

Physical Chemistry Experiments

UV-Vis Measurements

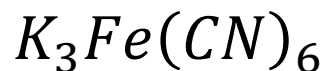
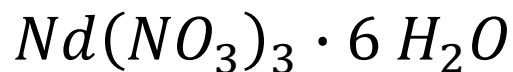
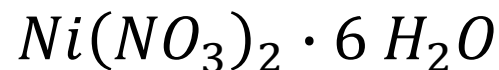
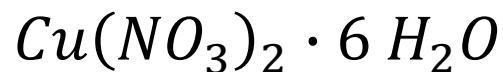
Example of a 4x4 matrix analysis

Propagation of error

NC State University

We will compare the analysis of each of four species to determine the molar absorptivity. This is obtained from the slope of the fit to the concentration vs. absorption.

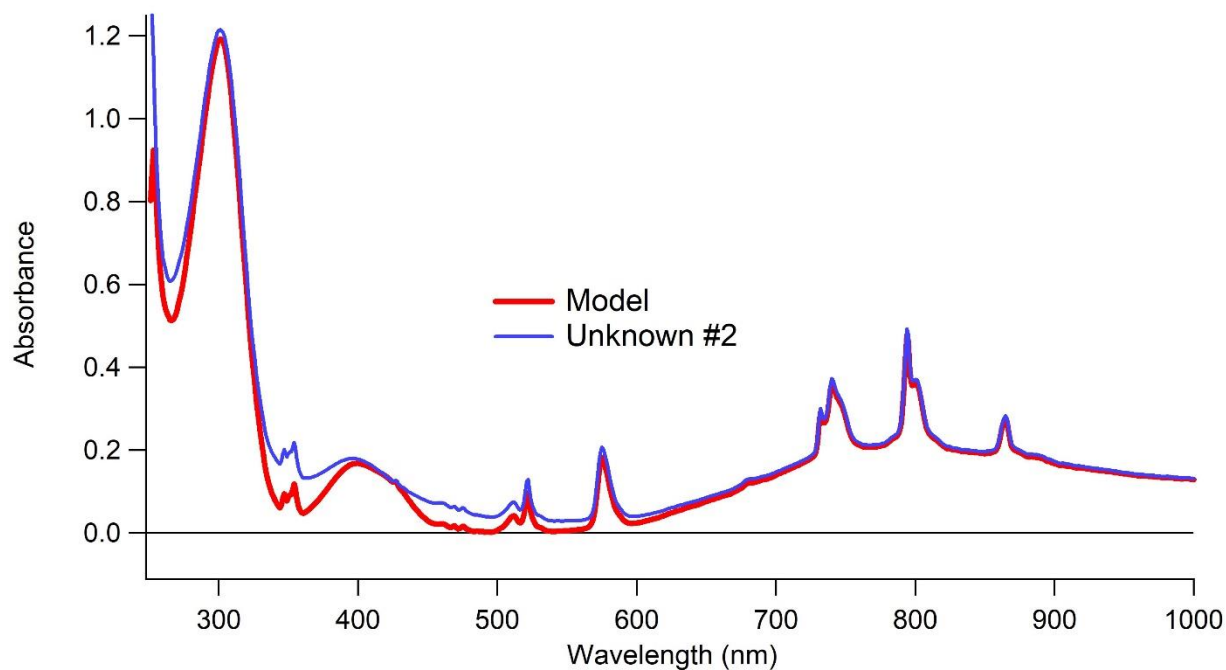
We could choose specific wavelengths for all four of the species we have tested. However, we do not know which wavelengths will be most beneficial. Rather than guess we have employed a Singular Value Decomposition method to determine the linear fits and error estimates for the molar absorptivity of each species.



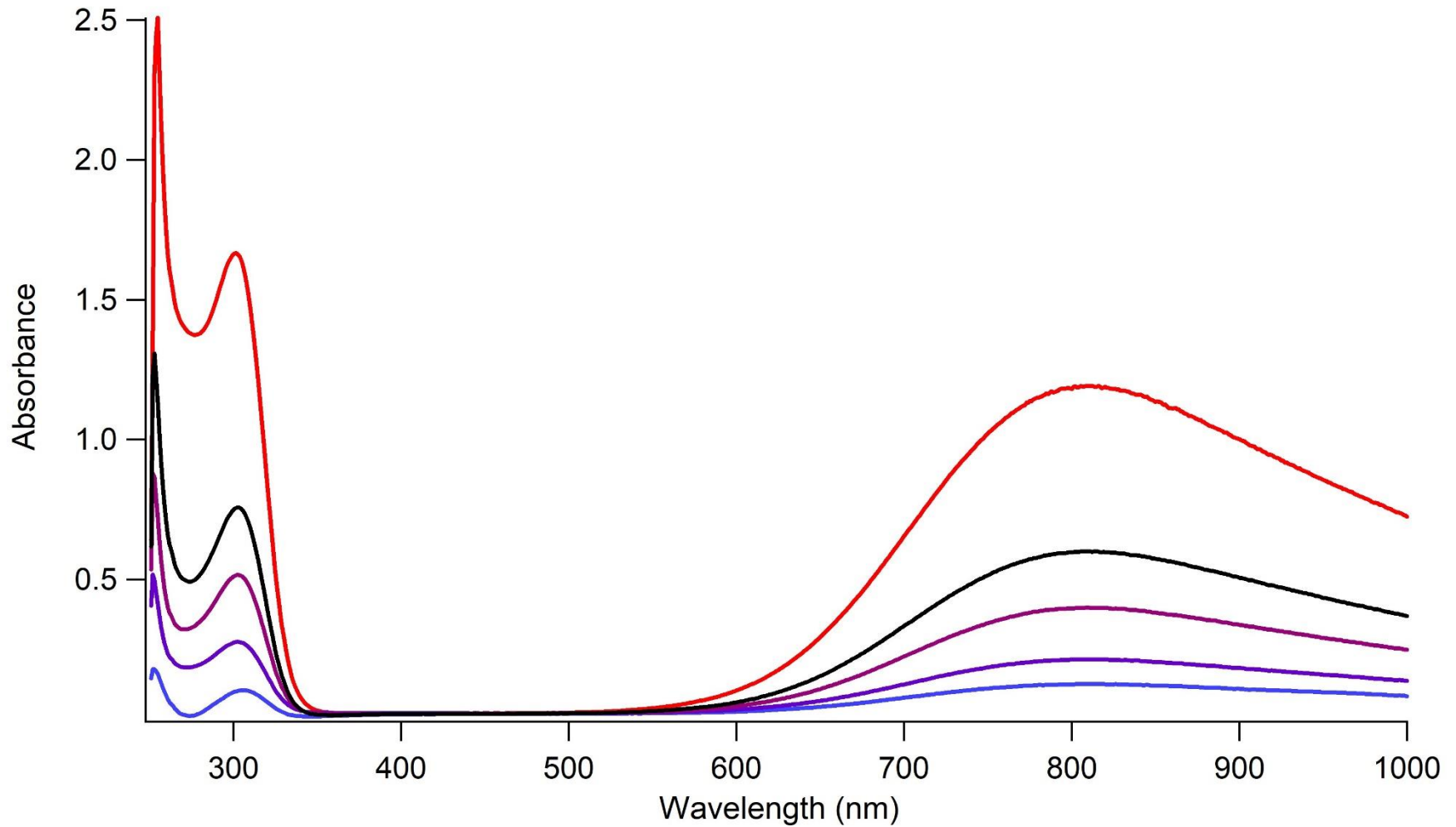
Matrix method

There are a number of ways to analyze spectra in order to determine the identity of compounds in mixtures in solution.

