2019학년도 1학기

고등분석화학 1: 강의 소개

담당교수: 이원용 (연구실: 과 443-C, 전화: 2123-2649, 전자우편: wylee@yonsei.ac.kr)

Principles of Instrumental Analysis, 6th edition. By Holler, Skoog, Crouch

분석화학 기초개념/원자분광분석법/전기분석/분리분석을 중심으로 강의

성적평가

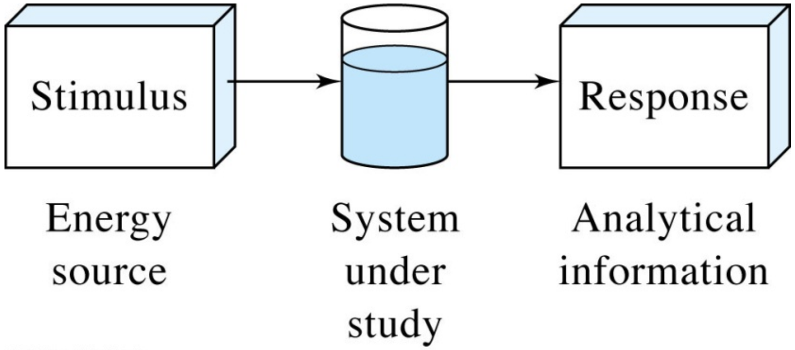
- 시험: 중간시험 (4월15일, 오후 6시-8시) 기말시험 (6월 3일, 오후 6시-8시)
- 출석점수: 없음, 단 1/3이상 결석은 F 학점,

2019년도 고등분석화학 1 강의 계획

일시	수업내용
2019.03.04	Chapter 1: Introduction
2019.03.11	Chapter 6: Review (Introduction to Spectrometric Methods) Chapter 7: Components of Optical Instrument
2019.03.18	Chapter 8-10: Atomic Spectrometry Chapter 10: Atomic Emission Spectrometry
2019.03.25	Chapter 11: Atomic Mass Spectrometry Chapter 20: Molecular Mass Spectrometry
2019.04.01	Chapter 21: Surface Characterization by Spectroscopy
2019.04.08	Chapter 22: Electroanalytical Chemistry
2019.04.15	중간시험 (오후 6시-8시)
2019.04.22	중간시험기간 (no class)
2019.04.29	Chapter 25: Volammetry
2019.05.06	대체공휴일(no class)
2019.05.13	Chapter 26. Introduction/ Chapter 27. Gas Chromatography
2019.05.20	Chapter 28. Liquid Chromatography
2019.05.27	Chapter 29. SFC/Chapter 30. Capillary Electrophoresis
2019.06.03	기말시험 (오후 6시-8시)

Instrumental Analysis

General concept



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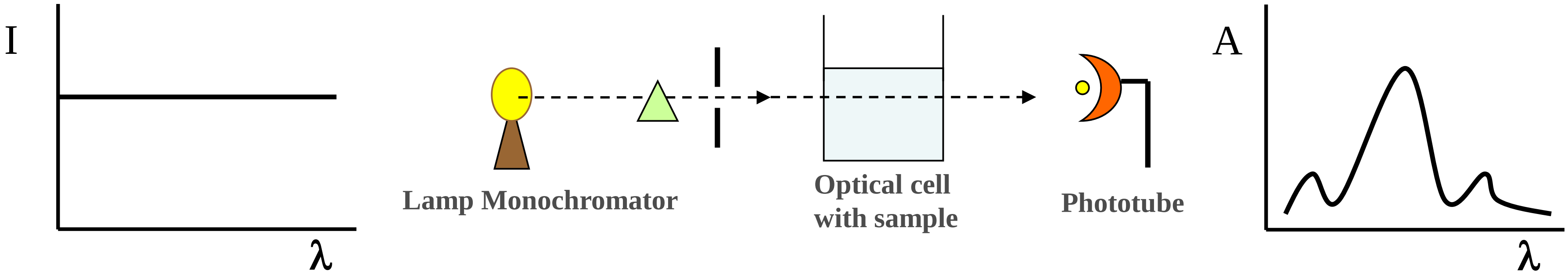
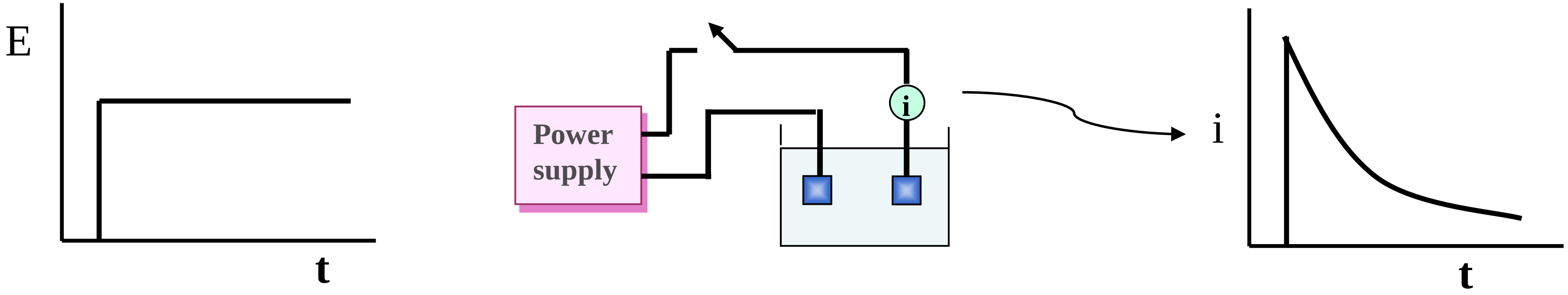
Spectrophotometric experiment



