

Temperature Dependent Solubility of Thioglycerol-Ligated ZnS Nanoparticles in 4:1 MeOH:H₂O Solution

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 - Nanoparticles (NPs) behave differently than bulk counterparts
 - Sparse literature on solubility of NPs

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- Treat monodisperse NP colloid in solvent as solution with temperature dependent solubility

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- Construct equilibrium phase diagram
 - Enthalpy of dissolution

Theory

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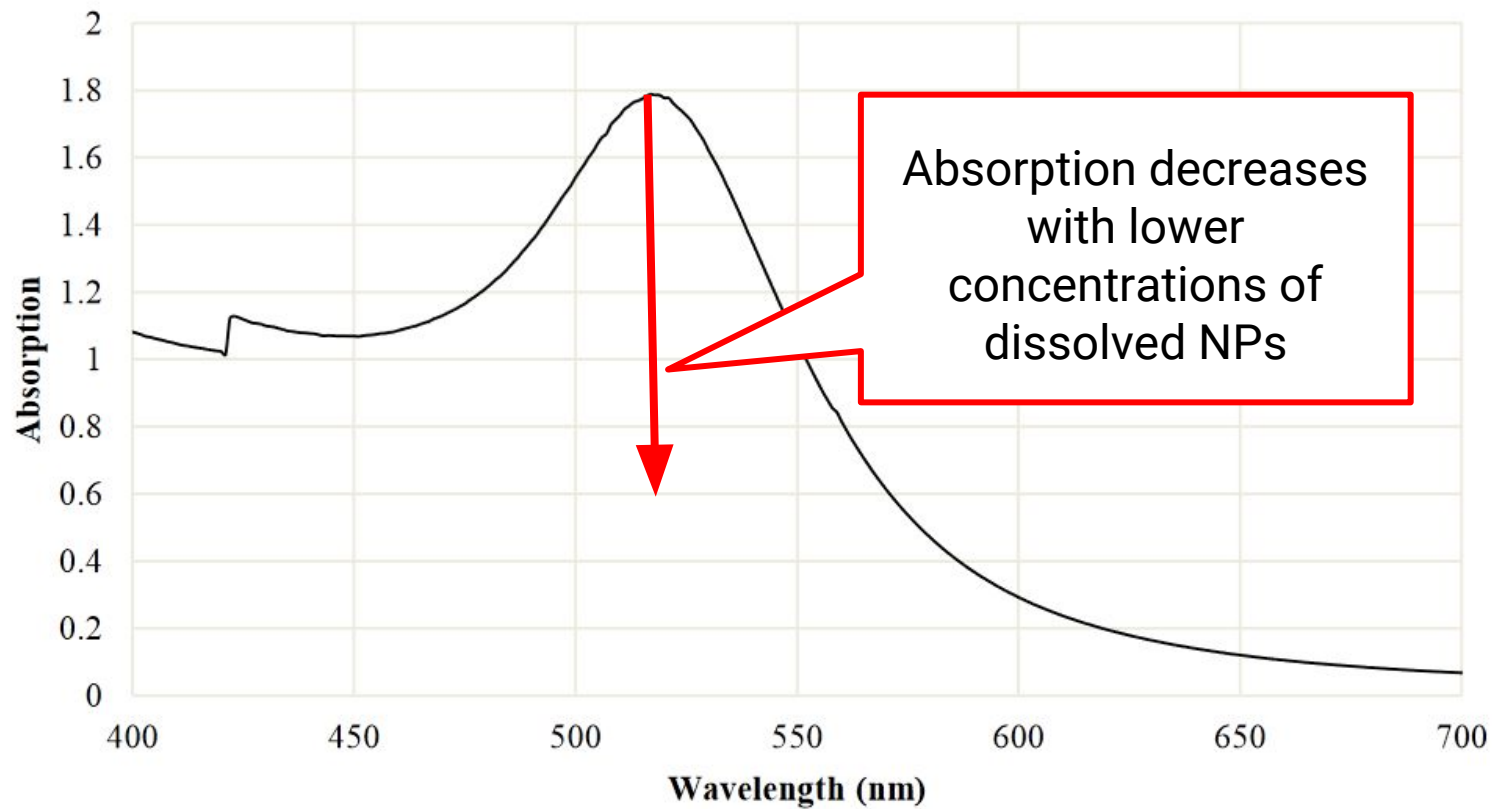
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 - Interaction between electrons on surface of NP with incident light
 - Causes unique light absorption profile characteristic to features such as NP material and size

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 - Interaction between electrons on surface of NP with incident light
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- UV-Vis spectrometer to view absorption spectrum
 - Higher concentration of dissolved NP gives greater absorption ($A = \epsilon \cdot l \cdot c$:: Beer-Lambert Law)