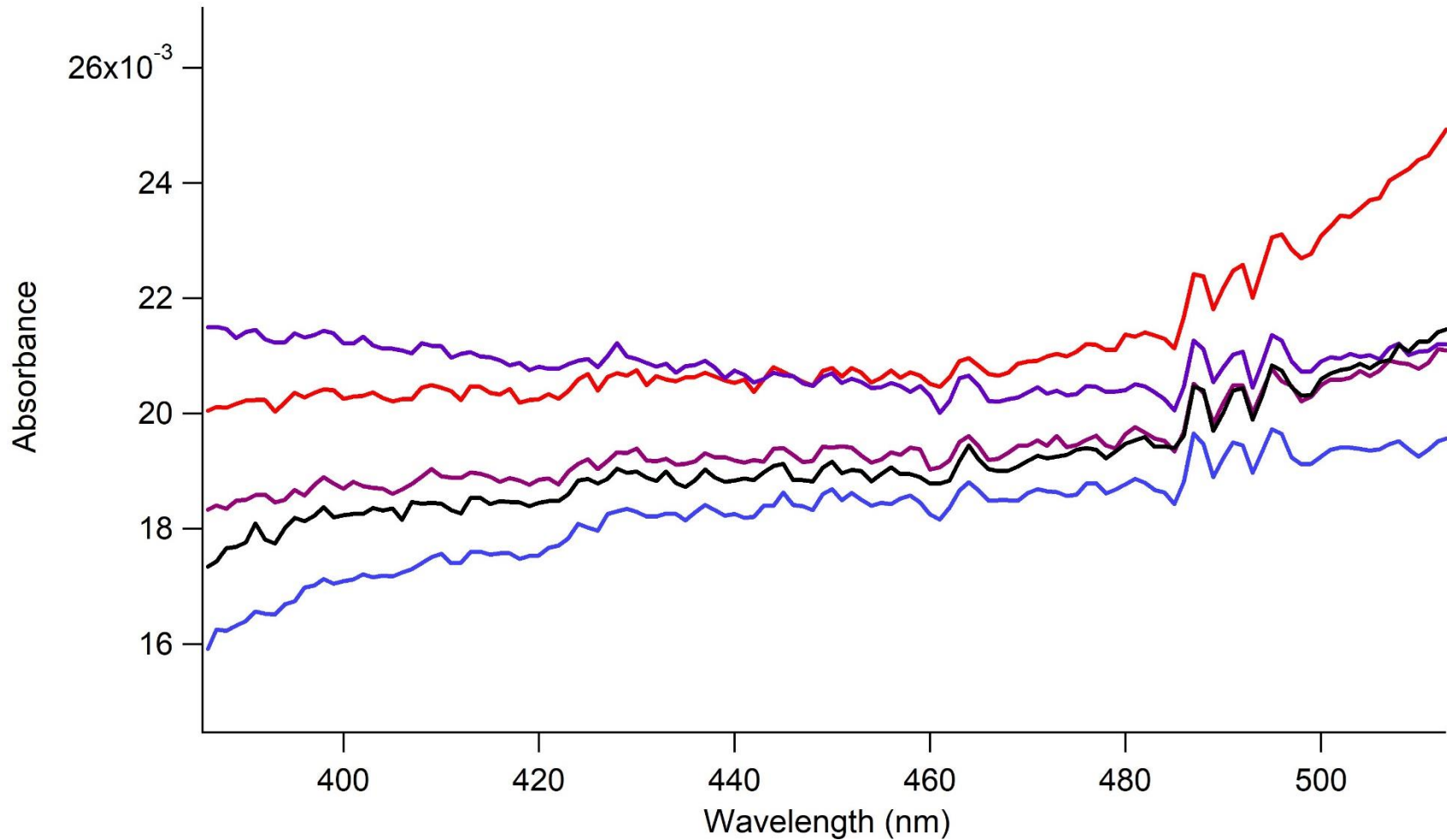
The most common is to obtain standard spectra of pure components. Using a concentration-dependent calibration, the molar absorptivity can be obtained.



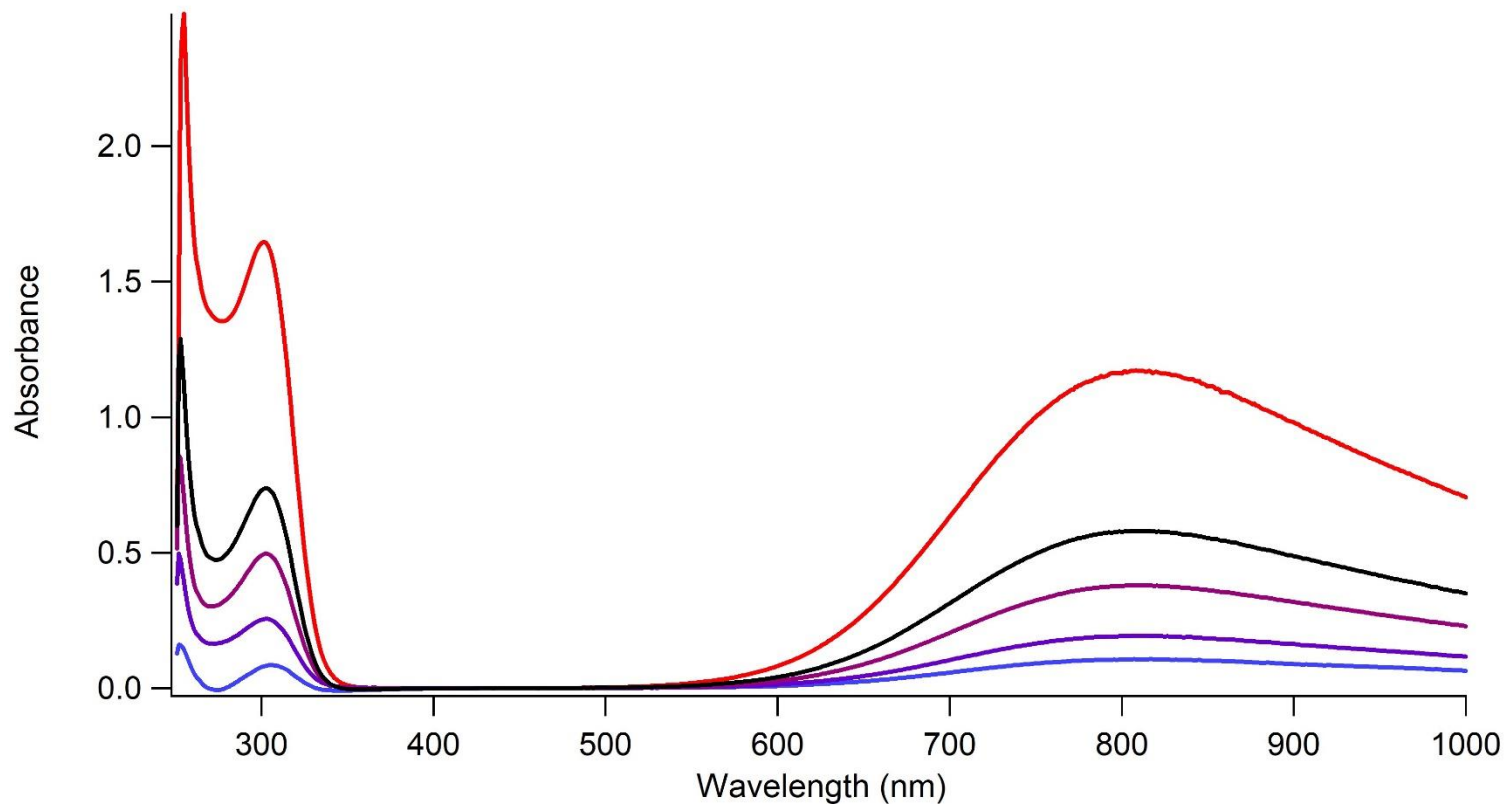
Raw data for $\text{Cu}(\text{NO}_3)_2$



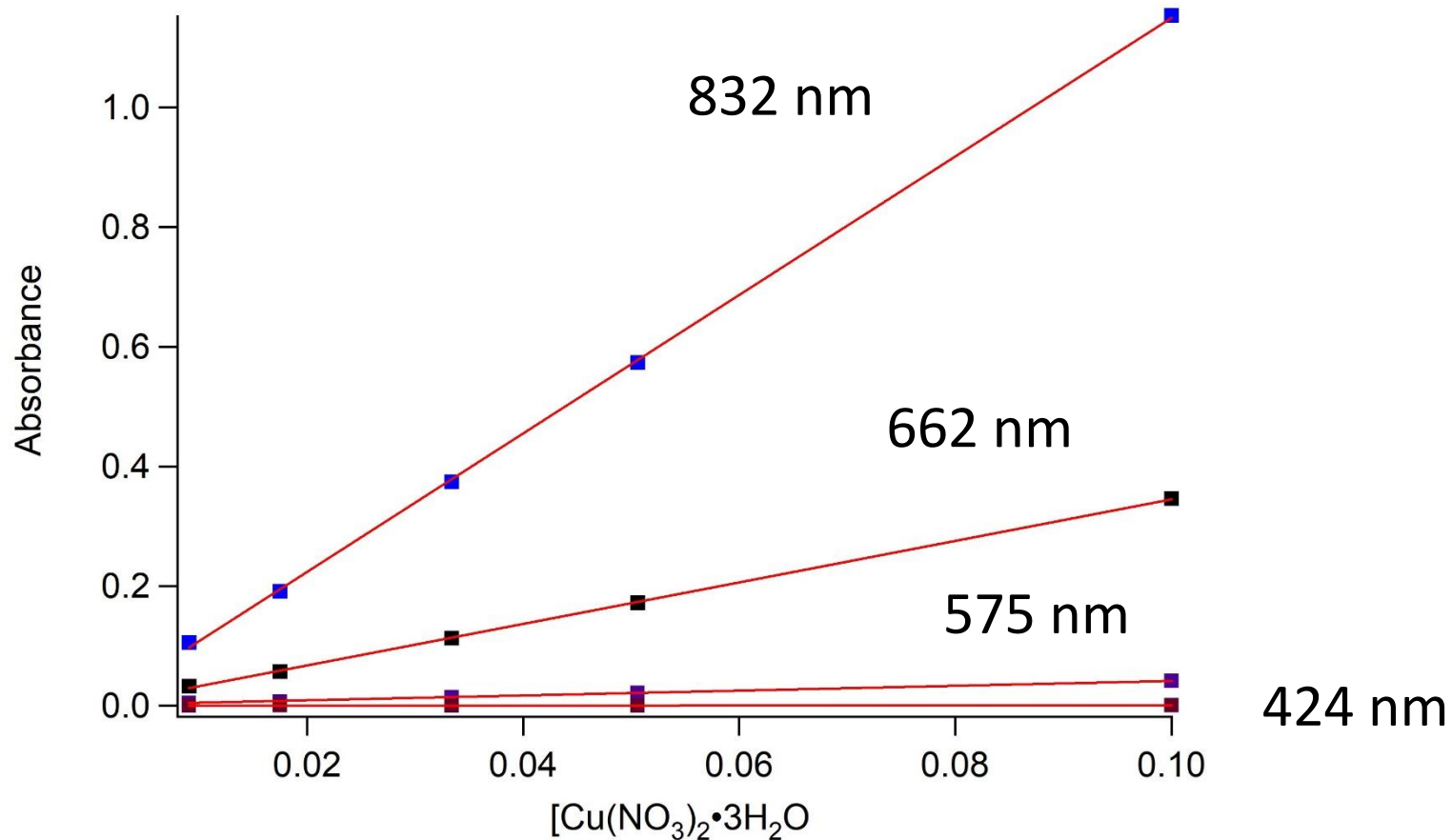
Expansion of the baseline of $\text{Cu}(\text{NO}_3)_2$