Electrochemical experiment



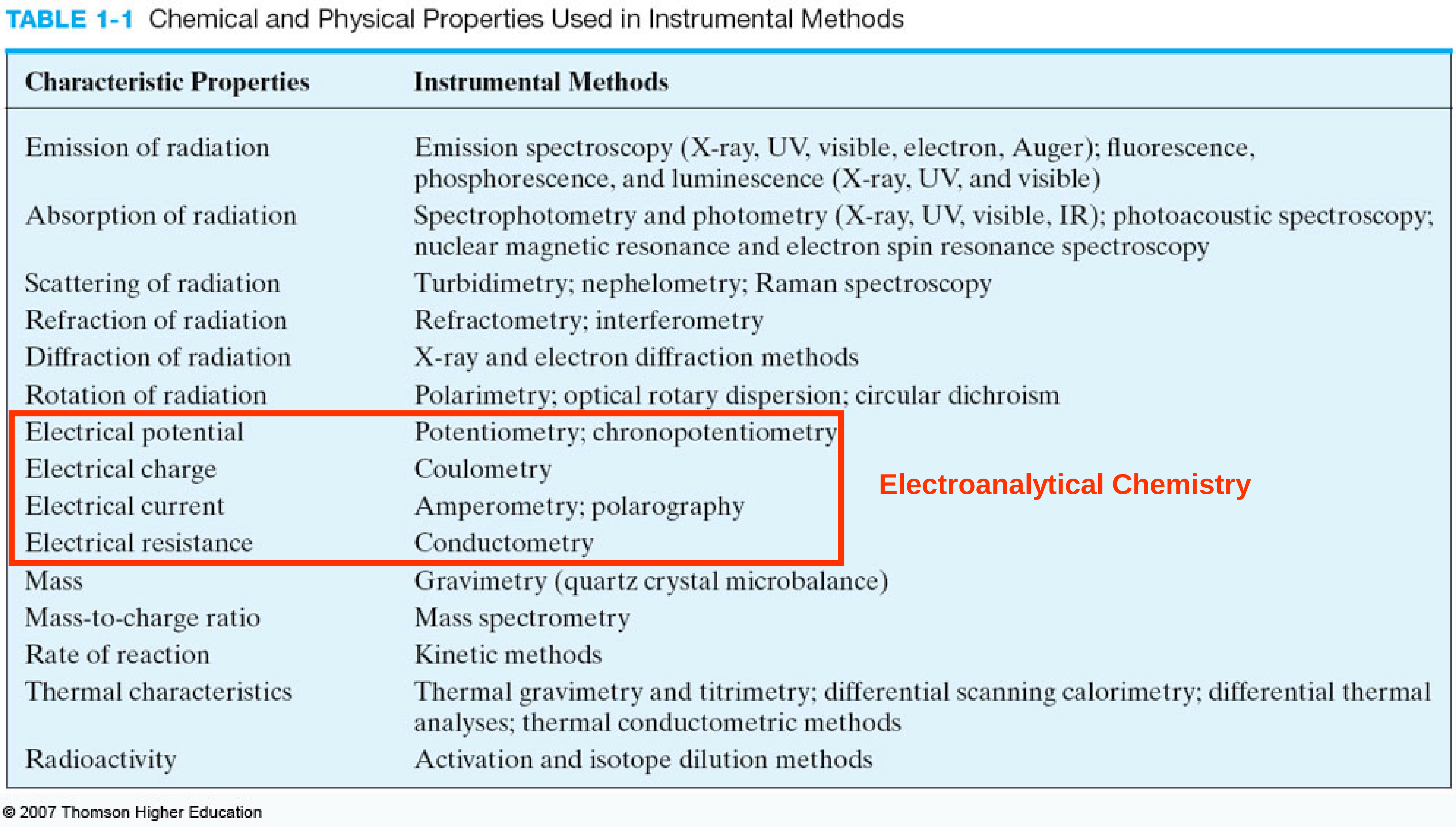


TABLE 1-1 Chemical and Physical Properties Used in Instrumental Methods

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

Electroanalytical Chemistry

Process for Analytical Chemistry

Defining the problem	sampling	pretreatment	measurement	evaluation
Obtain knowledge From Client Report Journal Cooking book	The sample Take Transfer Storage	Dissolution Clean up Concentration Separation	Select and/or Develop Best possible Methods	Interpreting the information Make clear and Meaningful report

Figure of Merit

: Performance characteristics of instruments

- Given instrumental method is suitable for attacking an analytical problem.
- Figure of merit permit the chemist to narrow the choice of instruments for given analytical problem to a relatively few.

