

## SPECTROPHOTOMETRIC ANALYSIS OF A PERMANGANATE- DICHROMATE MIXTURE

**DISCUSSION:** Permanganate and dichromate ion both absorb visible light though their absorbance maxima are fairly well separated. By measuring the absorbance at two different wavelengths of a solution containing both ions, it is possible to simultaneously determine the concentration of each ion in the solution.

In simultaneous determinations of two species it is necessary to generate two equations in order to determine the two unknown concentrations. In a spectrophotometric analysis these equations can be developed from the Beer-Lambert Law.

$$\text{Absorbance} = \mathbf{A} = e b C$$

Beer's Law requires the use of monochromatic radiation and it is under this restraint that the linear dependence of absorption and concentration occurs. If two or more species in a sample absorb at a specific wavelength, the instrument cannot distinguish between the individual species; it can only determine the total absorbance of the sample. For example, in a mixture in which *three* species, 1, 2 and 3, absorb at the same wavelength the total absorbance at that wavelength is:

$$\mathbf{A}_{\text{total}} = \mathbf{A}_1 + \mathbf{A}_2 + \mathbf{A}_3 \quad (\mathbf{A} = \text{absorbance})$$

and,

$$\mathbf{A}_{\text{total}} = e_1 b C_1 + e_2 b C_2 + e_3 b C_3$$

In order to determine the concentrations of each of the three species,  $C_1$ ,  $C_2$  and  $C_3$ , it is necessary to generate three equations (remember three unknowns require three equations for an exact solution). The most convenient way to construct three equations is to measure the total absorbance of the solution at three different wavelengths. The wavelengths chosen must be those at which the molar absorptivities,  $e$ , of the individual species are either known or can be experimentally determined.

In this experiment, a two component solution will be studied. The absorbing species are permanganate ion and dichromate ion, both of which absorb strongly in the visible spectrum. The two equations derived from the Beer-Lambert Law which will allow the

simultaneous determination of potassium dichromate (abbreviated below as Cr) and potassium permanganate (abbreviated as Mn) are:

(at wavelength *I*, the shorter wavelength)

$$A_{\text{total}}^I = e_{\text{Mn}}^I b C_{\text{Mn}} + e_{\text{Cr}}^I b C_{\text{Cr}}$$

(at wavelength *II*, the longer wavelength)

$$A_{\text{total}}^{II} = e_{\text{Mn}}^{II} b C_{\text{Mn}} + e_{\text{Cr}}^{II} b C_{\text{Cr}}$$

$A_{\text{total}}^I$  and  $A_{\text{total}}^{II}$  are determined experimentally. These equations require that the four molar absorptivities ( $e_{\text{Mn}}^I$ ,  $e_{\text{Cr}}^I$ ,  $e_{\text{Mn}}^{II}$ ,  $e_{\text{Cr}}^{II}$ ), the cell path length (*b*) and the total absorbance at both wavelengths, *I* and *II*, be known to calculate the permanganate (Mn) and dichromate (Cr) concentrations. The values of *e* and *b* will be determined together as the product "*eb*" from the slope of the straight line resulting from a Beer-Lambert plot of absorbance versus concentration (in units of molarity, *M*). This requires construction of four Beer-Lambert plots, one to determine each of the following terms:  $e_{\text{Mn}}^I b$ ,  $e_{\text{Cr}}^I b$ ,  $e_{\text{Mn}}^{II} b$  and  $e_{\text{Cr}}^{II} b$ . A typical B-L plot which will serve as a calibration curve in this determination is shown in figure 1.

