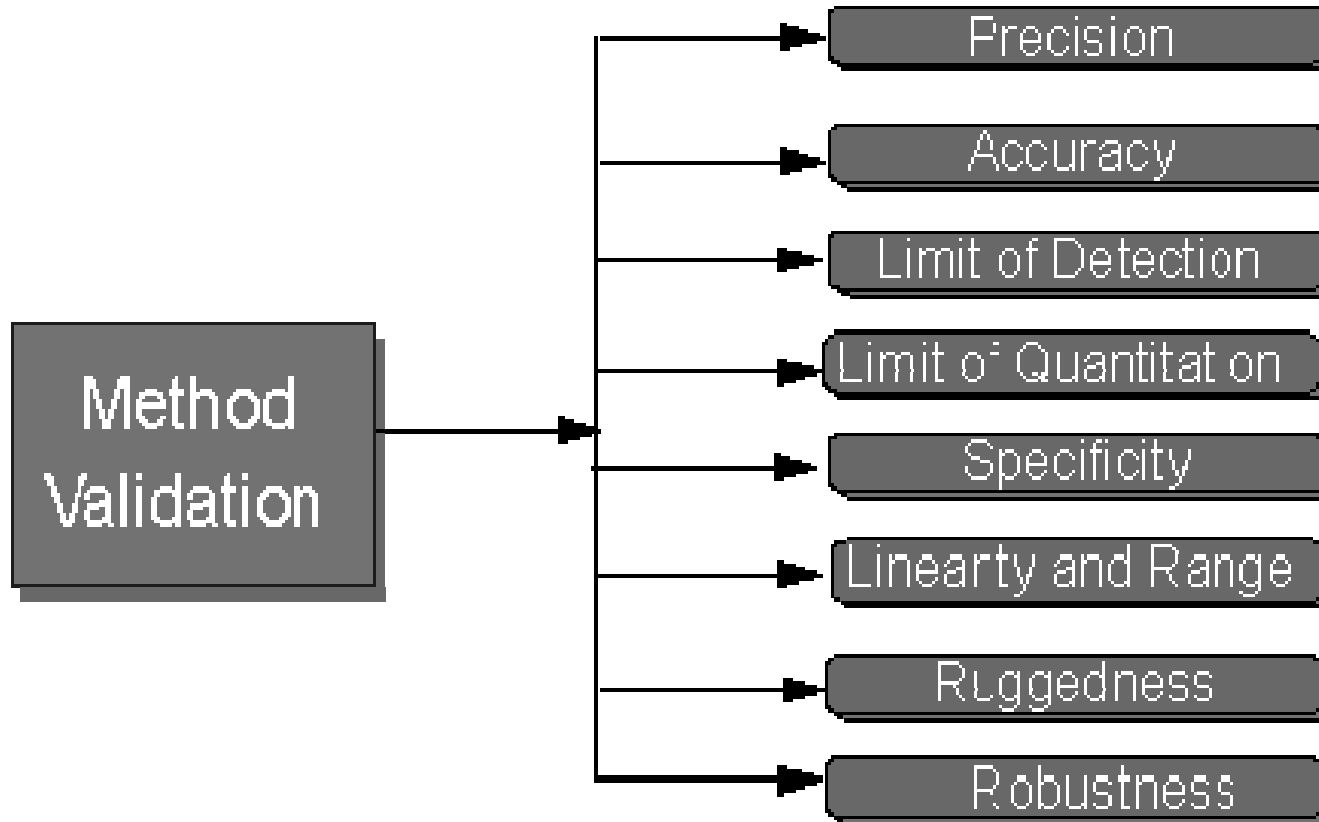
❖ Concentration Range

- Limit of Quantitation (LOQ)
- Limit of Linearity (LOL)

❖ Selectivity

- Effects of interferences
- Coefficient of Selectivity

What we need to know before jumping into it!



Evaluation of Analytical Data..

What do you want,
what do you get,
what does it mean?

Garbage in = garbage out!

Acceptable Data

“data [that are]... scientifically valid and defensible and of a level of precision and accuracy commensurate with [their] stated or intended use.” – *40.0017(1)*

Precision and Accuracy

Precision

Describes the reproducibility of a result

→ RANDOM ERRORS

Accuracy

Describes how close a measured value is to the “true value”

→ SYSTEMATIC ERRORS

Precision and Accuracy

Precise

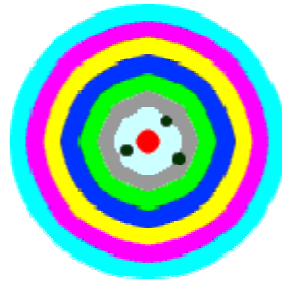


Precision and Accuracy

Precise



Accurate

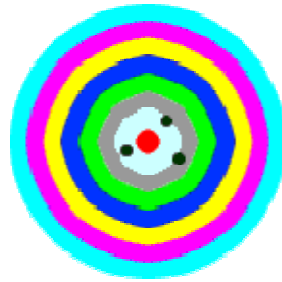


Precision and Accuracy

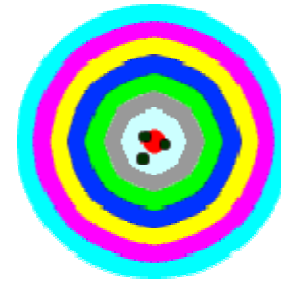
Precise



Accurate



Precise & Accurate



Types of Error

Systematic (Determinate) Error:

Flaw in experimental design or
equipment flaw

Random (Indeterminate) Error:

Effects of uncontrolled variables in
the measurement

Systematic (Determinate) Error:

Flaw in experimental design or equipment flaw
– affects accuracy of your results (how close they are to the “truth.”) Also called *instrumental bias*.

How would we control for systematic error?

1. Repeated measurements will not reveal systematic errors.
2. Unless the true value is known – and it seldom is – large systematic errors can go undetected for long periods of time.
3. **BUY A CERTIFIED STANDARD**

What are some other sources of **systematic** error?

- Improperly calibrated volumetric glassware.
- Improperly calibrated instruments.
- “Improperly calibrated” employees – e.g. in colorimetric tests, some people are colorblind and don’t know it.

How can we reduce **systematic** error?

In the design of an experiment or analysis, identify potential sources of systematic error. The final experimental design should minimize these errors.

Calibrate your equipment and instruments! This is part of quality assurance and is essential to providing valid and reliable results.

Independent analyses should be done at critical steps to verify the accuracy of your determinations.

Random (Indeterminate) Error:

Effects of **uncontrolled variables in the measurement – affects precision of your results.**

How can we control/minimize the effects of random errors?

1. High precision suggests low random error.
2. If there is no systematic error, **increasing the number of measurements** will decrease the influence of random error.
3. Decreasing the number of steps in an analysis or experiment is likely to decrease the random error.

Assessment of **accuracy**:

- $E_a = X - X_t$

Absolute Error

- $E_{rel} = \frac{X - X_t}{X_t} * 100\%$

Relative Error

Table 3-1 Summary of rules for propagation of uncertainty

Function	Uncertainty	Function ^a	Uncertainty ^b
$y = x_1 + x_2$	$e_y = 2 \sqrt{e_{x_1}^2 + e_{x_2}^2}$	$y = x^a$	$\%e_y = a\%e_x$
$y = x_1 - x_2$	$e_y = 2 \sqrt{e_{x_1}^2 + e_{x_2}^2}$	$y = \log x$	$e_y = \frac{1}{\ln 10} \frac{e_x}{x} \approx 0.434\ 29 \frac{e_x}{x}$
$y = x_1 \cdot x_2$	$\%e_y = 2 \sqrt{\%e_{x_1}^2 + \%e_{x_2}^2}$	$y = \ln x$	$e_y = \frac{e_x}{x}$
$y = \frac{x_1}{x_2}$	$\%e_y = 2 \sqrt{\%e_{x_1}^2 + \%e_{x_2}^2}$	$y = 10^x$	$\frac{e_y}{y} = (\ln 10)e_x \approx 2.302\ 6 e_x$
		$y = e^x$	$\frac{e_y}{y} = e_x$

a. x represents a variable and a represents a constant that has no uncertainty,

b. e_x/x is the relative error in x and $\%e_x$ is $100 \times e_x/x$.