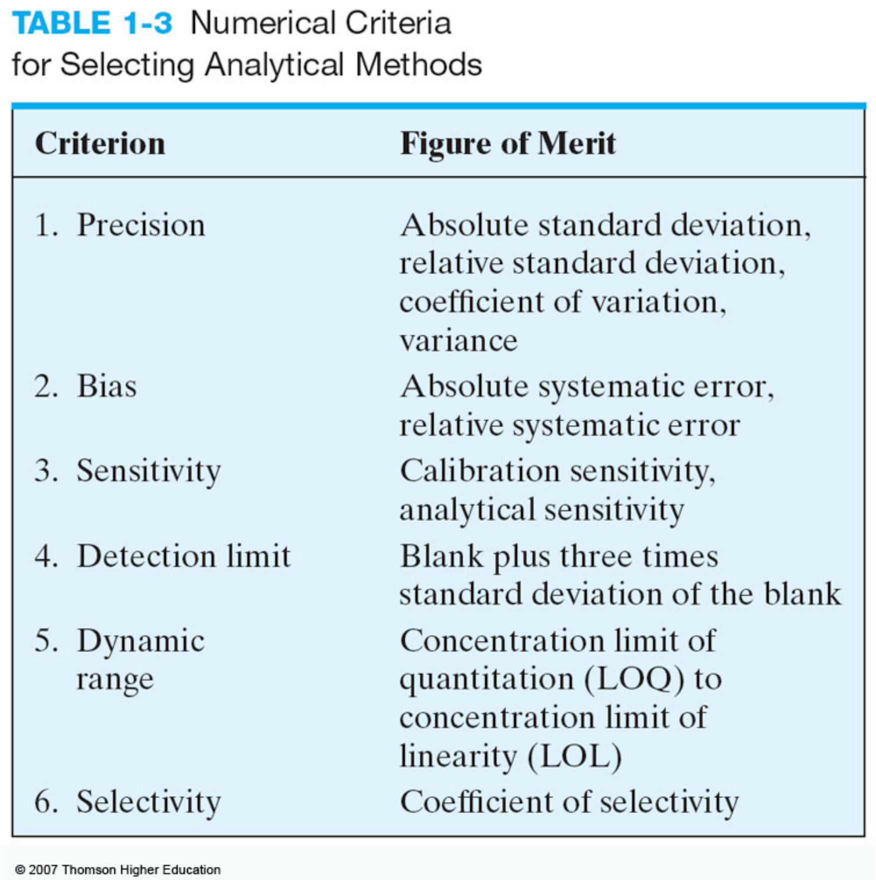


TABLE 1-3 Numerical Criteria for Selecting Analytical Methods

Criterion	Figure of Merit
1. Precision	Absolute standard deviation, relative standard deviation, coefficient of variation, variance
2. Bias	Absolute systematic error, relative systematic error
3. Sensitivity	Calibration sensitivity, analytical sensitivity
4. Detection limit	Blank plus three times standard deviation of the blank
5. Dynamic range	Concentration limit of quantitation (LOQ) to concentration limit of linearity (LOL)
6. Selectivity	Coefficient of selectivity

- Precision (reproducibility):

The degree of agreement between replicate measurement of the same quantity

- Accuracy:

The degree of agreement between the estimated concentration and true value (or certified value)

