2018학년도 1학기

기기분석: 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

/5th edition by Skoog, Holler and Nieman

- 분석화학 기초개념/분광분석/ 표면분석/질량분석/분리분석화학 을 중심으로 강의

성적평가

- 시험: 2회 (50% + 50%)
- 출석점수: 없음, 단 1/3이상 결석은 F 학점 (출석은 전자 출결시스템 활용: 학생증 지참 혹은 전자출결 어플리케이션 활용 요망)

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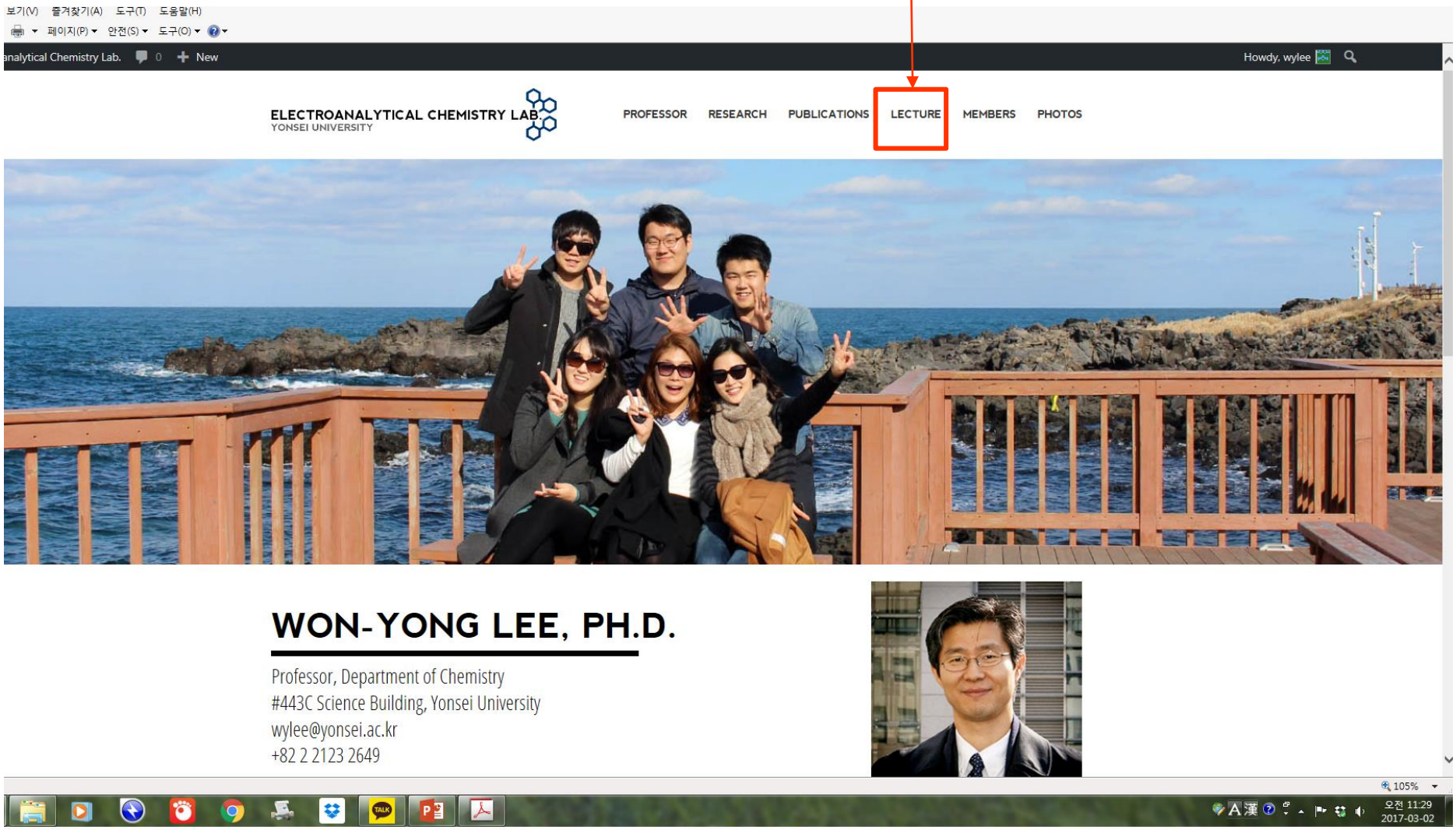
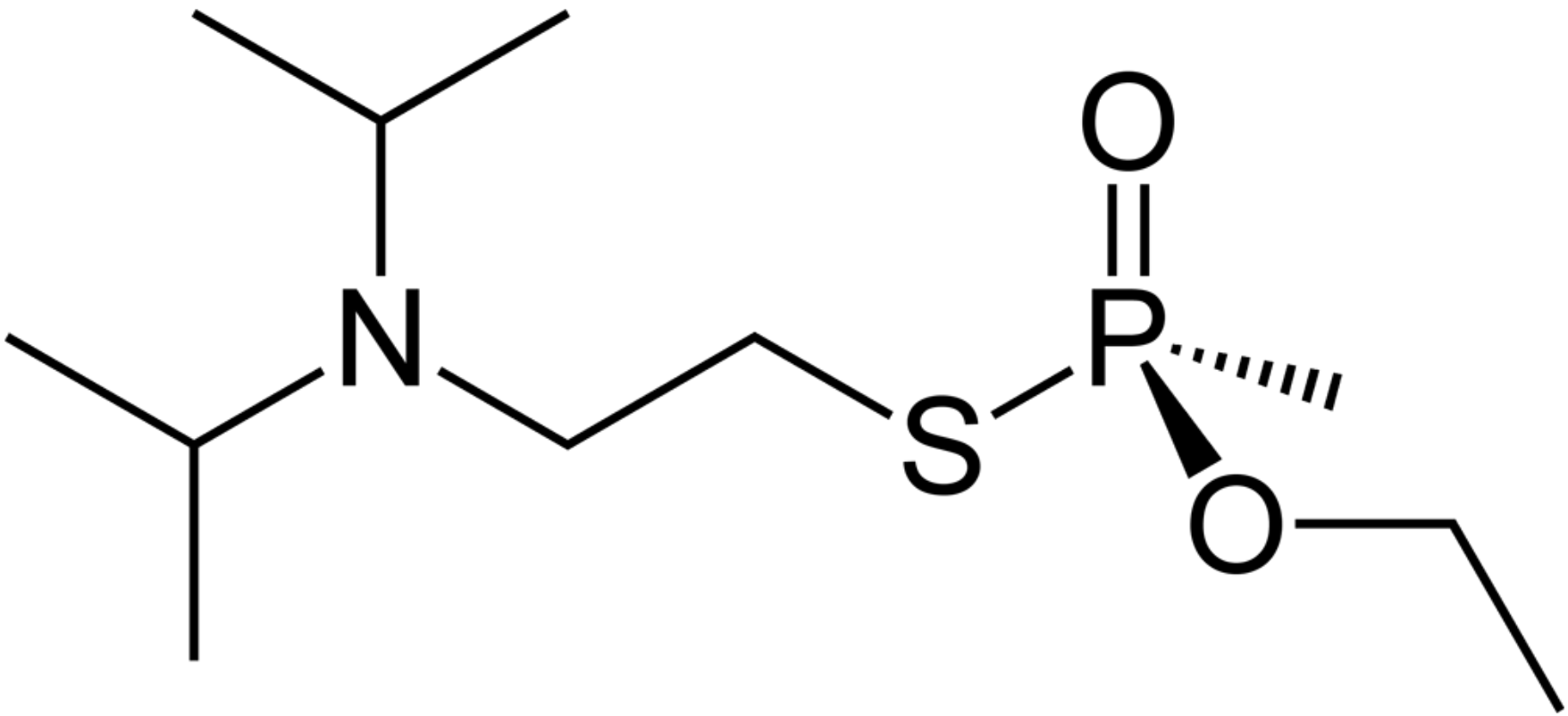