Evaluation of Analytical Data

Some Important Definitions

Mean (\bar{x}):

- also known as the *average*
- obtained by dividing the sum of replicate measurements by the number of measurements in the set
- given mathematically as

$$\bar{x} = \frac{\sum_{i=1}^N x_i}{N}$$

where x_i represents the individual values of x making up the set of N replicate measurements.

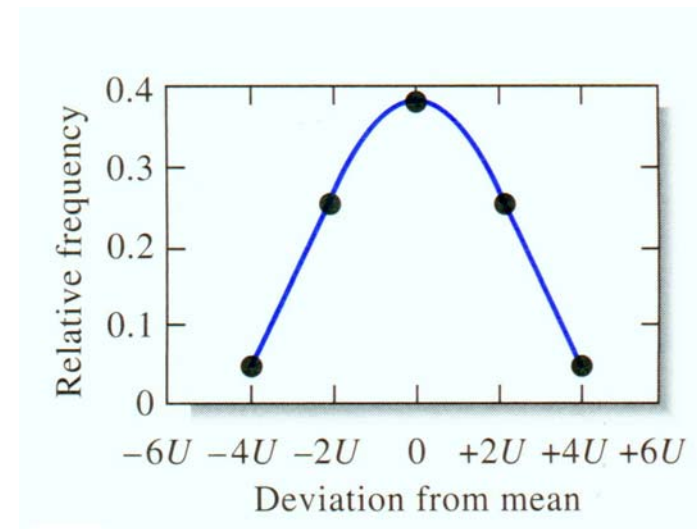
Evaluation of Analytical Data

Random Error Distribution:

- Consider **four** independent unknown random error sources (U) are imposed onto an analytical measurement
- Assume the magnitude of the error is identical for all four sources and that the magnitude of the error can either be added or subtracted from the analytical results.

TABLE 6-1

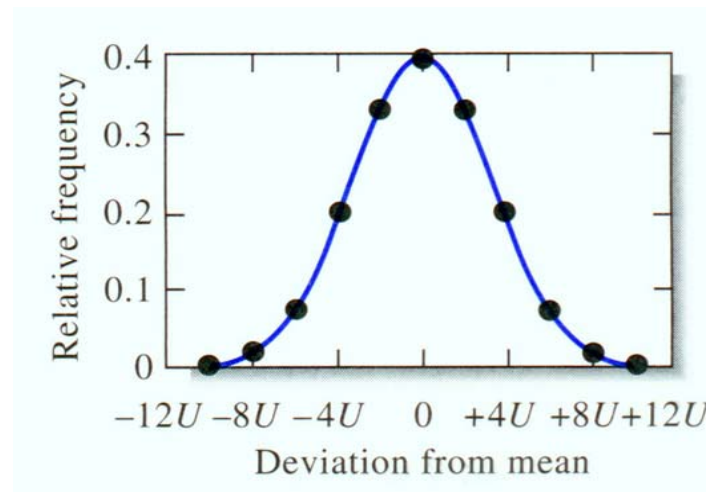
Possible Combinations of Four Equal-Sized Uncertainties			
Combinations of Uncertainties	Magnitude of Random Error	Number of Combinations	Relative Frequency
$+ U_1 + U_2 + U_3 + U_4$	$+ 4U$	1	$1/16 = 0.0625$
$- U_1 + U_2 + U_3 + U_4$	$+ 2U$	4	$4/16 = 0.250$
$+ U_1 - U_2 + U_3 + U_4$			
$+ U_1 + U_2 - U_3 + U_4$			
$+ U_1 + U_2 + U_3 - U_4$			
$- U_1 - U_2 + U_3 + U_4$	0	6	$6/16 = 0.375$
$+ U_1 + U_2 - U_3 - U_4$			
$+ U_1 - U_2 + U_3 - U_4$			
$- U_1 + U_2 - U_3 + U_4$			
$- U_1 + U_2 + U_3 - U_4$			
$+ U_1 - U_2 - U_3 + U_4$			
$+ U_1 - U_2 - U_3 - U_4$	$- 2U$	4	$4/16 = 0.250$
$- U_1 + U_2 - U_3 - U_4$			
$- U_1 - U_2 + U_3 - U_4$			
$- U_1 - U_2 - U_3 + U_4$			
$- U_1 - U_2 - U_3 - U_4$	$- 4U$	1	$1/16 = 0.0625$



Evaluation of Analytical Data

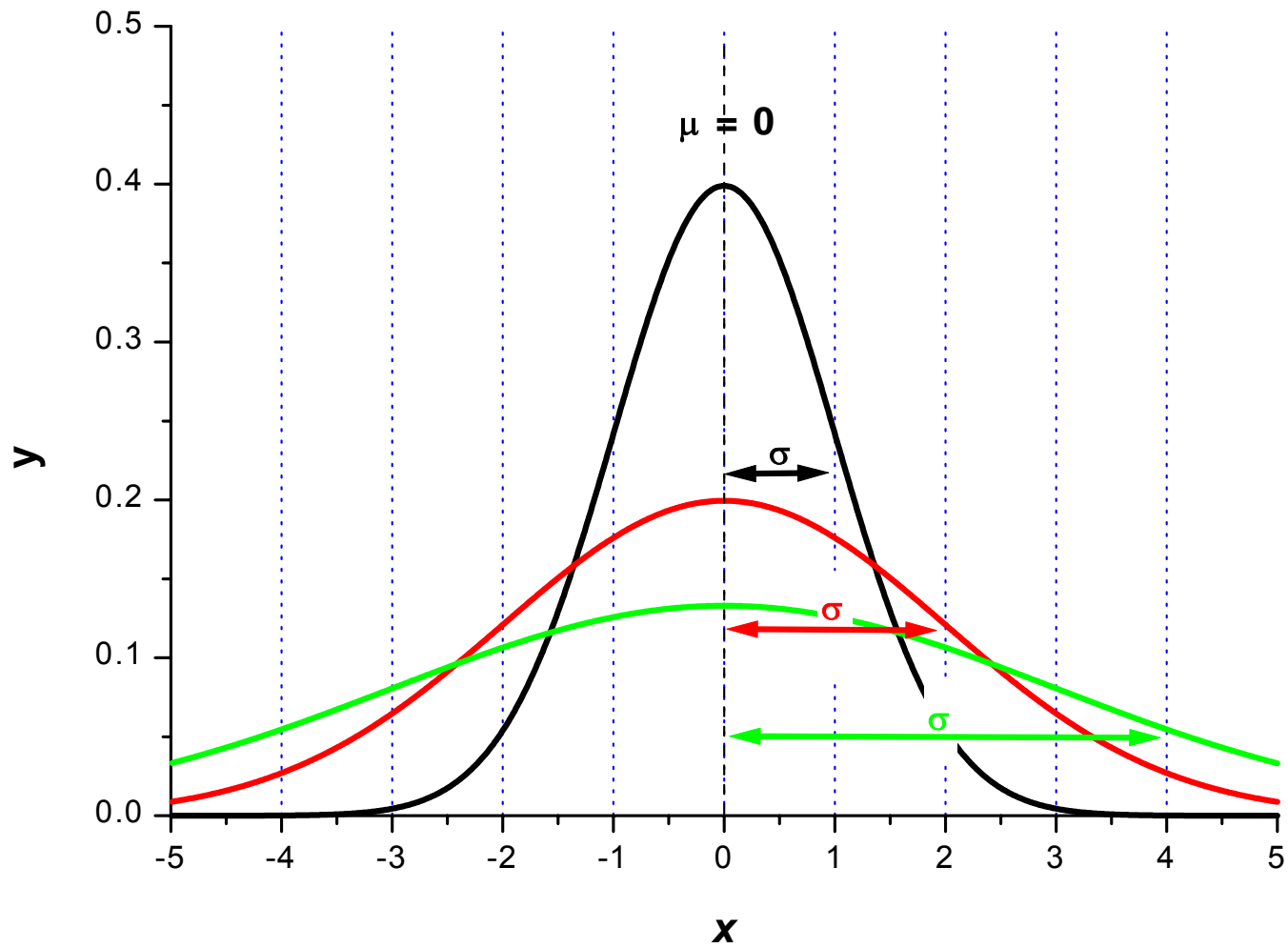
Random Error Distribution:

- Consider the case of **ten** independent unknown random error sources (U) are imposed onto an analytical measurement
- Assume the magnitude of the error is identical for all ten sources and that the magnitude of the error can either be added or subtracted from the analytical results.