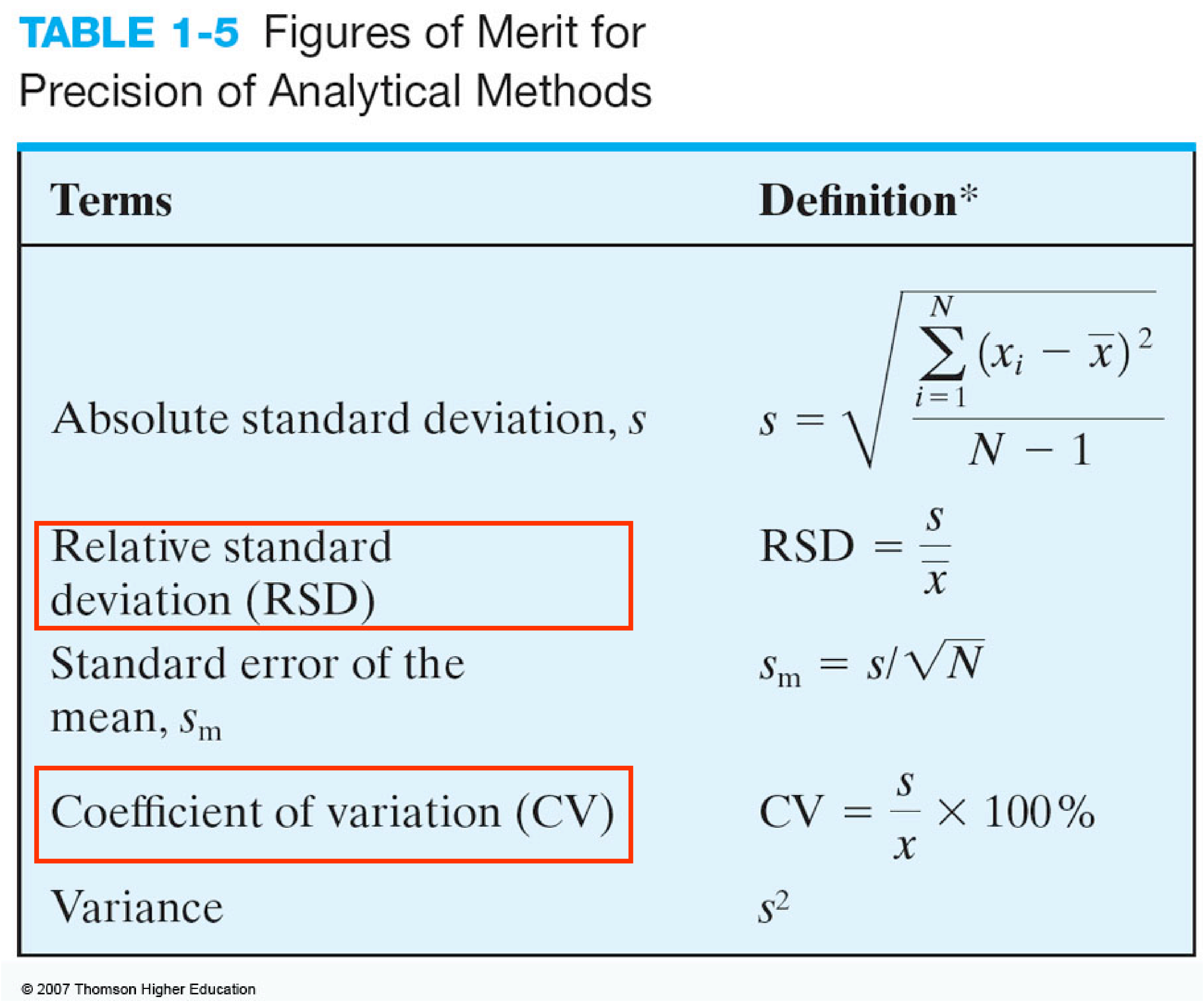


TABLE 1-5 Figures of Merit for Precision of Analytical Methods

Terms	**Definition***
Absolute standard deviation, s	$s = \sqrt{\dfrac{\sum_{i=1}^{N}(x_i - \overline{x})^2}{N - 1}}$
Relative standard deviation (RSD)	$\text{RSD} = \dfrac{s}{\overline{x}}$
Standard error of the mean, s_m	$s_m = s/\sqrt{N}$
Coefficient of variation (CV)	$\text{CV} = \dfrac{s}{\overline{x}} \times 100\%$
Variance	s^2

Experiment 1:

Signal 1 = 1001
Signal 2 = 1000
Signal 3 = 999

Average 1000
Standard deviation = 1
RSD = 1/1000 = 0.1%

Experiment 2:

Signal 1 = 0.005
Signal 2 = 0.007
Signal 3 = 0.003

Average 0.005
Standard deviation = 0.002
RSD = 0.002/0.005 = 40%

Bias

It provides a measure of the systematic or determinate error of an analytical method

bias = $\mu - \chi_t$

μ = population mean (certified value) χ_t = sample mean

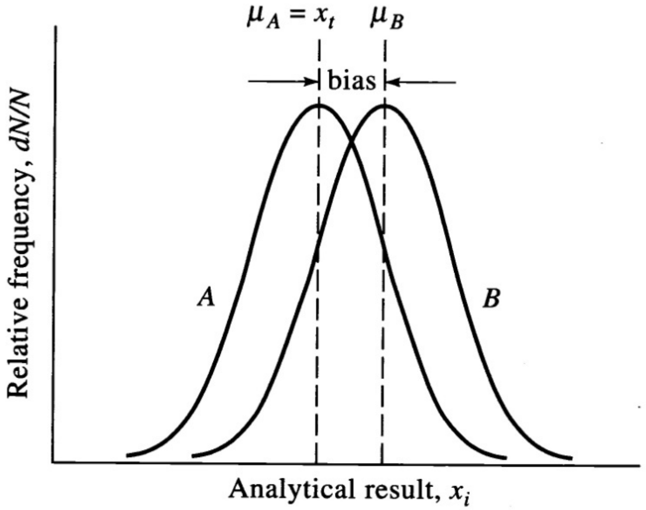


Figure a1-2 Illustration of bias = $\mu_B - \mu_A = \mu_B - x_i$

Systematic Error: Bias

: determinative error (고정오차, 가측 오차)

Instrumental error:

- **drift in electronic circuits**
- **calibration error**

Personal error:

Method errors:

Standard (certified) Reference Materials (SRM)
: validation

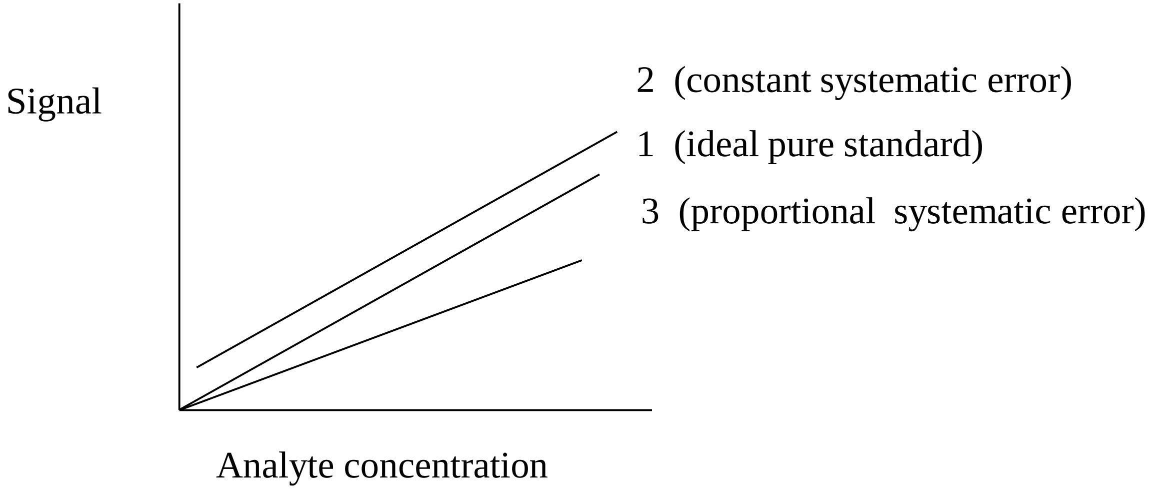


Fig. 3-3 Representation of systematic errors.

