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)

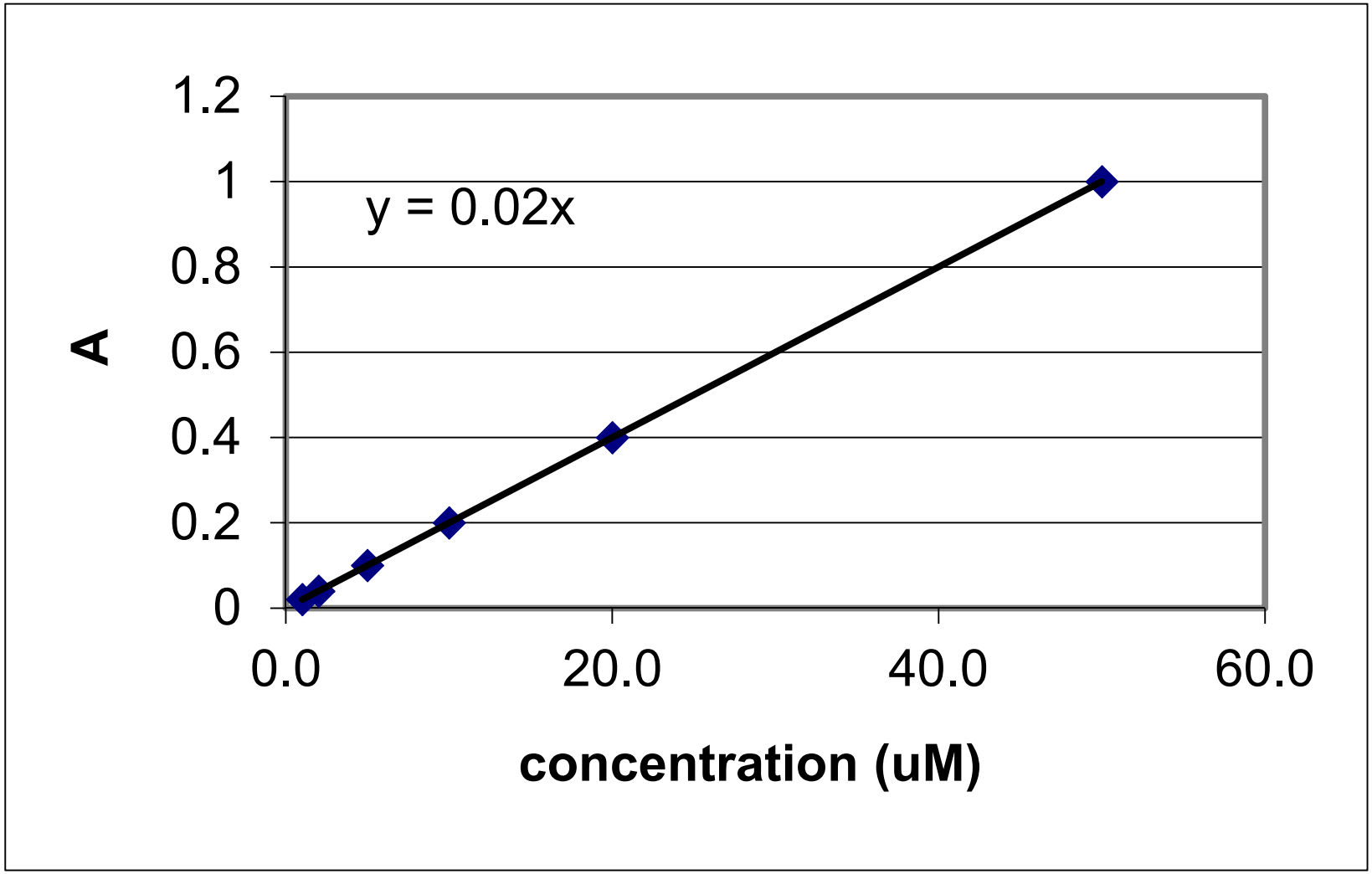
  b is path length