- This is distribution about the mean caused by random error produces a bell-shaped curve which is known as a **Gaussian Curve** or **Standard Error Curve**.

Gaussian Curve



Standard Deviation and Mean

Can never truly measure μ or σ . These are values for an infinite data set ($n = \text{infinity}$).

We can measure s and \bar{x} . These are values for a finite data set.

Evaluation of Analytical Data

Properties of Gaussian Curves:

- Gaussian curves can be described as a function two parameters, the **population mean**, μ , and the **standard deviation**, σ , where:

$$y = \frac{e^{-(x-\mu)^2 / 2\sigma}}{\sigma\sqrt{2\pi}}$$

- the **population mean**, μ , is calculated in the same manner as the mean calculation shown on the first slide, however, is based on the total number of measurements in the population and not a limited sample set. As such, in the absence of systematic error, the population mean should equal the true value of the measurement.
- the **population standard deviation**, σ , is a measure of the precision of a population of data and is given by:

$$\sigma = \sqrt{\frac{\sum_{i=1}^N (x_i - \mu)^2}{N}}$$

where N is the number of data points making up the population.

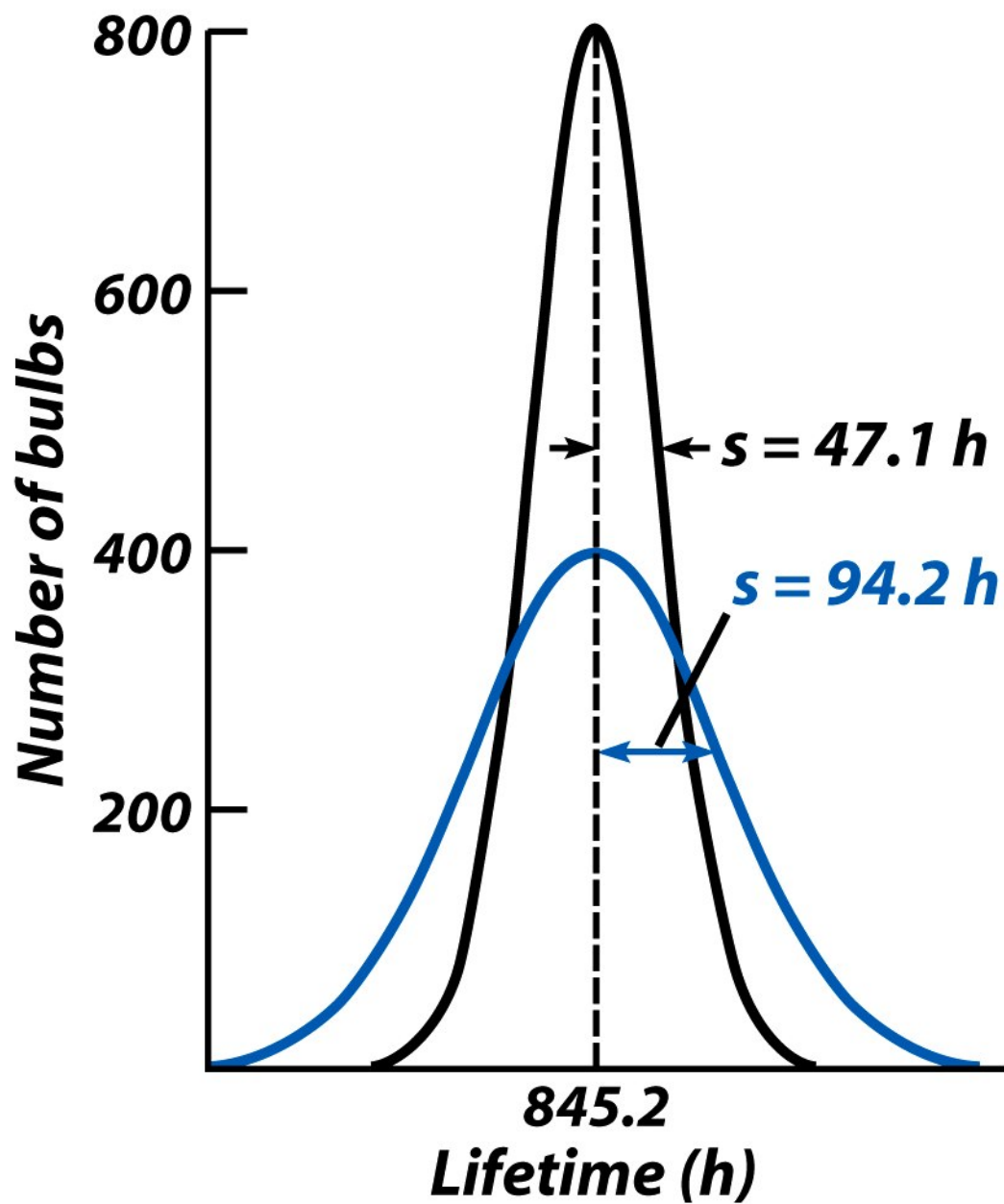


Figure 4-2
Quantitative Chemical Analysis, Seventh Edition
© 2007 W.H. Freeman and Company

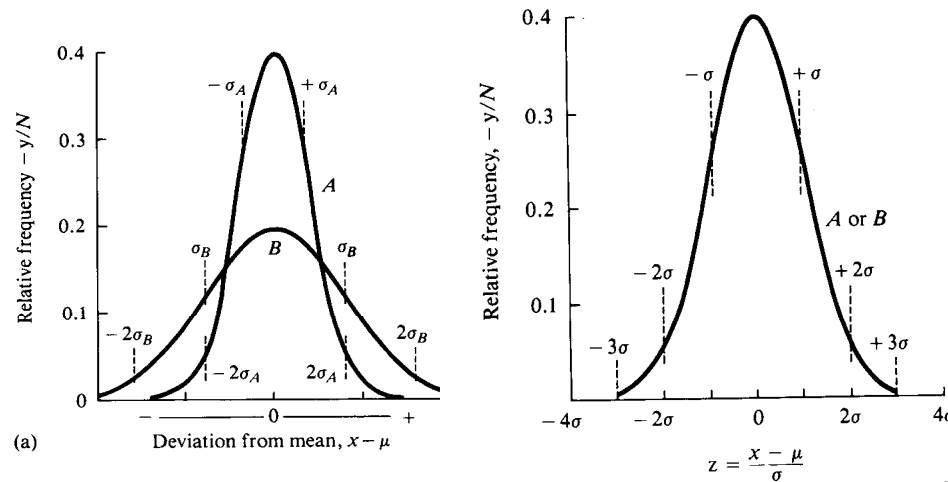
Evaluation of Analytical Data

Properties of Gaussian Curves: Standard deviation and probability

- A more conventional approach taken in the analysis of Gaussian distributions is to define the abscissa (x-axis) in terms of a parameter, z , which is the deviation of a data point from the mean relative to one standard deviation:

$$z = \frac{(x - \mu)}{\sigma}$$

- This serves to normalise error curves so that common statistical analysis of the data is facilitated. The resultant curve describes all populations of data, regardless of standard deviation. When $z = 1$, $x - \mu = \sigma$. When $z = 2$, $x - \mu = 2\sigma$. When $z = 3$, $x - \mu = 3\sigma$.