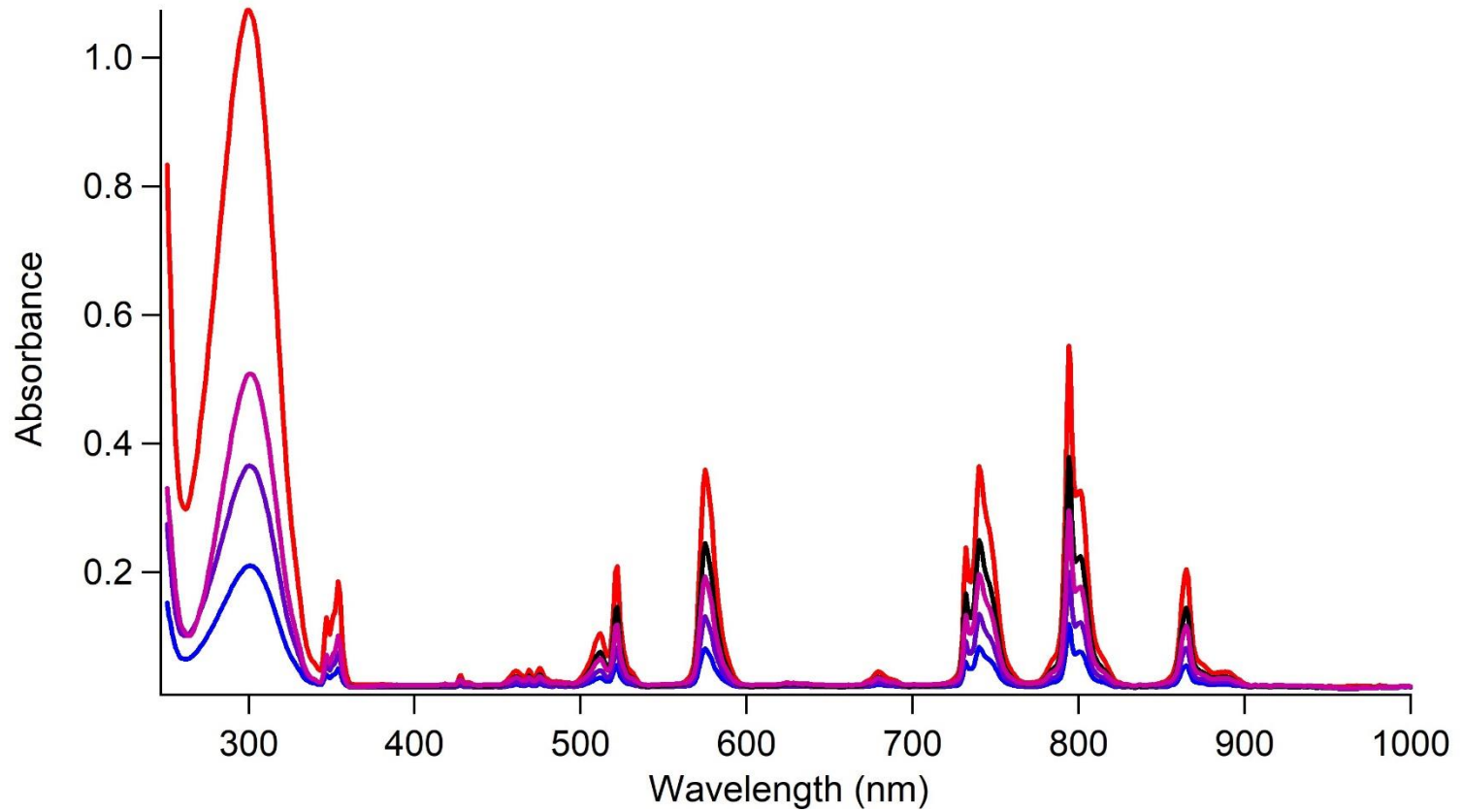
Baseline corrected data for $\text{Cu}(\text{NO}_3)_2$