Theory

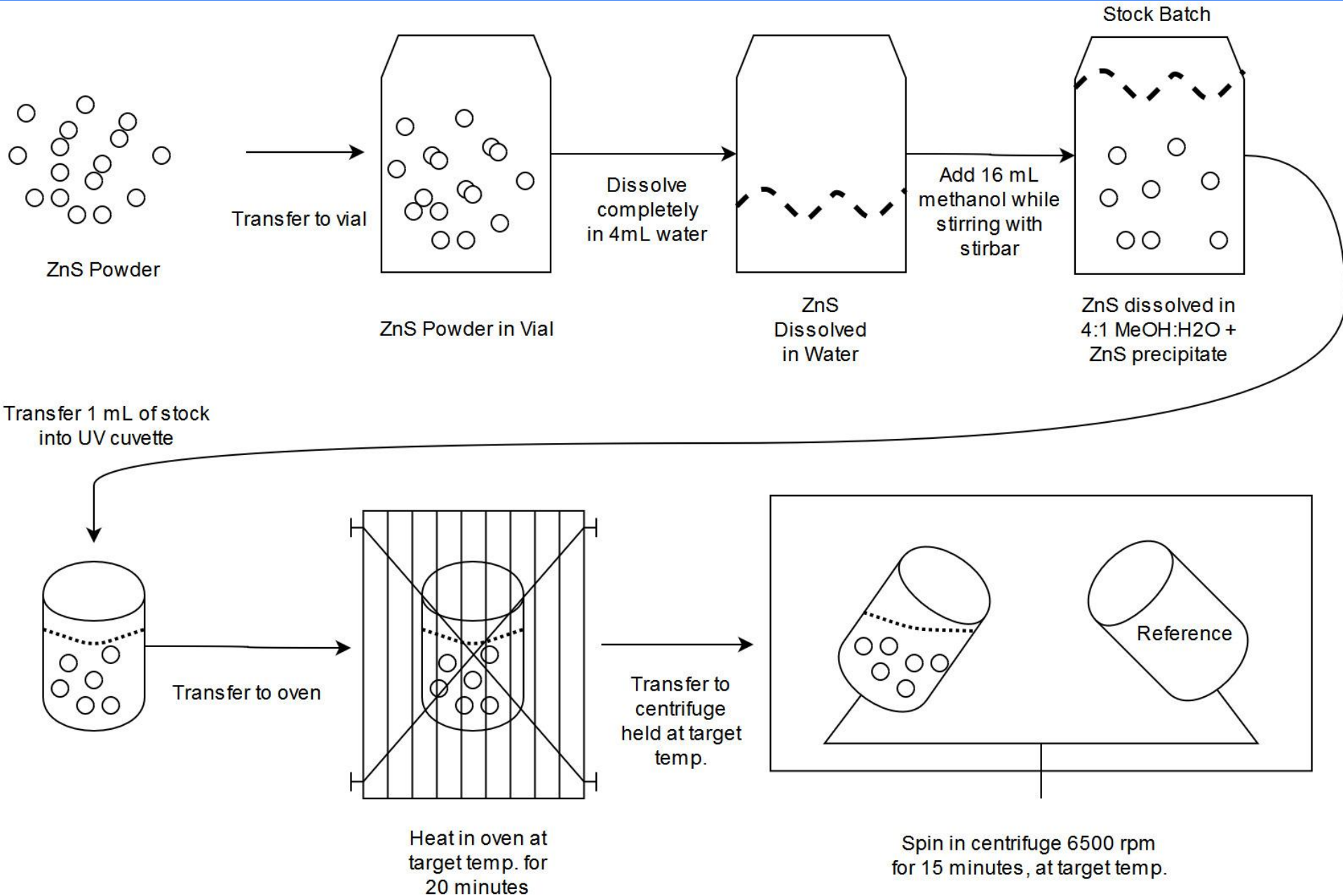
UV-VIS Data Collection



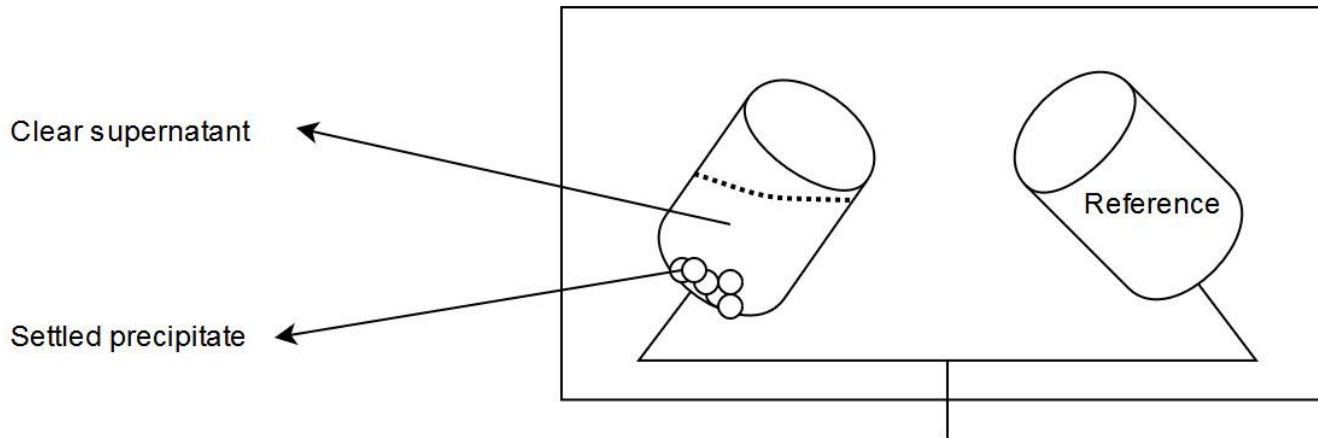
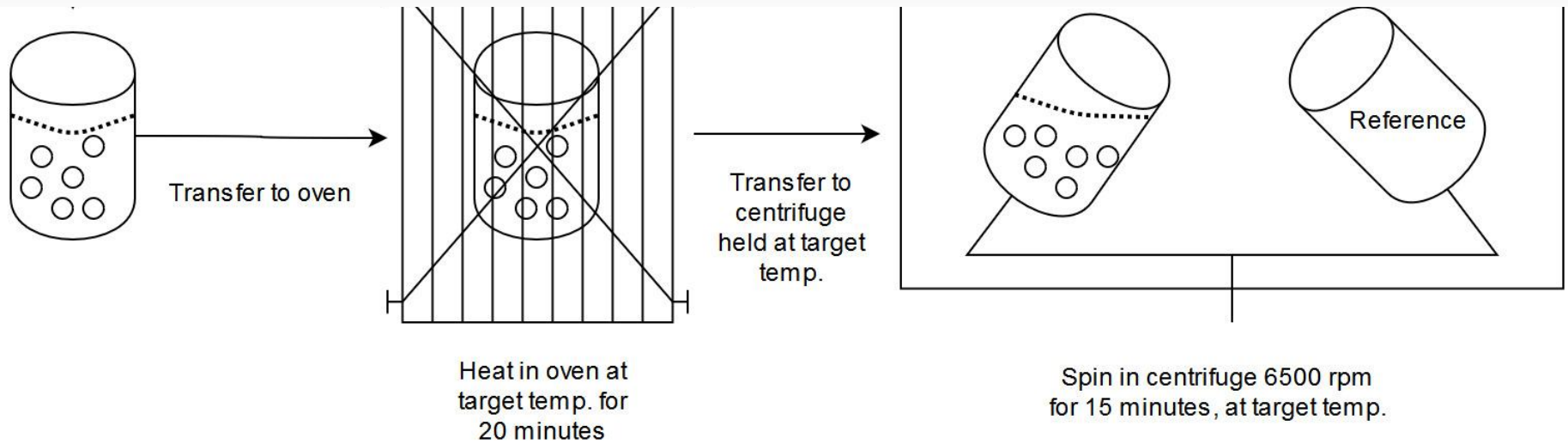
Our System