- The equation for the Gaussian curve is then written as:

$$y = \frac{e^{-z^2/2}}{\sigma\sqrt{2\pi}}$$

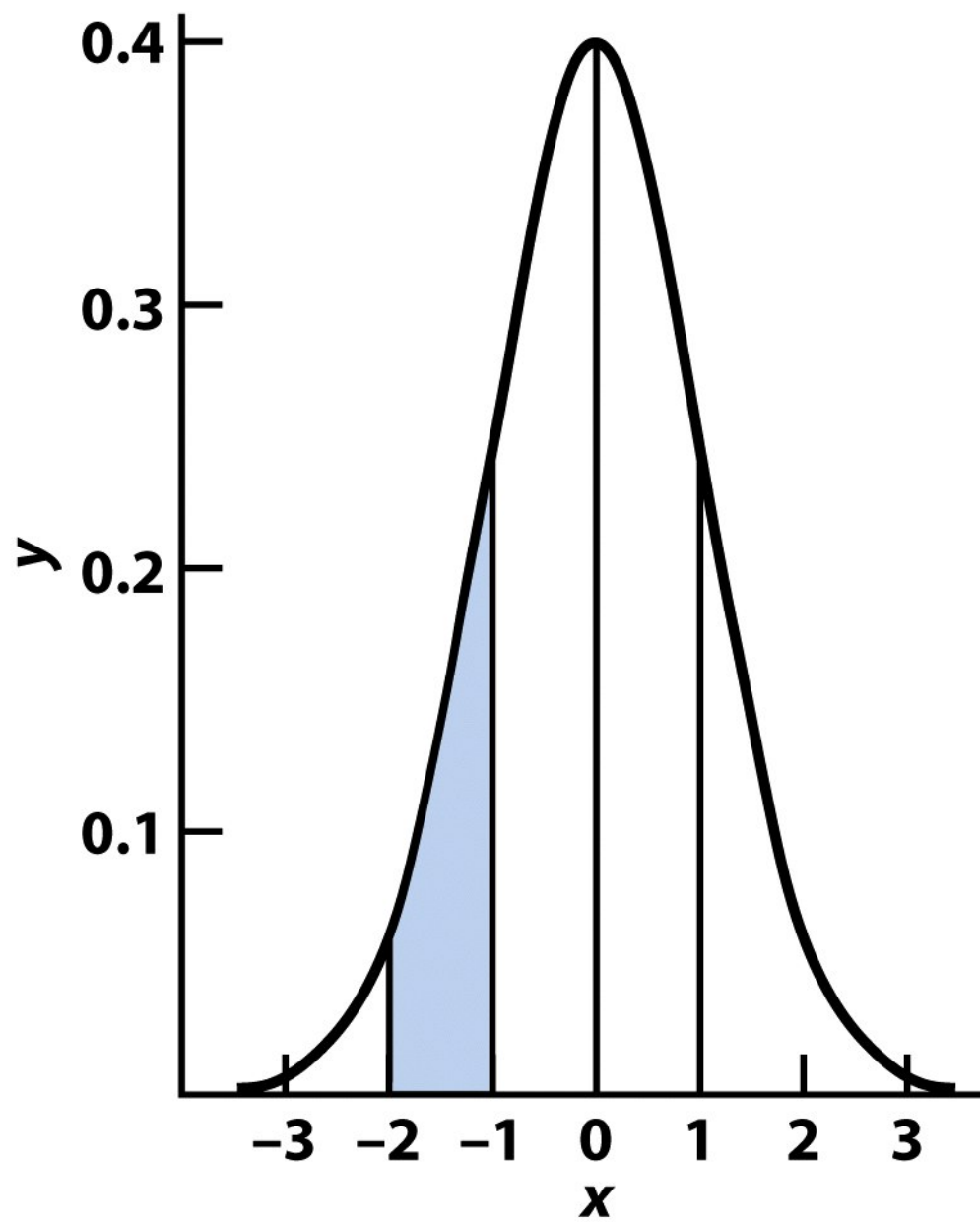
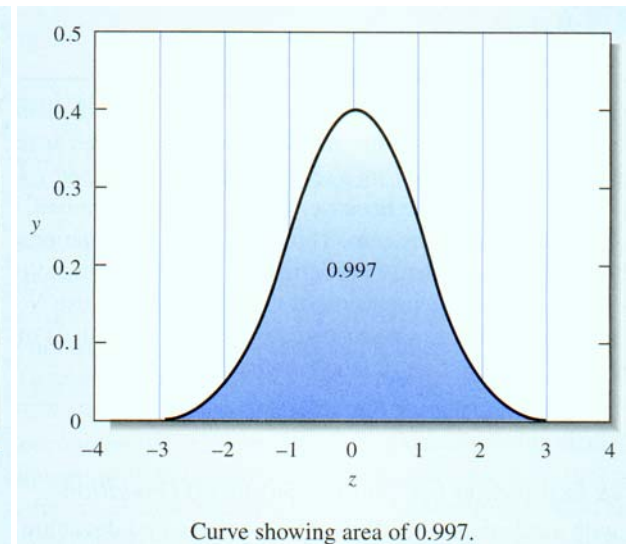
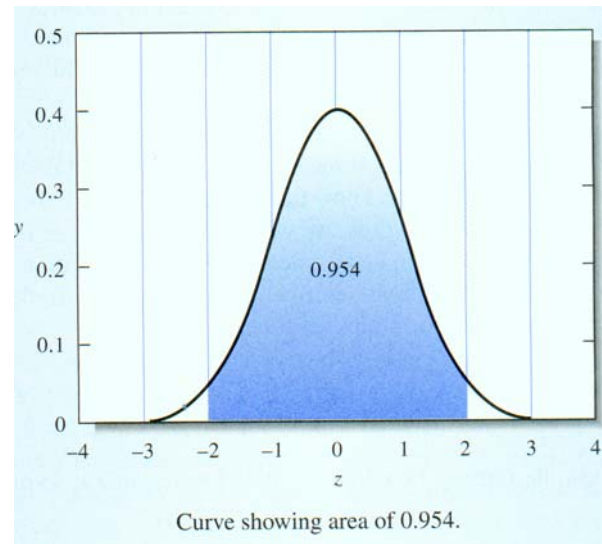
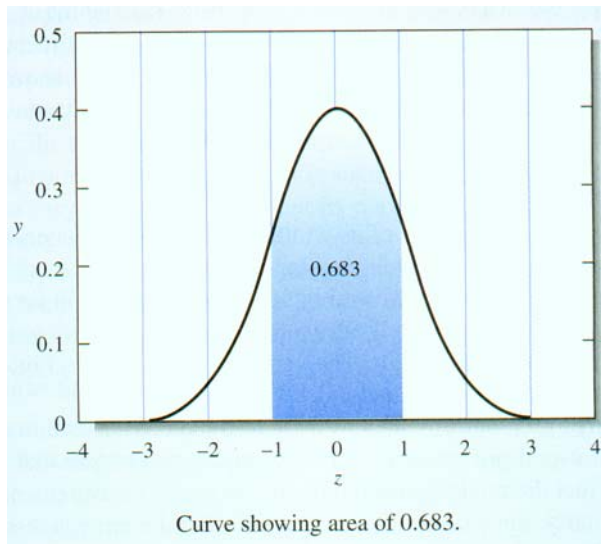


Figure 4-3
Quantitative Chemical Analysis, Seventh Edition
© 2007 W.H. Freeman and Company

Evaluation of Analytical Data

Properties of Gaussian Curves:

- Regardless of width:
 - 68.3% of the area beneath a Gaussian curve exists within **one** standard deviation ($\pm 1\sigma$) of the mean.
 - 95.4% of the area beneath a Gaussian curve exists within **two** standard deviations ($\pm 2\sigma$) of the mean.
 - 99.7% of the area beneath a Gaussian curve exists within **three** standard deviations ($\pm 3\sigma$) of the mean.



