

Determination of cobalt(II) nitrate and chromium(III) nitrate by UV/Vis absorption spectroscopy

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Abstract

In this experiment Analytical Ultraviolet-Visible Absorption Spectroscopy (UV/Vis)¹ was employed to determine absorption spectra, and therefore concentrations, of a mixture made up of $\text{Cr}(\text{NO}_3)_3$, $\text{Co}(\text{NO}_3)_2$, and de-ionized water. The absorption spectrum of this unknown mixture was compared analytically against a set of standard spectra and with the help of *Microsoft Excel* and a couple useful formulas the concentrations were found to be $0.0278M$ and $0.0063M$ for $\text{Cr}(\text{NO}_3)_3$ and $\text{Co}(\text{NO}_3)_2$, respectively.

0.1 Theory

In UV/Vis Spectroscopy photons are passed through a 1cm cuvette containing sample solution wherein some of the photons are absorbed unequally at various frequencies. By measuring the amount of photons transmitted through the cuvette compared to the amount going in, the transmittance of the sample, $T = \frac{I}{I_0}$ can be determined. Using transmittance, absorption values can be found: $A = \log_{10}(\frac{1}{T})$. However, an empirical law known as the *Beer-Lambert Law* is used instead, to attain the absorbance directly:

¹Beckman DU[®] 7400 Spectrophotometer

$A = b\epsilon C$ where b = path length through the cuvette (1cm here), ϵ = absorption coefficient (or extinction coefficient), and C = concentration of the sample in solution. By this equation one can therefore determine the concentration of a solution given an absorbance value, absorption coefficient, and path length. First off, it would be prudent to state immediately that the same 1cm cuvette was used for all measurements, which simplifies future calculations and is therefore favorable. ϵ values for both chromium and cobalt nitrate were determined at various wavelengths using a set of standards with known concentrations. From these trials were many Absorption vs. Concentration plots made. Employing regression analysis on each set of points yielded a line with slope equal to $b\epsilon$. Now since the unknown mixture was in fact a mixture of both chromium and cobalt species, concentration could not be determined directly from any of the given standards. But using regression-determined ϵ values and a set of two equations with two unknowns (both concentration) it was made possible to find the individual species concentrations. Note that throughout measurements absorption effects of the DI-H₂O were subtracted using a DI-H₂O blank as background on the device. The two equations were as follows: $A' = \epsilon'_x b[X] + \epsilon'_y b[Y]$ and $A'' = \epsilon''_x b[X] + \epsilon''_y b[Y]$ where A' = mix absorbance at 1st λ , A'' = mix absorbance 2nd λ , ϵ' = molar absorptivity at 1st λ , ϵ'' = molar absorptivity at 2nd λ , $[X]$ = concentration (M) of cobalt, and $[Y]$ = concentration (M) of chromium. These two equations were then solved for concentration using determinants:

$$[X] = \frac{\begin{vmatrix} A' & \epsilon'_y b \\ A'' & \epsilon''_y b \end{vmatrix}}{\begin{vmatrix} \epsilon'_x b & \epsilon'_y b \\ \epsilon''_x b & \epsilon''_y b \end{vmatrix}} = \frac{A' \epsilon''_y - A'' \epsilon'_y}{\epsilon'_x \epsilon''_y - \epsilon''_x \epsilon'_y}$$

$$[Y] = \frac{\begin{vmatrix} \epsilon'_x b & A' \\ \epsilon''_x b & A'' \end{vmatrix}}{\begin{vmatrix} \epsilon'_x b & \epsilon'_y b \\ \epsilon''_x b & \epsilon''_y b \end{vmatrix}} = \frac{A'' \epsilon'_x - A' \epsilon''_x}{\epsilon'_x \epsilon''_y - \epsilon''_x \epsilon'_y}$$

Plugging in all the appropriate values provides one with expected concentration values for both chromium and cobalt. It must also be noted that some reagents can interfere with one another. To make sure this is not the case a mixture of known concentration was run and its A_{mix} values were compared to $A_{Co} + A_{Cr}$ values at the same concentration. These values

would be expected to be nearly identical if the reagents did not interfere with one another.