2018학년도 기기분석 강의계획

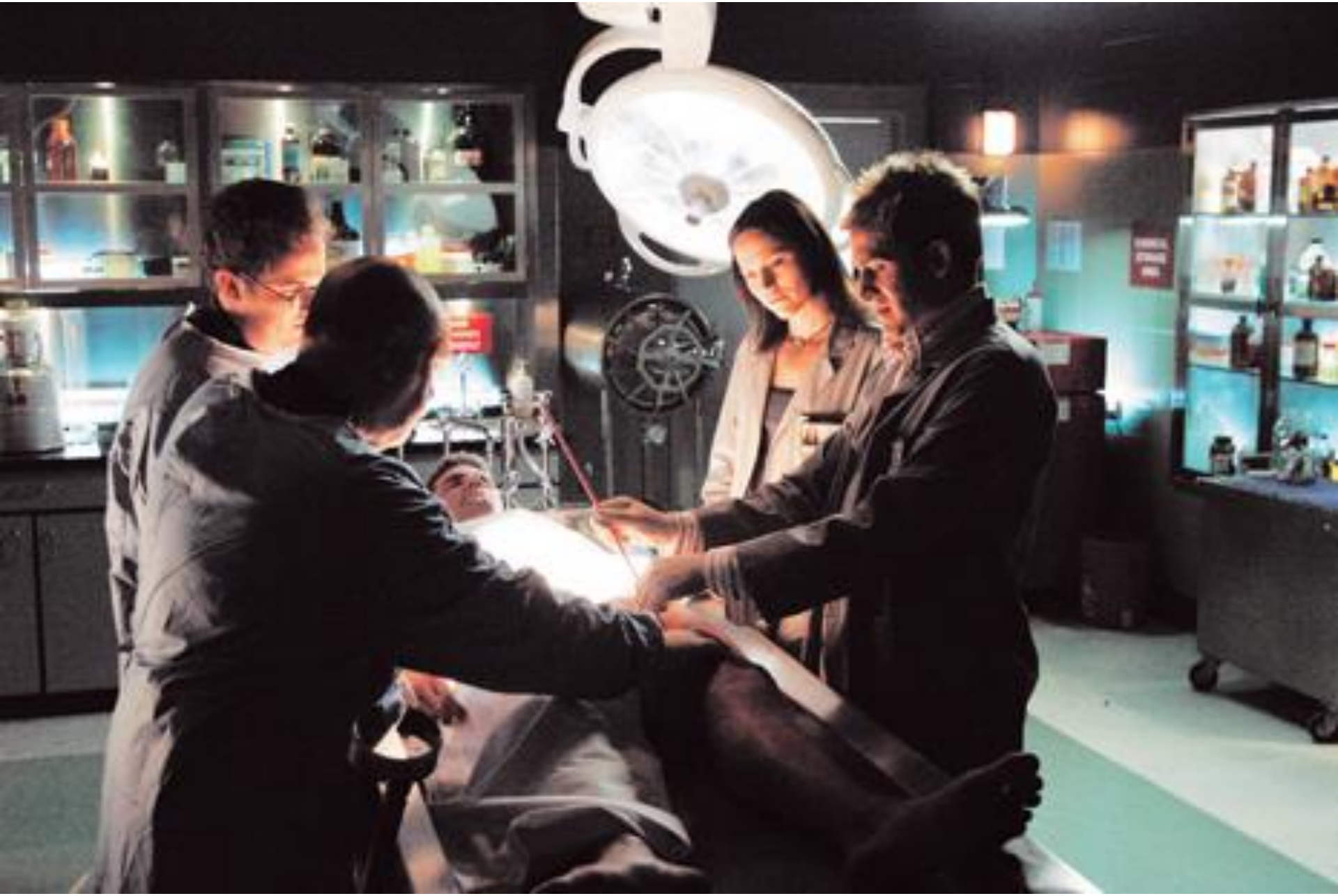
Chapter 1: Introduction
Chapter 2: Electrical Components and Circuits (시험범위제외)
Chapter 3: Operational Amplifiers in Chemical Instrumentation (시험범위제외)
Chapter 5: Signals and Noise
Chapter 6: Introduction to Spectrometric Methods
Chapter 7: Components of Optical Instruments
Chapter 8-10: Atomic Spectrometry
중간시험 (4월16일 수업시간)

Chapter 11: Atomic Mass Spectrometry
Chapter 15: Molecular Luminescence Spectrometry
Chapter 20: Molecular Mass Spectrometry
Chapter 21: Surface Characterization by Spectroscopy and Microscopy
Chapter 29: Supercritical Chromatography and Extraction
Chapter 30: Capillary Electrophoresis and Capillary Electrochromatography
기말시험 (6월11일, 자율학습 및 기말시험 기간)


김정남 시신 VX 검출
KBS1
9
KBSNEWS



VX: Ethyl-S-2-diisopropylaminoethyl-methyl phosphonothiolate




천재와 신참의 퍼펙트 만남
그들의 메스가 범죄를 해부한다!
국내 최초 메디컬 수사 드라마
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박신양 | 김아중 | 전광렬 | 엄지원 | 정겨운
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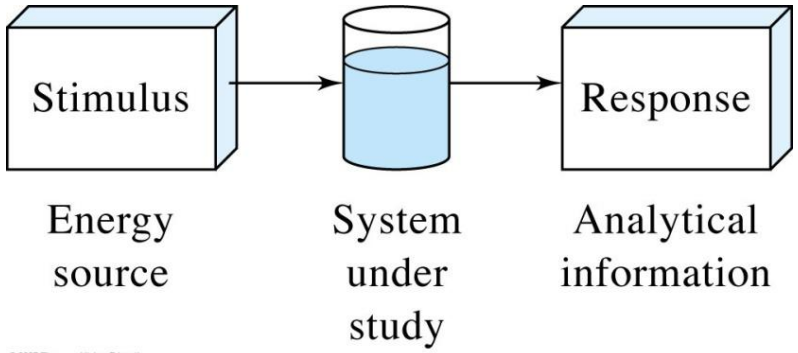
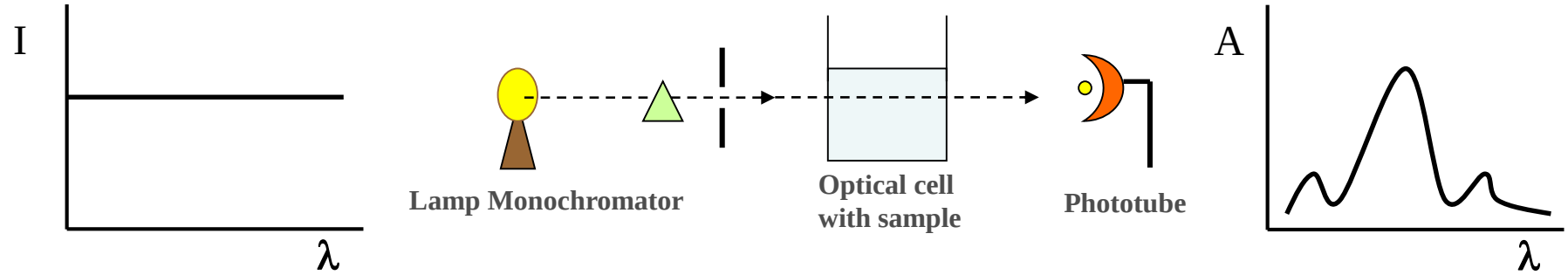
출입금지-POLICE LINE
과학 수사

Instrumental Analysis

General concept



Spectrophotometric experiment



Electrochemical experiment

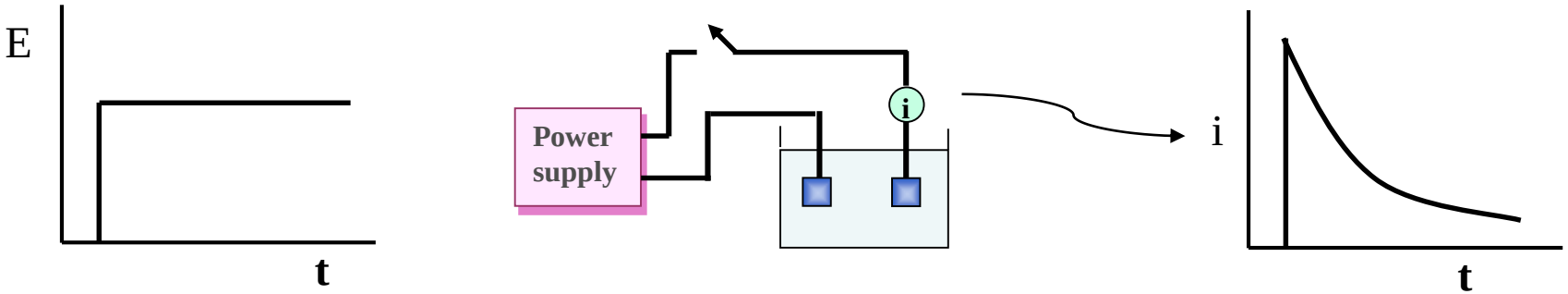


TABLE 1-1 Chemical and Physical Properties Used in Instrumental Methods

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

In instrument

One form —encoding→ **Another form**

Nonelectrical Domains:

- Length
- Density
- Chemical composition
- Pressure
- Mass

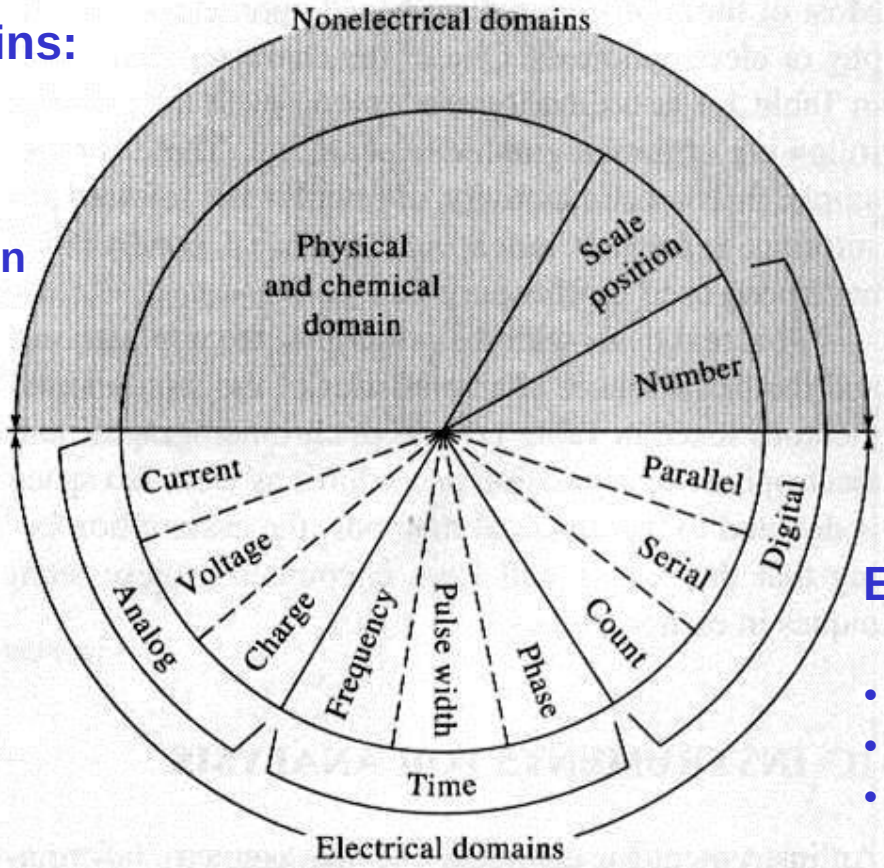
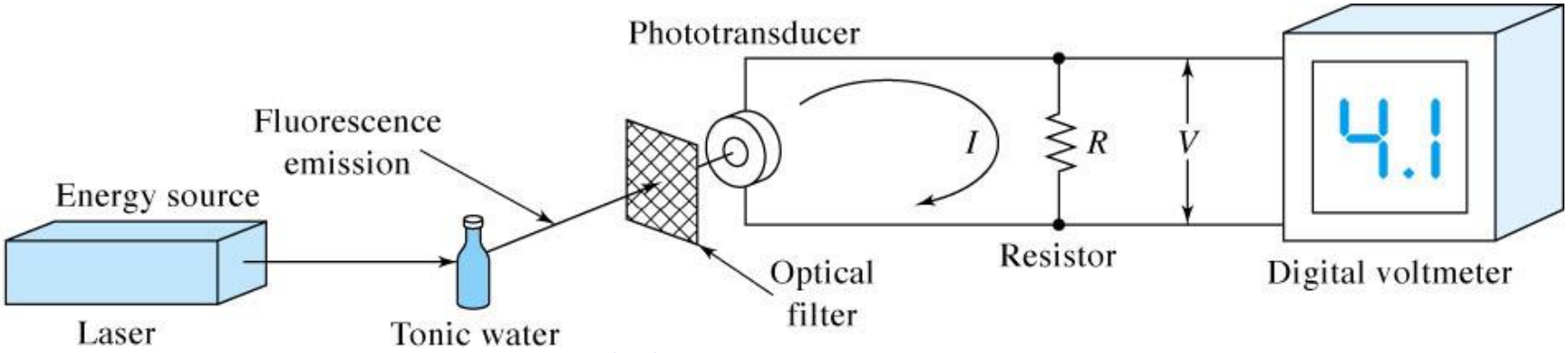