Random Error:

indeterminate error

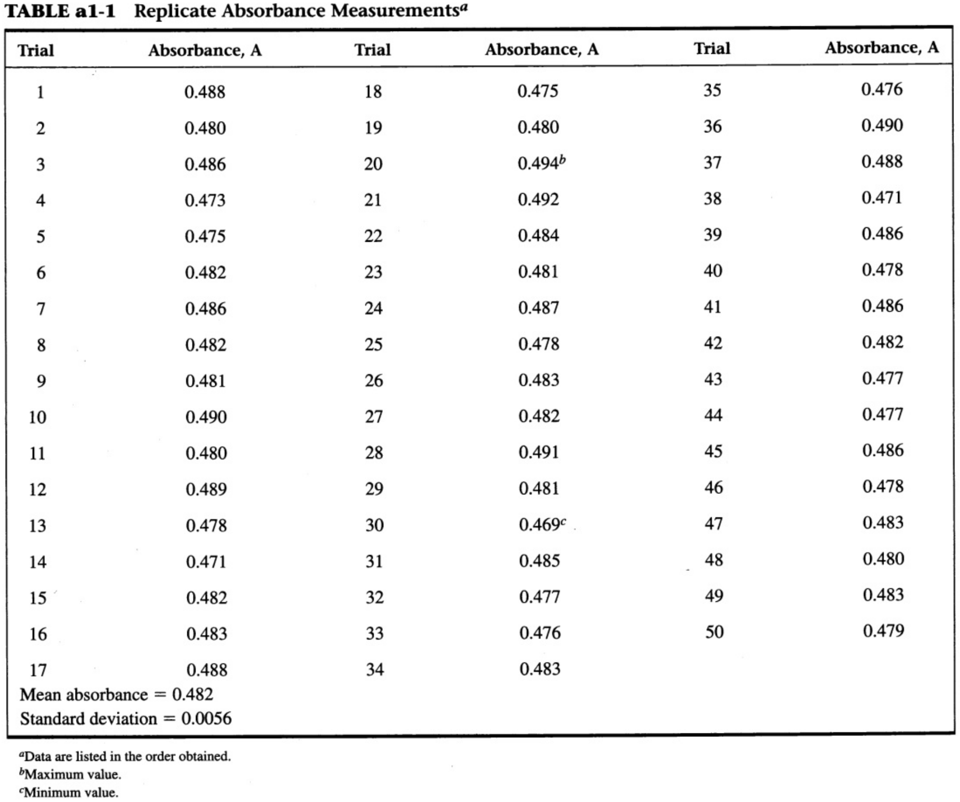


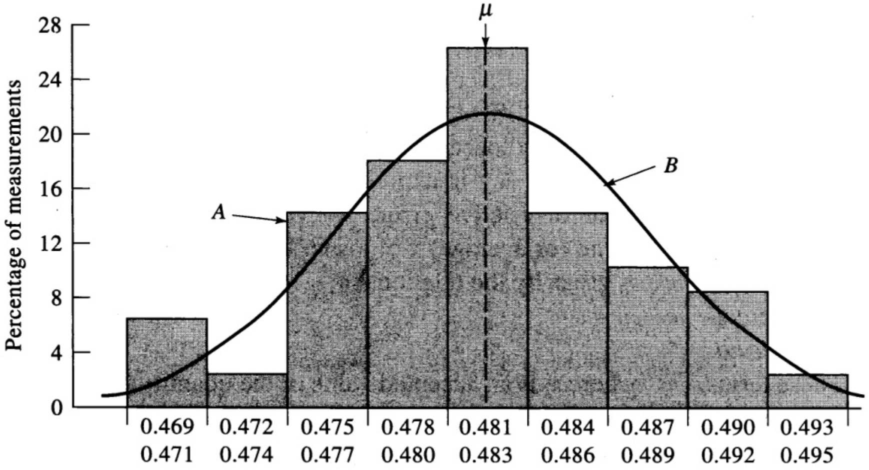
TABLE a1-1 Replicate Absorbance Measurements[a]

Trial	Absorbance, A	Trial	Absorbance, A	Trial	Absorbance, A
1	0.488	18	0.475	35	0.476
2	0.480	19	0.480	36	0.490
3	0.486	20	0.494[b]	37	0.488
4	0.473	21	0.492	38	0.471
5	0.475	22	0.484	39	0.486
6	0.482	23	0.481	40	0.478
7	0.486	24	0.487	41	0.486
8	0.482	25	0.478	42	0.482
9	0.481	26	0.483	43	0.477
10	0.490	27	0.482	44	0.477
11	0.480	28	0.491	45	0.486
12	0.489	29	0.481	46	0.478
13	0.478	30	0.469[c]	47	0.483
14	0.471	31	0.485	48	0.480
15	0.482	32	0.477	49	0.483
16	0.483	33	0.476	50	0.479
17	0.488	34	0.483		

Mean absorbance = 0.482
Standard deviation = 0.0056

[a] Data are listed in the order obtained.
[b] Maximum value.
[c] Minimum value.