- ZnS NPs ligated with thioglycerol (3-mercapto-1,2-propanediol)
 - Highly soluble in water
 - Insoluble in methanol
 - SPR peak at ~251nm
 - Requires UV-transparent cuvette

Procedure

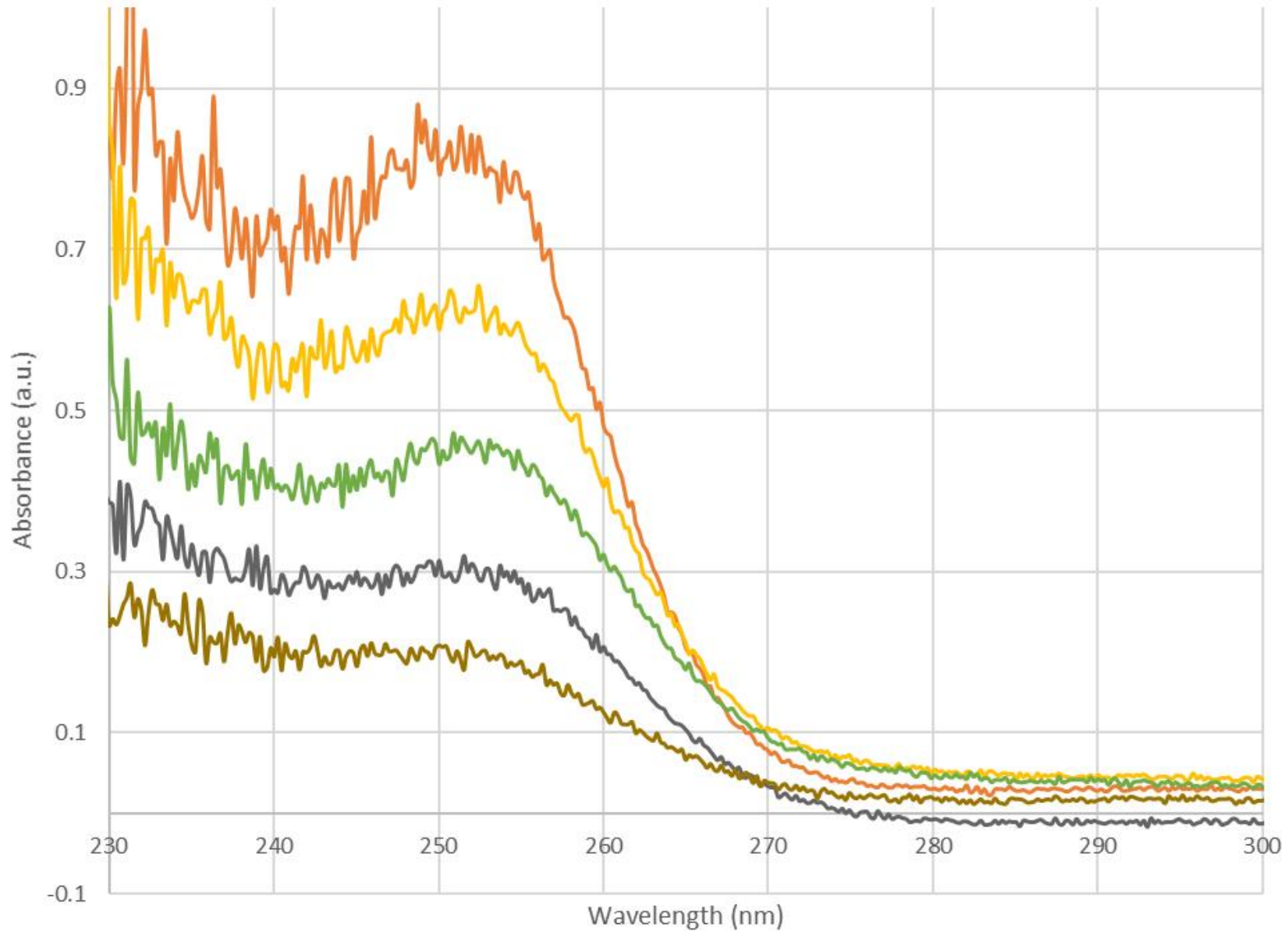