  c concentration

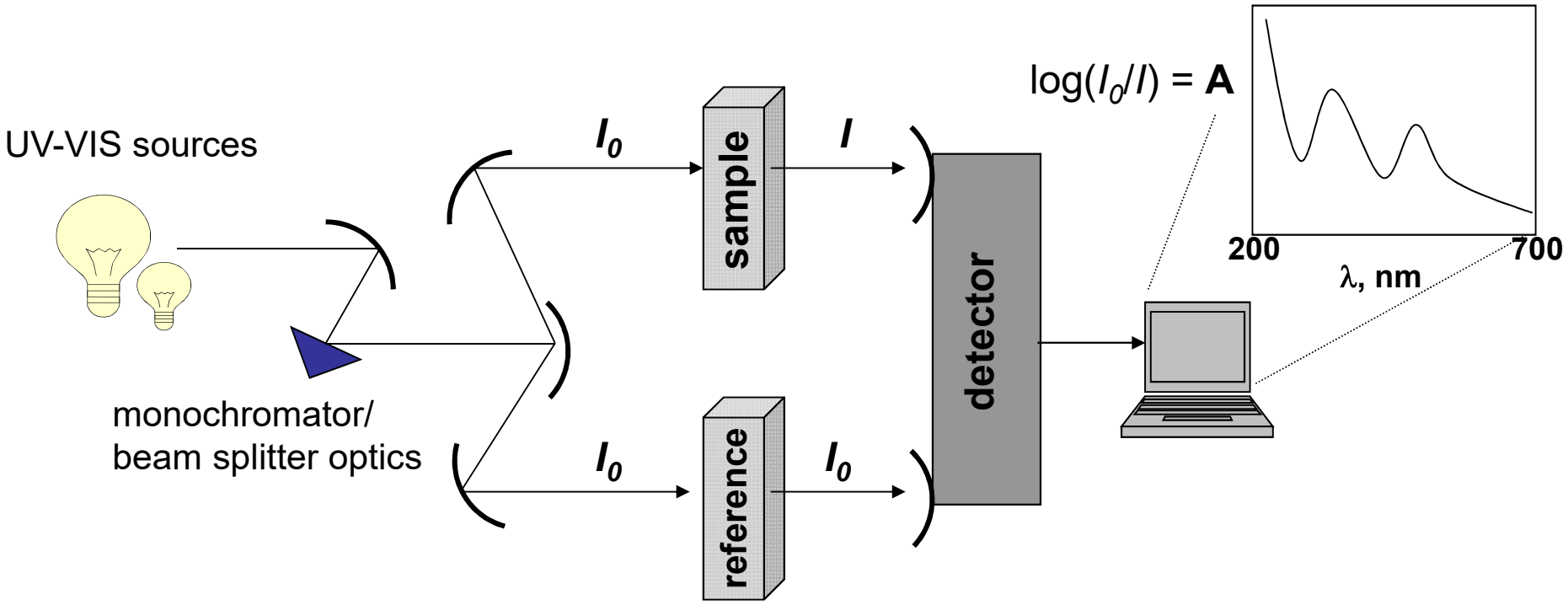
Standard Practice

- 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