In the absence of systematic error,
the measurement of a large set of data
Approaches the true value



Sensitivity

Sensitivity (감도)

- A measure of its ability to distinguish between small differences in analyte concentration
- Quantitative definition of sensitivity by IUPAC:

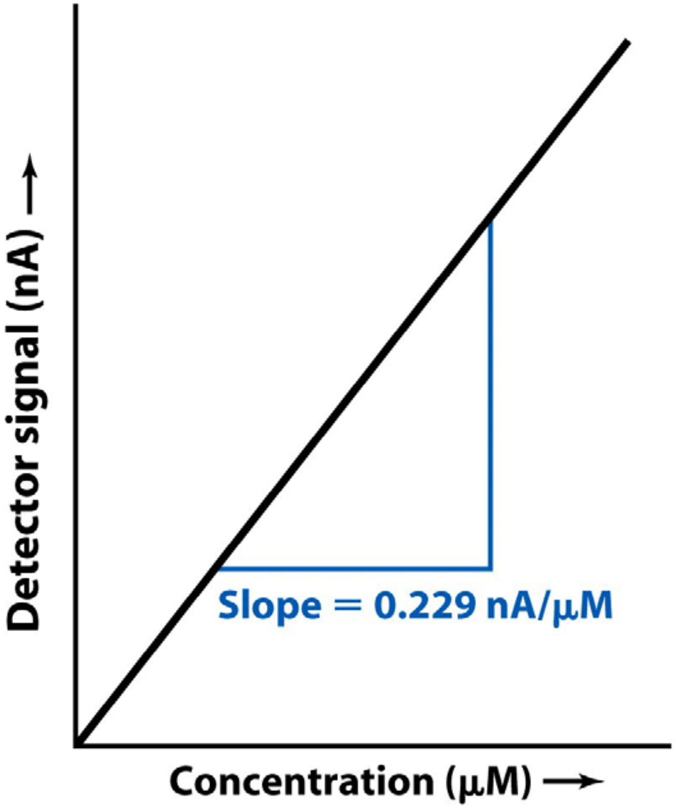
Calibration sensitivity

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

S: measured signal

S_{bl} can: blank signal

m: slope of calibration curve = calibration sensitivity



Unnumbered figure pg 86
Quantitative Chemical Analysis, Seventh Edition
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Detection Limit

Detection limit (limit of detection; C_m)

: the minimum concentration or mass of analyte that can be detected at a known confidence level

- Depends upon the ratio of the analytical signal to the size of the statistical fluctuations in the blank signal (S/N)

- S_m: minimum distinguishable analytical signal (S/N =3)

- $S_m = \overline{S}_{bl} + k\, s_{bl}$ (k =$\underline{3}$ or 2)
- $\overline{S}_{bl}$ (average blank signal), s_{bl} (standard deviation of blank signal)
- S_m can be determined by performing 20 to 30 blank measurements.
- $C_m = (S_m - \overline{S}_{bl})/m$

Example 1-1.

Determination of lead (based on flame emission spectrum)

