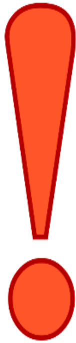

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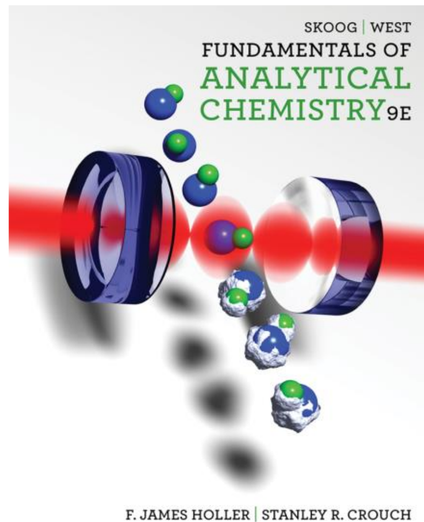
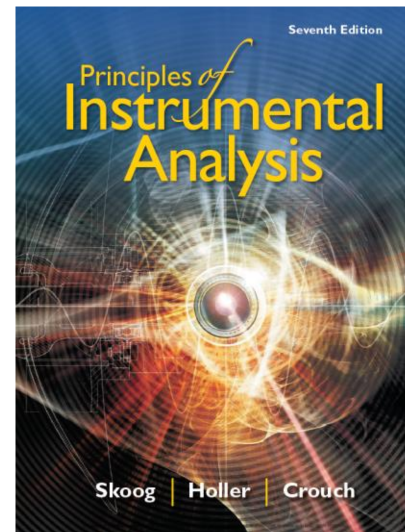
1.



2.



3.

ATAKOL's lecture notes

1. Skoog, D.A., West, D.M., Holler, J.F., Crouch, S.R. 2013. Fundamentals of Analytical Chemistry (9E). Cengage Learning, Belmont, USA.
2. Skoog, D.A., Holler, J.F., Crouch, S.R. 2016. Principles of Instrumental Analysis (7E). Cengage Learning, Boston, USA.
3. Prof. Dr. Orhan ATAKOL's lecture notes.

LAMBERT-BEER LAW and UV-VIS DEVICES

Lambert-Beer Law

- According to Beer's law, absorbance is directly proportional to the concentration of the absorbing species, ***c***, and to the path length, ***b***, of the absorbing medium.

$$A = \log (P_0 / P) = a\ b\ c$$

- In Equation, ***a*** is a proportionality constant called the absorptivity. Because absorbance is a unitless quantity, the absorptivity must have units that cancel the units of ***b*** and ***c***.
- When we express the concentration in Equation in moles per liter and b in cm, the proportionality constant is called the molar absorptivity and is given the symbol **ε**. Thus,

$$A = \varepsilon\ b\ c$$

The Lambert-Beer Law can be used in several different ways:

- We can calculate molar absorptivities of species if the concentration is known.

Absorptivities, are functions of such variables as solvent, solution composition, and temperature. Because of variations in absorptivity with conditions, it is never a good idea to depend on literature values for quantitative work. Hence, a standard solution of the analyte in the same solvent and at a similar temperature is used to obtain the absorptivity at the time of the analysis.

- We can use the measured value of absorbance to obtain concentration if absorptivity and path length are known.

Most often, we use a series of standard solutions of the analyte to construct a calibration curve, or working curve, of A versus c or to obtain a linear regression equation. It may also be necessary to duplicate closely the overall composition of the analyte solution in order to compensate for matrix effects. Alternatively, the method of standard additions is used for the same purpose.

- We can use UV-visible absorption to monitor titrations and to study the composition of complex ions.

UV-VIS DEVICES

Source → **Wavelenght selector** → **Sample** → **Detector** → **Signal processor**

Source

A source must generate a beam of radiation that is sufficiently powerful for easy detection and measurement

Wavelenght selector

Wavelenght selectors are devices to restrict the radiation being measured to a narrow band that is absorbed or emitted by the analyte. Such devices greatly enhance both the selectivity and the sensitivity of an instrument.

Sample

Sample containers, which are usually called cells or cuvettes, must have windows that are transparent in the spectral region of interest.

Detector

A detector is a device that identifies, records, or indicates a change in one of the variables in its environment such as pressure, temperature, or electromagnetic radiation

Signal processor

A signal processor is an electronic device that may amplify the electrical signal from the detector. In addition, it may convert the signal from dc to ac, change the phase of the signal, and filter it to remove unwanted components. The signal processor may also perform some mathematical operations on the signal. Digital meters and computer monitors are two examples of readout devices . Computers are often used to control various instrumental parameters, to process and store data, to print results and spectra, and to compare results with various databases.

SOURCES

Spectroscopic sources are of two types:

1. **Continuum sources**, which emit radiation that changes in intensity only slowly as a function of wavelength.
    - Xenon arc lamp (Molecular fluorescence)
    - H_2 and D_2 lamps (UV molecular absorption)
    - Tungsten/halogen lamp (UV/visible/near-IR molecular absorption)
    - Tungsten lamp (Visible/near-IR molecular absorption)
    - Nernst glower (IR molecular absorption)
    - Nichrome wire (IR molecular absorption)
    - Globar (IR molecular absorption)
2. **Line sources**, which emit a limited number of spectral lines, each of which spans a very narrow wavelength range.
    - Low-pressure mercury arc lamps (in liquid chromatography detectors)
    - Hollow cathode lamps (Atomic absorption spectroscopy)
    - Lasers (Emission spectroscopy)

WAVELENGTH SELECTORS

to isolate the desired wavelength band so that only the band of interest is detected and measured.

Monochromators (*with grating)*
The Echellete Grating
The Echelle Grating
Concave Gratings
Holographic Gratings

A **monochromator** is a device that contains an entrance slit and an exit slit. The exit slit is used to isolate a small band of wavelengths. One band at a time is isolated and different bands can be transmitted sequentially by rotating the grating.

Monochromators (*with prism)*
Bunsen
Litrow

Filters
Interference Filters
Absorption Filters

Spectrographs

A **spectrograph** is a device that uses a grating to disperse a spectrum. It contains an entrance slit to define the area of the source to be viewed. A large opening at its exit allows a range of wavelengths to strike a multiwavelength detector.

Polychromators

A **polychromator** contains multiple exit slits so that several wavelength bands can be isolated simultaneously.

Photon Detectors

Phototubes
Photomultiplier tubes
Silicon photodiodes
Photoconductive cells

Thermal Detectors

Thermocouples
Bolometers
Pneumatic cells
Pyroelectric devices

Ultraviolet/Visible Photometers and Spectrophotometers

In a singlebeam instrument radiation from the filter or monochromator passes through either the reference cell or the sample cell before striking the photodetector.

In a doublebeam instrument, radiation from the filter or monochromator is split into two beams that simultaneously pass through the reference and sample cells before striking two matched photodetectors.