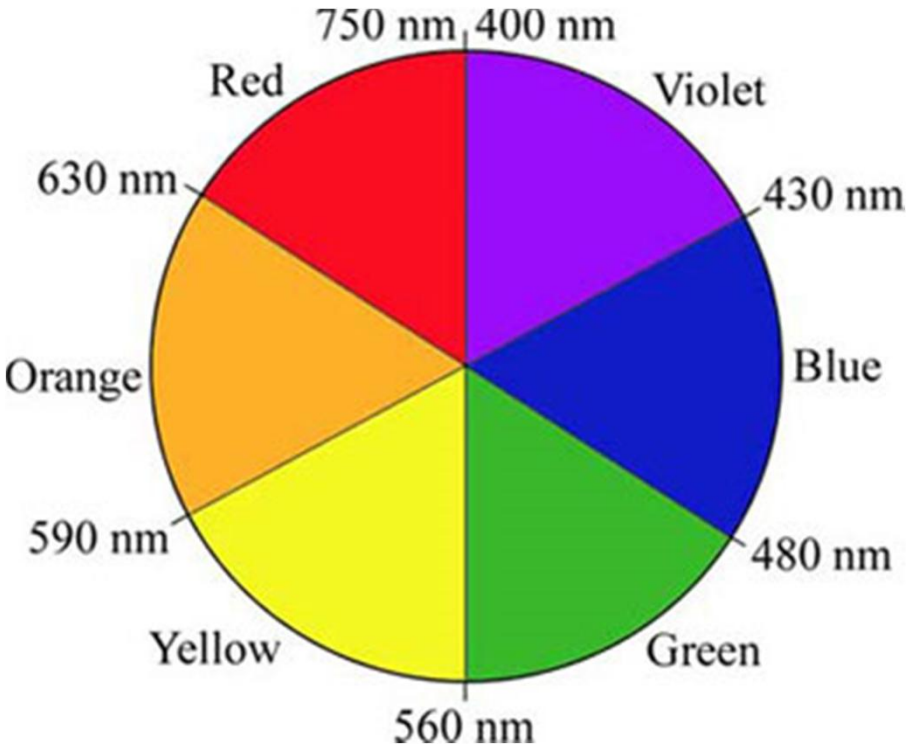


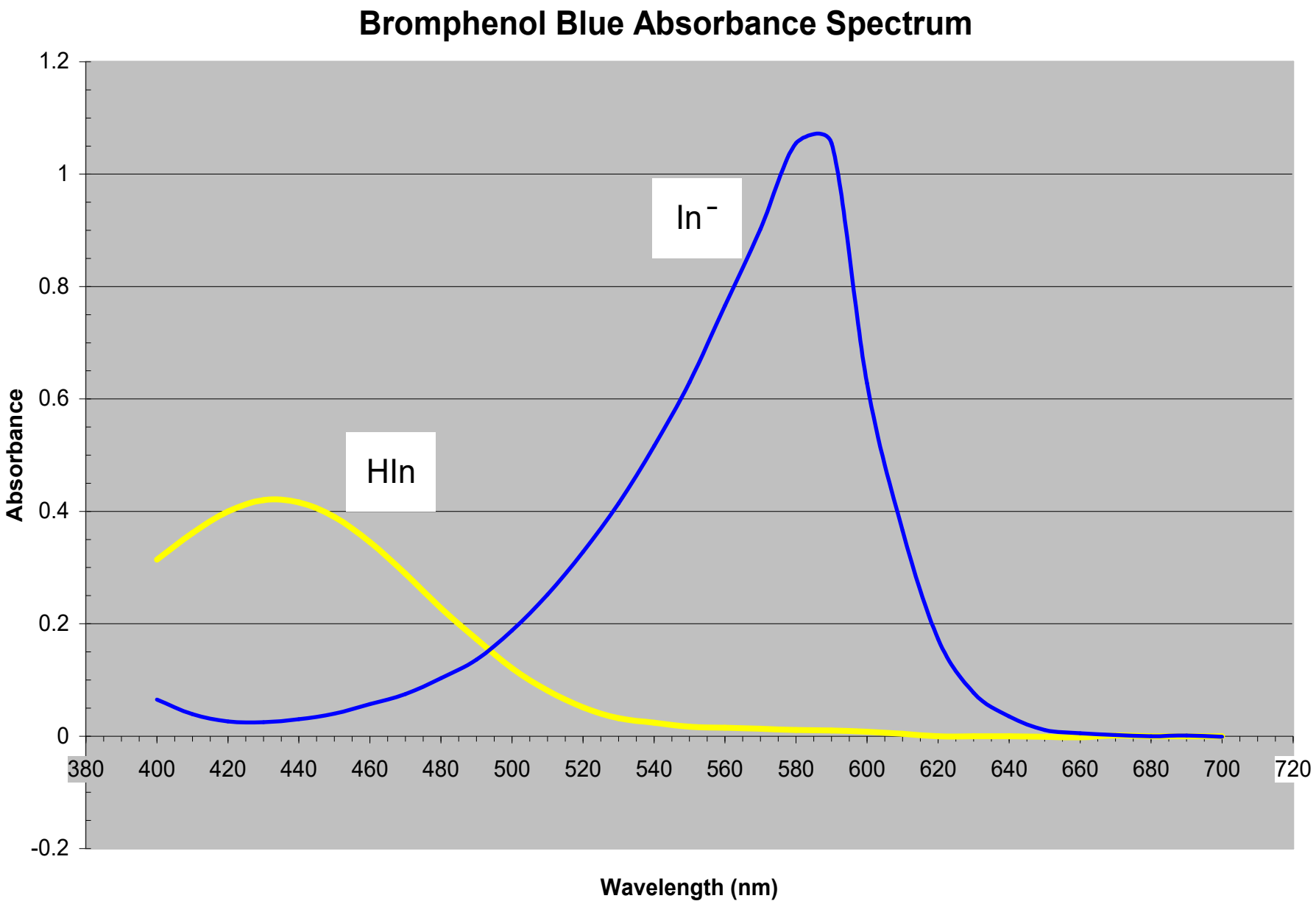
UV-vis spectrometer