Calibration data : $s = 1.12\ C_{Pb} + 0.312$

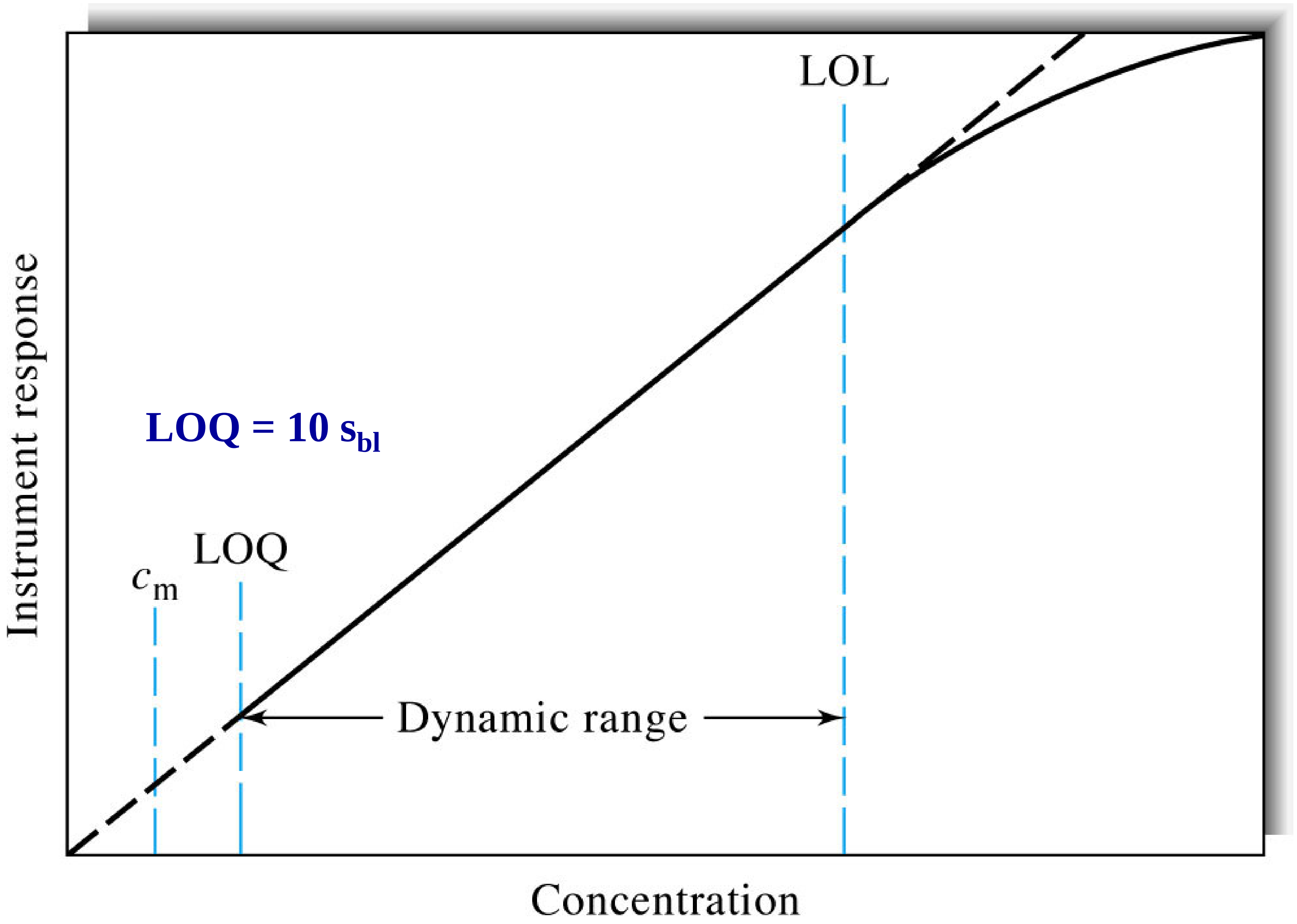
Conc, ppm, Pb	No. of replications	Mean value of *S*,	*s*
10.0	10	11.62	0.15
1.00	10	1.12	0.025
0.000 (blank)	24	0.0296	0.0082

(a) Calibration sensitivity = ? → slope = 1.12

(b) Detection limit = ? → $S_m = S_{bl} + 3 \times s_{bl} = 0.0296 + 3 \times 0.0082 = 0.054$

Detection limit, $C_m = (0.054-0.0296)/1.12 = 0.022$ ppm Pb

Linear Dynamic range = LOQ ~ LOL



LOQ = 10 s_{bl}

Calibration

A process that relates the measured signal to the concentration of analytes

- Simple (external) calibration method

(no matrix effect or pre-separation step)

The plot between series of standards and signal

- Standard addition method

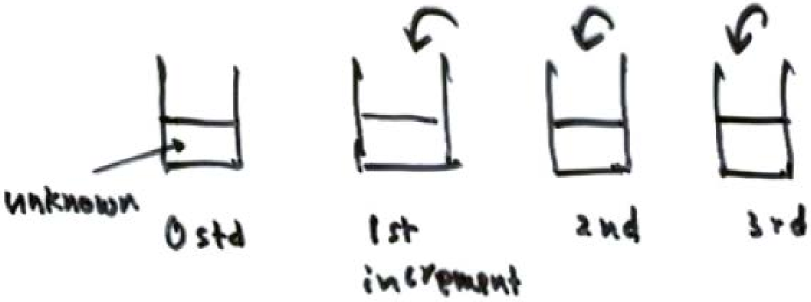
Add standard solutions to sample
(several aliquot of the same size)

- Internal standard method

A substance is added in a constant amount to all samples, blank and calibration standards

Standard Addition Method

- Useful for analyzing complex samples in which matrix effect is substantial.
- Known quantities of analyte are added to the unknown: from the increase in signal, concentration of analyte in original unknown can be deduced.



