

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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Earvin P Eugene



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