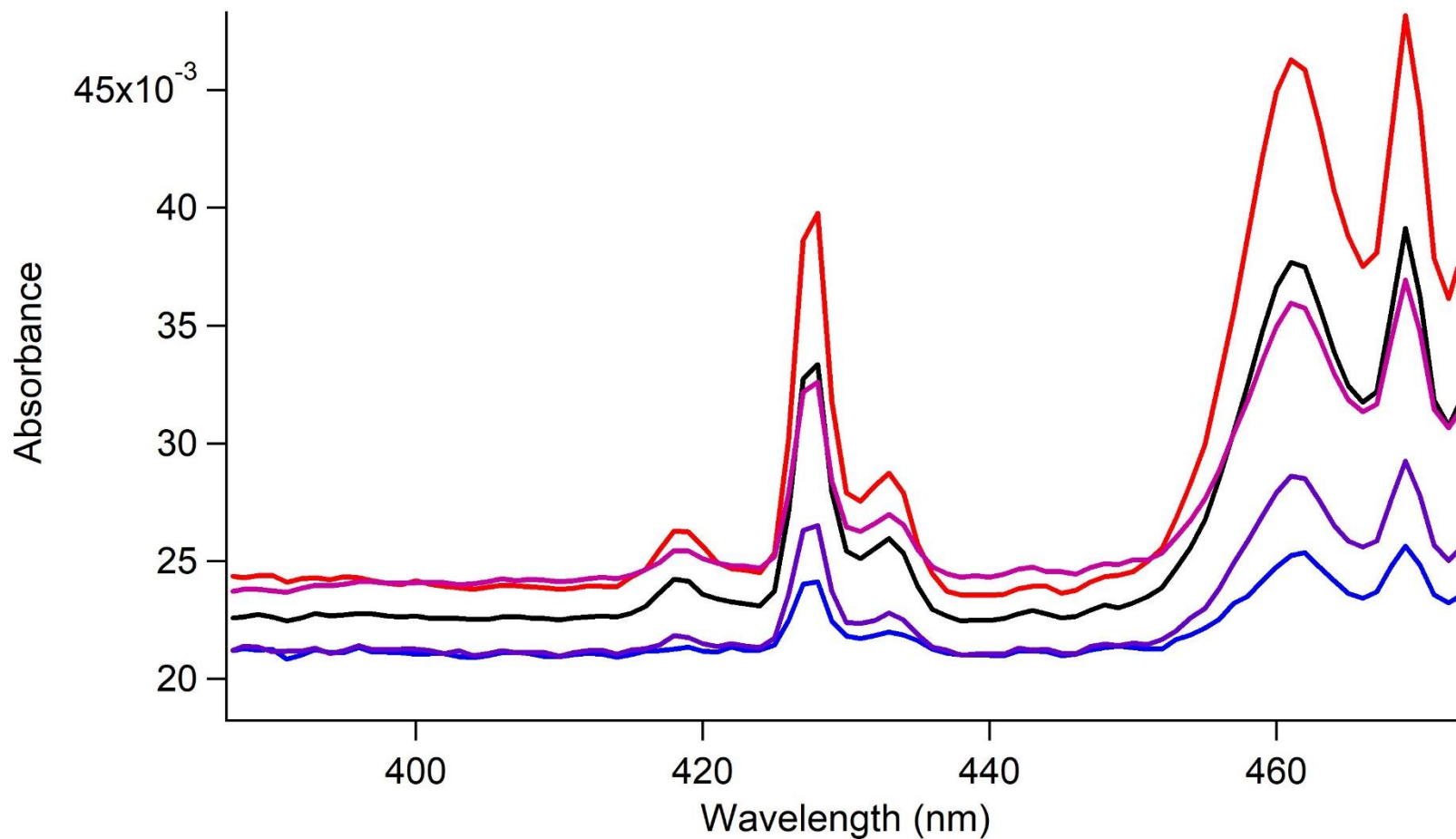
Linear regressions for four wavelengths



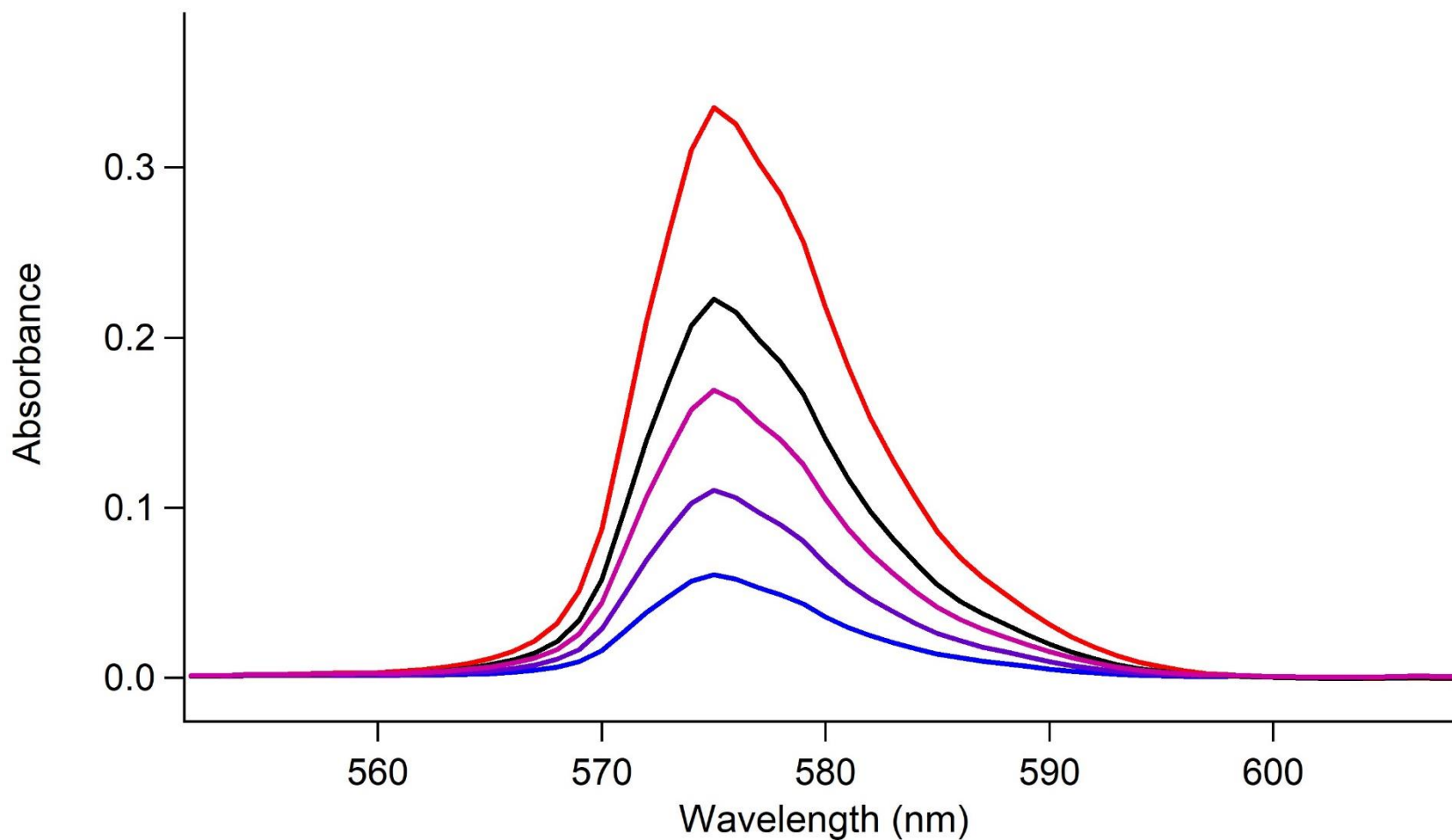
Raw data for $\text{Nd}(\text{NO}_3)_3$



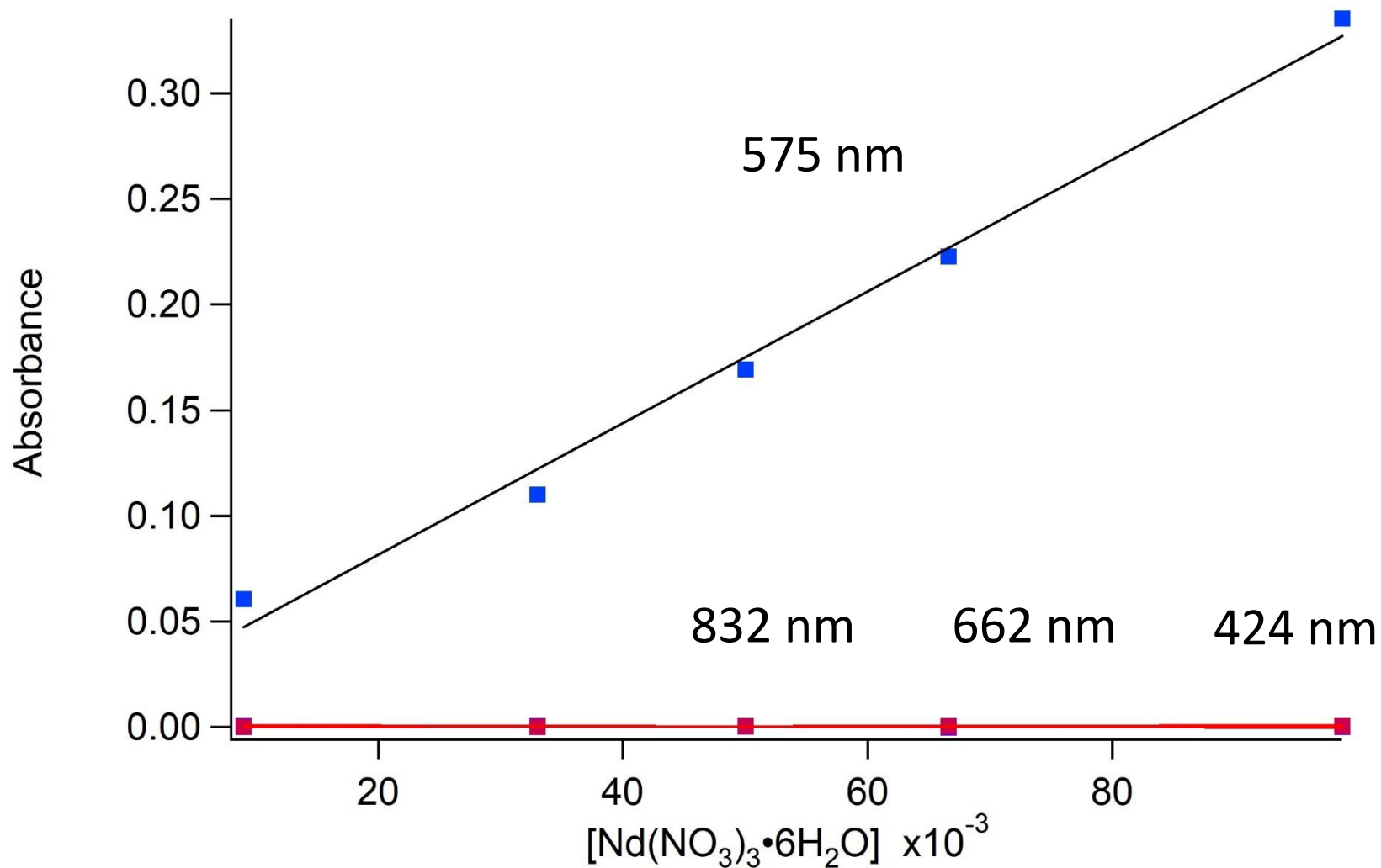
Expansion of the baseline of $\text{Nd}(\text{NO}_3)_3$