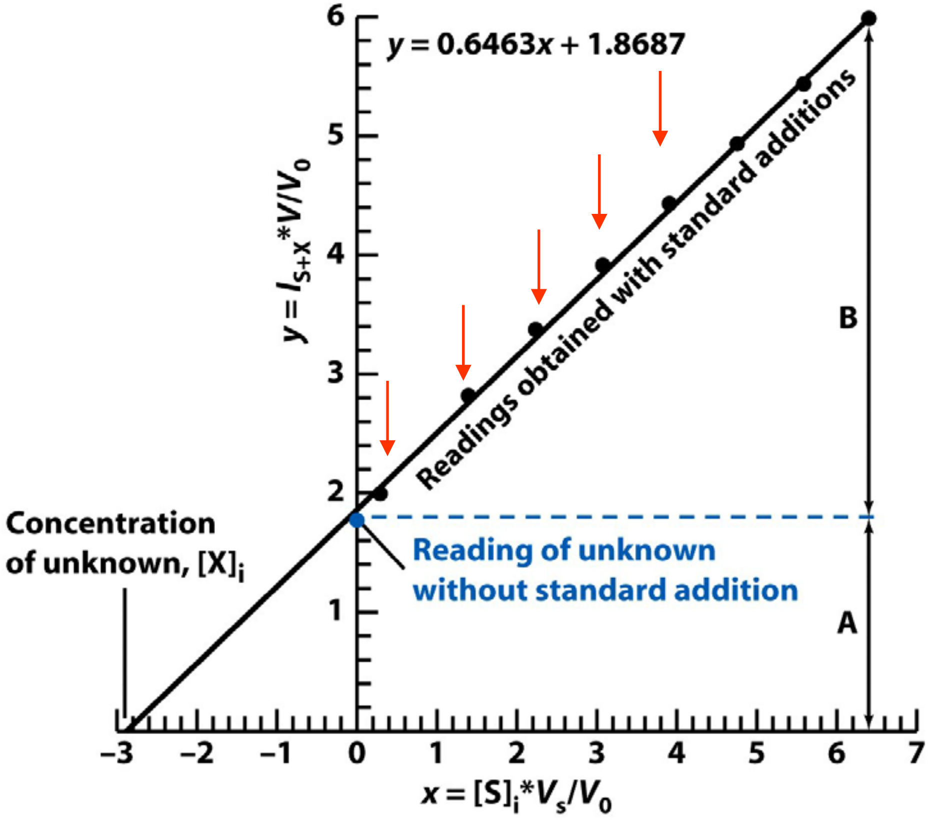


Figure 5-6
Quantitative Chemical Analysis, Seventh Edition

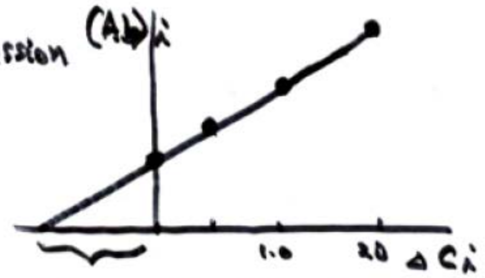
Standard Addition Method

Example

Det. of Zn^{2+} solution by AAS using standard addition method

step #	conc. of added Zn (ppm)	Absorbance
1	0.0	0.196
2	0.5	0.289
3	1.0	0.383
4	2.0	0.555

By linear regression



Conc. of original

$$A_i = 0.199 + 0.179\,\Delta C_i$$

$$A_i = 0 = 0.199 + 0.179\,\Delta C_i$$

$$\Delta C_i = \frac{0.199}{0.179} = 1.11 \text{ ppm}$$

$\therefore$ Original $[Zn^{2+}]$ = 1.11 ppm

Internal Standard

An internal standard (IS) is a known amount of compound, different from analyte, that is added to the unknown sample.

IS: useful in analyses in which the quantity of sample analyzed or the instrument response varies slightly from run to run for reasons that are difficult to control

Gas and liquid chromatography:
- flow rate change → response change
- small quantity of solution is injected: not reproducible

Relative response of the detector to the analyte and standard is constant:
(e.g) flow rate change → S(IS) 5% increase → S(analyte) 5% increase

The concentration of IS is known → correct concentration of analyte can be derived.

IS is also desirable when sample loss can occur during sample preparation before analysis.

Internal Standard

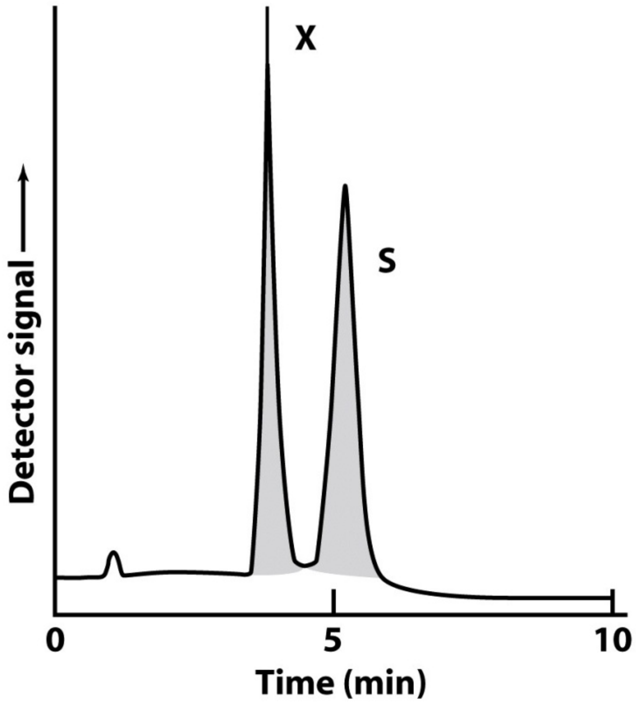


Figure 5-7
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If [X] = [S] = 1.0 mM, area Ax = 2.5 area S,
then response factor = 2.5

Ax/[X] = R (As/[S]) ; R = response factor

Example:
(1) Preliminary experiment to determine R:
[X] = 0.0837M, [S] = 0.0666M → Ax =423, As = 347

423/0.0837 = R (347/0.666) → R = 0.970

(2) To analyze the unknown ([X]= ?),
10.0 mL of 0.146 M standard was added to the 10 mL unknown
and diluted to 25 mL → Ax = 553, As = 582

[S] = 0.146 M x dilution factor (10.0/25.0) = 0.0584 M
553/[X] = 0.970 (582/0.0584) → [X] = 0.0572 M

Thus, original concentration of X in unknown is 0.0572 x (25.0 mL/10.0mL) = 0.143M