0.2 Procedure

A set of three handouts were given by the instructor to facilitate a coherent procedure, each one containing information that the other two lacked. Nevertheless one in particular² was used as the master procedure and gave clear instructions as to starting up and shutting down the instrument and what generally needed to be accomplished in the experiment. Suffice it to say that the instrument covered a wavelength range from 350nm to 650nm and quantitatively highlighted absorbances at 410.0, 450.0, 510.0, 540.0, 575.0, and 625.0nm. The standard dilutions were of concentrations listed below and the known mixture in particular had concentrations of 0.0100M-Cr(NO₃)₃ and 0.0752M-Co(NO₃)₂. All standard solutions were prepared in 25-mL volumetric flasks.

Cr(NO ₃) ₃ (M)	Stock Sol'n (mL)	Co(NO ₃) ₂ (M)
0.0100	5	0.0376
0.0200	10	0.0752
0.0300	15	0.1128
0.0400	20	0.1504
0.0500	25	.188

Table 0.1: Standard Solution Specifications

0.3 Results

Most of the results are listed in various tables below. table 0.2 and 0.3 show experimentally determined absorbance values for the Cr and Co standard dilutions, respectively. Similarly, table 0.4 lists absorbances for both

²Determination of cobalt(II) nitrate and chromium(III) nitrate by UV/Vis absorption spectroscopy, revised Fall 2006

the known mixture and unknown mixture at the given wavelengths. Table 0.5 lists slope values harvested from the regression lines in figures 0.1 and 0.2 which represent $\epsilon * b$ in the Beer-Lambert Law mentioned in section 0.1. Also determined (in table 0.6) were percent error values between expected absorbances in the known mixture (as calculated using 0.0200M-Cr and 0.0752M-Co absorbances added together) compared to the actual absorbance of the mixture. The added singular standards were taken as the true value in the percent error³ calculation to produce the given results. Figure 0.3 has also been supplied below for qualitative purposes.

Conc (M)	@410nm	@450nm	@510nm	@540nm	@575nm	@625nm
0.0100	0.1500	0.0794	0.0476	0.0895	0.1242	0.0705
0.0200	0.3052	0.1502	0.0981	0.1856	0.2553	0.1482
0.0300	0.4652	0.2205	0.1511	0.2842	0.3878	0.2216
0.0400	0.6151	0.2854	0.2004	0.3799	0.5165	.2918
0.0500	0.7763	0.3549	0.2526	0.4815	0.6548	0.3709

Table 0.2: Chromium Standard Absorbances

0.4 Discussion

As mentioned earlier, the standards were prepared in 25-mL volumetric flasks. This allowed for very precise measurements of concentration. One difficulty was due to this choice, however, as these flasks had no caps for them for mixing. This problem was solved using parafilm to close off the opening while mixing. For this reason it should be expected that relatively little error in the end could be attributed to improper mixing. It should be noted that the chromium and cobalt solutions were prepared by two different respective people, as this allows for precision at least within each set of dilutions. The computer-interfaced instrument took readings very quickly so that the main bottleneck in the experiment in terms of time came from mixing the solutions. This step is necessary, however, and