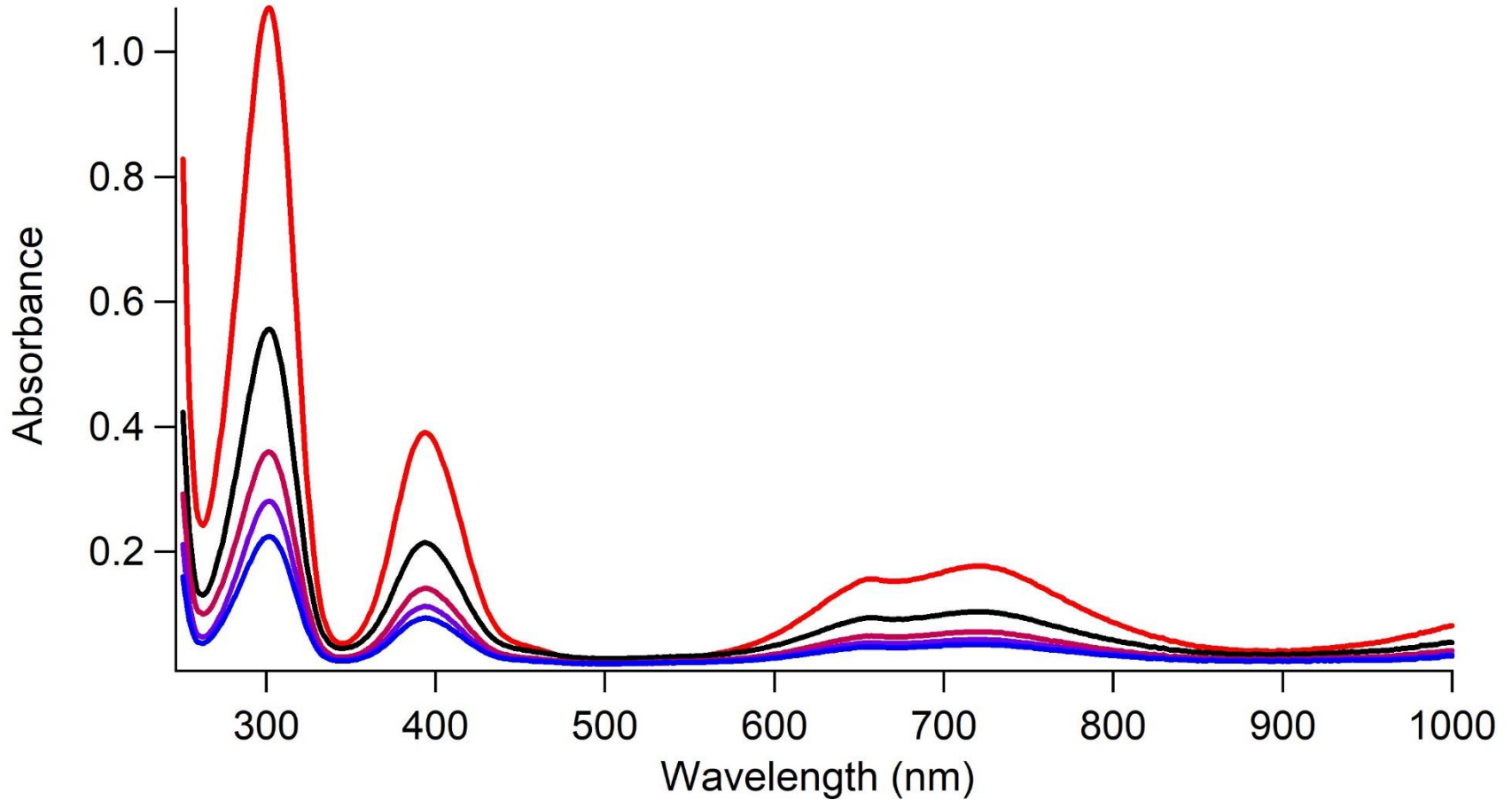
Baseline corrected data for $\text{Nd}(\text{NO}_3)_3$



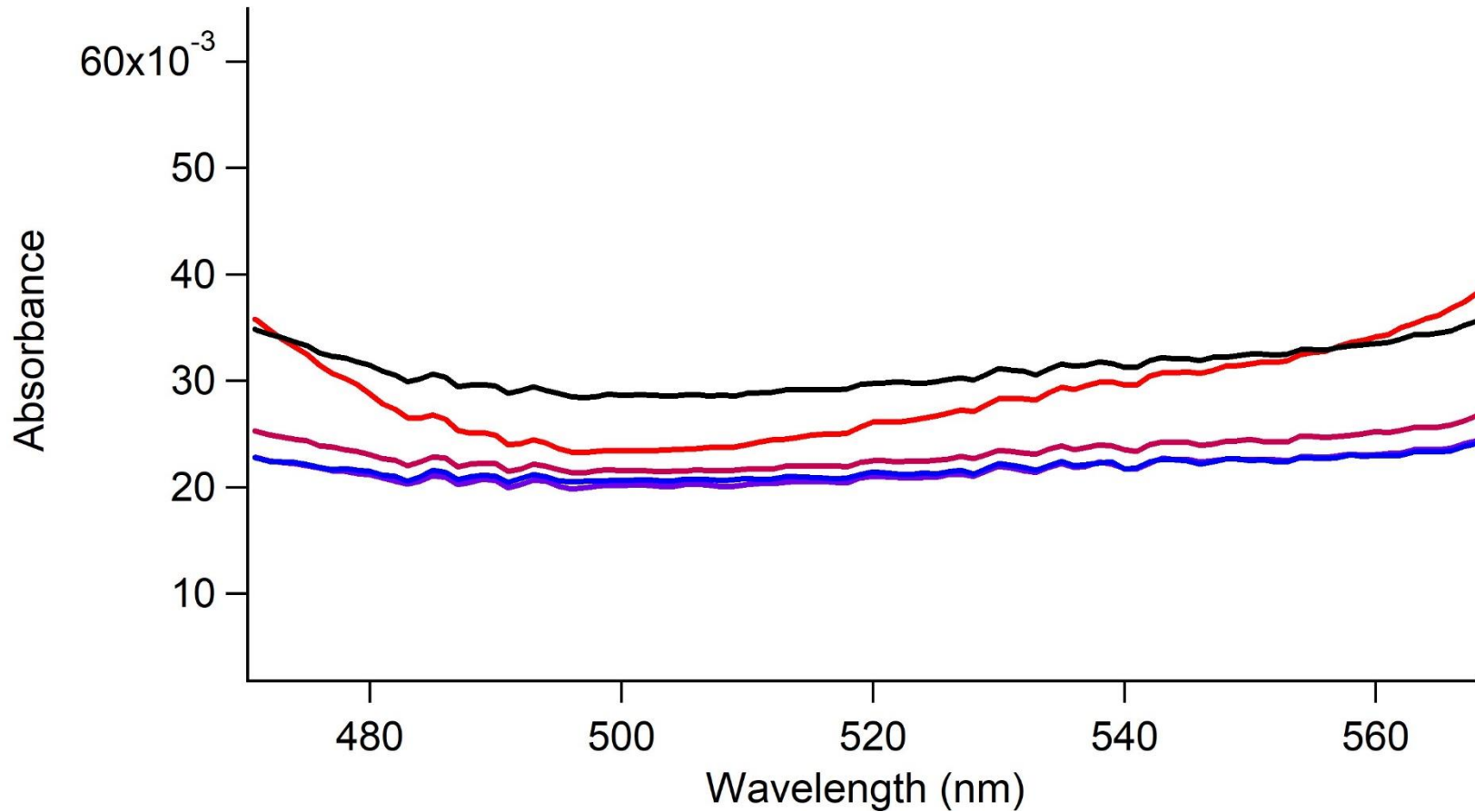
Linear regression calibration for $\text{Nd}(\text{NO}_3)_3$



