

Kinetics-Based Indirect Spectrophotometric Method for Simultaneous Determination of MnO_4^- and $\text{Cr}_2\text{O}_7^{2-}$

A Modern Instrumental Analysis Laboratory Experiment

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UV-visible absorption spectroscopy provides a very convenient experimental means for determining percentage compositions and solution concentrations of unknown samples, for measuring reaction rate constants, and for determining both 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 :

$$A = \epsilon_i b C \quad (1)$$

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

$$A_{\text{Total}} = A_i + A_j = \epsilon_i b C_i + \epsilon_j b C_j \quad (2)$$

if no interaction or reaction between components i and j occurs. Absorbance measurements at two different wavelengths provide two equations in two unknowns. By solving both equations simultaneously,

$$A_{\text{Total}@\lambda_1} = \epsilon_{i@\lambda_1} b C_i + \epsilon_{j@\lambda_1} b C_j \quad (3)$$

$$A_{\text{Total}@\lambda_2} = \epsilon_{i@\lambda_2} b C_i + \epsilon_{j@\lambda_2} b C_j \quad (4)$$

one can obtain concentrations of the two components. The four ϵ -values needed in this computation are calculated from Beer–Lambert law plots (or linear-least squares analysis) for the separate components in standard solutions of known concentrations. This method has been used numerous times in our quantitative analysis course to determine MnO_4^- and $\text{Cr}_2\text{O}_7^{2-}$ concentrations in unknown liquid mixtures. The two wavelengths selected for these analyses are 545 nm and 440 nm, which correspond to wavelengths of near-maximum absorbances for MnO_4^- and $\text{Cr}_2\text{O}_7^{2-}$, 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 involves a relatively interesting kinetics-based indirect spectrophotometric method for the simultaneous determination of MnO_4^- and $\text{Cr}_2\text{O}_7^{2-}$. It draws heavily upon two published analyses for permanganate and vanadate ions (11, 12), which we have modified to enable quantitative determination of $\text{Cr}_2\text{O}_7^{2-}$ concentration. From an educational point of view, the modification affords our undergraduate chemistry majors the rare opportunity to critically compare direct and indirect analytical methods for a common unknown mixture. Most students will have performed the direct analysis based upon eq 2 as an experiment in our quantitative analysis course. Method selection and method evaluation are two problems that practicing analytical chemists routinely encounter.

The kinetics-based indirect spectrophotometric method is relatively straightforward and takes advantage of the fact that the oxidation of pyrogallol red (PGR) by permanganate occurs much faster than oxidation of PGR by dichromate. One follows the extent of oxidation by monitoring the absorbance of the solution at 488 nm, which corresponds to the broad band maximum in the PGR absorption spectrum. Measured absorbances at two fixed times, A_{t_1} and A_{t_2} , are directly proportional to the molar concentrations of the added oxidizing agents

$$A_{t_1} = A_{\text{PGR}} + m_{t_1, \text{Cr}_2\text{O}_7^{2-}} C_{\text{Cr}_2\text{O}_7^{2-}} + m_{t_1, \text{MnO}_4^-} C_{\text{MnO}_4^-} \quad (5)$$

$$A_{t_2} = A_{\text{PGR}} + m_{t_2, \text{Cr}_2\text{O}_7^{2-}} C_{\text{Cr}_2\text{O}_7^{2-}} + m_{t_2, \text{MnO}_4^-} C_{\text{MnO}_4^-} \quad (6)$$

where A_{PGR} represents the solution absorbance in the absence of both MnO_4^- and $\text{Cr}_2\text{O}_7^{2-}$, and m_{t_i} is the numerical value of the calibration curve slope for each time i and component j . We have found 3 and 8 min to be suitable reaction times. Oxidation of PGR by permanganate is complete in the first three minutes. Reduction in the observed absorbance between 3 and 8 min results entirely from the oxidation of PGR by the dichromate ion. The above method generates the two equations that must be solved simultaneously from absorbance measurements at two fixed times, rather than at two different analysis wavelengths. This can potentially eliminate problems encountered in the analysis of mixtures containing components having severely overlapping absorption spectra (10), as is the case with $\text{Cr}_2\text{O}_7^{2-}$ and MnO_4^- (see Fig. 1). The permanganate ion has an appreciable absorbance at both 350 and 440 nm, which are the analysis wavelengths for the dichromate ion. Moreover, students are shown that chemical reactions need not occur instantaneously to be of analytical significance. Kinetics-based techniques represent an important part of the experimental methods available to practicing

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analytical chemists (13–16).