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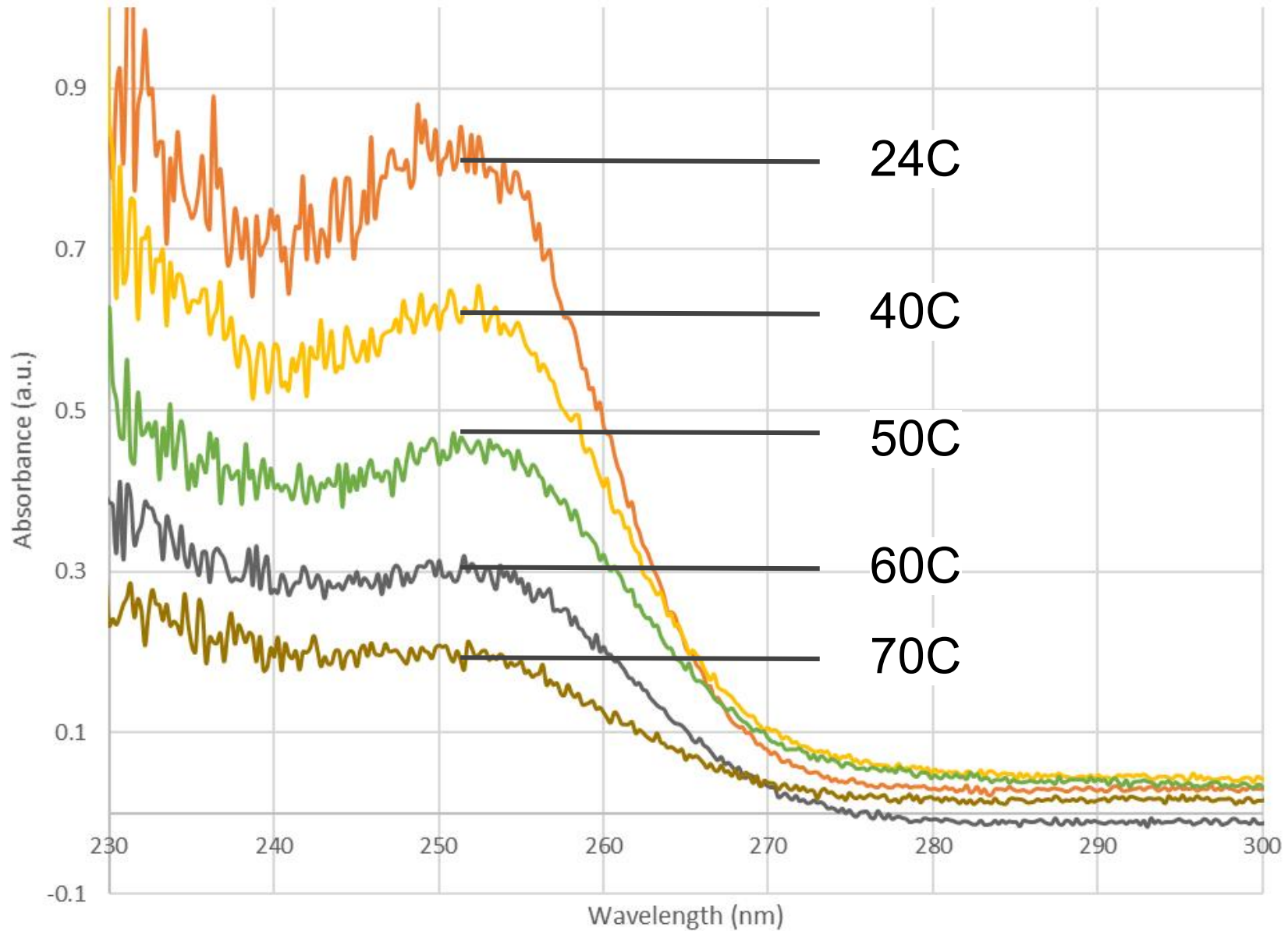


Measure absorbance spectrum of clear supernatant, use reference (4:1 MeOH:H₂O with no ZnS) as background spectrum