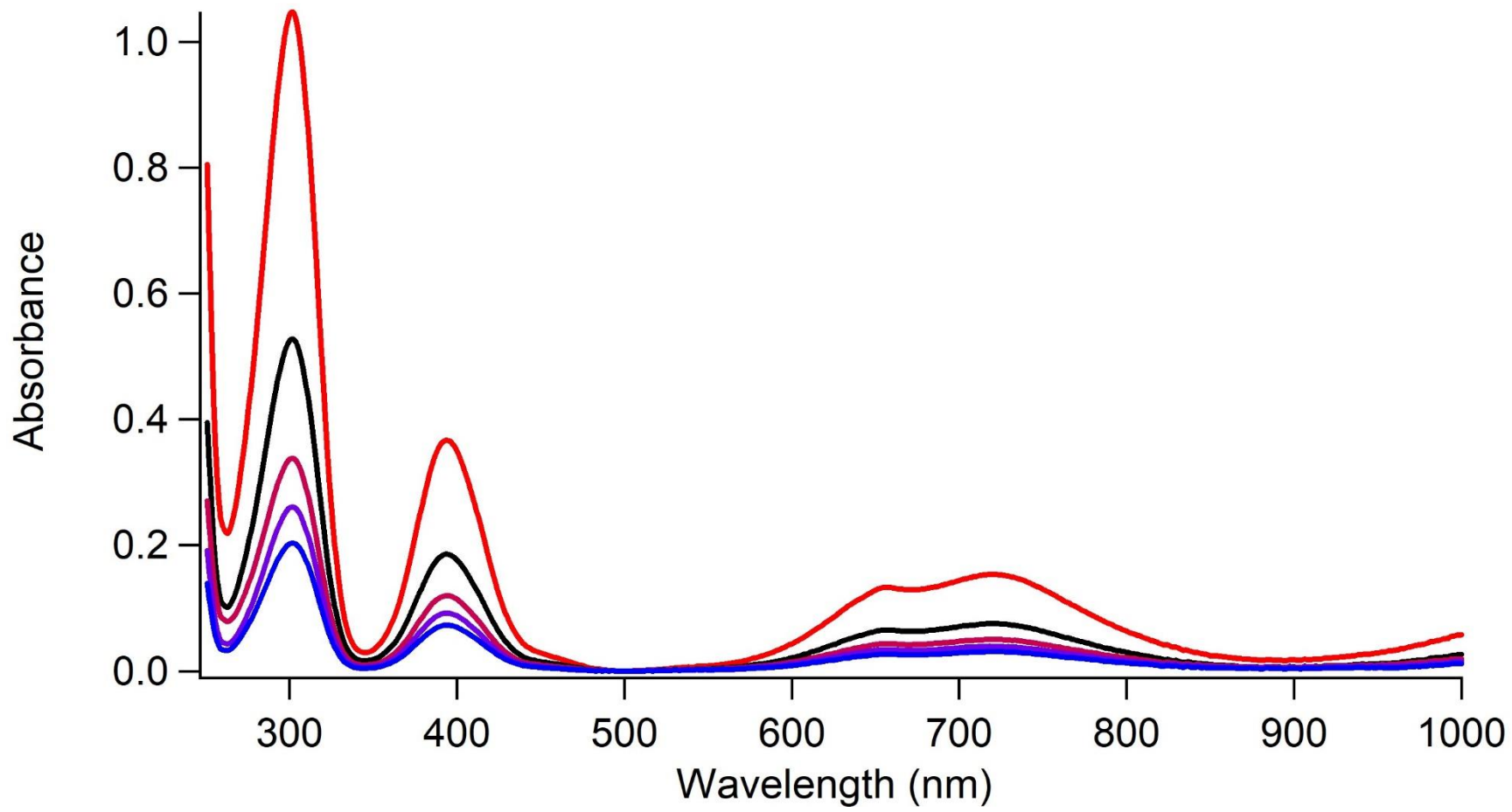
Raw data for Ni(NO₃)₂



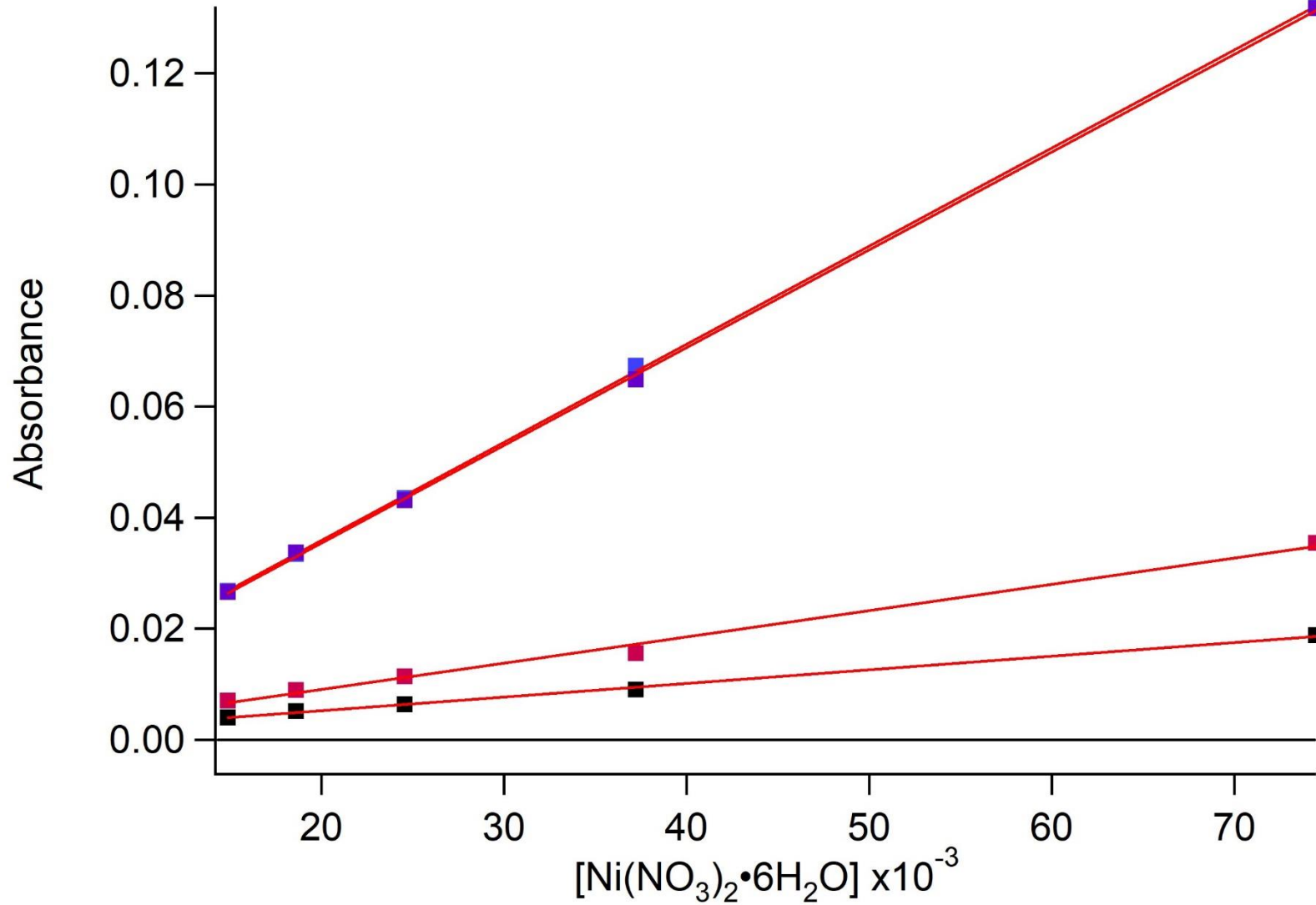
Expansion of the baseline for Ni(NO₃)₂