$$3\%_{err} = \frac{|A_{true} - A_{exp}|}{A_{true}} \times 100\%$$

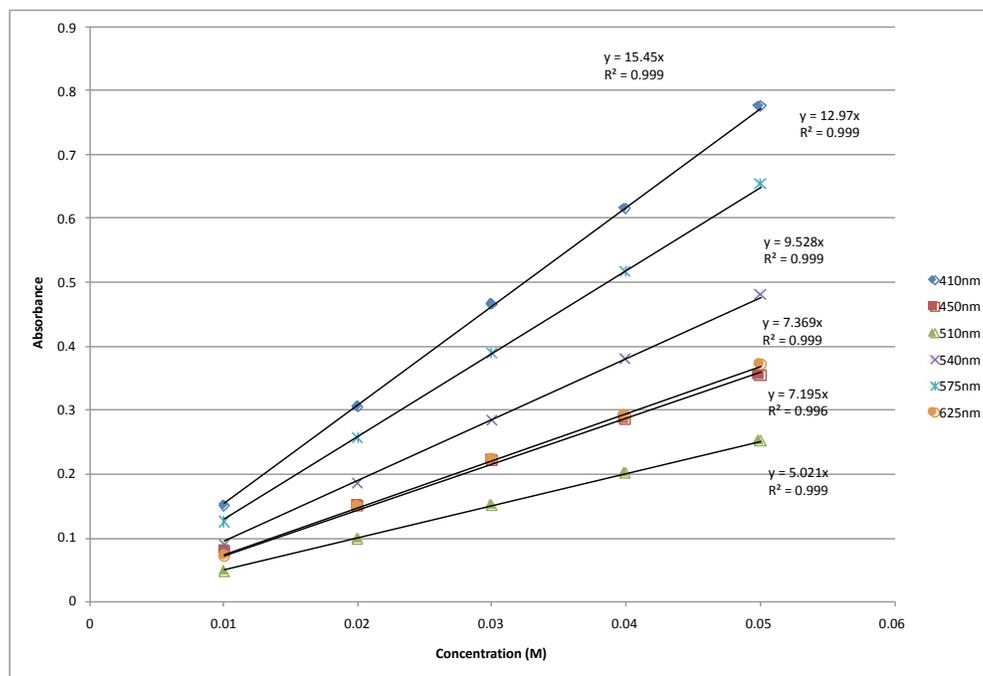


Figure 0.1: Absorbance vs Concentration (M) for $\text{Cr}(\text{NO}_3)_3$

Conc (M)	@410nm	@450nm	@510nm	@540nm	@575nm	@625nm
0.0376	0.0104	0.0746	0.1782	0.1114	0.0217	0.0068
0.0752	0.0276	0.1553	0.3620	0.2292	0.0486	0.0231
0.1128	0.0429	0.2345	0.5433	0.3449	0.0739	0.0357
0.1504	0.0584	0.3132	0.7274	0.4585	0.0987	0.0474
0.1880	0.0764	0.3991	0.9202	0.5811	0.1240	0.0557