Experimental Methods

The experimental work can easily be completed in a three-hour laboratory period. We suggest that students work in groups of two in order to reduce the time needed to prepare solutions. Each group is given 25 mL of an unknown solution containing between 5.00×10^{-5} and 2.00×10^{-4} M KMnO_4 and 2.50×10^{-5} to 1.00×10^{-4} M $\text{K}_2\text{Cr}_2\text{O}_7$. Separate stock solutions of 2.00×10^{-4} M KMnO_4 and 1.00×10^{-4} M $\text{K}_2\text{Cr}_2\text{O}_7$ are prepared ahead of time by the instructor or laboratory assistant. Each group will also need approximately 300 mL of “reaction” solvent. The reaction solvent is prepared by transferring 250 mL of pH 4.0 acetic acid–sodium acetate buffer (2.2 M acetic acid + 0.5 M sodium acetate) and 75 mL of 8.0×10^{-4} M pyrogallol red (dissolved in ethanol) to a 500-mL volumetric flask and diluting to the mark with deionized water.

Students are instructed to use a buret to transfer 20.00 mL of the reaction solvent into each of twelve 25-mL volumetric flasks. The first flask is filled to the mark with deionized water and the absorbance is measured after 3 and 8 min have elapsed. To the next five flasks are added 1.0, 2.0, 3.0, 4.0, and 5.0 mL, by pipet, of 1.00×10^{-4} M $\text{K}_2\text{Cr}_2\text{O}_7$ stock solution. Each flask is then filled to the mark with deionized water and the absorbances are recorded at the two fixed times. Students are cautioned that the fixed time intervals are critical and that all solutions should be analyzed in a stepwise manner. The oxidizing agent is added to the next solution in the series only after the 8-min data point has been recorded for the preceding solution. The five KMnO_4 standard solutions and unknown solution (3-mL aliquot) are prepared and analyzed in a similar manner. If necessary, the aliquot size of the unknown can be increased (or decreased) to give a suitable reduction in the measured absorbance. (NOTE: All chemical and waste solutions should be discarded according to proper disposal procedures; see refs 17 and 18.) The ambient room temperature is maintained fairly constant in our laboratory. If temperature fluctuations become a problem, our spectrophotometers are equipped with a thermostated, water-jacketed cell holder that can be used to maintain better temperature control.

Discussion of Results

Typical student results are listed in Table 1 for the determination of MnO_4^- and $\text{Cr}_2\text{O}_7^{2-}$ by means of the kinetics-based indirect spectrophotometric method. The first six solutions pertain to the calibration curves for dichromate, needed to determine the numerical values of the two proportionality constants, $m_{t,\text{Cr}_2\text{O}_7^{2-}}$ and $m_{t,\text{Cr}_2\text{O}_7^{2-}}$, that govern the change in the measured absorbance. Solutions 7–11 are standards containing known amounts of MnO_4^- . Linear least-squares analysis of the experimental data for the two sets of standard solutions yields slopes of $m_{t,\text{Cr}_2\text{O}_7^{2-}} = -16,060 \pm 730$ ($r^2 = .9917$), $m_{t,\text{Cr}_2\text{O}_7^{2-}} = -23,550 \pm 940$ ($r^2 = .9936$) and $m_{t,\text{MnO}_4^-} = m_{t,\text{MnO}_4^-} = -18,560 \pm 210$ ($r^2 = .9995$). Near-unity squared correlation coefficients indicate that the measured absorbance does decrease linearly with the molar concentrations of both added oxidizing agents. By solving eqs 5 and 6

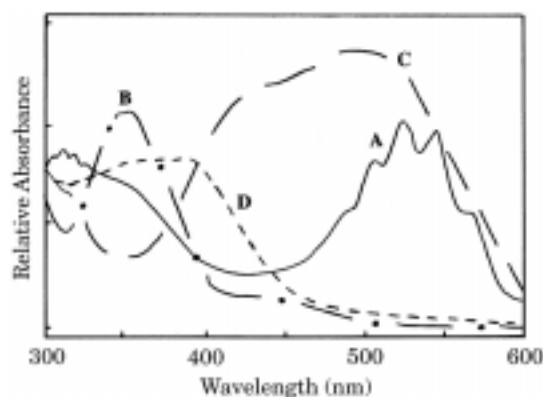


Figure 1. Absorbance spectra of (A) MnO_4^- ; (B) $\text{Cr}_2\text{O}_7^{2-}$; (C) PGR and (D) its oxidized form.

simultaneously, one obtains numerical values of $C_{\text{Cr}_2\text{O}_7^{2-}} = 5.87 \times 10^{-6}$ M and $C_{\text{MnO}_4^-} = 1.19 \times 10^{-5}$ M for the molar concentrations of the diluted unknown solution.