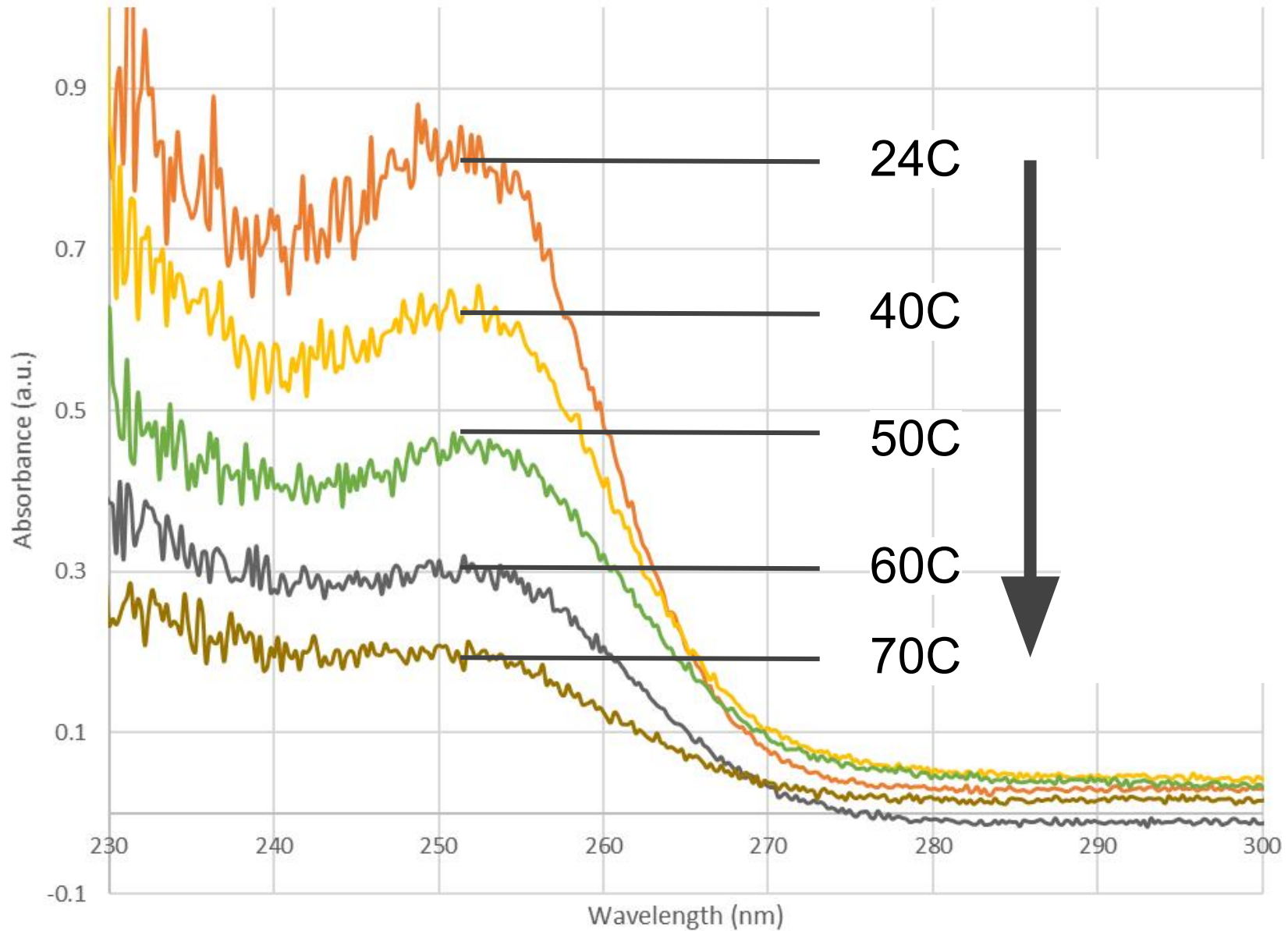
Spectral results



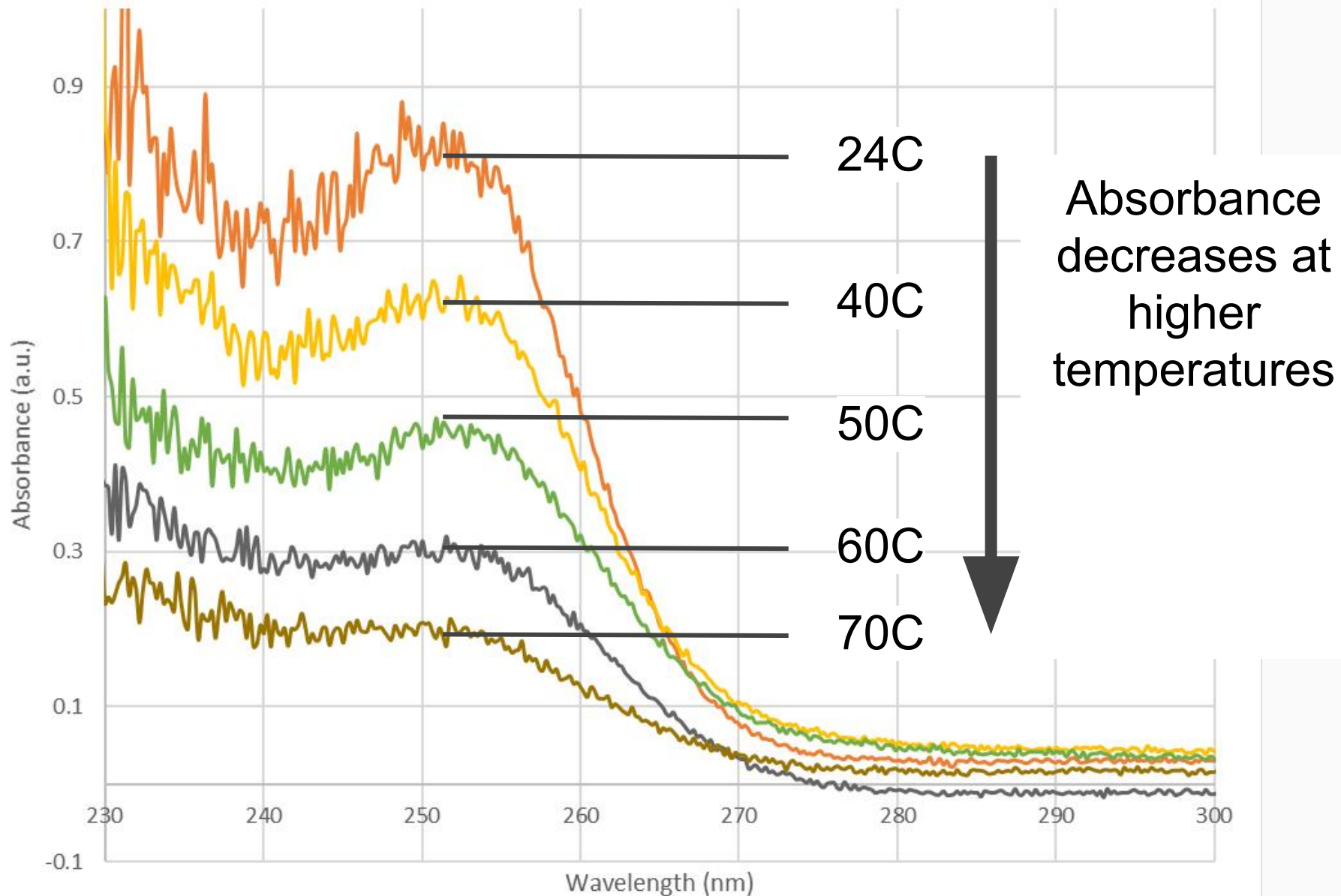
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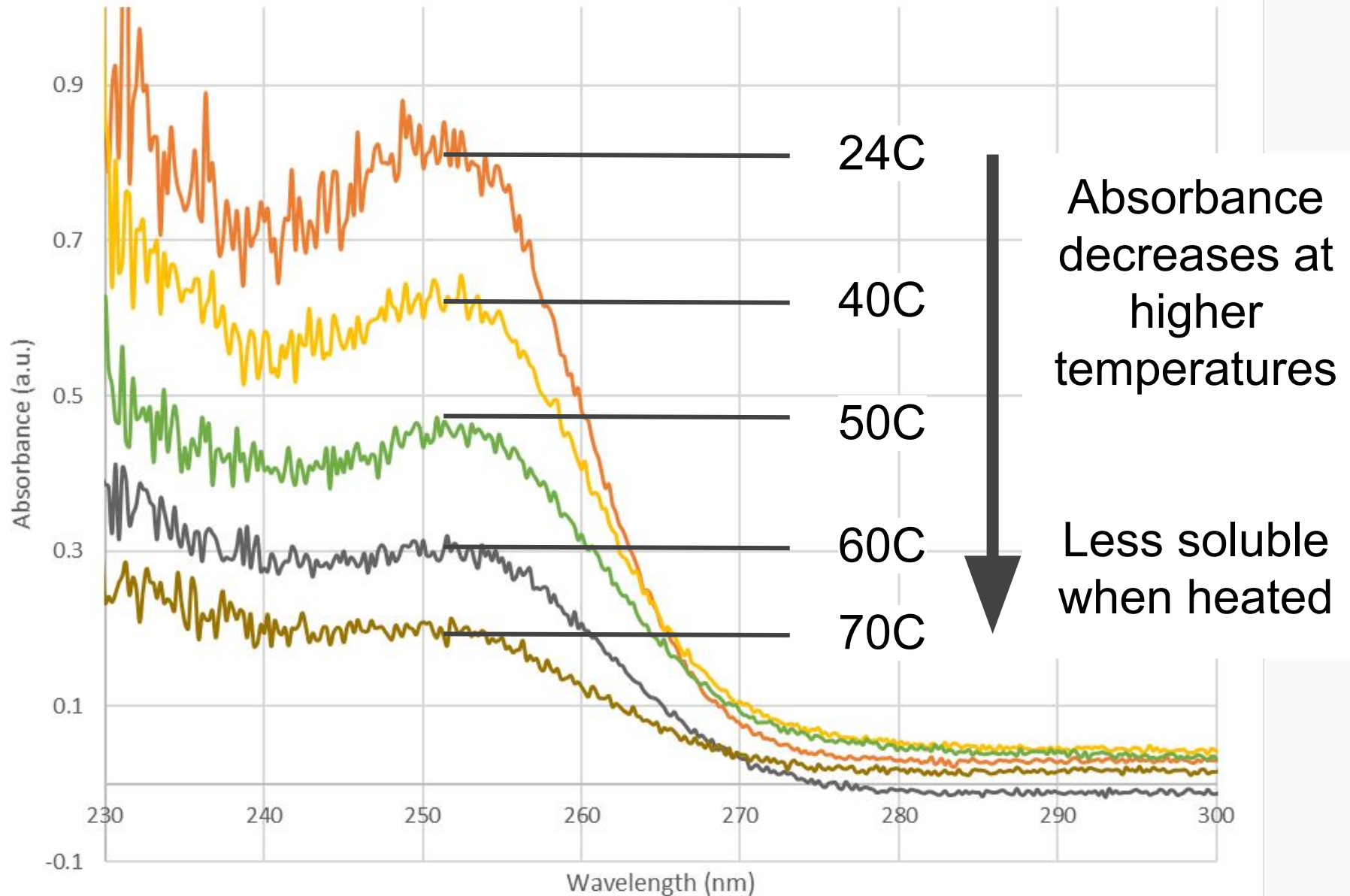
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Equilibrium reaction, thus Le Chatelier's principle tells us excess heat would favor the left-hand side