Evaluation of Analytical Data

Reporting errors in experimental data:

- Most commonly, the standard deviation is used to report the precision of analytical data.
- The standard deviation can also be put into a relative context. The two most common relative precision measures used are the *relative standard deviation (RSD)* and the *coefficient of variation (CV)*.
- *Relative standard deviation (RSD)* is calculated by dividing the standard deviation by the mean value of the data set as follows:

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

- The **Coefficient of Variation (CV)** is simply the RSD multiplied by 100%:

$$CV = \frac{s}{\bar{x}} \times 100 \%$$

Evaluation of Analytical Data

Confidence Intervals:

- True values (*i.e.* real population means) are never known in the real world.
- However, if numerous measurements are made, the mean value (\bar{x}) of the set containing many experimental outcomes may closely approach the true value (μ).
- It is often the case that resources available to us (quantity of sample, time and \$\$\$) only permit for a limited set of data to be collected for any experiment.
- We can establish a *confidence interval* (CI) surrounding an experimentally determined mean within which the population mean should exist
- *Vice versa*, a suitable number of experiments to conduct that will provide us with the confidence required in the experimental outcome can be established *a priori*.
- ***NOTE: This assumes there is an absence of determinate error!!!***

Evaluation of Analytical Data

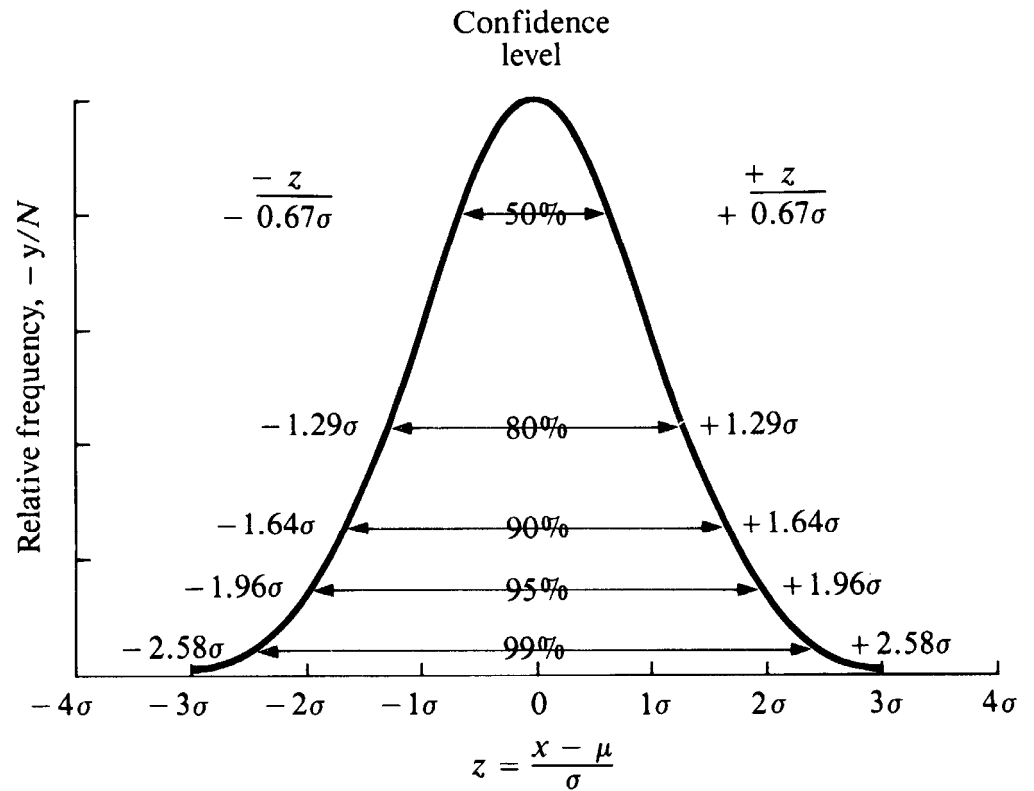
Confidence Intervals:

If a good estimate of σ exists,

$$\text{CI for } \mu = \bar{x} \pm \frac{z\sigma}{\sqrt{N}}$$

Confidence Levels for Various Values of z

Confidence Level, %	z
50	0.67
68	1.00
80	1.28
90	1.64
95	1.96
95.4	2.00
99	2.58
99.7	3.00
99.9	3.29



Evaluation of Analytical Data

Confidence Intervals for Limited Sets of Data:

- for the calculation of confidence intervals for limited sets of data, look up values of t from the t -table, which is based on the confidence required and the degrees of freedom.

Degrees of Freedom	80%	90%	95%	99%	99.9%
1	3.08	6.31	12.7	63.7	637
2	1.89	2.92	4.30	9.92	31.6
3	1.64	2.35	3.18	5.84	12.9
4	1.53	2.13	2.78	4.60	8.61
5	1.48	2.02	2.57	4.03	6.87
6	1.44	1.94	2.45	3.71	5.96
7	1.42	1.90	2.36	3.50	5.41
8	1.40	1.86	2.31	3.36	5.04
9	1.38	1.83	2.26	3.25	4.78
10	1.37	1.81	2.23	3.17	4.59
15	1.34	1.75	2.13	2.95	4.07
20	1.32	1.73	2.09	2.84	3.85
40	1.30	1.68	2.02	2.70	3.55
60	1.30	1.67	2.00	2.62	3.46
∞	1.28	1.64	1.96	2.58	3.29

- Then use the following equation to determine the confidence interval (CI) based on the selected t value:

$$\text{CI for } \mu = \bar{x} \pm \frac{ts}{\sqrt{N}}$$

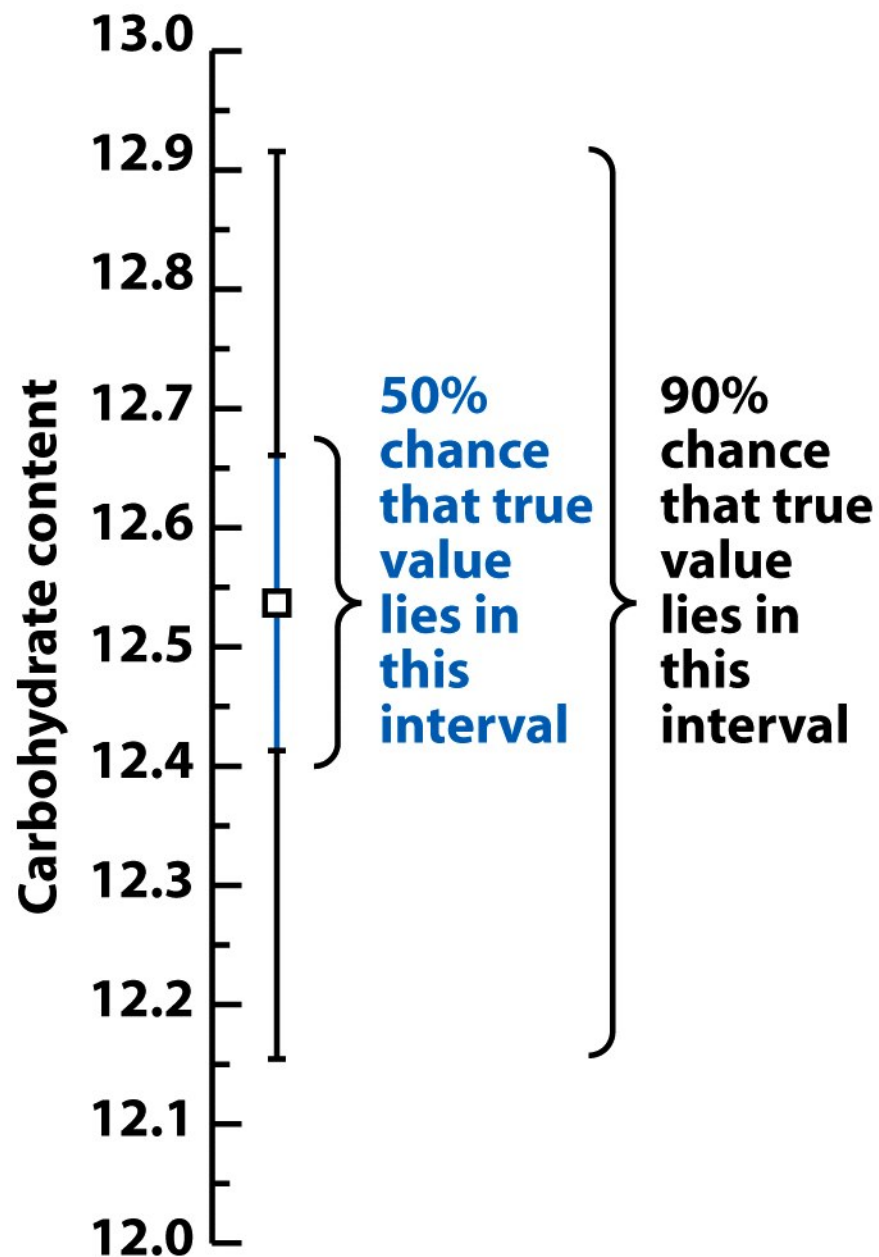
Problem

- The carbohydrate content of a glycoprotein is determined to be 12.6, 11.9, 13.0, 12.7 and 12.5 g of carbohydrate per 100 g of protein in replicate analyses. Find the 50% and 90% confidence intervals for the carbohydrate content.