Students are reminded during the brief pre-laboratory lecture that analytical chemists always report the concentrations in the original unknown samples, and that one must always take into account any dilutions that may have been made during the course of the chemical analysis. The experimentally determined molar concentrations of $\text{Cr}_2\text{O}_7^{2-}$ and MnO_4^- in the original unknown sample, $C_{\text{Cr}_2\text{O}_7^{2-}} = 4.90 \times 10^{-5}$ M and $C_{\text{MnO}_4^-} = 9.91 \times 10^{-5}$ M, are in agreement with the so-called “true” values of $C_{\text{Cr}_2\text{O}_7^{2-}} = 5.00 \times 10^{-5}$ M and $C_{\text{MnO}_4^-} = 1.00 \times 10^{-4}$ M. Other student values reported for this sample were $C_{\text{Cr}_2\text{O}_7^{2-}} = 4.81 \times 10^{-5}$, 5.13×10^{-5} , and 5.17×10^{-5} M and $C_{\text{MnO}_4^-} = 9.71 \times 10^{-5}$, 9.89×10^{-5} , and 1.03×10^{-4} M for the molar concentrations of the dichromate and permanganate ions. On the basis of our past experiences with the kinetics-based indirect spectrophotometric method, students should be able to get within $\pm 5\%$ of the correct values.

Table 1. Absorbance Data for Simultaneous Determination of MnO_4^- and $\text{Cr}_2\text{O}_7^{2-}$ by Kinetics-Based Indirect Spectrophotometric Method

Soln	C ($\text{Cr}_2\text{O}_7^{2-}$) (M)	C (MnO_4^-) (M)	Absorbance ^a	
			3 min	8 min
1	0	0	1.23	1.23
2	4.00×10^{-6}	0	1.171	1.136
3	8.00×10^{-6}	0	1.103	1.033
4	1.20×10^{-5}	0	1.041	0.958
5	1.60×10^{-5}	0	0.954	0.827
6	2.00×10^{-5}	0	0.923	0.771
7	0	8.00×10^{-6}	1.094	1.093
8	0	1.60×10^{-5}	0.939	0.938
9	0	2.40×10^{-5}	0.787	0.786
10	0	3.20×10^{-5}	0.632	0.631
11	0	4.00×10^{-5}	0.498	0.497
12	Unknown ^b	Unknown ^b	0.915	0.871

^a Measured absorbances recorded at 488 nm on a Bausch and Lomb Spectronic 2000.

^b A 3-mL aliquot of the unknown solution was used.

As part of the laboratory instruction, students in our instrumental analysis course are given the analytical results ($C_{Cr_2O_7}$ and $C_{MnO_4^-}$ values) for their unknown sample, which were determined using the more conventional two-wavelength spectrophotometric method (see eqs 3 and 4) by undergraduate students enrolled in the preceding semester's quantitative analysis course. They are asked to statistically analyze data from the kinetics-based and two-wavelength methods and to determine if there is a significant difference between the two methods. The statistical treatment is discussed in most standard analytical textbooks (19–21). Rarely are undergraduate students afforded the opportunity to actually apply the treatment to their experimental data. Such analysis leads into a discussion of factors that are considered in selecting an analytical method. Selection of an appropriate analytical method is a decision that practicing analytical chemists encounter daily.

From an educational standpoint, we prefer the kinetics-based experiment to the more traditional two-component, two-wavelength spectrophotometric methods published in standard laboratory manuals. The experiment not only incorporates the important fundamental principles associated with spectroscopic analysis, but it also exposes students to kinetics-based techniques, which are often encountered in enzyme and drug determinations. Moreover, the kinetics-based method presented above provides students who have already performed a two-component spectroscopic analysis based upon eq 2 in their quantitative analysis course a suitable alternative laboratory experiment. If desired, the experiment can be shortened so as to analyze only one of the two ions.

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