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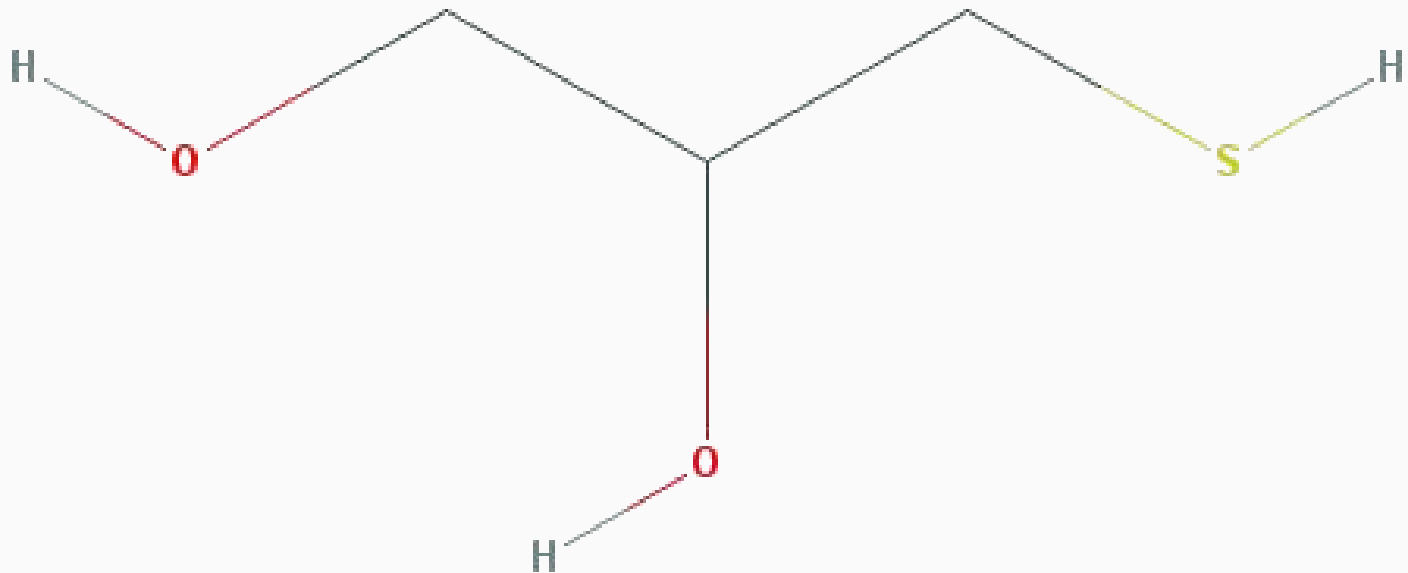
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 - Higher entropy (disorder) in precipitate than dissolved

Dissolved: Less Disorder

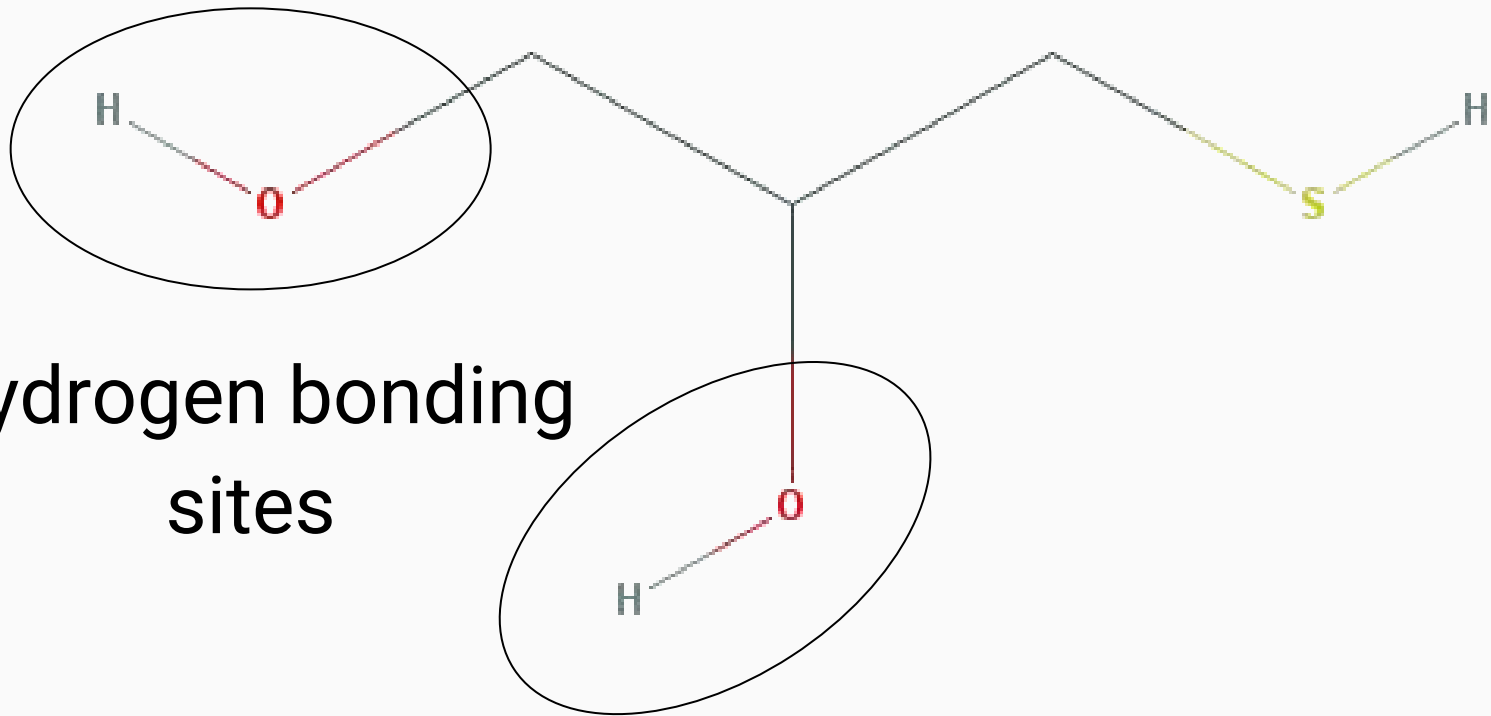
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- Dissolved ZnS with hydrogen bonds is more ordered (less disordered) than undissolved as ZnS precipitate