Table 4-2 Values of Student's t

Degrees of freedom	Confidence level (%)						
	50	90	95	98	99	99.5	99.9
1	1.000	6.314	12.706	31.821	63.656	127.321	636.578
2	0.816	2.920	4.303	6.965	9.925	14.089	31.598
3	0.765	2.353	3.182	4.541	5.841	7.453	12.924
4	0.741	2.132	2.776	3.747	4.604	5.598	8.610
5	0.727	2.015	2.571	3.365	4.032	4.773	6.869
6	0.718	1.943	2.447	3.143	3.707	4.317	5.959
7	0.711	1.895	2.365	2.998	3.500	4.029	5.408
8	0.706	1.860	2.306	2.896	3.355	3.832	5.041
9	0.703	1.833	2.262	2.821	3.250	3.690	4.781
10	0.700	1.812	2.228	2.764	3.169	3.581	4.587
15	0.691	1.753	2.131	2.602	2.947	3.252	4.073
20	0.687	1.725	2.086	2.528	2.845	3.153	3.850
25	0.684	1.708	2.060	2.485	2.787	3.078	3.725
30	0.683	1.697	2.042	2.457	2.750	3.030	3.646
40	0.681	1.684	2.021	2.423	2.704	2.971	3.551
60	0.679	1.671	2.000	2.390	2.660	2.915	3.460
120	0.677	1.658	1.980	2.358	2.617	2.860	3.373
∞	0.674	1.645	1.960	2.326	2.576	2.807	3.291

NOTE: In calculating confidence intervals, σ may be substituted for s in Equation 4-6 if you have a great deal of experience with a particular method and have therefore determined its "true" population standard deviation. If σ is used instead of s , the value of t to use in Equation 4-6 comes from the bottom row of Table 4-2.



Unnumbered figure pg 58a
Quantitative Chemical Analysis, Seventh Edition
© 2007 W.H. Freeman and Company

Evaluation of Analytical Data

Comparing an Experimental Mean with a Known Value: t Test

Example:

A sample of swimming pool chlorine is known to contain 30.0% NaOCl. An analyst conducted an independent experiment and measured values of 30.4%, 30.5%, 30.6%, 30.4% and 30.3%. Can it be said that the mean of the Analyst's determination is accurate with 95% confidence?

$$\bar{x} = 30.4\%$$

$$s = 0.12$$

$$\text{degrees of freedom} = N - 1 = 4$$

$$t \text{ at } 95\% \text{ confidence and } 4 \text{ degrees of freedom} = 2.78$$

$$\mu = \bar{x} \pm \frac{ts}{\sqrt{N}}$$

$$30.0\% = 30.4 \pm \frac{2.78 \cdot 0.12}{\sqrt{5}} \%$$

$$30.0\% \neq 30.4 \pm 0.15\% \therefore \text{Determinant Error}$$

Uncertainty in a Measurement

3 Ways

1. : $\bar{x} \pm s$ **Okay, but report N!!!**

2. : $\bar{x} \pm \sigma_m$ **Better**

3. : $\bar{x} \pm C.L.$ **Best**

QA/QC Program

QA/QC stands for Quality Assurance and Quality Control

A QA/QC program is a set of guidelines developed to ensure the validity of results.

QA/QC Program

Typical Components

1) Chain of Custody

Keep track of who, what, where, and when the sample has been handled.

2) Sample Blank

Blank sample (e.g. water, sand) that accompanies sample in its journey

3) Method Blank

This is a blank sample prepared during analysis

QA/QC Program

Typical Components

4) Blank Spike (Method Spike)

A known amount of analyte is added to a blank sample. A percent recovery for the analyte is calculated.

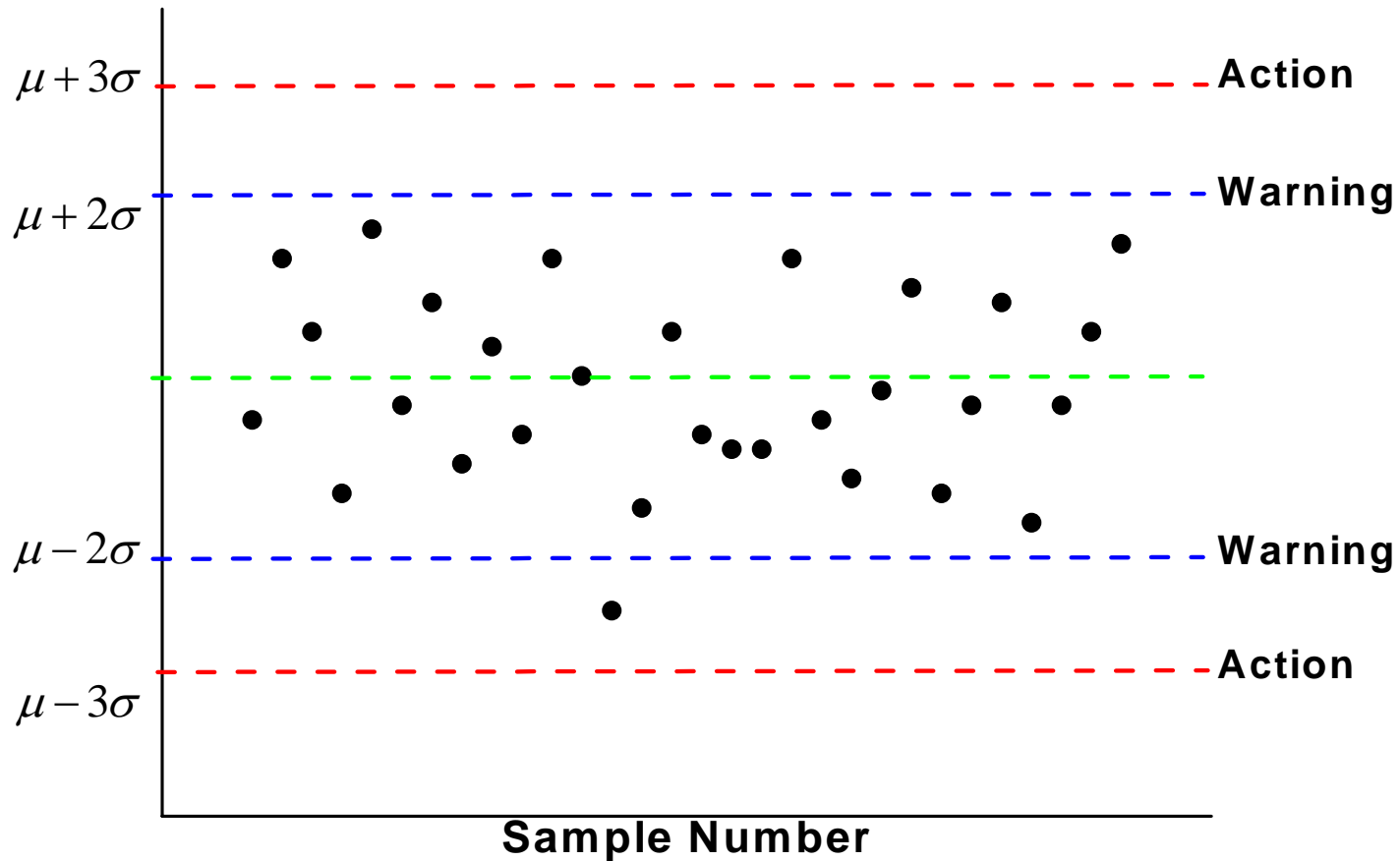
5) Matrix Spike

A known amount of analyte is added (“spiked”) to the sample. A percent recovery for the analyte is calculated.

6) Check Standard

A standard from a source other than the standards used to construct the calibration curve is analyzed.

