Quantitative Determination of Cr(III) and Co(II) Using a Spectroscopic H-Point Standard Addition Method

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UV-vis absorption spectroscopy provides a very convenient experimental means for determining percentage compositions and solution concentrations of unknown samples, measuring reaction rate constants, and determining the stoichiometry and equilibrium constant of metal-ligand complexes. During the past few years many experimental spectroscopic methods have appeared in this *Journal* (1-10) and in standard laboratory manuals for use in general chemistry, physical chemistry, or quantitative analysis.

Spectroscopic methods are based upon application of the Beer-Lambert law, which states that the measured absorbance, A , is directly proportional to the molar concentration of the light-absorbing species i :

$$A = \epsilon_{\text{species } i} b C_{\text{species } i} \quad (1)$$

where b is the path length (in cm) through the solution and ϵ is the molar absorptivity (in $\text{M}^{-1} \text{cm}^{-1}$) at the absorption wavelength. When two light-absorbing species are present, the individual absorbances are additive:

$$\begin{aligned} A_{\text{total}} &= A_{\text{species } i} + A_{\text{species } j} \\ &= \epsilon_{\text{species } i} b C_{\text{species } i} + \epsilon_{\text{species } j} b C_{\text{species } j} \end{aligned} \quad (2)$$

assuming that no interaction/reaction occurs between components i and j . Absorbance measurements at two different wavelengths provide two equations in two unknowns. By solving both equations simultaneously, concentrations of the two components can be obtained. The four ϵ -values needed in this computation are calculated from Beer-Lambert law plots (or linear least squares analysis) for the separate components using standard solutions of known concentrations. This method has been used numerous times in our Instrumental Analysis course to determine Co(II) and Cr(III) concentrations in unknown liquid mixtures. The two wavelengths selected for these analyses were 510 nm and 575 nm, which correspond to wavelengths of near maximum absorbances for Co(II) and Cr(III), respectively.

During the past two years we have continually upgraded the laboratory experiments students perform in our undergraduate Instrumental Analysis course to incorporate as much as possible new analytical methods and data treatments published in recent chemical literature. One of the experiments designed involved a relatively interesting spectroscopic H-point standard addition method (HPSAM) for simultaneous determination of both Co(II) and Cr(III). The HPSAM experiment replaced the more conventional absorption method discussed above. Advantages associated with the HPSAM (11-13) include elimination of sample matrix effects, reduction of both constant and systematic errors, and a decrease in the number of absorbance measurements that must be made. The method is applicable to determine an analyte concentration in the presence of an interfering impurity. If the identity of the impurity is known, its concentration can be determined. From an educational standpoint, the HPSAM exposes students to a graphical data

Figure 1. Absorbance spectra of 0.188 M Co(II) (---) and 0.0500 M Cr(III) (—) solutions.

treatment not found in standard textbooks, but which is published in the recent chemical literature. Moreover, incorporation of journal articles into the laboratory portion of the course encourages students to read the chemical literature for new ideas. Published applications using HPSAM include quantitative determination of phenol and *o*-cresol in unknown mixtures (14), simultaneous determination of manganese and vanadium by oxidation of pyrogallol red (15), and determination of creatinine and albumin with alkaline picrate (15). The last two examples involve kinetic

Figure 2. Plot of A_{total} vs. $C_{\text{Co(II) added}}$ used in H-point standard addition method. x and y coordinates of common point of intersection of the two linear lines ($-C_{\text{Co(II) unknown}}$, $A_{\text{unknown Cr(III)}}$) correspond to minus molar concentration of Co(II) and to Cr(III) absorbance in the unknown mixture, respectively. The plot was generated using $A_{520.4}(\lambda_1)$ and $A_{630.0}(\lambda_2)$ data from Table 1

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methods, in which, the absorbance is measured at two different reaction times rather than at two different wavelengths, as is the case considered here. Kinetic-based HPSAM equations are explained in detail elsewhere (15).