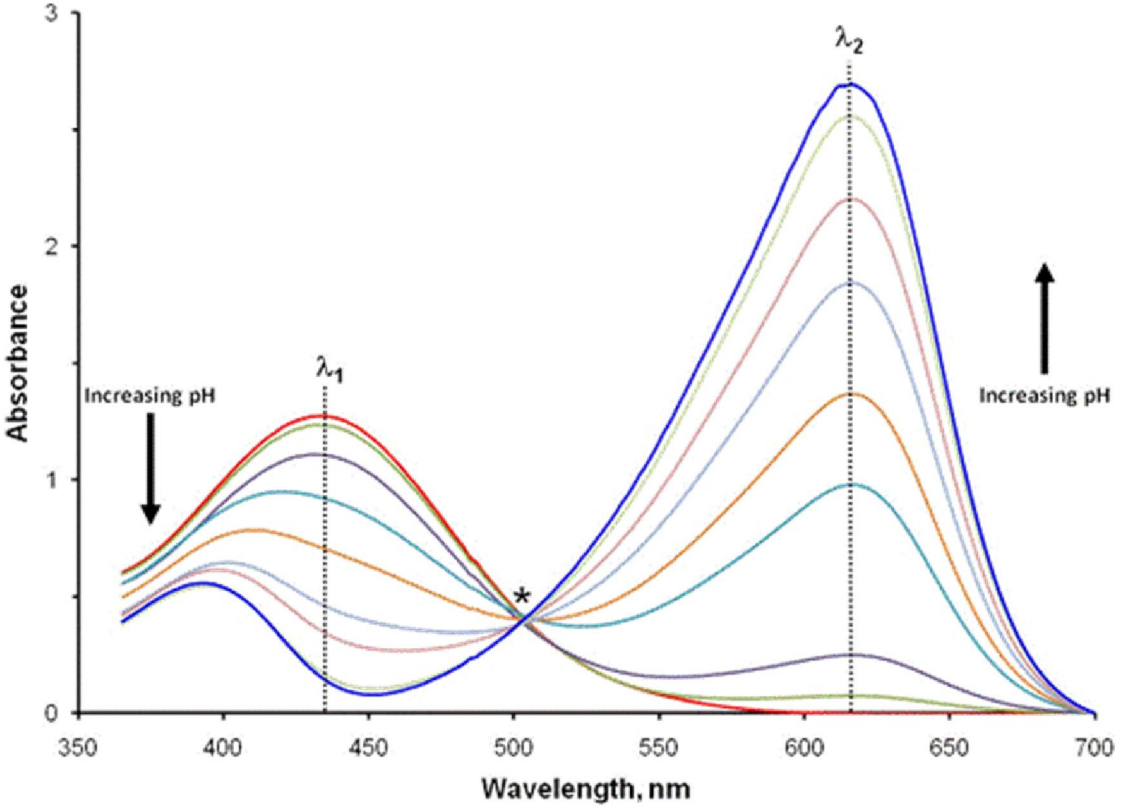
Spectroscopy

- Indicators give fairly broad visible absorption spectra