Table 0.3: Cobalt Standard Absorbances

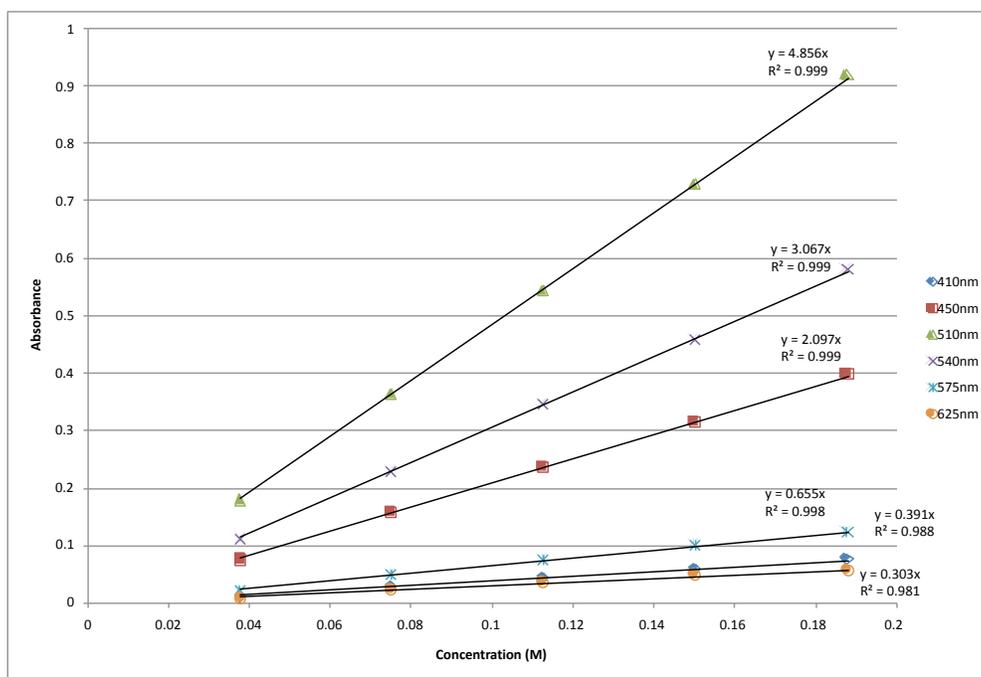


Figure 0.2: Absorbance vs Concentration (M) for $\text{Co}(\text{NO}_3)_2$

Wavelength, λ (nm)	A, known mixture	A, unknown mixture
410	0.3432	0.3932
450	0.3090	0.2228
510	0.4681	0.2147
540	0.4262	0.2934
575	0.3124	0.3342
625	0.1755	0.1911

Table 0.4: Absorbance of Known and Unknown mixtures

Solution	@410nm	@450nm	@510nm	@540nm	@575nm	@625nm
Cr(NO ₃) ₃	15.45	7.195	5.021	9.528	12.97	7.369
Co(NO ₃) ₂	0.655	2.097	4.865	3.067	0.391	0.303

Table 0.5: Experimentally determined ϵ values

Wavelength, λ (nm)	% error
410	3.12
450	1.15
510	1.74
540	2.75
575	2.80
625	2.45

Table 0.6: % error for known mixture

should not be omitted (read: done by instructor beforehand) because it allows the student to practice his technique and get a quantitative output showcasing his own handiwork, as represented by the accuracy and precision (or lack thereof) revealed in the final calculations. By color alone it could be deduced that the unknown mixture contained more chromium than cobalt, for the solutions were different colors and the color of the unknown more closely matched the chromium standards. Similarly, the chart (see attached) for the unknown mixture resembled the chromium standards in between 0.0200M and 0.0300M yet at the same time it was clear some cobalt existed because the absorption peak at $\lambda = 510nm$ on the unknown chart reached a value beyond that in the 0.0300M chromium standard and was known to be a cobalt-sensitive wavelength. The calculated concentrations for the components chromium and cobalt were found to be 0.0278M and 0.0063M, respectively, using the determinant equations listed in section 0.1. These values correlate correctly with qualitative preliminary observations. As stated before, it was important to determine whether or not the mixture components would react with one another. Worries about this were