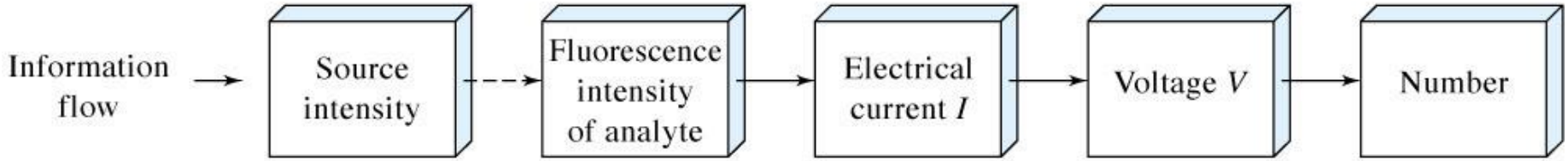
Figure 1-2 Data domains map. The upper (shaded) half of the map comprises nonelectrical domains. The bottom half is made up of electrical domains. Note that the digital domain spans both electrical and nonelectrical domains.

Electrical Domains:

- Analog domains
- Digital domains
- Time domains

Any measurement process can be represented as a series of ***interdomain conversions***



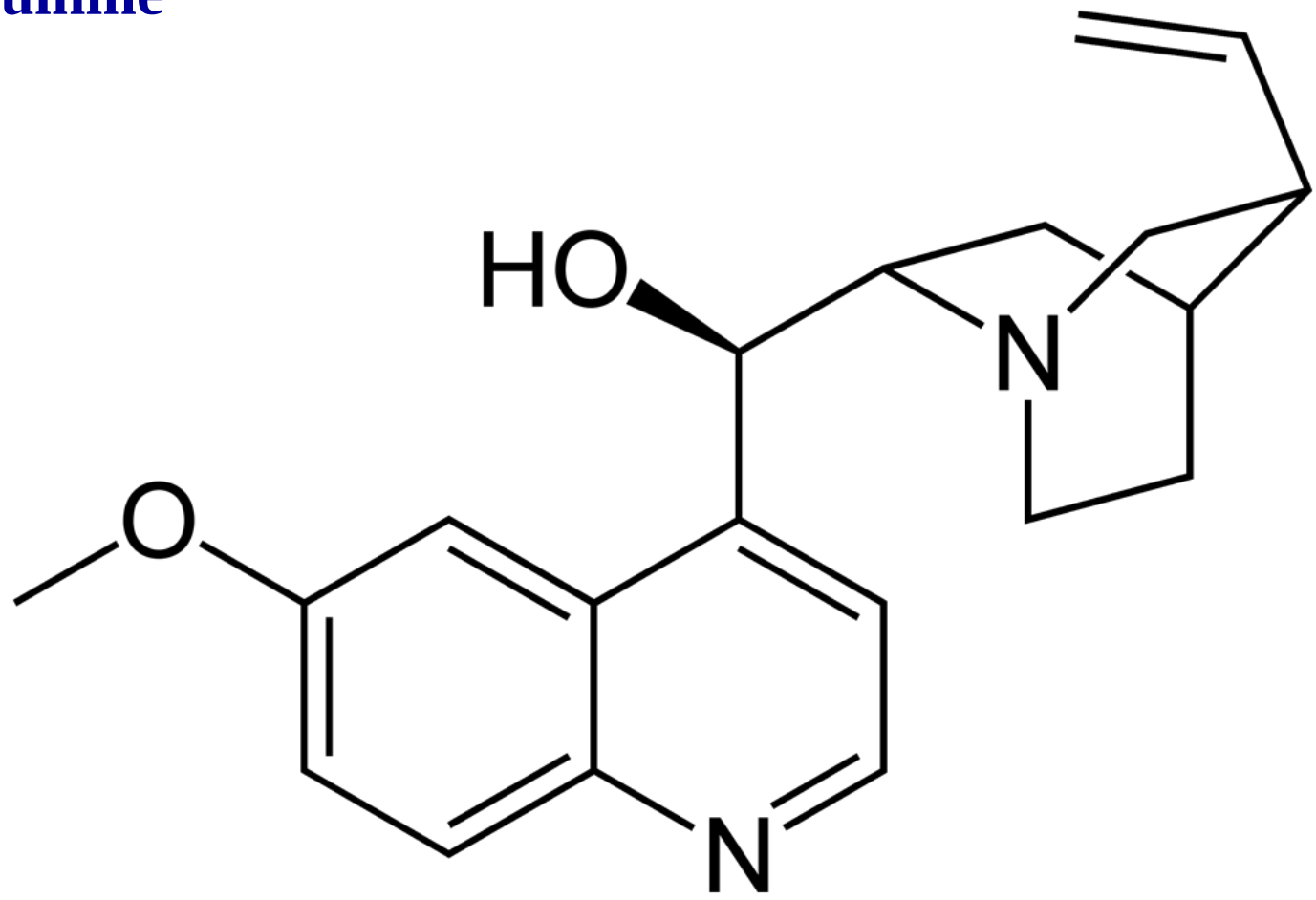


Non-electrical domain (b) **electrical domain**

Governed by →	Laws of chemistry and physics	Transducer transfer function	Ohm's law $V = IR$	Meter transfer function

(c)

Quinine



Natural alkaloid:
antipyretic (fever-reducing), antimalarial, analgesic (painkilling)

Cinchona

Bottle of tonic water

Under regular light

Under UV light

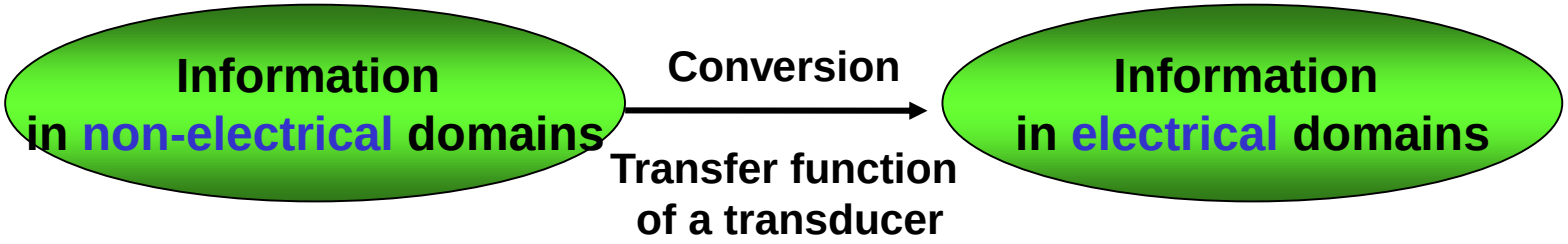
TABLE 1-2 Some Examples of Instrument Components

Instrument	Energy Source (stimulus)	Analytical Information	Information Sorter	Input Transducer	Data Domain of Transduced Information	Signal Processor/ Readout
Photometer	Tungsten lamp	Attenuated light beam	Filter	Photodiode	Electrical current	Amplifier, digitizer, LED display
Atomic emission spectrometer	Inductively coupled plasma	UV or visible radiation	Monochromator	Photomultiplier tube	Electrical current	Amplifier, digitizer, digital display
Coulometer	Direct-current source	Charge required to reduce or oxidize analyte	Cell potential	Electrodes	Time	Amplifier, digital timer
pH meter	Sample/ glass electrode	Hydrogen ion activity	Glass electrode	Glass-calomel electrodes	Electrical voltage	Amplifier, digitizer, digital display
Mass spectrometer	Ion source	Mass-to-charge ratio	Mass analyzer	Electron multiplier	Electrical current	Amplifier, digitizer, computer system
Gas chromatograph with flame ionization	Flame	Ion concentration vs. time	Chromatographic column	Biased electrodes	Electrical current	Electrometer, digitizer, computer system

Detector, Transducer, and Sensors

Detector: the most general term

Transducer:

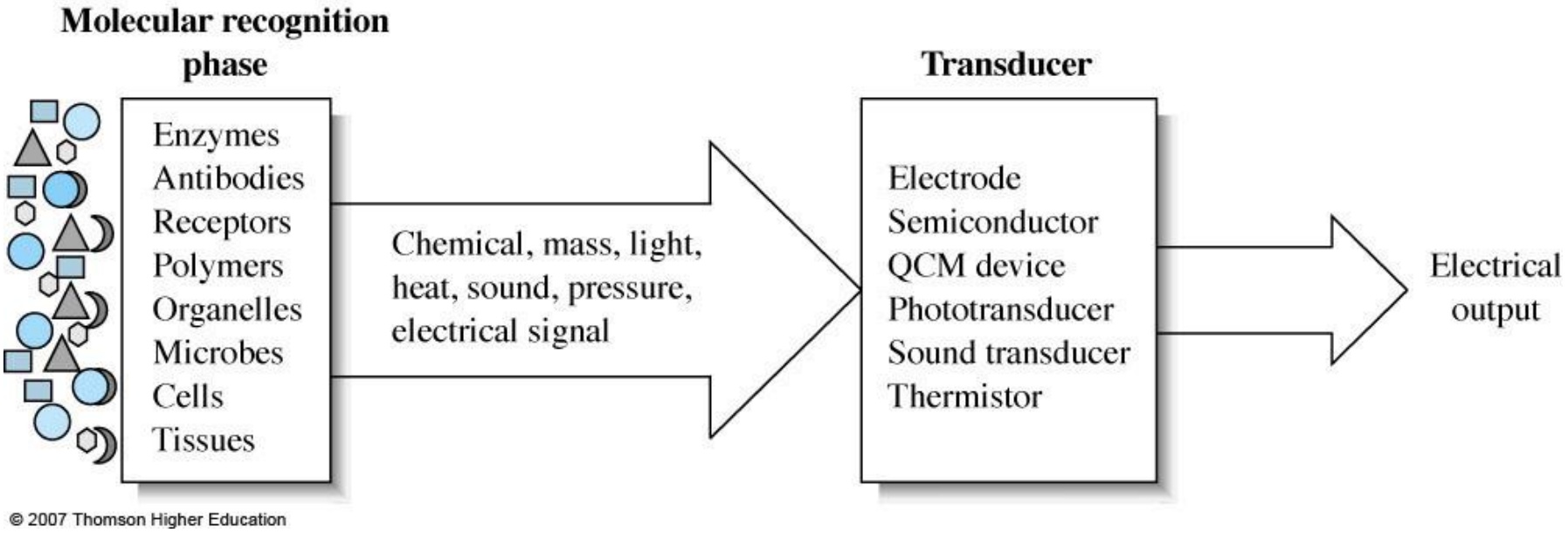


Example:

- **Photodiode, Photomultiplier tube (PMT)**
- **Electrode**
- **Quartz crystal**
- **Thermister**

Chemical Sensor and Biosensor

selective recognition phase + transducer



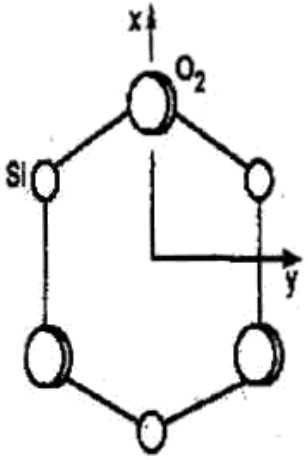
Chemical sensor: chemical recognition phase (polymer, ionomer, semiconductor etc)
Biosensor; biological components (enzyme, antibody, DNA, cell …)

Characteristics of Chemical Sensor and Biosensor: small and portable

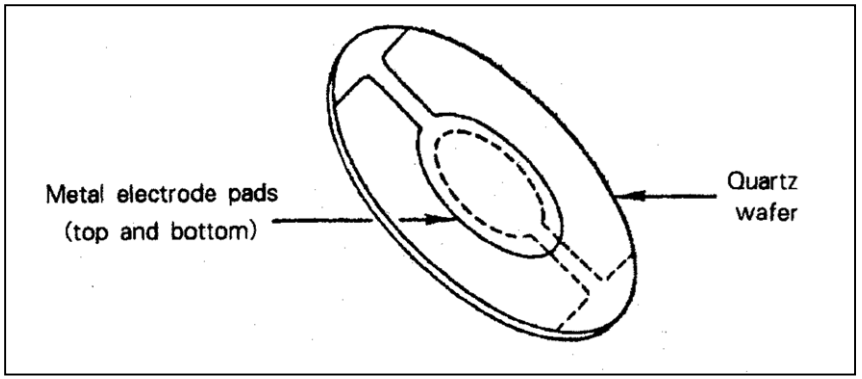
QCM (Quartz Crystal Microbalance)

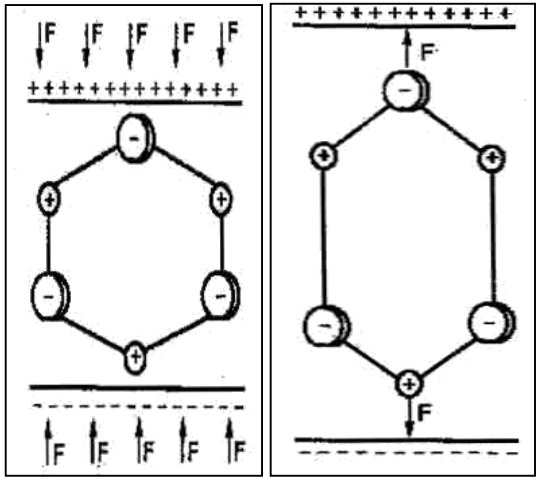
For piezoelectric material such as quartz crystal,

Mechanical Deformation ⟷ *Electric Potential*



PZ (piezoelectric crystal)
→ centroasymmetry





converse piezoelectric effect

piezoelectric effect (in 1880, Pierre Curie discovered): piezo = stress in Greek

QCM (Quartz Crystal Microbalance)

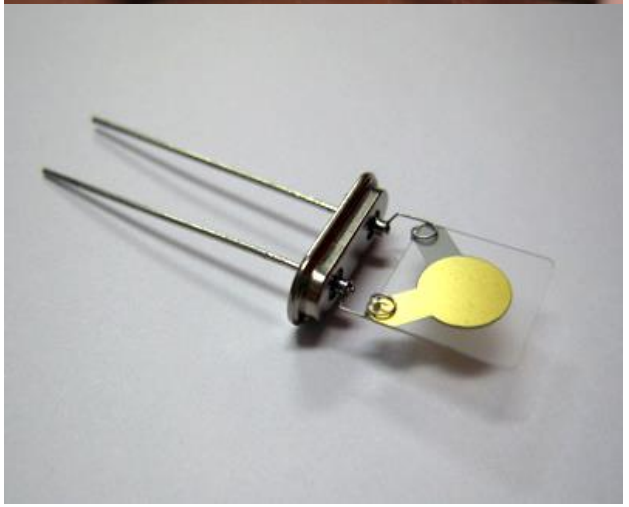
Saubery's equation

$$\Delta mass = \frac{-\Delta freq \times A \times \sqrt{\mu_q \times \rho_q}}{2 \times F_q^{\,2}}$$

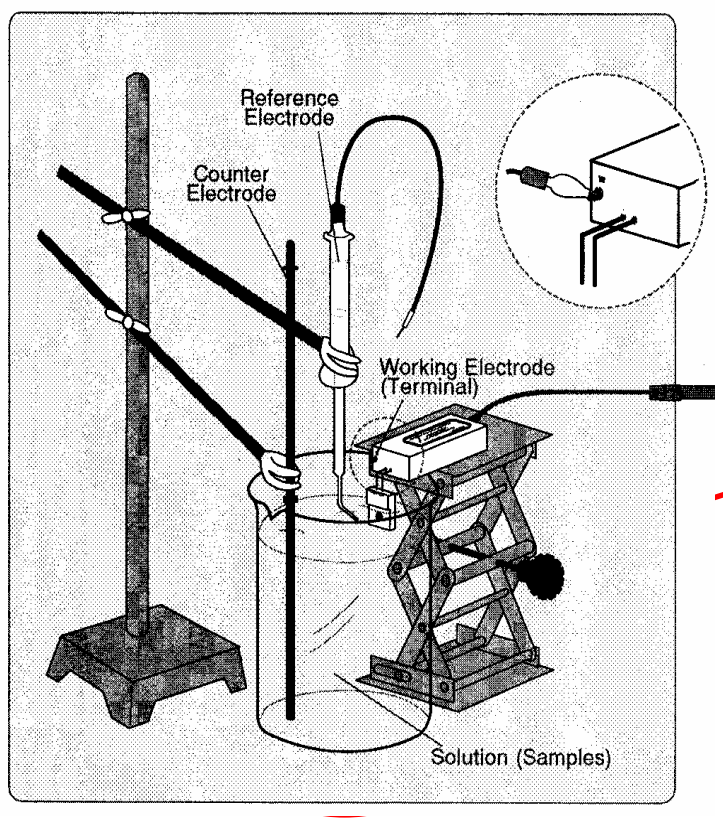
Δ mass : Mass change
Δ freq : Resonant frequency change
μ_q : AT-cut quartz crystal constant (2.947*1011 g/Cmsec^2)
ρ_q : Quartz crystal density (2.648 g/Cm^2)
F_q : Reference frequency (9.00 MHz)
A : Quartz crystal surface area (0.196 Cm^2)

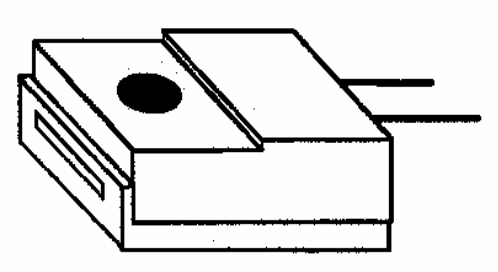
$$\longrightarrow \quad \Delta mass = -\Delta freq \times 5.453 \times A$$
$$= -\Delta freq \times 1.068$$