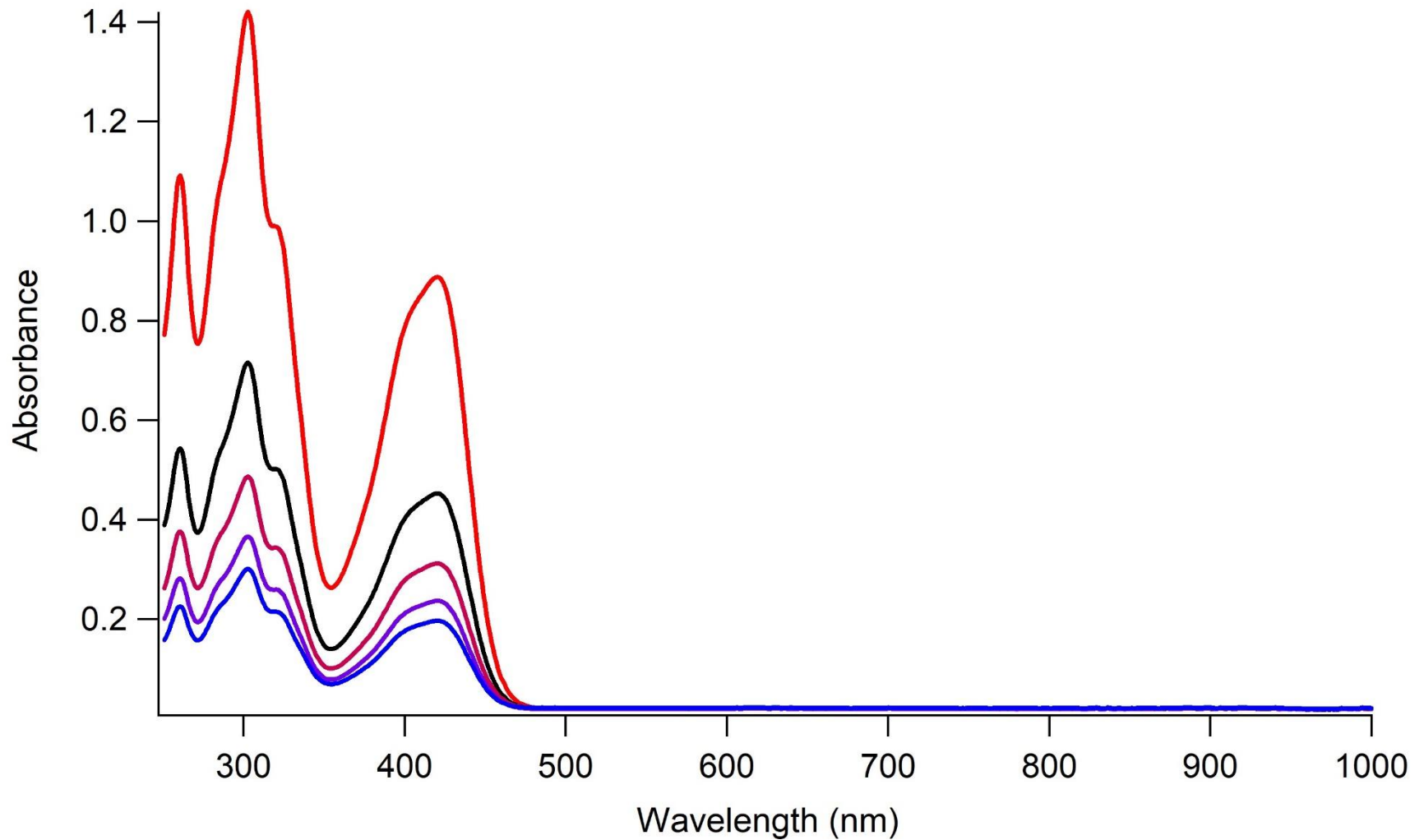
Baseline corrected data for Ni(NO₃)₂



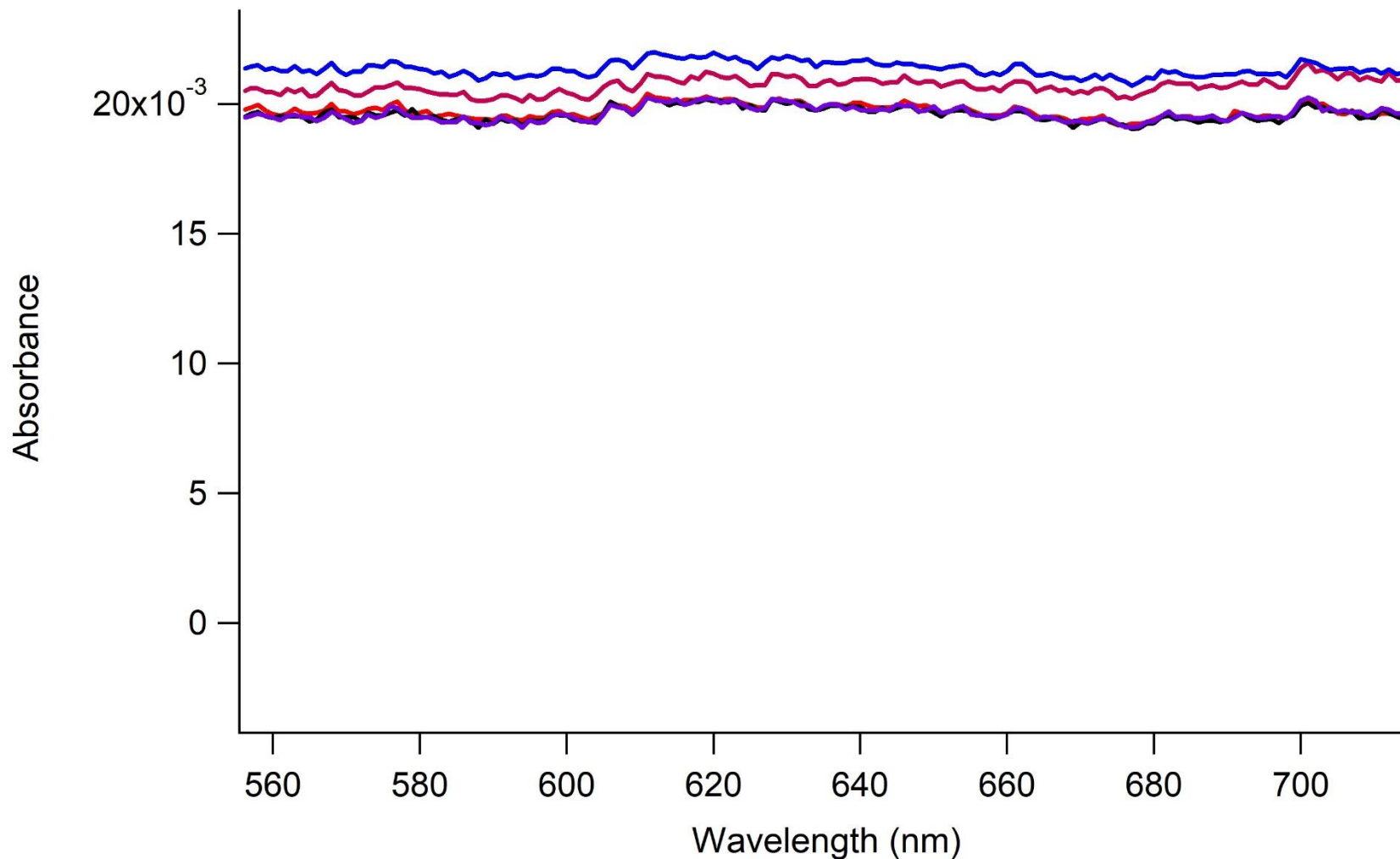
Linear regression calibration for Ni(NO₃)₂