The H-point standard addition method is relatively straightforward, and will be discussed in terms of the individual absorption spectrum of Co(II) and Cr(III) depicted in Figure 1. Determination of Co(II) concentration is achieved by judiciously selecting two wavelengths, λ_1 and λ_2 , lying on both sides of the maximum absorption of Cr(III), such that the absorbances of Cr(III) are identical at both wavelengths: $A_{\text{Cr(III)}@ \lambda_1} = A_{\text{Cr(III)}@ \lambda_2}$. In addition, the difference in $\epsilon_{\text{Co(II)}@ \lambda_1}$ and $\epsilon_{\text{Co(II)}@ \lambda_2}$ should be as large as possible to improve the method's accuracy. Note that the observed spectrum of Cr(III) in the 350–700 nm spectral region contains two absorption bands; hence, two pairs of analysis wavelengths (λ_1 and λ_2) and (λ_1' and λ_2') can be used if students are instructed to think of a method for perhaps evaluating the reliability of the H-point standard addition method. Measurements at (λ_1 and λ_2) and (λ_1' and λ_2') should yield identical values of $C_{\text{Co(II) unknown}}$ and $C_{\text{Cr(III) unknown}}$, at least to within the method's experimental uncertainty.

Known amounts of Co(II) are successively added to the unknown mixture and the resulting absorbances are recorded. Mathematically, the absorbances vary linearly with the added Co(II) concentration, $C_{\text{Co(II) added}}$, according to

$$A_{\text{total}@ \lambda_1} = \epsilon_{\text{Co(II)}@ \lambda_1} b C_{\text{Co(II) added}} + A_{\text{unknown Cr(III)}@ \lambda_1} + A_{\text{unknown Co(II)}@ \lambda_1} \quad (3)$$

$$A_{\text{total}@ \lambda_2} = \epsilon_{\text{Co(II)}@ \lambda_2} b C_{\text{Co(II) added}} + A_{\text{unknown Cr(III)}@ \lambda_2} + A_{\text{unknown Co(II)}@ \lambda_2} \quad (4)$$

where the slopes and intercepts are given by $\epsilon_{\text{Co(II)}@ \lambda_i} b$ and $A_{\text{unknown Cr(III)}@ \lambda_i} + A_{\text{unknown Co(II)}@ \lambda_i}$, respectively.

Careful examination of eqs 3 and 4 reveals that plots of A_{total} vs. $C_{\text{Co(II) added}}$ result in two straight lines that have a common point of intersection with coordinates ($-C_{\text{Co(II) unknown}}, A_{\text{unknown Cr(III)}@ \lambda_1 \text{ and } \lambda_2}$), as shown in Figure 2. The x-coordinate yields directly the molar concentration of Co(II) in the unknown sample, whereas the y-coordinate corresponds to the Cr(III) absorbance in the unknown at both λ_1 and λ_2 . The molar concentration of the second mixture component, $C_{\text{Cr(III) unknown}}$, can be calculated by dividing the y-coordinate by $\epsilon_{\text{Cr(III)}@ \lambda_1}$ (or by $\epsilon_{\text{Cr(III)}@ \lambda_2}$), this latter quantity determined from measured absorbance values for standard solutions of known Cr(III) molarity.

Experimental Measurements

The experimental work can be completed easily in a standard 3-hour laboratory period. We suggest that the students work in groups of two in order to reduce the time needed to prepare solutions, and that absorbance measurements be made at both pairs (λ_1 and λ_2) and (λ_1' and λ_2') of analysis wavelengths. Each group is given 100 mL of an unknown solution containing 0.100–0.200 M $\text{Co(NO}_3)_2$ and 0.0300–0.0600 M $\text{Cr(NO}_3)_3$. Separate stock solutions of 0.188 M $\text{Co(NO}_3)_2$ and 0.0500 M $\text{Cr(NO}_3)_3$ are prepared ahead of time by the instructor or laboratory assistant. Students are instructed to transfer 15 mL of their unknown solution into each of five 50-mL volumetric flasks, using a

Table 1. Experimental Absorbance Data for Simultaneous Determination of Co(II) and Cr(III) Using H-Point Standard Addition Method

Vol. of unknown (mL)	$C_{\text{Co(II) added}}$ (M)	$C_{\text{Cr(III) added}}$ (M)	Absorbances			
			367.2 nm	454.0 nm	520.4 nm	630 nm
15.0	0	0	0.104	0.242	0.360	0.121
15.0	0.0188	0	0.106	0.290	0.447	0.128
15.0	0.0376	0	0.108	0.333	0.530	0.133
15.0	0.0564	0	0.109	0.379	0.617	0.139
15.0	0.0752	0	0.112	0.427	0.703	0.145
0	0	0.0050	0.034	0.034	0.034	0.036
0	0	0.0100	0.066	0.067	0.068	0.070
0	0	0.0150	0.098	0.098	0.102	0.104
0	0	0.0200	0.133	0.131	0.138	0.140
0	0	0.0250	0.163	0.159	0.169	0.171