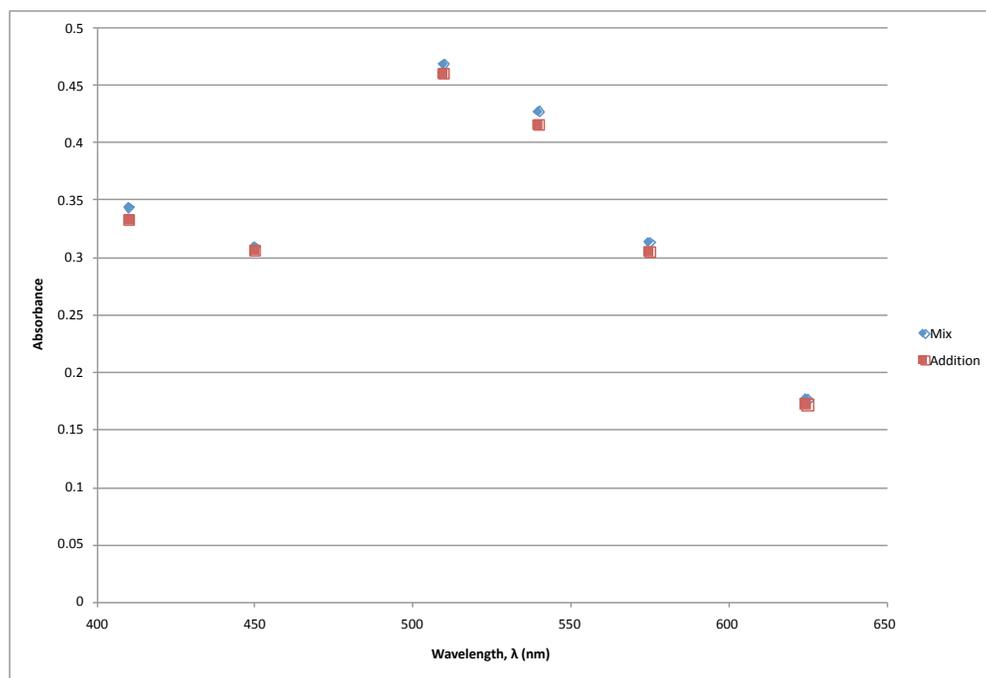


Figure 0.3: A vs. λ comparing mix and addition

assuaged by comparing the known mixture with equal concentrations of stand-alone solutions from the standard dilutions. From table 0.6 It can be seen that the percent error is within reasonable means. Similarly, figure 0.3 showed comparative absorbances almost identical at given wavelengths. However, it can also be noted that the mixture consistently returned slightly greater absorbance values than the additions. So while this leads one to believe that the substances do in fact affect the absorbance values, this is the case to an acceptably minuscule degree. The wavelength values for this experiment were chosen by the instructor, and it appears they were picked for a couple reasons. To really get a good idea of what's happening across a spectrum while at the same time not laboriously chugging away at every wavelength conceivable one must choose a handful of important values over a reasonably consistent spread. That is to say, The known important wavelengths, such as 410 and 575nm for chromium and 510 and 540nm for cobalt, are chosen initially and then other wavelengths along the spectrum are picked to fill out the spectrum. At least, this is what has been deduced

as the logic behind choosing the given wavelengths. Of course, a more definitive way of finding this information out would involve simply asking the instructor. Similarly, It can be noted that the cobalt concentrations are considerably larger and cover a greater range than the chromium concentrations. These respective concentration ranges were chosen in such a way that they would allow for one component's absorption values to be similar to the other, and therefore avoid one component dominating the printout. Then again, this is exactly what happened in the unknown mixture. Figures 0.1 and 0.2 also serve to reinforce the empirical notion that there is a linear relationship between concentration and absorbance; this expectation is further backed up on the figures, as they show impressive linear correlation (R^2) values, keeping a tight range from 0.996 to 0.999. This entire process is made nearly effortless with the help of a streamlined computer-interfaced instrument using proprietary software and high-quality cuvettes. More information is given with each handout than is even needed for this report. Sources of error were few, and cut down further by certain choices. Using the same cuvette for each run allowed for precision because the path length and general integrity of the cuvette remained consistent throughout. Using a computer-interfaced instrument further disallowed user error because it automated the sample presentation and data collection allowing for further consistency. In general, the more done by machines (and therefore less done by humans) the better, quantitatively speaking. The main sources of error, then, could be found in human-dictated parts of the experiment. Attaining the correct standard concentrations requires one to be precise in measuring the solution volumes and transferring them to the flask, and these values can be thrown off by such inconsistencies as liquid droplets remaining in the tip of pipets or on the surface. Error can further present itself in measuring the correct volume within the volumetric flask, as liquid is known to stick along the neck of the flask and therefore not contribute to the recorded volume but, of course, contribute to the actual volume and therefore the actual concentration.

0.5 Conclusion

This experiment involved attaining absorbance values for standard concentration solutions at various wavelengths for use in determining the concentrations in a mixture of known components but unknown singular con-

centrations. While it will not be determined until afterward whether or not the calculated concentrations align favorably with the actual concentrations, it does appear that the numbers add up correctly such that the unknown plot attained gives an accurate representation of what would be expected for a mixture of the calculated respective concentrations. It was also determined in the course of completing this experiment that the two reagent components, $\text{Cr}(\text{NO}_3)_3$ and $\text{Co}(\text{NO}_3)_2$, interfered with one another at such a negligible level that, for scholastic endeavors at least, these chemicals can be determined as essentially isolated from one another in terms of absorbance, though if one wants to harvest any qualitative observation from the comparison it would be that in general, the overall absorbance is increased slightly when these two chemicals are found simultaneously in a solution.