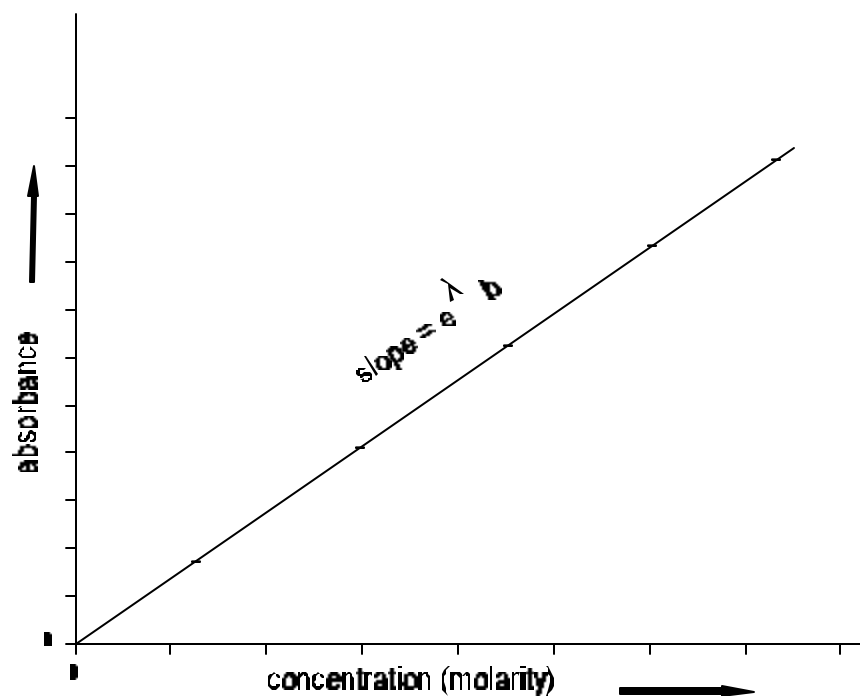


Figure 1

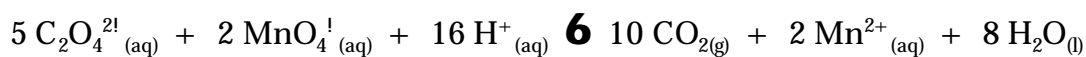
After the four "eb" terms are evaluated from the four calibration curves, and the total absorbance of the dichromate-permanganate mixtures are known at the two selected wavelengths, the two equations that result can be solved simultaneously for  $C_{Mn}$  and  $C_{Cr}$ . A convenient method for solving the equations simultaneously is by using determinants. Remember, the operation symbolized in a determinant as

$$\begin{array}{c} \left| \begin{array}{cc} a & b \\ c & d \end{array} \right| \\ \text{means} \\ (ad - bc) \end{array}$$

$$C_{Mn} = [MnO_4^-] = \frac{\begin{vmatrix} A_{tot}^I & e_{Cr}^I b \\ A_{tot}^{II} & e_{Cr}^{II} b \end{vmatrix}}{\begin{vmatrix} e_{Mn}^I b & e_{Cr}^I b \\ e_{Mn}^{II} b & e_{Cr}^{II} b \end{vmatrix}}$$

$$C_{Cr} = [Cr_2O_7^{2-}] = \frac{\begin{vmatrix} e_{Mn}^I b & A_{tot}^I \\ e_{Mn}^{II} b & A_{tot}^{II} \end{vmatrix}}{\begin{vmatrix} e_{Mn}^I b & e_{Cr}^I b \\ e_{Mn}^{II} b & e_{Cr}^{II} b \end{vmatrix}}$$

To simultaneously determine the concentrations of dichromate ion and permanganate ion in a mixture requires knowing each of the terms in the above determinates. The calibration curves will provide the four "eb" products and you will measure the total absorbances at the two wavelengths. Standard solutions of potassium permanganate and potassium dichromate must be prepared to generate the calibration curve. Potassium dichromate is itself a primary standard and therefore does not need to be standardized. However, potassium permanganate is not a primary standard and therefore does need to be standardized by the McBride method.



**PREPARATION  
OF REAGENTS:**

**0.75 M H<sub>2</sub>SO<sub>4</sub>:** Measure the calculated volume of 18.0 M H<sub>2</sub>SO<sub>4</sub> into 500 mL of deionized water. Mix well and store the solution in a 1 L screw-top bottle.

**0.25 M H<sub>2</sub>SO<sub>4</sub>:** Measure the calculated volume of 18.0 M H<sub>2</sub>SO<sub>4</sub> into 1500 mL of deionized water. Mix well and store the solution in an acid bottle.

**0.02 M K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> (Stock Solution):** Prepare 100 mL of about 0.02 M K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> by weighing 0.55 to 0.60 g (record exactly) of the reagent grade substance (dried 1 to 2 hours at 110°C) on the analytical balance, dissolving in water, and diluting to 100 mL in a volumetric flask. Mix the solution well.