1 Hz $\longrightarrow$ 1.068 ngcm^{-2}

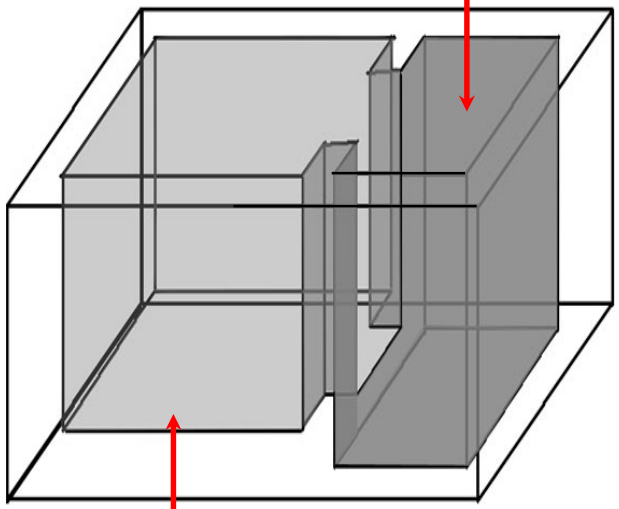


Experimental Set-Up for EQCM



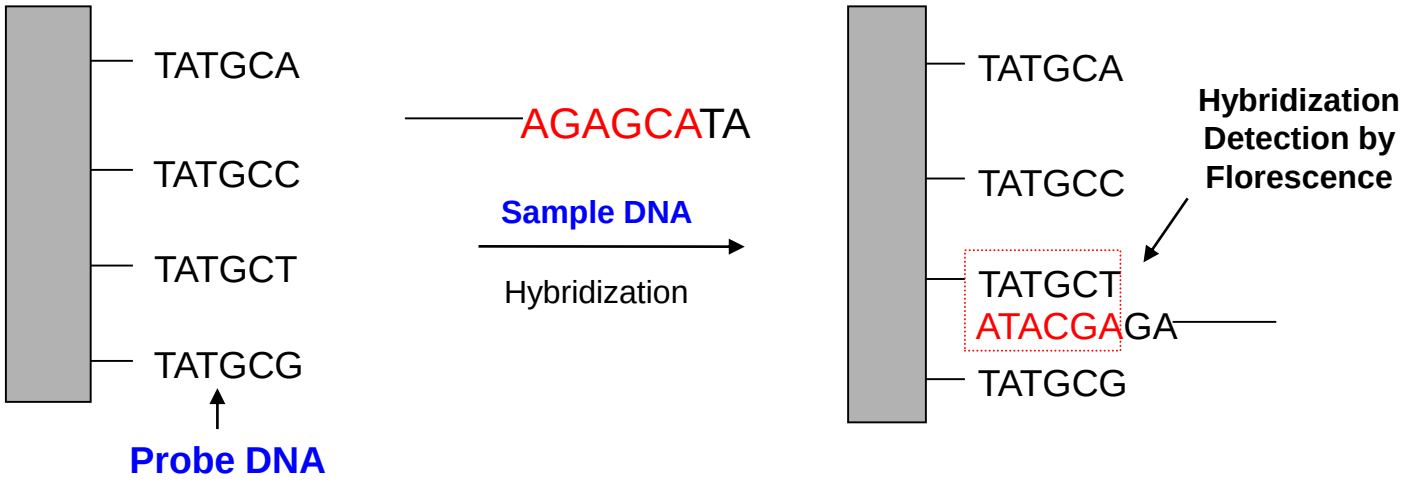


Working Electrode



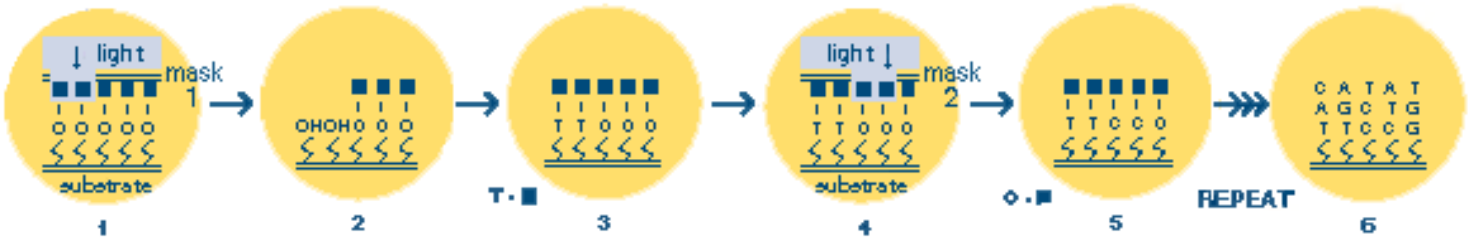
Cell Volume : 5-6 mL

DNA Chip: ordered array of a variety of immobilized DNA molecules



Applications

- Identification of complex genetic disease and pathogen analysis
- Drug discovery and expression information of genes over time, between tissues, and disease states



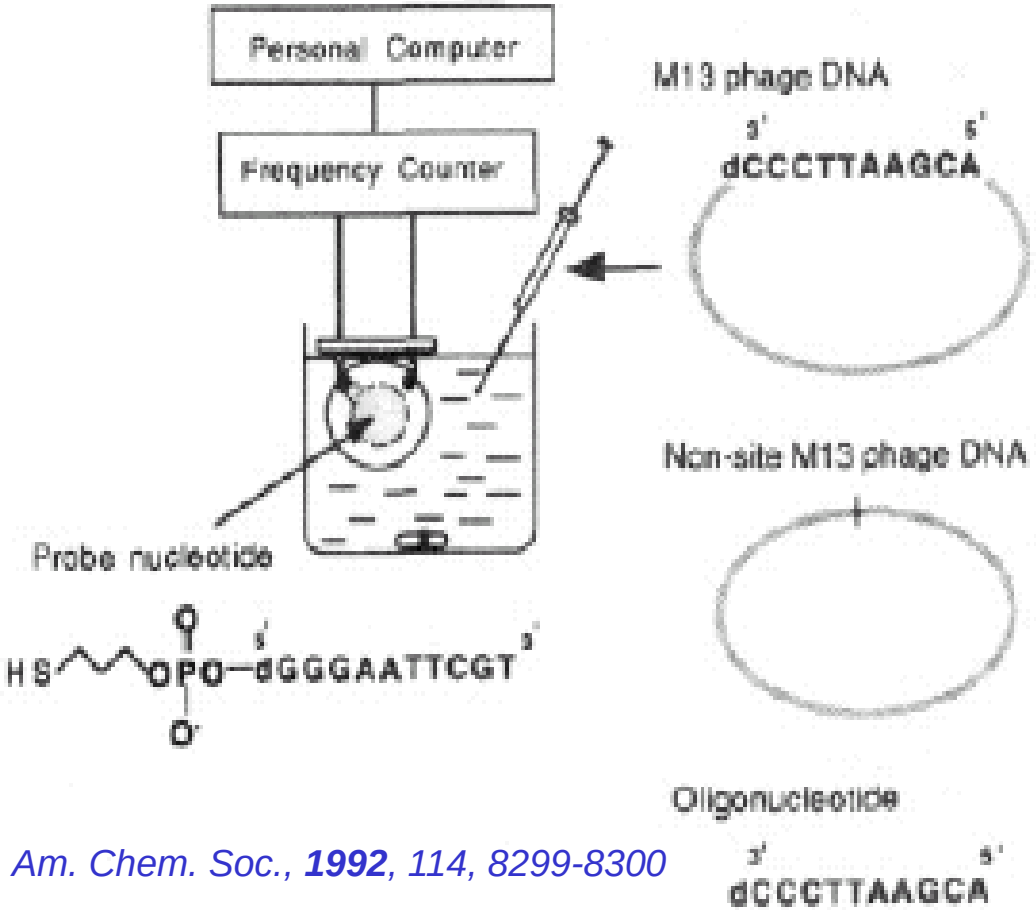
R. J. Lipshultz, et. al., *Nature, Genetics*, **1999**, *21*, 20-24

Hybridization of Nucleic Acids Immobilized on a Quartz Crystal Microbalance

Yoshio Okahata,*[1a] Yuka Matsunobu,[1a] Kuniharu Ijiro,[1a] Masayuki Mukae,[1b] Akira Murakami,[1b] and Keisuke Makino[1b]

Department of Biomolecular Engineering Tokyo Institute of Technology Ookayama, Meguro-ku, Tokyo 152, Japan Faculty of Textile Science, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606, Japan