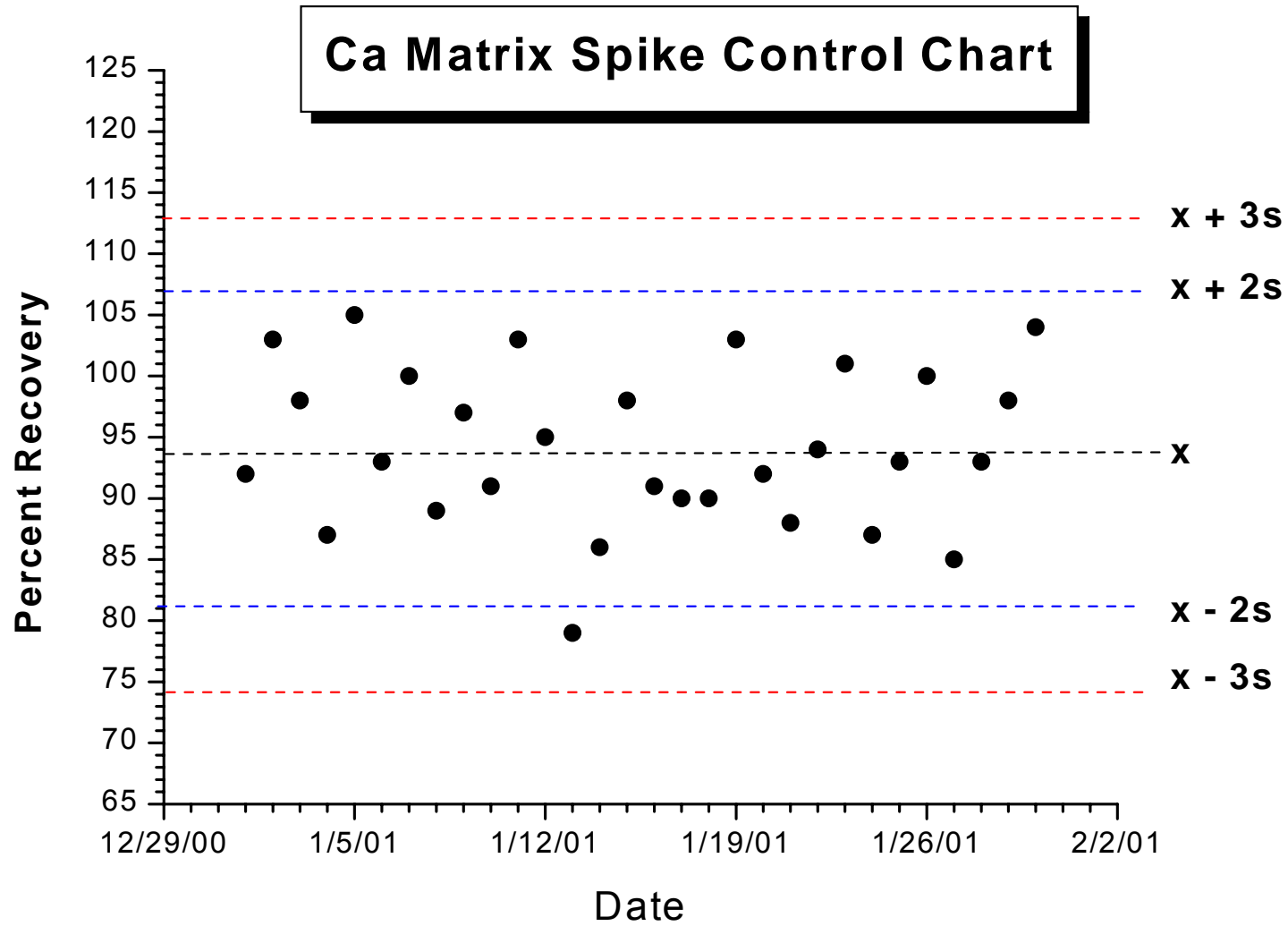
Control Charts: Process Monitoring



95.5 % between $\mu \pm 2\sigma$

99.7 % between $\mu \pm 3\sigma$

Control Charts: Matrix Spikes



Precision – Figures of Merit

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

Relative standard deviation $RDS = \frac{s}{\bar{x}}$

Coefficient of variation $CV = \frac{s}{\bar{x}} \times 100\%$

Standard deviation of the mean $s_m = s / \sqrt{n}$,

where n = number of times the mean was determined.

Calibration Sensitivity

$$S = mc + S_{bl}$$

where

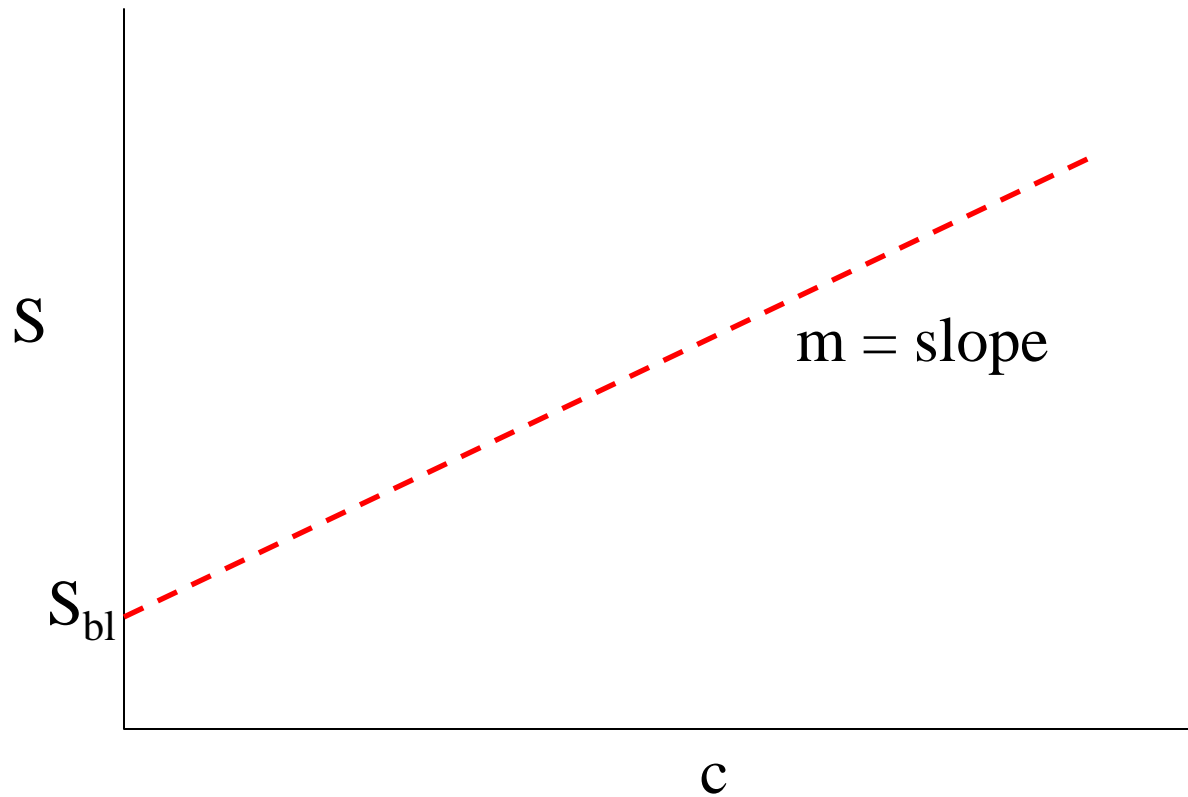
S = signal

c = concentration

S_{bl} = signal of blank

m = slope (Calibration Sensitivity)

