Determining the k_a of an acid-base indicator

Indicator

$HIn + H_2O \leftrightarrow In^- + H_3O^+$
Red Blue

$Ka = [H_3O^+] [In^-]/[HIn]$

$[H_3O^+] = Ka [HIn]/[In^-]$
$(-\log [H_3O^+]) = (-\log Ka) + (\log [In^-]/[HIn])$
$pH = pKa + \log [In^-]/[HIn]$

Quantitative Spectroscopy

- Beer's Law

  $A_{\lambda 1} = e_{\lambda 1}bc$

  ε is molar absorptivity (unique for a given compound at λ_1)

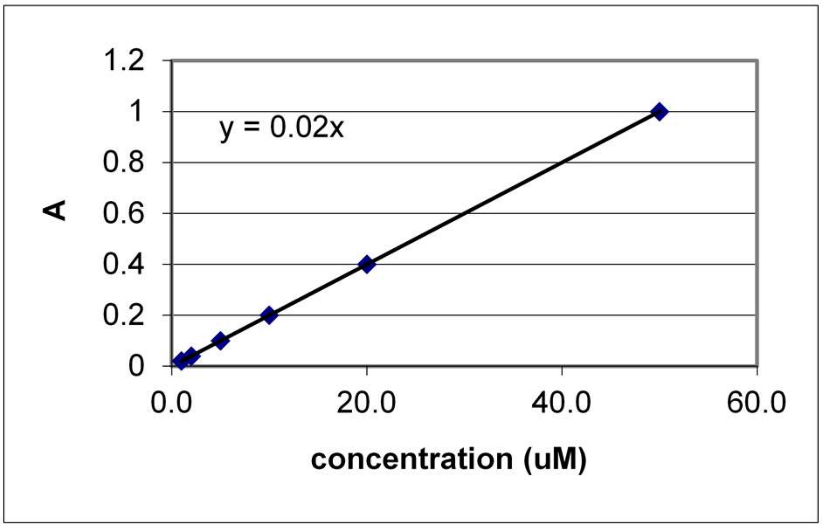
  b is path length

  c concentration

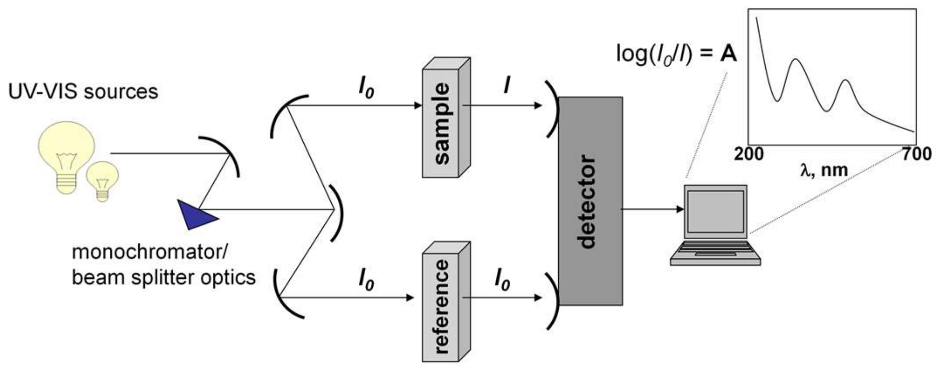
Standard Practice

- Prepare standards of known concentration
- Measure absorbance at λ_{MAX}
- Plot A vs. concentration
- Obtain slope
- Use slope (and intercept) to determine the concentration of the analyte in the unknown