pipet. The solution in the first flask is diluted to the mark with deionized water. To the remaining four flasks are added (by pipet) 5.0, 10.0, 15.0, and 20.0 mL, respectively, of the 0.188 M $\text{Co(NO}_3)_2$ stock solution. Each flask is then filled to the mark with deionized water. Students also prepare standard solutions containing 0.0050, 0.0100, 0.0150, 0.0200, and 0.0250 M $\text{Cr(NO}_3)_3$ by transferring by pipet appropriate quantities of the Cr(III) stock solution into 50-mL volumetric flasks and diluting to the mark with deionized water. If a scanning UV/vis spectrophotometer is available, students should record the absorption spectrum of the 0.188 M Co(II) and 0.050 M Cr(III) stock solutions in order to select the proper analysis wavelengths (see Fig. 1). Alternatively, one can simply tell the students that (367.2 and 454.0 nm) and (520.4 and 630.0 nm) are two sets of many possible suitable wavelength pairs. Finally, absorbances of all ten solutions are measured at the four (or two) wavelengths selected. (NOTE: All chemical and waste solutions should be discarded using proper disposal procedures; see references 16 and 17.)

Discussion of Results

Typical results are listed in Table 1 for the determination of Co(II) and Cr(III) using the H-point standard addition method. The first five solutions pertain to the unknown sample containing both metal ions. Solutions 6–10 are standards containing known amounts of Cr(III), from which students will calculate the molar absorptivity of Cr(III), $\epsilon_{\text{Cr(III)}}$, at the four wavelengths studied. Linear least squares analysis of the experimental data for the five unknown solutions at $\lambda = 520.4$ and 630.0 nm shows

$$A_{\text{total}@ 520.4 \text{ nm}} = 0.360 + 4.553 C_{\text{Co(II) added}} \quad (r^2 = .9999) \quad (5)$$

$$A_{\text{total}@ 630.0 \text{ nm}} = 0.121 + 0.314 C_{\text{Co(II) added}} \quad (r^2 = .9980) \quad (6)$$

that A does increase linearly with $C_{\text{Co(II) added}}$ in accordance with the Beer–Lambert law. Numerical values for $C_{\text{Co(II) unknown}}$ of 0.0564 M (diluted sample) and for $A_{\text{Cr(III) unknown}}$ of 0.103 are obtained by solving eqs 5 and 6 simultaneously for their common point of intersection.

Linear least squares analysis of absorbance data for the five Cr(III) standard solutions gives $\epsilon_{\text{Cr(III)}} = 6.800 \text{ M}^{-1} \text{ cm}^{-1}$ for the Cr(III) molar absorptivity at both 520.4 and 630.0 nm. The two molar absorptivities should be *nearly identical* because this was one of the conditions required when the analysis wavelengths were selected initially. The Cr(III) concentration in the unknown sample (after dilu-

tion) is obtained from $C_{\text{Cr(III) unknown}} = A_{\text{Cr(III) unknown}}/e_{\text{Cr(III)}} = 0.103/6.800 = 0.0151$ M. Similar results are obtained from absorbance data at 367.2 and 454.0 nm.

Students are reminded during the brief prelaboratory lecture that analytical chemists always report the concentrations in the original unknown solutions, and that one must always take into account any dilutions made during the course of the analysis. The experimentally determined molar concentrations of Co(II) and Cr(III), $C_{\text{Co(II) unknown}} = 0.188$ M and $C_{\text{Cr(III) unknown}} = 0.0505$ M, are in excellent agreement with the so-called "true" values of $C_{\text{Co(II) unknown}} = 0.188$ M and $C_{\text{Cr(III) unknown}} = 0.0500$ M. Based upon our past experiences with HPSAM, students should be able to get within 1–2% of the correct values. A more sophisticated data analysis might include computation of upper and lower bounds of the found concentrations, as well as the test for linearity, using equations given in ref 13. Such computations could provide a convenient way to introduce the use of statistics into the laboratory experiment.

The H-point standard addition method affords a convenient experimental means for simultaneous determination of Co(II) and Cr(III) in unknown mixtures. Students are exposed to the general method of standard addition, which is an important, often-used analytical technique for eliminating sample matrix effects. Absorbance measurements at two different pairs of analysis wavelengths allows students to assess the method's reliability. The data analysis is relatively simple, and the two metal-ion concentrations can be computed by linear least squares analysis or

graphic methods. We have now introduced the HPSAM into our Instrumental Analysis course as replacement for the more conventional laboratory experiment involving the simultaneous determination of Co(II) and Cr(III) in unknown mixtures based upon absorbance measurements at 510 and 575 nm.

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