Calibration Sensitivity (m)



$$S = mc + S_{bl}$$

Analytical Sensitivity

$$\gamma = m / s_s$$

where

m = slope

s_s = standard deviation
of the measurement

Signal Detection Limit

$$S_m = \bar{S}_{bl} + k s_{bl}$$

where,

S_m = minimum distinguishable signal

\bar{S}_{bl} = mean blank signal

s_{bl} = standard deviation of blank signal

k = 3 for Detect. Limit and 10 for LOQ

Concentration Detection Limit

$$S_m = \bar{S}_{bl} + k s_{bl}$$

$$S = mc + S_{bl}$$

$$c = \frac{S - S_{bl}}{m}$$

$$c_m = \frac{S_m - S_{bl}}{m}$$

Limits of Quantitation and Linearity

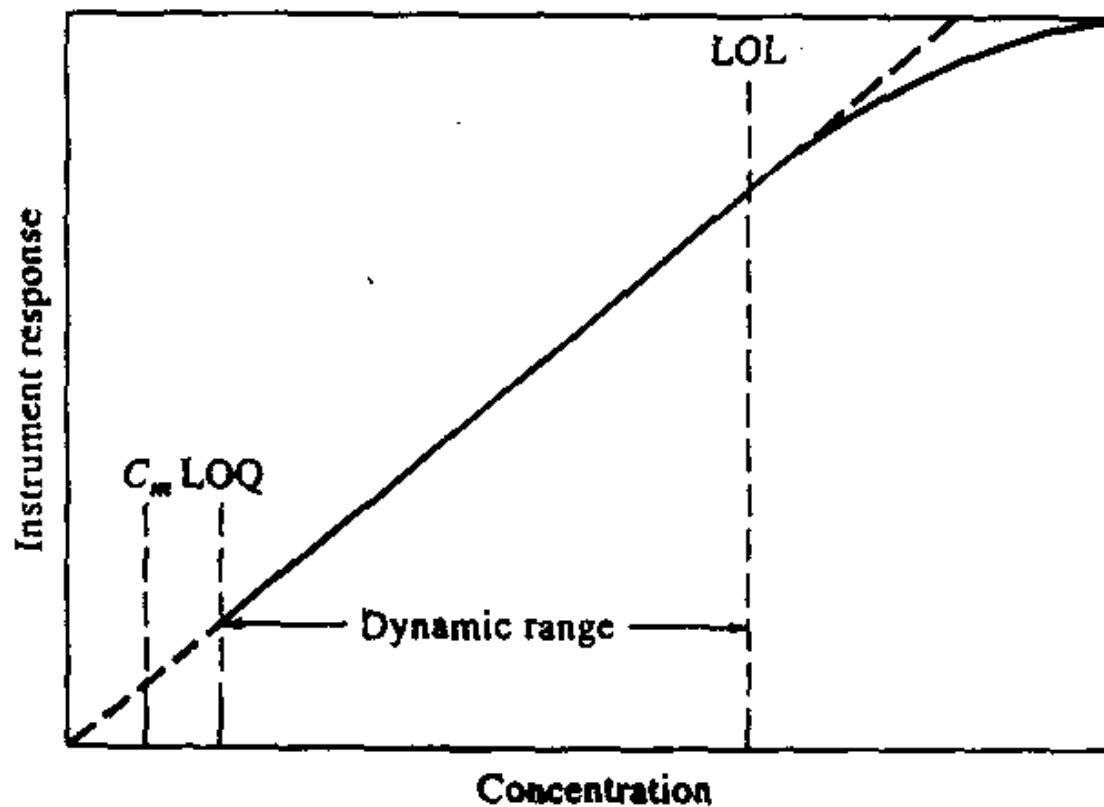


Figure 1-7 Useful range of an analytical method. LOQ = limit of quantitative measurement; LOL = limit of linear response.

Example-Sensitivity

EXAMPLE 1-1

A least-squares analysis of calibration data for the determination of lead based upon its flame emission spectrum yielded the equation

$$S = 1.12 c_{\text{Pb}} + 0.312$$

where c_{Pb} is the lead concentration in parts per million and S is a measure of the relative intensity of the lead emission line. The following replicate data were then obtained:

Concn, ppm Pb	No. of Replications	Mean Value of S	s
10.0	10	11.62	0.15
1.00	10	1.12	0.025
0.000	24	0.0296	0.0082

Calculate (a) the calibration sensitivity, (b) the analytical sensitivity at 1 and 10 ppm of Pb, and (c) the detection limit.

- (a) By definition, the calibration sensitivity m is the slope of the straight line. Thus, $m = 1.12$.
(b) At 10 ppm Pb, $\gamma = m/s_S = 1.12/0.15 = 7.5$.
At 1 ppm Pb, $\gamma = 1.12/0.025 = 45$.
(c) Applying Equation 1-4,

$$S_m = 0.0296 + 3 \times 0.0082 = 0.054$$

Substituting into Equation 1-5 gives

$$c_m = \frac{0.054 - 0.0296}{1.12} = 0.022 \text{ ppm Pb.}$$

Selectivity

$$S = m_A c_A + m_B c_B + m_C c_C + S_{bl}$$

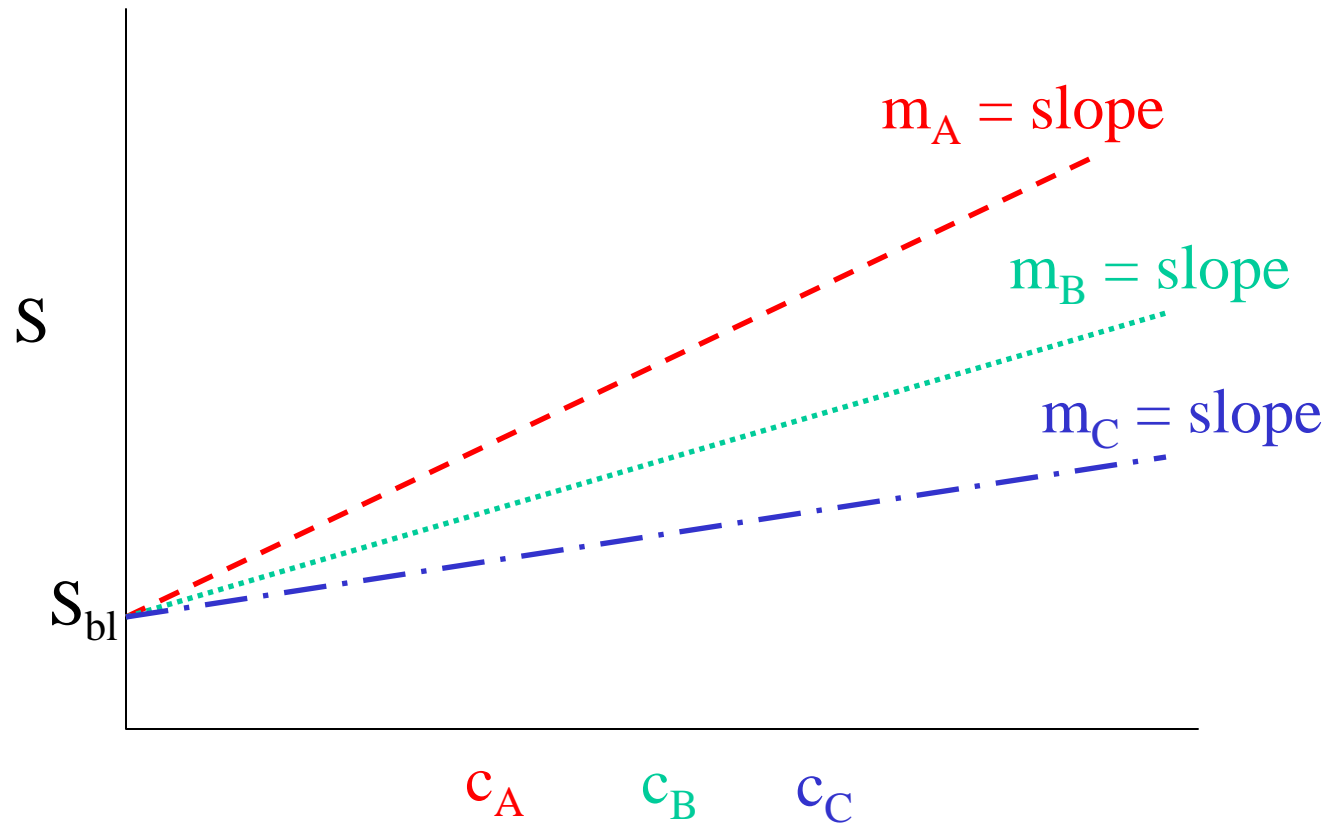
$$k_{B,A} = m_B / m_A$$

$$k_{C,A} = m_C / m_A$$

$$S = m_A (c_A + k_{B,A} c_B + k_{C,A} c_C) + S_{bl}$$

where the k's are the selectivity coefficients

Calibration Selectivity



Problems – Chapter 1

All problems 1 - 11