Typical Beer's Law Plot

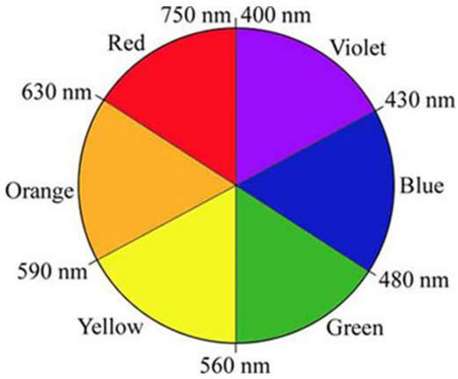


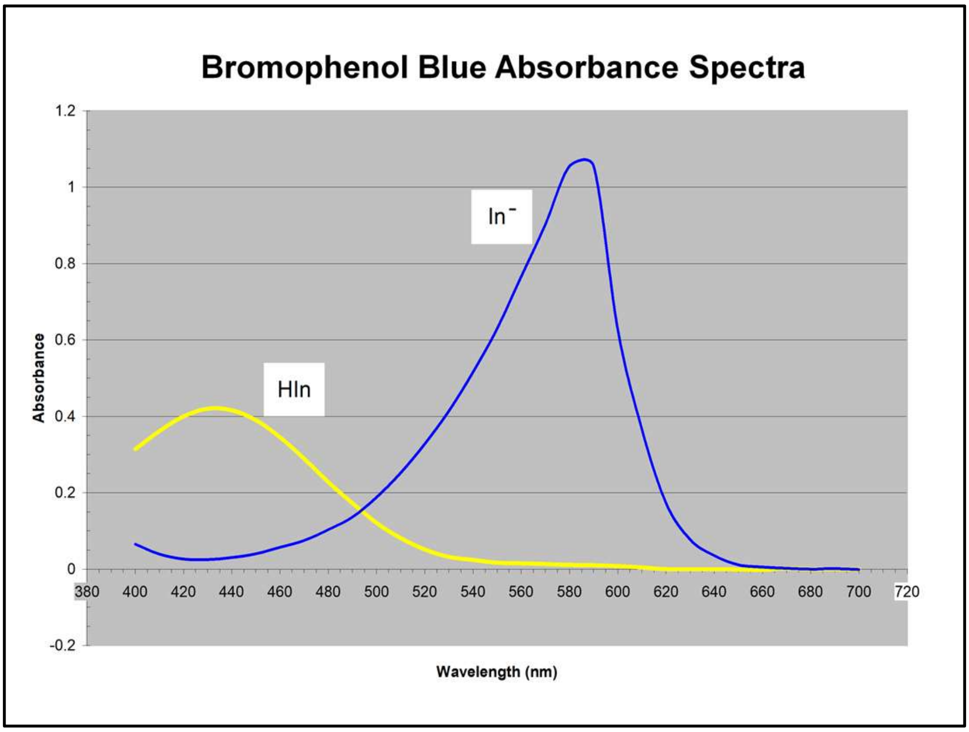
UV-vis spectrometer



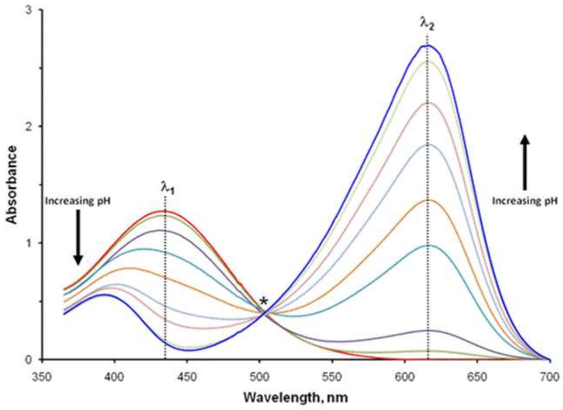
Spectroscopy

- Indicators give fairly broad visible absorption spectra



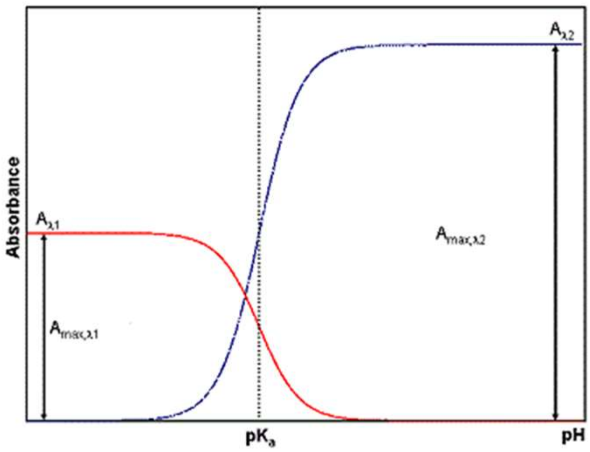

Bromophenol Blue Absorbance Spectra
Absorbance
Wavelength (nm)
1.2
1
0.8
0.6
0.4
0.2
0
-0.2
380
400
420
440
460
480
500
520
540
560
580
600
620
640
660
680
700
720
In⁻
HIn