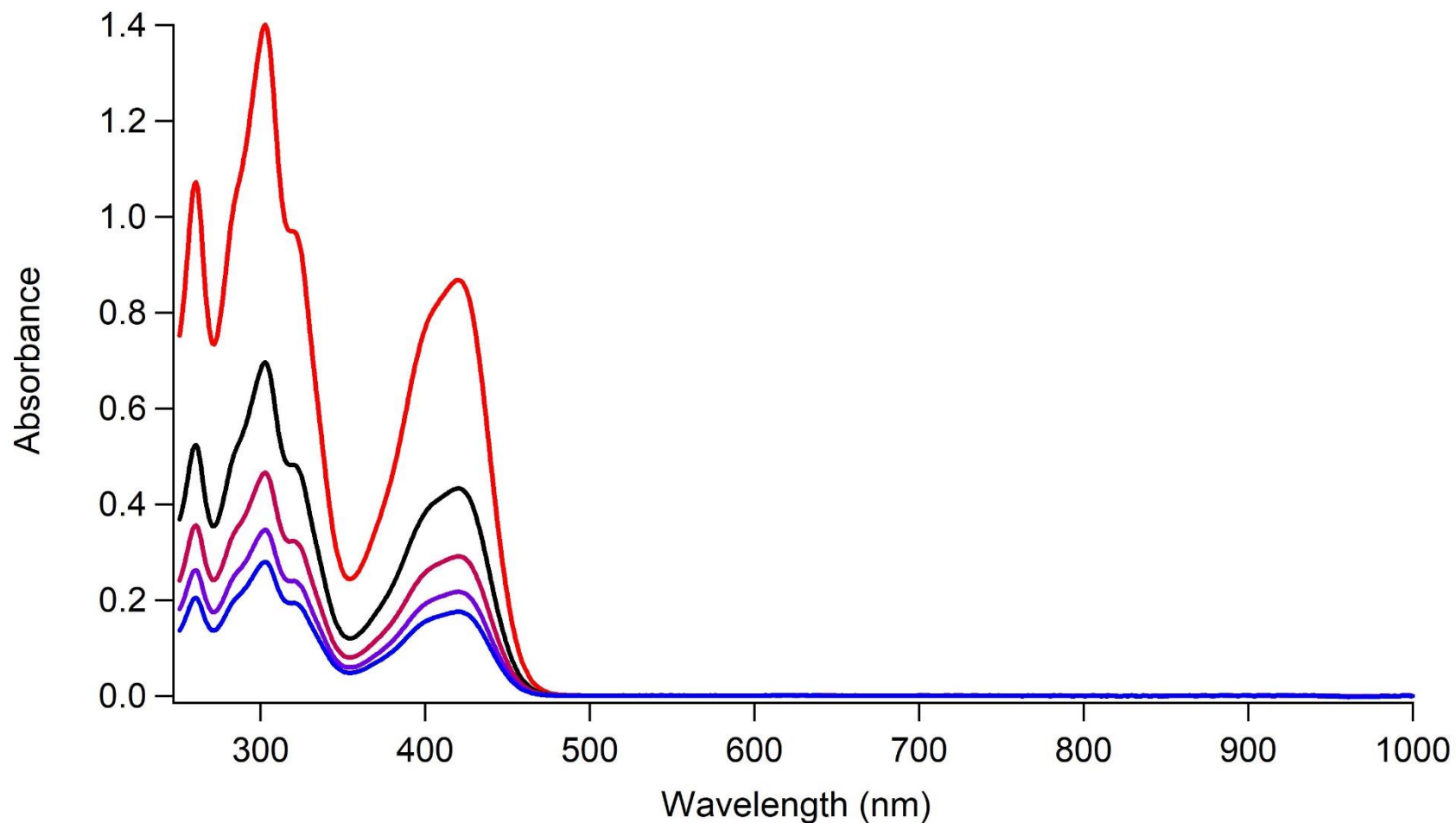
Raw data for $K_3Fe(CN)_6$



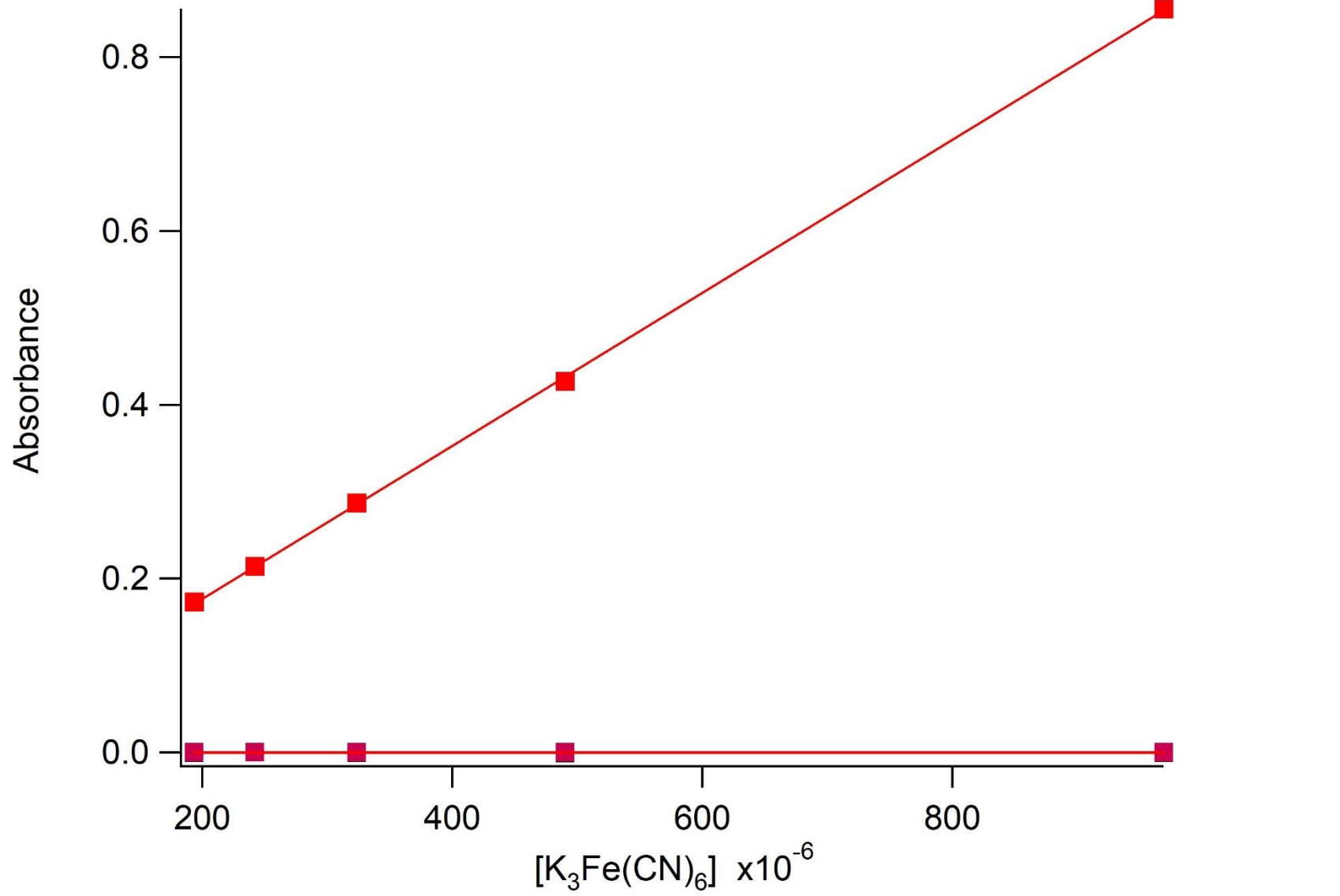
Expansion of the baseline for $K_3Fe(CN)_6$



Baseline corrected data for $\text{K}_3\text{Fe}(\text{CN})_6$



Linear regression calibration for $\text{K}_3\text{Fe}(\text{CN})_6$



Concentration of unknown using absorption spectroscopy

The wavelengths selected for analysis were 424 nm, 575 nm, 662 nm, and 832 nm. I attempted to find wavelengths that had absorption mainly from one species. This was most difficult for $\text{K}_3\text{Fe}(\text{CN})_6$, which only has absorption below 450 nm and that overlaps with both Ni and Nd complexes.

$$\varepsilon = \begin{pmatrix} 0 & 0 & 1.829 & 879.5 \\ 0 & 6.85 & 0.307 & 0 \\ 3.59 & 0 & 1.82 & 0 \\ 11.5 & 0 & 0.535 & 0 \end{pmatrix}$$

$$\varepsilon^{-1} = \begin{pmatrix} 0 & 0 & -0.028 & 0.0956 \\ 0 & 0.145 & -0.027 & 0.0084 \\ 0 & 0 & 0.603 & -0.1885 \\ 0.00113 & 0 & -0.0012 & 0.00039 \end{pmatrix}$$

$$c = \varepsilon^{-1}A$$

For unknown 2 after baseline correction

$$A = \begin{pmatrix} 0.149 \\ 0.178 \\ 0.118 \\ 0.143 \end{pmatrix}$$

$$c = \begin{pmatrix} 0.0104 \\ 0.02405 \\ 0.0441 \\ 7.7e - 5 \end{pmatrix}$$

To be compared with the original dilutions

$$c = \begin{pmatrix} 0.0166 \\ 0.0263 \\ 0.0148 \\ 9.7e - 5 \end{pmatrix}$$

| Species | Matrix | Exmpt | Diff% |
|---------|----------------------|----------------------|-------|
| Cu | 0.01043 | 0.0166 | -37.5 |
| Nd | 0.02405 | 0.0263 | -9 |
| Ni | 0.0441 | 0.0148 | 196 |
| Fe | 7.7×10^{-5} | 9.7×10^{-5} | -19.7 |

The errors are most easily handled using the individual 95% confidence limits for individual concentrations combined in a weighted formula as follows

$$\sigma_{c1} = \sqrt{\varepsilon_{11}^{-2} A_1^2 \sigma_{11}^2 + \varepsilon_{12}^{-2} A_2^2 \sigma_{12}^2 + \varepsilon_{13}^{-2} A_3^2 \sigma_{13}^2 + \varepsilon_{14}^{-2} A_4^2 \sigma_{14}^2}$$

With similar formulae for the other concentrations.

Generalized propagation of error

For the general case of a function that depends on multiple variables, $f(x,y,z)$, we

Can expand the function in a Taylor's series

$$f(x, y, z) \approx f^0 + \frac{\partial f}{\partial x} x + \frac{\partial f}{\partial y} y + \frac{\partial f}{\partial z} z$$

To see that the function depends in a linear fashion on each variable with a slope equal to the first derivative of the function with respect to that variable. The combined error with respect to all of the variables is root-mean-square average

$$\sigma = \sqrt{\left(\frac{\partial f}{\partial x}\right)^2 \Delta x^2 + \left(\frac{\partial f}{\partial y}\right)^2 \Delta y^2 + \left(\frac{\partial f}{\partial z}\right)^2 \Delta z^2 + \dots}$$

Propagation of error

If we calculate a quantity Q from a number of measured values (A, B, C, \dots) each with their respective uncertainties ($\sigma(A), \sigma(B), \sigma(C), \dots$) we can calculate how the uncertainties *propagate* into the value of Q as follows. If $Q = f(x, y, z)$ then

$$\sigma^2(Q) \cong \left(\frac{\partial f}{\partial x}\right)^2 \sigma^2(x) + \left(\frac{\partial f}{\partial y}\right)^2 \sigma^2(y) + \left(\frac{\partial f}{\partial z}\right)^2 \sigma^2(z)$$

Please note that we take derivatives versus '**x, y, z etc**' here. Then we evaluate the derivative at the average or best fit value for a given parameter.

This formula is an *approximation* that only holds true if the error sources $\sigma(x), \sigma(y), \sigma(z), \dots$ are independent (i.e. uncorrelated). If x and y represent e.g. the intercept and slope from the same regression this is generally not true. In addition we tacitly assume that we can replace the σ 's by their estimates (i.e. s_e 's)

Propagation of error

Most commonly, the error on a quantity, Δx , is given as the standard deviation, σ

The standard deviation is the positive square root of variance, σ^2

The value of a quantity and its error are often expressed as an interval $x \pm \Delta x$

If the statistical probability distribution of the variable is known, it is possible to derive confidence limits to describe the region within which the true value of the variable may be found.

In the case of a line $y = mx + b$

We can calculate the error of y relative x as $\Delta y = m \Delta x$

Propagation of error in a polynomial

For example if $Q = f(x) = x^n$.

$$\frac{\partial f}{\partial x} = nx^{n-1}$$

$$\sigma^2(Q) = (nx^{n-1})^2 \sigma^2(x)$$

$$\sigma(Q) = \frac{\sigma(x)nx^n}{x}$$

$$\frac{\sigma(Q)}{Q} = n \frac{\sigma(x)}{x}$$

From propagation of error we can conclude that the relative error in Q is n times larger than the relative error in x if the relationship is $Q = x^n$.

Example relevant to UV-vis laboratory

From the standard line you obtain the slope at each measured wavelength, which is equal to the extinction coefficient, ϵ_{λ} . Each extinction coefficient has an associated standard error s_e that comes from the linear least square fitting. When reporting the extinction coefficient in a table we would like to see the error (usually in parentheses to indicate that it is a standard error and not a 95% confidence limit).

There is an error associated with the measurement of the absorbance. This can be estimated from replicates (3 or more) or from an analysis of the noise on the spectra. To obtain the noise on the spectra you would select a flat region of the spectrum and then determine the width of the Gaussian noise by taking the average and standard deviation.

Example relevant to UV-vis laboratory

The equation for the calculation of concentration uses two equations and two unknowns, c_1 and c_2 .

$$A_1 = \epsilon_{11}c_1 + \epsilon_{12}c_2$$

$$A_2 = \epsilon_{21}c_1 + \epsilon_{22}c_2$$

Therefore,

$$c_1 = (\epsilon_{11})^{-1}A_1 + (\epsilon_{21})^{-1}A_2$$

$$c_2 = (\epsilon_{12})^{-1}A_1 + (\epsilon_{22})^{-1}A_2$$

The error propagation of error in this equation is

$$\sigma(c_1) = \sqrt{\sum_n (\epsilon_{n1})^{-2} \sigma(A_n)^2 + ((\epsilon_{n1})^{-2} A_n)^2 \sigma(\epsilon_{n1})^2}$$