**Dichromate Working Standards:** Using a 10 mL buret, deliver 2.00, 4.00, 6.00, 8.00, and 10.00 mL portions of the stock solution into five 100 mL volumetric flasks numbered 1 to 5. Dilute each solution to the mark with 0.25 M H<sub>2</sub>SO<sub>4</sub>. Calculate and record the concentration (molarity) of each standard.

**0.01 M KMnO<sub>4</sub> (Stock Solution):** Dissolve the calculated mass of KMnO<sub>4</sub> in 250 mL of deionized water in a 500 mL screw-top bottle. KMnO<sub>4</sub> dissolves slowly, so shake the mixture well. Store this solution in this bottle. Standardize this solution using the McBride method.

**Permanganate Working Standards:** Using a 10 mL buret, deliver 0.50, 1.00, 2.00, 3.00, and 4.00 mL portions of your stock solution into five 100 mL volumetric flasks numbered 1 to 5. Dilute each solution to the mark with 0.25 M H<sub>2</sub>SO<sub>4</sub>. Calculate and record the concentration (in molarity) of each standard. Use these solutions the same day they are prepared.

Dispose of all permanganate solutions in the designated waste bottle at the end of the laboratory period.

**EXPERIMENTAL  
PROCEDURE:****The McBride Method of Standardizing KMnO<sub>4</sub>:**

Weigh accurately (to four places after the decimal) four samples of about 0.10 to 0.15 g each of dried sodium oxalate (dried 1 to 2 hours at 110°C) into clean, labeled, 500 mL Erlenmeyer flasks. Dissolve each sample in about 75 mL of the 0.75 M sulfuric acid. Then heat the first solution **almost** to boiling and titrate slowly with permanganate with constant swirling. The **end point** is marked by the appearance of a **faint pink color** that persists at least

30 sec. The temperature should not drop below 60°C during the titration. Titrate the other three solutions in the same manner.

To determine the blank, place about 100 mL of the 0.75 M sulfuric acid in an Erlenmeyer flask and add permanganate solution dropwise until the color matches that of the titrated solution. This volume should be subtracted from the volume used in the titration. Calculate the molarity of the permanganate solution. *Use this solution the same day it is prepared and standardized.*

**Absorption Spectra and Beer's Law Check:** Measure the absorbance of the permanganate solution with the highest concentration over the wavelength interval of 360 to 650 nm using 0.25 M H<sub>2</sub>SO<sub>4</sub> as the blank. The Shimadzu 160 UV-VIS scanning spectrophotometer should be used for this measurement. The operation of the Shimadzu 160 is described below. Repeat the procedure with the most concentrated dichromate standard solution. From each scan, determine the wavelength of an absorbance peak which absorbs well but with an absorbance *less than 1.0*.

Measure the absorbance of **all standard solutions at each of these two wavelengths**, using the Shimadzu 160 or a SPEC 20D.

Consult Appendix A-2 if you use the SPEC 20D. Remember, when using the SPEC 20D, you must calibrate the instrument at each wavelength, (setting the 0% and 100% Transmittance points), before taking analytical data.

Generate four calibration curves on the computer, plotting absorbance on the Y axis and concentration *in units of molarity* on the X axis. Use regression analysis to calculate the slope, (which equals "eb") for both ions at each of the two wavelengths.

**Analysis of Unknown:** Obtain an unknown from the instructor in a 100 mL volumetric flask and dilute it to the mark with 0.25 M H<sub>2</sub>SO<sub>4</sub>. Measure the total absorbance ( $A_{\text{tot}}^I$  and  $A_{\text{tot}}^{II}$ ) at the two chosen wavelengths, and, using the determinate method, calculate the concentrations of permanganate and dichromate in the unknown.

**THE SHIMADZU  
160 UV-VIS  
SPECTRO-  
PHOTOMETER:**

1. Turn the machine on (switch is on the left side), and while you wait for it to warm up and give you the menu, obtain 3 cuvettes from your instructor. Notice that the cuvettes have two clear sides opposite one another and two frosted sides. Do not touch the clear sides since a dirty cuvette may result in an inaccurate absorbance.