Received July 6, 1992



Y. Okahata, et. Al. J. Am. Chem. Soc., ***1992****, 114, 8299-8300*

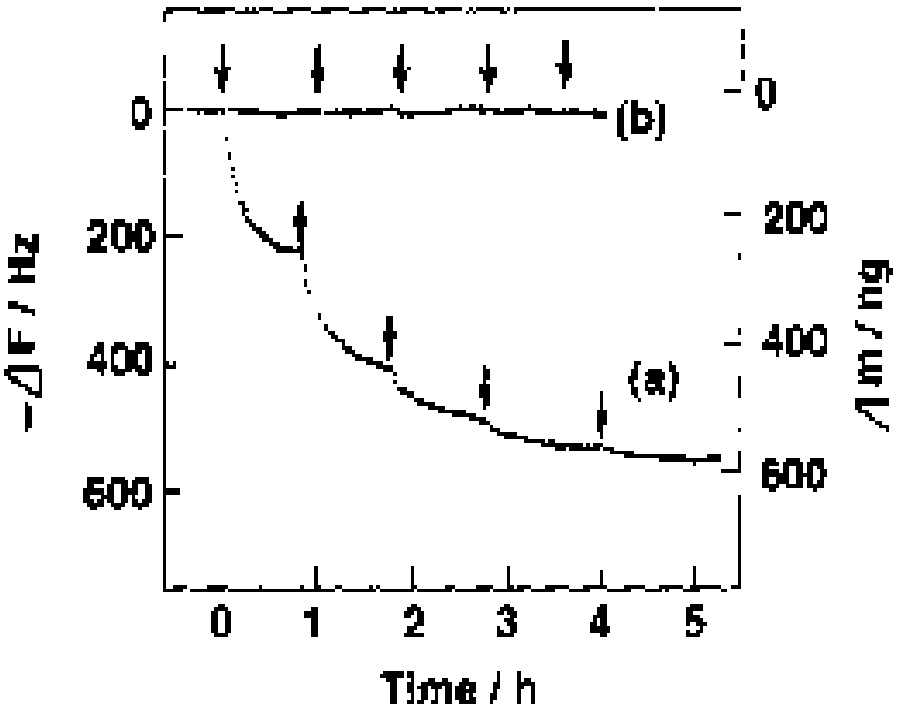
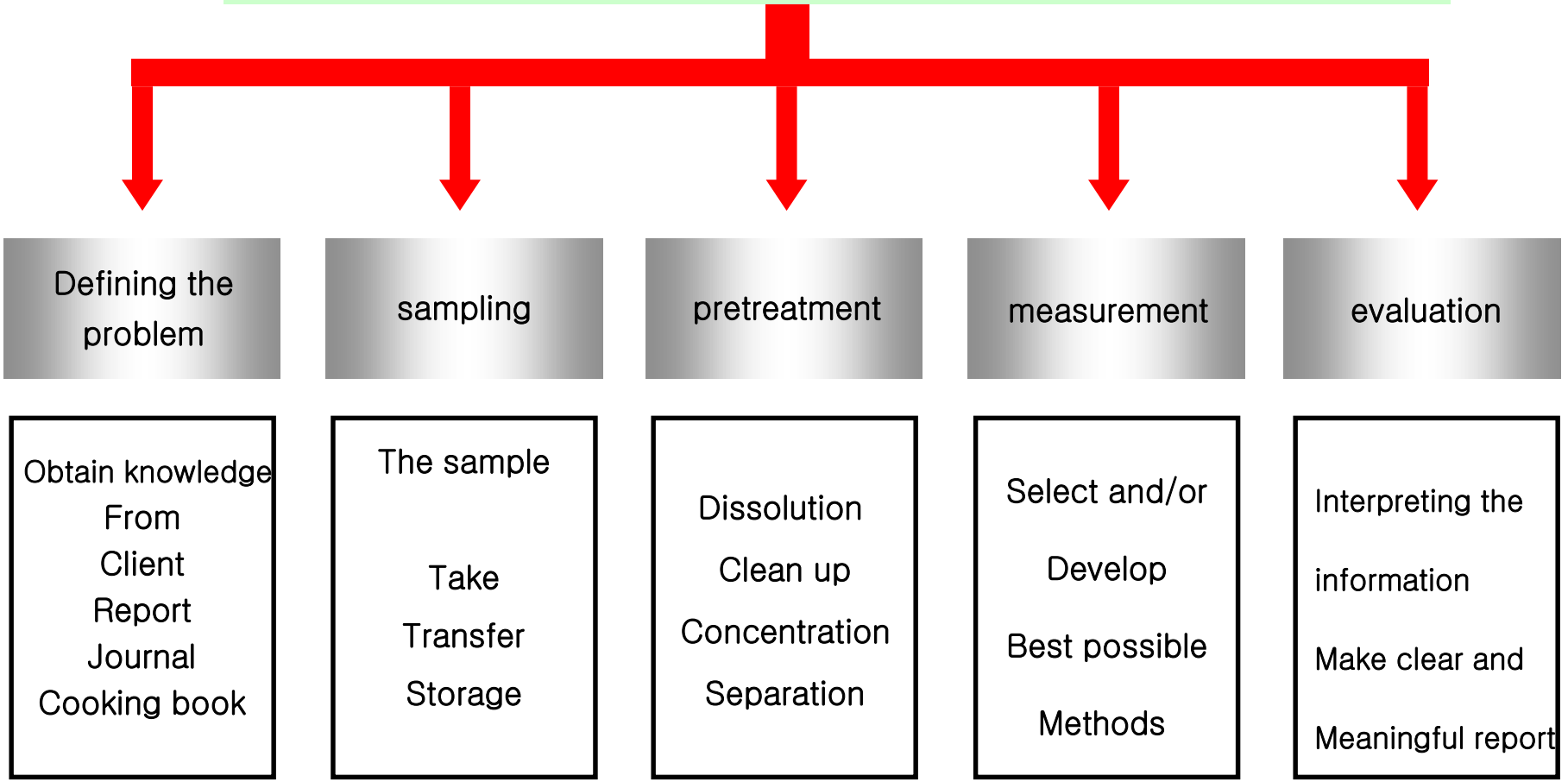


Figure 1. Typical frequency changes of 30-mer nucleotide (106 ng, 35 pmol) immobilized QCM, responding to each addition (120 ng, 0.05 pmol) of (a) M13 phage DNA and (b) nonsite M13 phage DNA in a 10-mL aqueous solution at 50 °C.

Process for Analytical Chemistry



Defining Problem for Analytical Chemistry

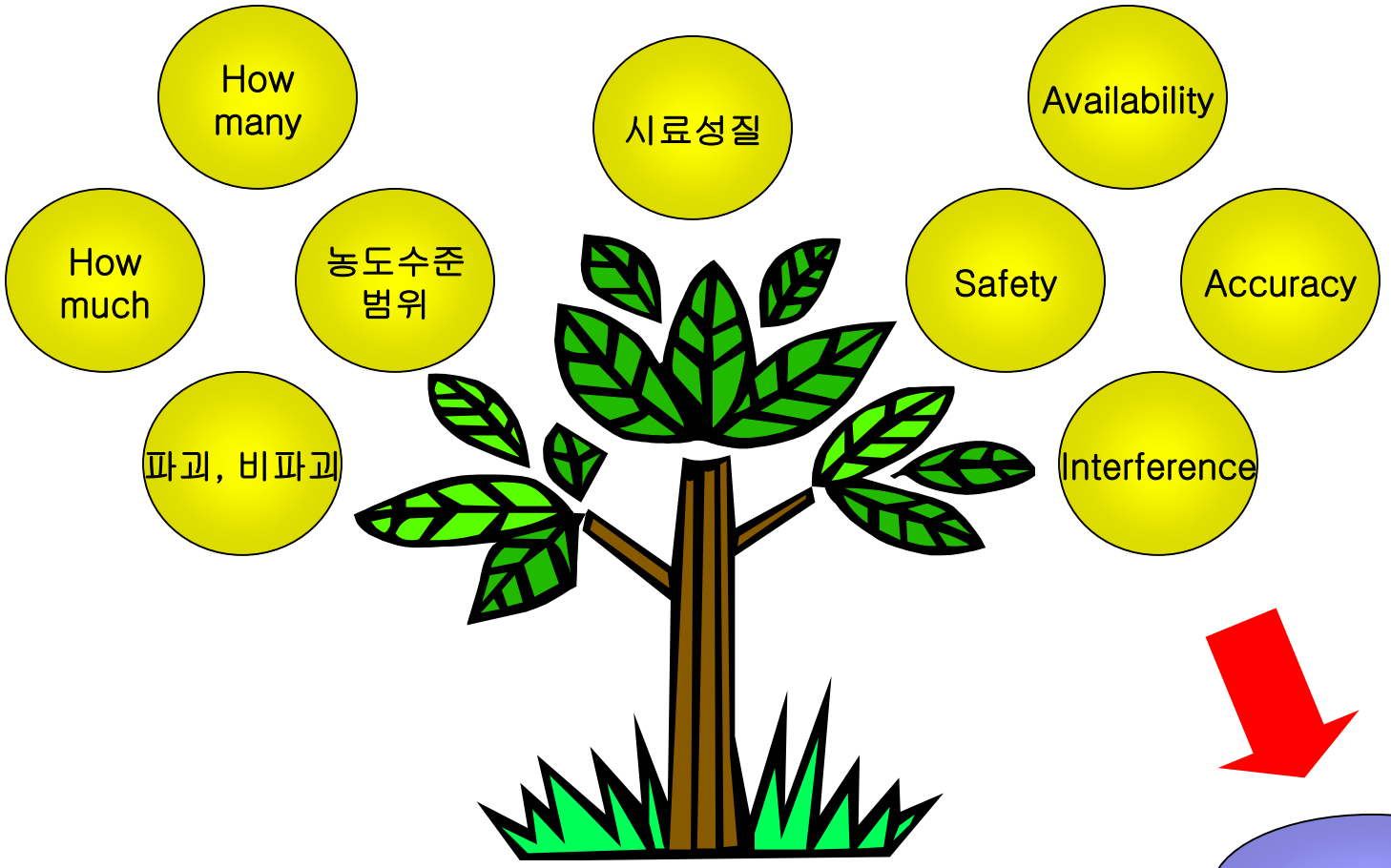


Figure of Merit

: 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

TABLE 1-4 Other Characteristics to Be Considered in Method Choice

1. Speed
2. Ease and convenience
3. Skill required of operator
4. Cost and availability of equipment
5. Per-sample cost

- Precision:

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)