Calculating ΔH_{dis}

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- By van't Hoff equation: $\ln(x) = -(\Delta H_{\text{dis}}/RT) + c$
 - x: mole fraction
 - R: gas constant (8.314×10^{-3} kJ/mol K)
 - T: temperature (Kelvin)
 - c: constant related to activity coefficient

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- Then $x=bA$
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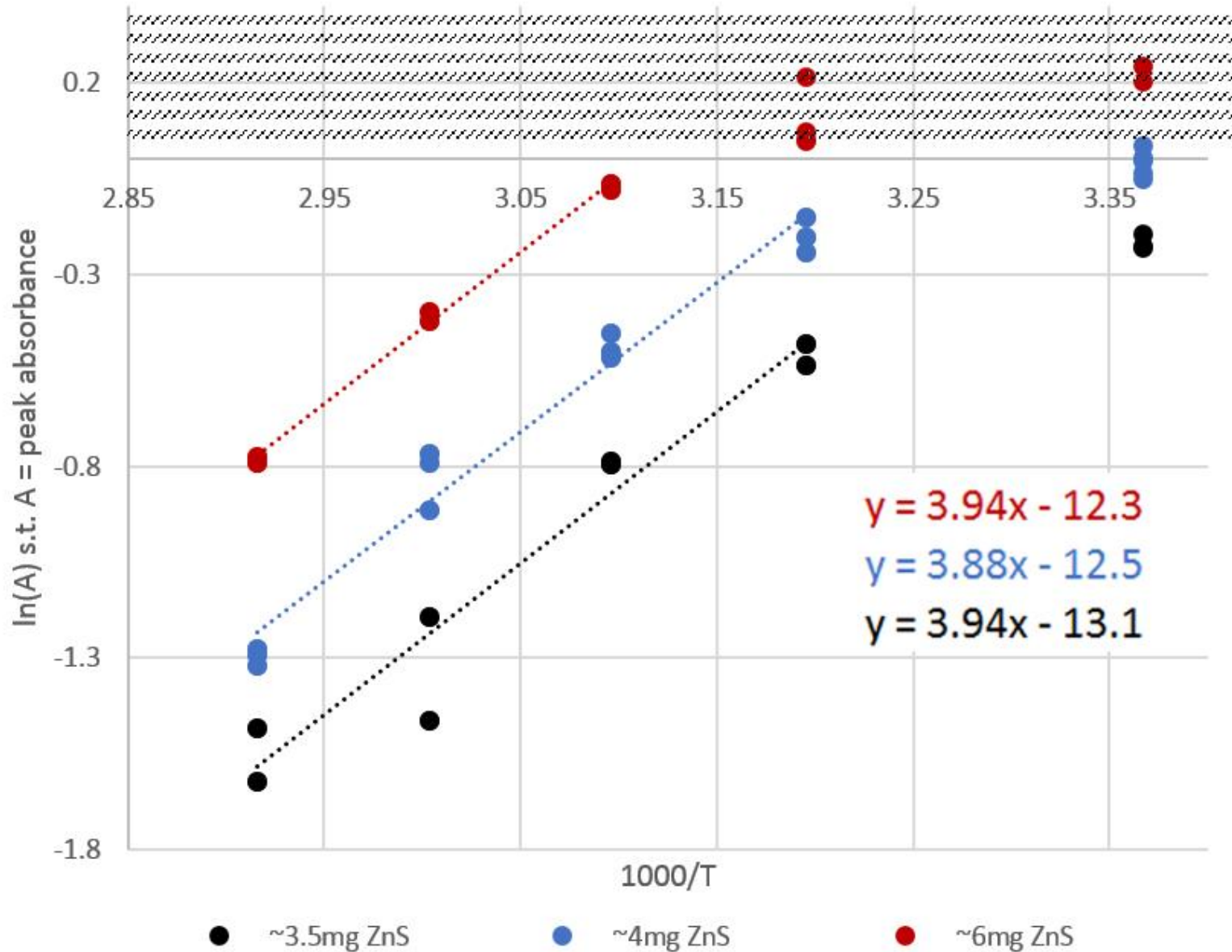
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- Proportionality b does not affect slope

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- Dissolution is exothermic
- $\Delta H_{\text{dis}} = -3 \times 10^1 \text{ kJ/mol K}$ (for 4:1 ratio MeOH:H₂O in the region of 40C-70C)

Acknowledgements

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