2. Rinse each cuvette with the solution to be placed in it. Fill the cuvette (the one that you rinsed with your blank solution) to about 3/4 with your blank solution of 0.25 M sulfuric acid. Wipe the outside dry with a Kimwipe® and place the lid on. Open the slide door on the top of the UV-VIS, notice that there are two cell holders in which to put cuvettes. The cell holder toward the back of the instrument is for the blank, and the one in the front is for the sample to be analyzed. Carefully place the blank in the rear cell holder, making certain the *clear* sides (not the frosted sides) are facing right-left.
3. Fill the remaining two cuvettes with your **most concentrated** permanganate and dichromate standards to 3/4 full. Place the cuvette containing the permanganate standard in the front cell (make certain the cuvette exterior is wiped dry), again with the clear sides right-left. Once both cuvettes are properly in place, slide the sample chamber door fully closed.
4. By now you should be able to see a list of choices on the screen in the **Main Menu**, as shown in Figure 2.

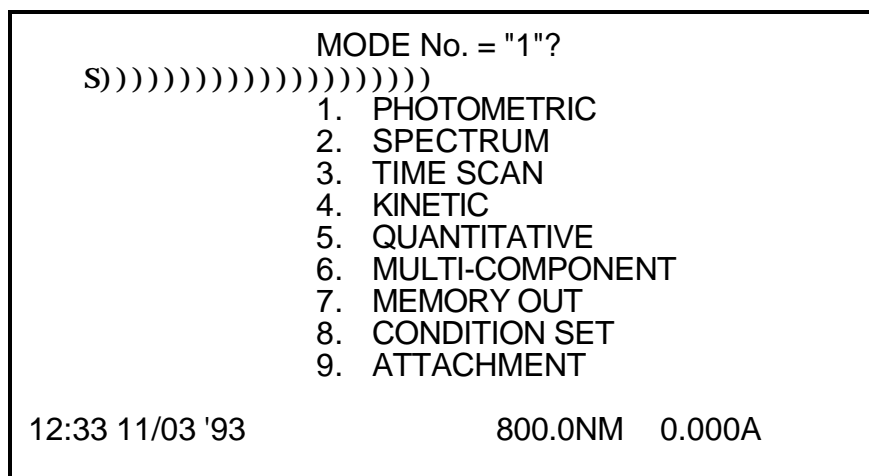


Figure 2

Choose **SPECTRUM** by pressing its number followed by **ENTER**. The screen will change and you will see another menu. Press **YES** when asked "**PARAMETER CHANGE Y/N?**" Enter the number of the parameter to be changed followed by **ENTER**, until your screen has the parameters shown in Figure 3. Once this is done, press **NO**, and when prompted to

do so, press **START**. If you want to go back to this screen to make a change, press **RETURN**.

SPECTRUM	PARAMETER CHANGE Y/N?
S))))))))))))))))))))))))))	
1. 8S= 650.0NM	8E = 360.0NM
2. MEASURE(ABS/T%)=ABS	
3. UPPER=+2.00a	LOWER =+0.00A
4. SCAN SPEED=FAST	
5. CYCLE T= 60SEC	N= 1
6. OVERLAY	NO
7. COPY	YES
8. SURVEY SCAN	NO
9. FILE	
12:34 11/03 '93	650.0NM 0.000A

Figure 3

- After your scan has been printed, answer **YES** to the question "**DATA PROCESSING Y/N?**" that appears on the top of the screen. Choose the option **PEAK-PICK** followed by **ENTER**. This option determines the maxima and minima wavelengths of the spectrum and concurrently generates a printout of these values. Press **COPY** to obtain a copy of your last screen. Repeat for your dichromate standard. Note: The Peak-Pick option for the dichromate may not show a maximum less than 1.0, therefore choose an operating wavelength that is located on the shoulder, somewhere around 440 nm (this will allow you to select a wavelength where the absorbance is less than 1.0).