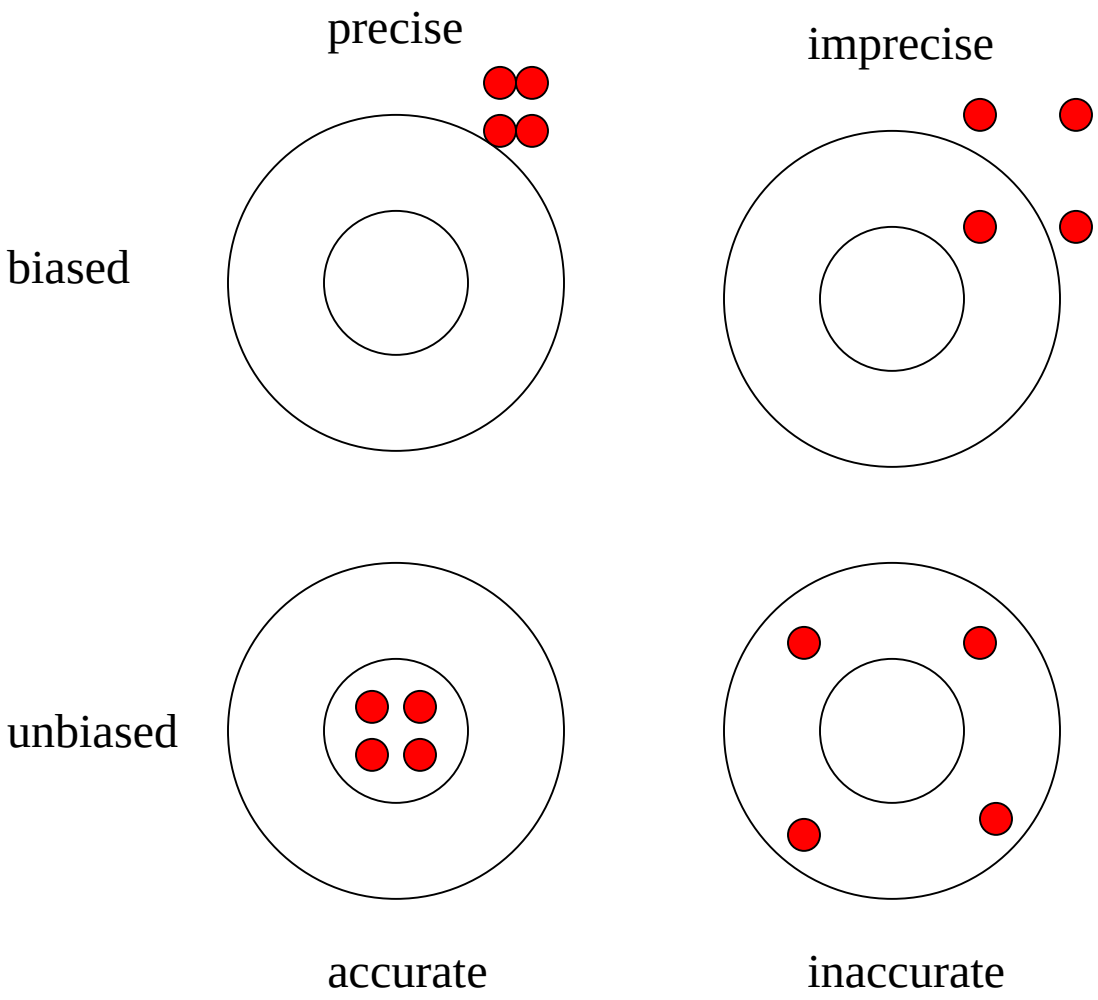


Diagram illustrating bias, precision and accuracy.
EI Stearns, *Chem. Met. Eng*. 53, 119, 1946.
C. Eisenhart, *Photogrammetric Eng*. 18, 3, 1952.

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

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

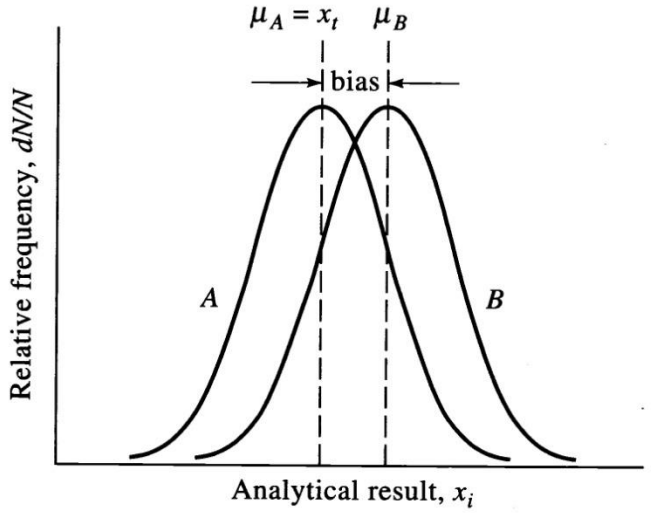


Figure a1-2 Illustration of bias = $\mu_B - \mu_A = \mu_B - x_i$

Systematic Error: Bias

: determinative error (고정오차, 가측오차)

Instrumental error:

- drift in electronic circuits

- calibration error

Personal error:

Method errors:

Standard (certified) Reference Materials (SRM)

: validation

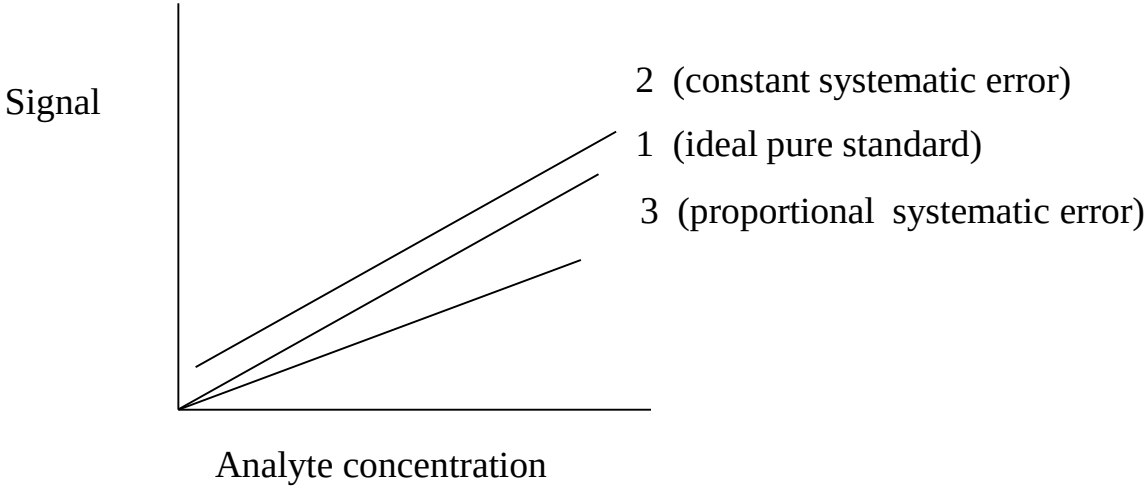


Fig. 3-3 Representation of systematic errors.

Random Error:

indeterminate error

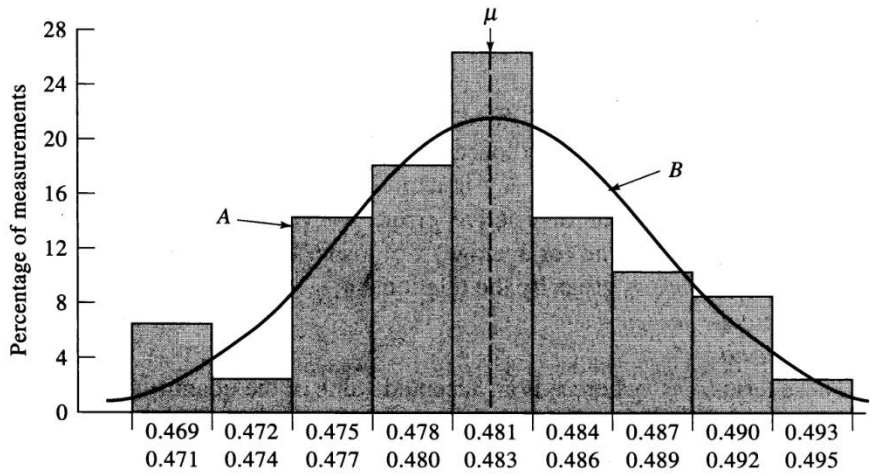
TABLE a1-1 Replicate Absorbance Measurements[a]

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:

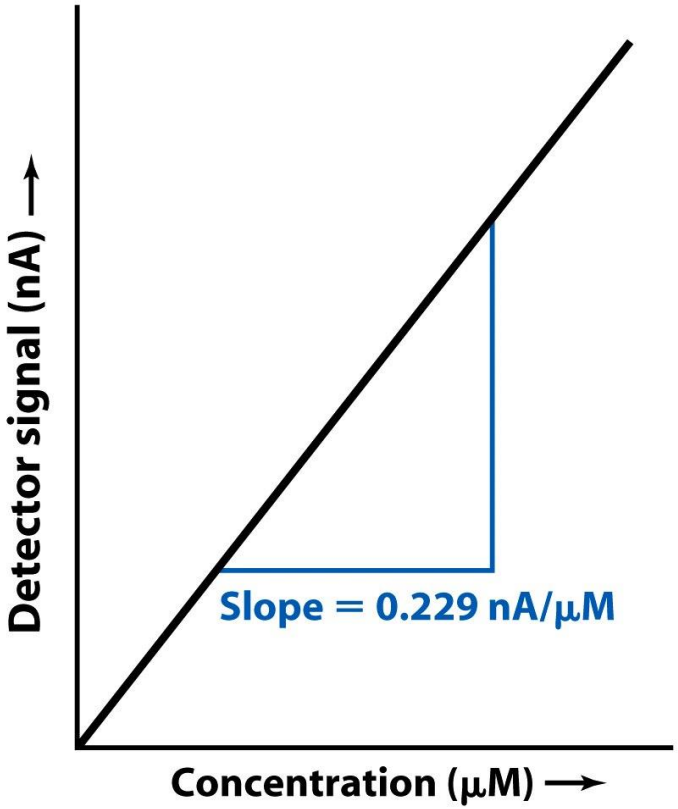
Calibration sensitivity

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

S: measured signal

S_{bl} can: blank signal

m: slope of calibration curve = calibration sensitivity



Unnumbered figure pg 86
Quantitative Chemical Analysis, Seventh Edition

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

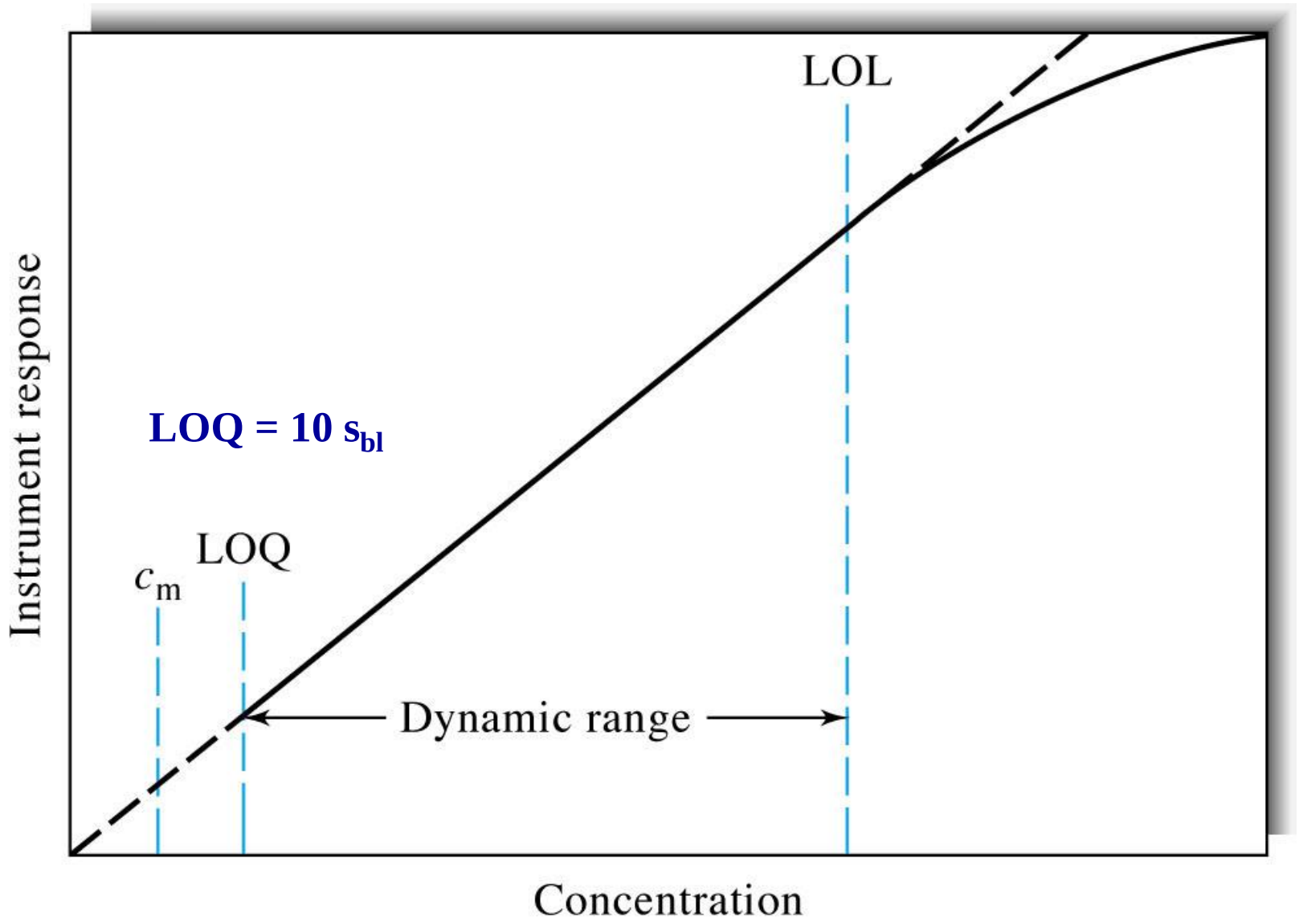
Conc, ppm, Pb	No. of replications	Mean value of *S*,	*s*
10.0	10	11.62	0.15
1.00	10	1.12	0.025
0.000 (blank)	24	0.0296	0.0082

(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



Selectivity

Selectivity: the degree to which the method is free from interferences by other species contained in the sample matrix

-No analytical method is totally free from interference from other species.

- A sample containing an analyte A as well as potential interferents B

- Selectivity coefficient for B with respect to A, $k_{A,\,B}$ = response B/response A

- Not widely used except for ion-selective electrode

- (ISE) $k_{Li^+,\,K^+}$ = response K^+/response Li^+

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

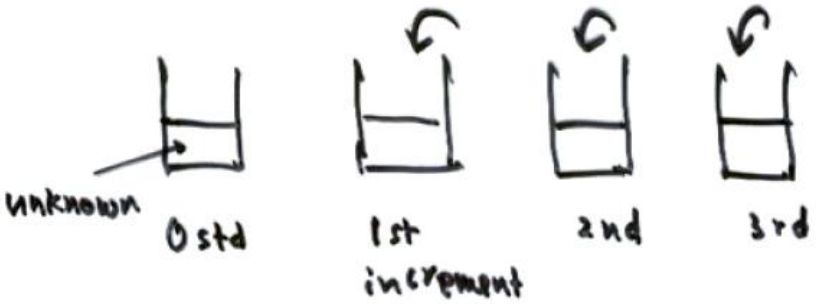
→ **Add standard solutions to sample (several aliquot of the same size)**

- 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.



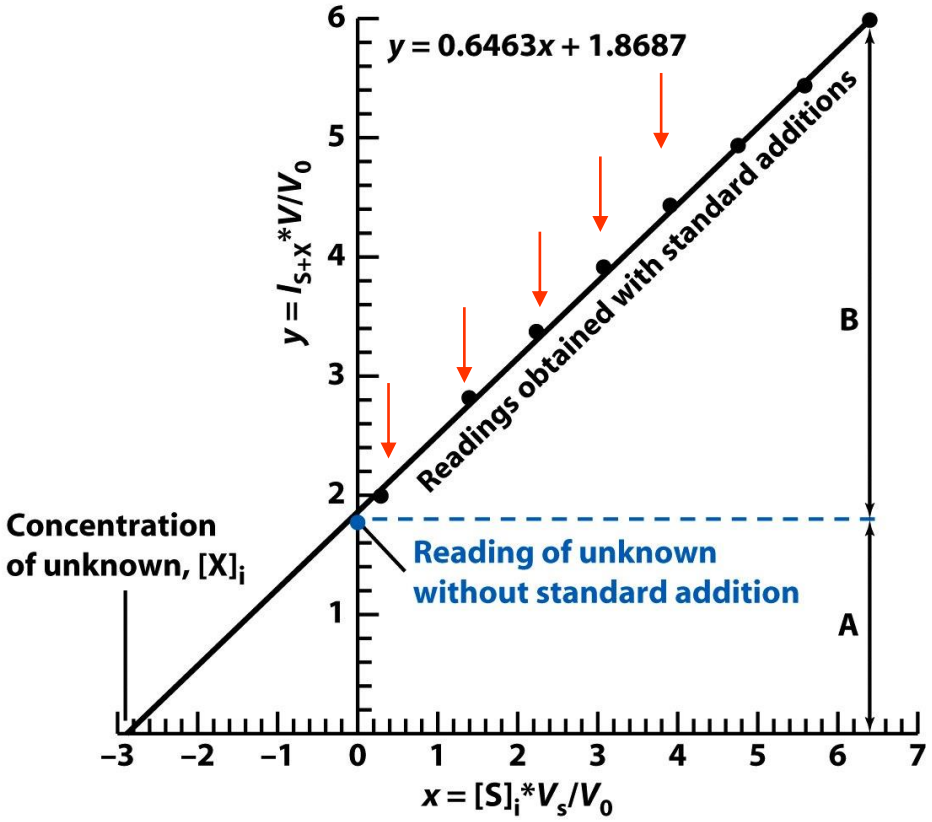


Figure 5-6
Quantitative Chemical Analysis, Seventh Edition

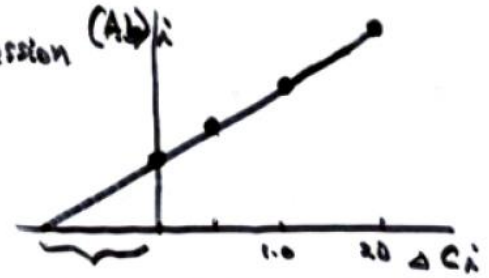
Standard Addition Method

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	0.535

By linear regression



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

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

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

$\therefore$ 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

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

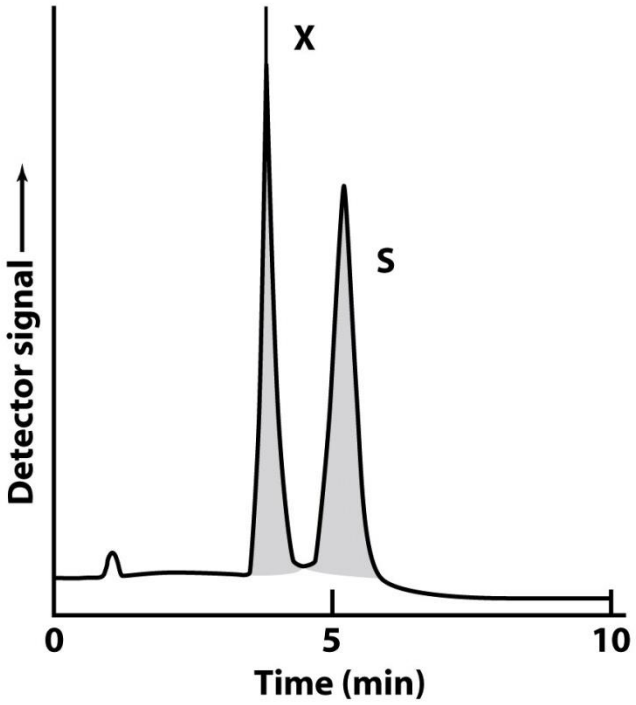


Figure 5-7
Quantitative Chemical Analysis, Seventh Edition

(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