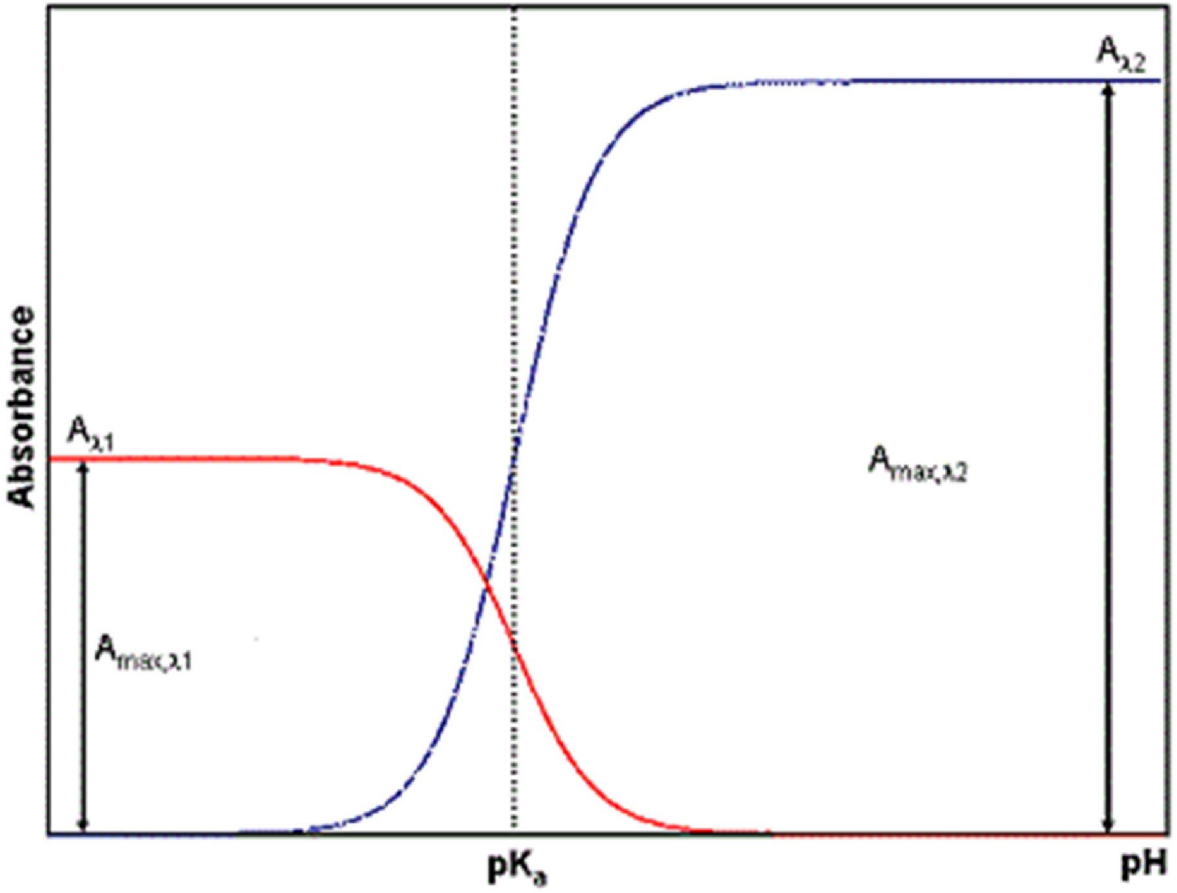


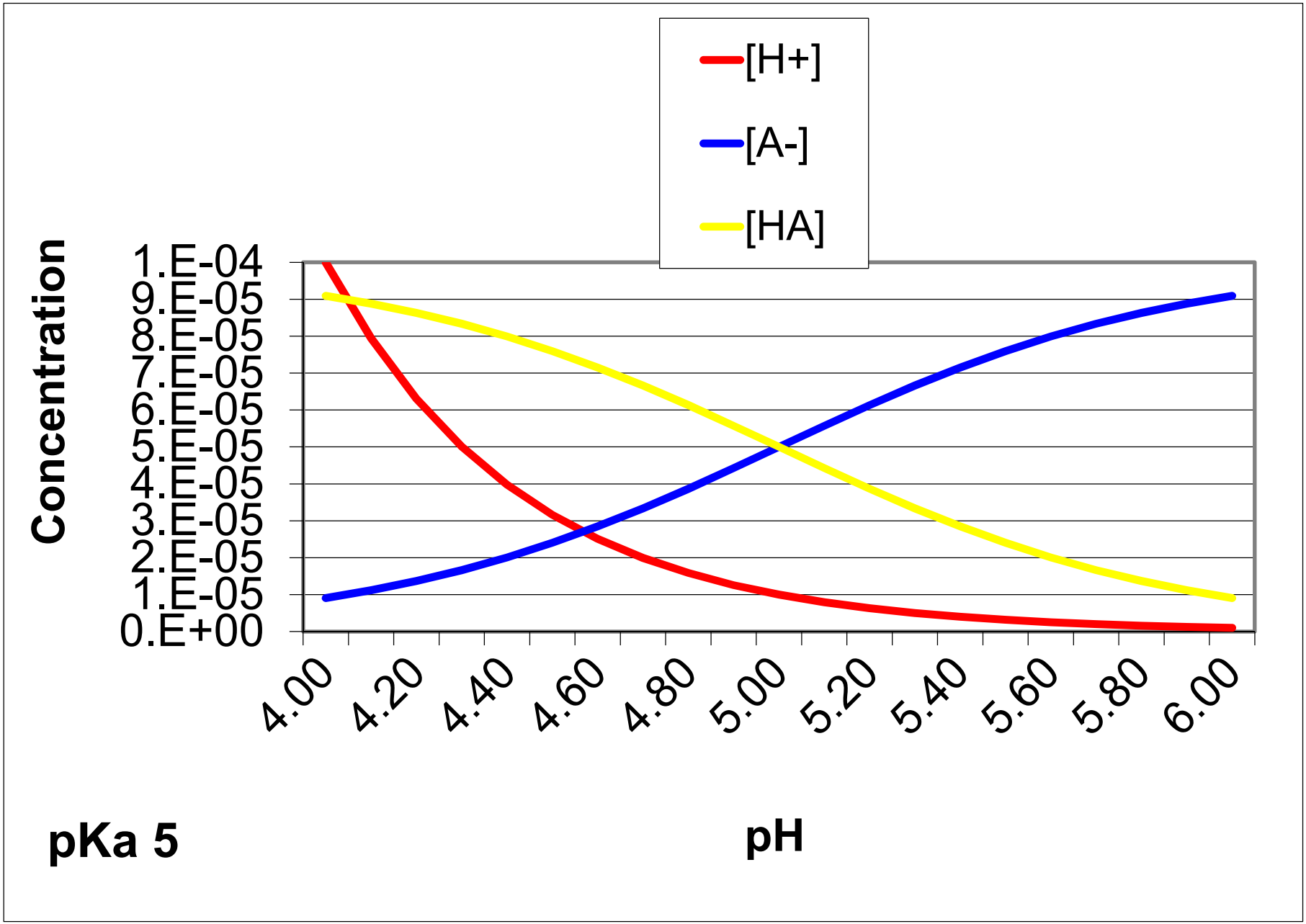

Bromphenol Blue Absorbance Spectrum
1.2
1
0.8
0.6
0.4
0.2
0
-0.2
Absorbance
In⁻
HIn
380
400
420
440
460
480
500
520
540
560
580
600
620
640
660
680
700
720
Wavelength (nm)