- CALIBRATION CURVES:**
- Return to the main menu by depressing the **RETURN** key followed by depressing the **MODE** key. Choose the **photometric** option by depressing "1" then **ENTER**.
  - The screen will change and you will see another menu. Press **YES** when asked "**PARAMETER CHANGE Y/N?**". Enter the number of the parameter to be changed followed by **ENTER**. You will initially choose to change option "5". When at option "5", choose 2, in order to analyze at two wavelengths. After entering the two wavelength determination option, you will be prompted to enter the actual wavelengths of which you have

chosen to analyze at. Once this is done, make sure the rest of the screen looks like that in Figure 4.

```

PHOTOMETRIC    PARAMETER CHANGE Y/N?
S))))))))))))))))))))))))))))))))))
  1. GOTO 8= 525.0NM           81 = 525.0
                                82 = 440.0
  2. MEASURE(ABS/T%)=ABS
  3. SAMPLE No. = 1
  4. CYCLE T= 60SEC
      N= 1
  5. PROCESSING=28

  6. DATA PRINT           YES
  7. FILE

12:37 11/03 '93           525.0NM  0.000A

```

Figure 4

3. At this point you are ready to read absorbance values of your standards and unknown. Depress **NO** once all of your parameter changes have been make. Place your sample in the holder, close the door and press **START**. Repeat this procedure until all samples have been determined (a total of eleven). The printout should look similar to that in figure 5.

```

*** PHOTOMETRIC ***
  8 525.0 440.0
No.      A1      A2      A1! A2      A1/A2
S))))))))))))))))))))))))))))))))))
  1      0.123    0.005    0.118    26.474
  2      0.247    0.010    0.238    25.962
  3      0.494    0.019    0.475    26.090
  .      .        .        .        .
  .      .        .        .        .
  8      0.031    0.475   -0.444    0.0658
  9      0.037    0.641   -0.604    0.0584
 10      0.047    0.808   -0.761    0.0582
 11      0.545    0.385    0.159    1.4126

```

Figure 5

## REPORT SHEET: SPECTROPHOTOMETRIC ANALYSIS OF A PERMANGANATE-DICHROMATE MIXTURE

Name \_\_\_\_\_  
Please print; last name first

Sample Number: \_\_\_\_\_

Name \_\_\_\_\_  
Please print; last name first

Date: \_\_\_\_\_

**Molarity of stock standards:**  $K_2Cr_2O_7$  \_\_\_\_\_

$KMnO_4$  \_\_\_\_\_

**Optimum wavelengths:**  $K_2Cr_2O_7$  \_\_\_\_\_

$KMnO_4$  \_\_\_\_\_

**Products of Molar absorptivities x path length:** Record each slope, "eb", to 4 significant figures and record the corresponding regression coefficient, R2, to 4 digits in the brackets, [ ].

Shorter wavelength (*I*)

Longer wavelength (*II*)

$e'_{Cr} b =$  \_\_\_\_\_ [     ]

$e''_{Cr} b =$  \_\_\_\_\_ [     ]

$e'_{Mn} b =$  \_\_\_\_\_ [     ]

$e''_{Mn} b =$  \_\_\_\_\_ [     ]

**Experimentally measured absorbance of the unknown mixtures:**

Shorter wavelength *I*:  $A'_{total} =$  \_\_\_\_\_

Longer wavelength *II*:  $A''_{total} =$  \_\_\_\_\_

**Calculated concentrations (M) of the unknown to three significant figures:**

$K_2Cr_2O_7$  \_\_\_\_\_

$KMnO_4$  \_\_\_\_\_

**Graphical concentrations (M) of the unknown to three significant figures:**

$K_2Cr_2O_7$  \_\_\_\_\_

$KMnO_4$  \_\_\_\_\_

<b>Standardization of stock <math>\text{KMnO}_4</math> with <math>\text{Na}_2\text{C}_2\text{O}_4</math>:</b>				
	Trial 1	Trial 2	Trial 3	Trial 4
mass of standard $\text{Na}_2\text{C}_2\text{O}_4$				
volume of $\text{KMnO}_4$ required to reach the end point (after blank is subtracted)				
$M_{\text{KMnO}_4}$				
Average molarity of $\text{KMnO}_4$ : _____				
Show calculations of one trial:				

**Calculations:**

Molarity of the $\text{K}_2\text{Cr}_2\text{O}_7$ stock standard:
Molarity of the dichromate ion in the unknown:
Molarity of the permanganate ion in the unknown:

If additional space is needed for calculations, use the back side of this page.