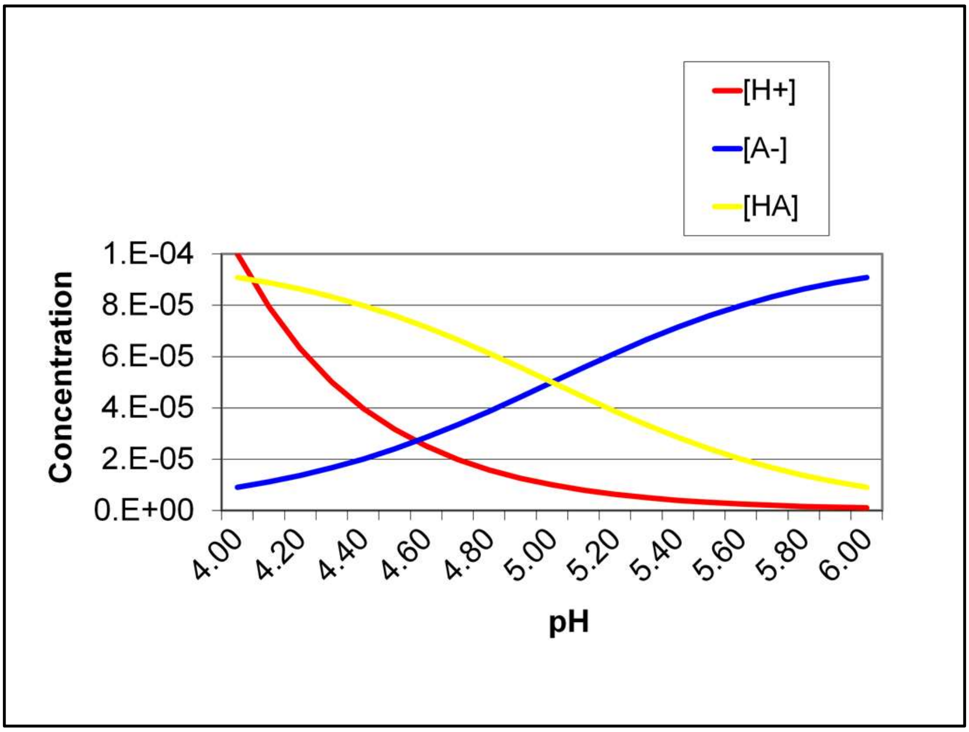
Changing pH



Absorbance
Wavelength, nm
Increasing pH
Increasing pH
λ1
λ2
*
0
1
2
3
350
400
450
500
550
600
650
700

Absorption measurement



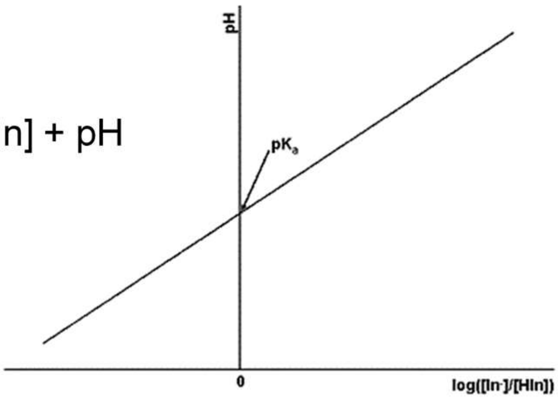


[H+]
[A-]
[HA]
1.E-04
8.E-05
6.E-05
4.E-05
2.E-05
0.E+00
Concentration
4.00
4.20
4.40
4.60
4.80
5.00
5.20
5.40
5.60
5.80
6.00
pH

Changing pH

$pH = pKa + \log [In^-]/[HIn]$

$pKa = \log [In^-]/[HIn] + pH$



Absorption measurement

Must make measurements at two wavelengths

$$A_{\lambda 1} = \varepsilon_{\lambda 1 HIn} b C_{HIn} + \varepsilon_{\lambda 1 In} b C_{In-}$$

$$A_{\lambda 2} = \varepsilon_{\lambda 2 HIn} b C_{HIn} + \varepsilon_{\lambda 2 In} b C_{In-}$$

$$C_T = C_{HIn} + C_{In-}$$

Absorption measurement

At low pH:

$A_{\lambda 1}^{low} = \varepsilon_{\lambda 1 HIn} b C_T$ $A_{\lambda 2}^{low} = \varepsilon_{\lambda 2 HIn} b C_T$

At high pH:

$A_{\lambda 1}^{high} = \varepsilon_{\lambda 1 In} b C_T$ $A_{\lambda 2}^{high} = \varepsilon_{\lambda 2 In} b C_T$

Calculate ε for Hin and In^- at both λ.

In the lab

- Prepare Indicator solution adjusted to the proper pH with HA/A^- buffer
- Measure UV-vis spectra and identify $\lambda 1$ and $\lambda 2$
- Calculate [In^-]/[Hin] from UV-vis data
- Calculate pH for each buffer solution
- Report pH vs log [In^-]/[Hin] and draw the straight line.
- Calculate pKa as intercept