

Colorimetric Analysis Tutorial Answers

1. a) The limitations of the Beer-Lambert Law are:

- Deviations in absorption coefficients at high concentrations (>0.01M) due to electrostatic interactions between molecules in close proximity
- Scattering of light due to particulates in the sample
- Fluorescence or phosphorescence of the sample
- Refractive index changes with analyte concentration
- Shifts in chemical equilibrium as a function of concentration
- Non-monochromatic radiation (deviations can be minimized by using a relatively flat part of the absorption spectrum such as the maximum of an absorption band)
- Stray light
- Unmatched cells

See D A Skoog, F J Holler, S R Crouch, (2007) "Principles of Instrumental Analysis", 6th Ed., p 336-343 for a full description.

b) Colorimetric analysis of mixtures requires/assumes no interaction between the various species present i.e. they do not change each other's colour/absorbance spectrum.

2. Break the problem down into steps and use equations for propagation of errors.

	Value	SD
A_1	0.312	0.003
A_2	0.092	0.002
l	1.000	0.005
ϵ_{A1}	70.660	2.165
ϵ_{A2}	3.510	0.197
ϵ_{B1}	16.910	0.786
ϵ_{B2}	107.230	3.055

Step	Value	Error
$\epsilon_{B1} A_2$	1.5557	0.0798
$\epsilon_{B2} A_1$	33.4558	1.0060
$\epsilon_{A2} \epsilon_{B1}$	59.3541	4.3254
$\epsilon_{A1} \epsilon_{B2}$	7576.8718	317.0067
$\epsilon_{B1} A_2 - \epsilon_{B2} A_1$	-31.9000	1.0091
$\epsilon_{A2} \epsilon_{B1} - \epsilon_{A1} \epsilon_{B2}$	7517.5177	317.0362
c_A	0.004243	0.0002247

$$= 1.5557 \times \sqrt{[(0.786/16.91)^2 + (0.002/0.092)^2]}$$

$$= 33.4558 \times \sqrt{[(3.055/107.23)^2 + (0.003/0.312)^2]}$$

$$= 59.3541 \times \sqrt{[(0.197/3.51)^2 + (0.786/16.91)^2]}$$

$$= 7576.8718 \times \sqrt{[(2.165/70.66)^2 + (3.055/107.23)^2]}$$

$$= \sqrt{[(0.0798)^2 + (1.0060)^2]}$$

$$= \sqrt{[(4.3254)^2 + (317.0067)^2]}$$

$$= 0.004243 \times \sqrt{[(1.0091/-31.9000)^2 + (317.0362/-7517.5177)^2 + (0.005/1)^2]}$$

Step	Value	Error
$\epsilon_{A1} A_2$	1.0951	0.0624
$\epsilon_{A2} A_1$	6.5007	0.2442
$\epsilon_{B1} \epsilon_{A2}$	59.3541	4.3254
$\epsilon_{B2} \epsilon_{A1}$	7576.8718	317.0067
$\epsilon_{A1} A_2 - \epsilon_{A2} A_1$	-5.4056	0.2521
$\epsilon_{B2} \epsilon_{A1} - \epsilon_{B1} \epsilon_{A2}$	-7517.5177	317.0362
c_B	0.000719	0.000045

Therefore: $c_A = 0.00424 \pm 0.00022$ M and $c_B = 0.00072 \pm 0.00005$ M

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B Lingard



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