Changing pH


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

Absorption measurement

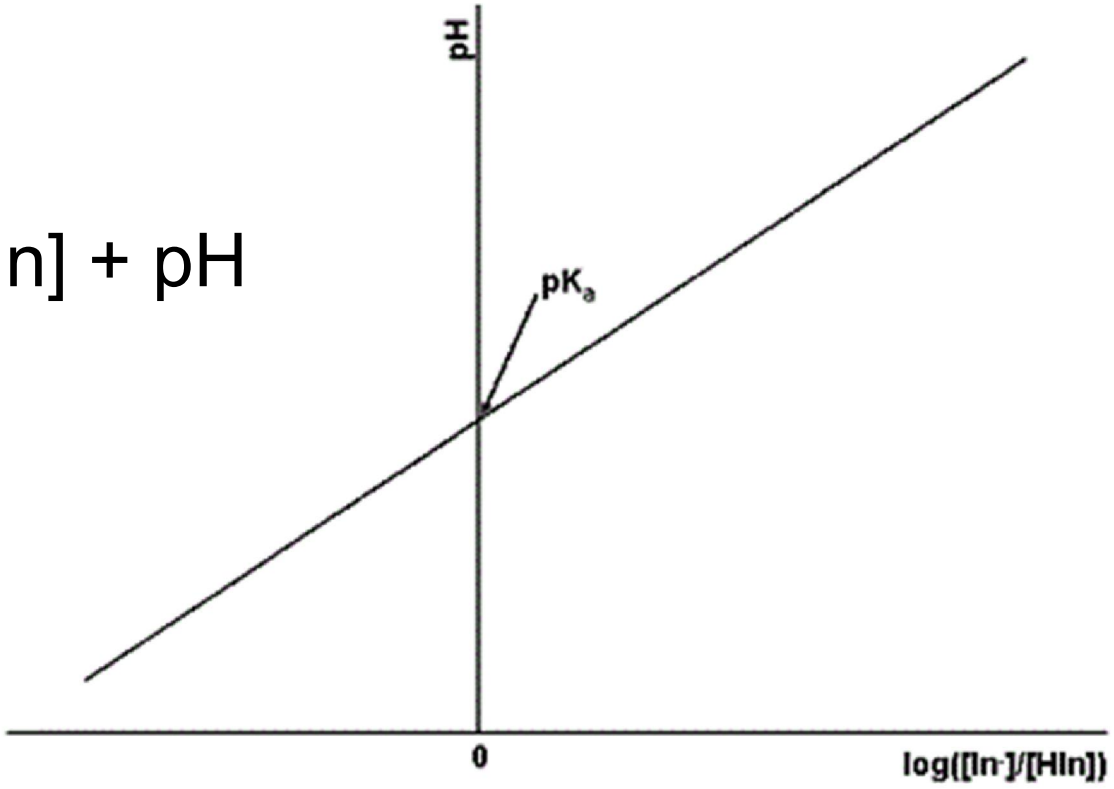



[H+]
[A-]
[HA]
Concentration
1.E-04
9.E-05
8.E-05
7.E-05
6.E-05
5.E-05
4.E-05
3.E-05
2.E-05
1.E-05
0.E+00
4.00
4.20
4.40
4.60
4.80
5.00
5.20
5.40
5.60
5.80
6.00
pKa 5
pH

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:

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

At high pH:

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

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