COLORIMETRIC DETERMINATION OF MANGANESE (Chemistry 51 Version)

The objective of this experiment is to determine the percentage of manganese in a steel sample, using colorimetric methods of analysis.

PRINCIPLES

This analysis is accomplished by dissolving the steel sample, converting all of the manganese to the intensely colored MnO_4^- ion, and then determining the percentage of light absorbed by the MnO_4^- for a set of reproducible conditions such as degree of dilution, wave length, and light path length. The problems associated with each of these factors are discussed below.

Light Absorption

When a chemical species absorbs visible light, electrons in the normal ground state are raised to a higher energy excited state. The difference in energy between the two states of the absorbing species is equal to the energy of the light quantum absorbed. As a beam of monochromatic light, i.e., light of a single wavelength, passes through an absorbing solution, the intensity of the light decreases as photons are removed from the beam. It is reasonable to assume that the more light-absorbing entities there are in the light path and the more light quanta there are available to begin with, the greater is the amont of light that will be absorbed. We can express this in equation form as

$$\text{Total quanta absorbed/sec} \propto \text{(light intensity) (number of absorbing entities)} \qquad (1)$$

In order to evaluate this expression for the light which is absorbed from a light beam whose cross section is 1 cm^2 as it passes through a very thin layer of solution *dx*, as in Fig. 1, we define

$$\text{Light intensity} = I = \text{quanta/cm}^2\text{sec}$$

For a solution whose concentration is c moles/liter, the total number of moles (n) of the light-absorbing chemical, in length dx of a light beam whose cross section is 1 cm^2, is

$$n = \left[c \ \frac{\text{moles}}{\text{liter}} \right] \left[\frac{1 \text{ liter}}{1000 \text{ cm}^3} \right] \ (dx \ \text{cm}^3)$$

$$= \frac{c \ dx}{1000} \quad \text{moles}$$

If the 1-cm^2 layer of solution of length dx cm absorbs dI light quanta/sec (a minus sign indicates that I is getting smaller; the quanta are absorbed), we can rewqrite Eq. (l) as

$$-dI \ \propto \ (I) \ \frac{c \ dx}{1000}$$

We can convert the proportionality to an equality by introducing a proportionality constant K, which is characteristic of the material absorbing the light as well as of the wavelength.

$$-dI = \frac{KIc}{1000} \ dx = kIc \ dx$$

$$-\frac{dI}{I} = kc \ dx$$

In actual practice, we do not use very thin layers of absorbing material; instead we use a vessel containing a large amount of solution which may be thought of as being a whole succession of thin layers, as in Fig. 2, each layer having an incident light intensity equal to the intensity of the emergent beam from the preceding layer. The way to find how the intensity (I) of the final emergent beam compares with the initial ilntensity (I_o) is to take the sum of all the little absorptions brought about by each thin layer of thickness dx. This is a problem ideally suited for the methods of calculus, and if you've had such a course, you will understand that the following notation describes just such a summation: on the left, the summation of the changes in light intensity as it goes from I_o to I; on the right, the summation of the layers as they go from the first surface to a total thickness of b cm.

$$-\int_{I_o}^{I} \frac{dI}{I} = kc \int_{0}^{b} dx$$

If you have not had calculus, then you will have to have confidence in those who have, and accept these summations to be

$$-\ln \frac{I}{I_o} = kcb$$

By inverting the ratio of light intensities and converting to log base 10, we have

$$\log \frac{I_o}{I} = \frac{kcb}{2.303} = \varepsilon cb \qquad (2)$$

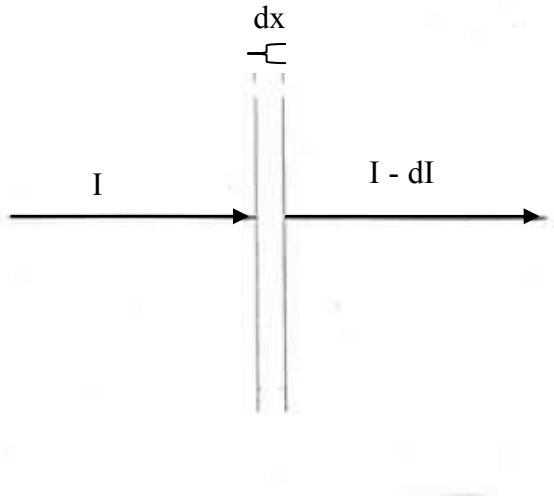

Figure 1

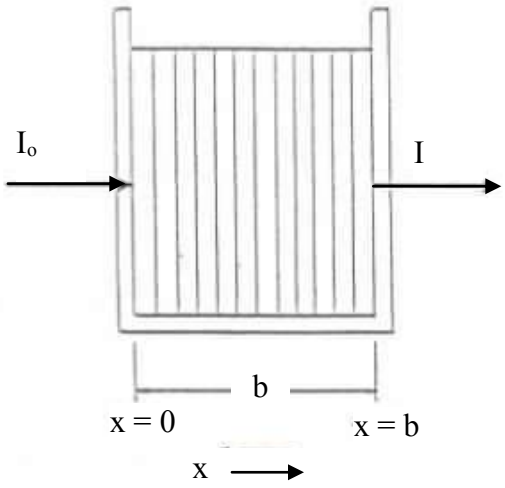

Figure 2

Equation (2) is known as Beer's Law. The molar absorptivity, ε, is a constant which is characteristic of the substance absorbing the light and of the wave-length. The quantity I/I_o, which represents the fraction of the incident light which passes through unabsorbed, is called **the transmittance,** T, and is often expressed as a percentage. The quantity log I_O/I, which is termed **absorbance,** is very irnportant in analytical work because it is proportional to the concentration of the absorbing species. The relationship between these quantities is summarized in the equation

$$A = \varepsilon c b = \log \frac{I_o}{I} = \log \frac{1}{T} = \log \frac{100}{\%T} \quad (3)$$

If several light-absorbing entities are present in a cell length b, each absorbs the light independently according to Eq. (2) so that the total absorbance of the solution is the sum of the absorbances of the individual species

$$A_T = A_1 + A_2 + A_3 = \varepsilon_1 c_1 b + \varepsilon_2 c_2 b + \varepsilon_3 c_3 b = b \sum \varepsilon_i c_i \quad (4)$$

The best way to show the light-absorbing characteristics of a substance is to plot its value of ε vs wavelength as has been done for the MnO_4^- ion in Fig. 3. This is called the absorption spectrum of the MnO_4^- ion. The MnO_4^- ion strongly absorbs the green light in the region 4800 - 5800 Å, leaving the color of the solution to be determined by the red and blue light that is transmitted; it is magenta.

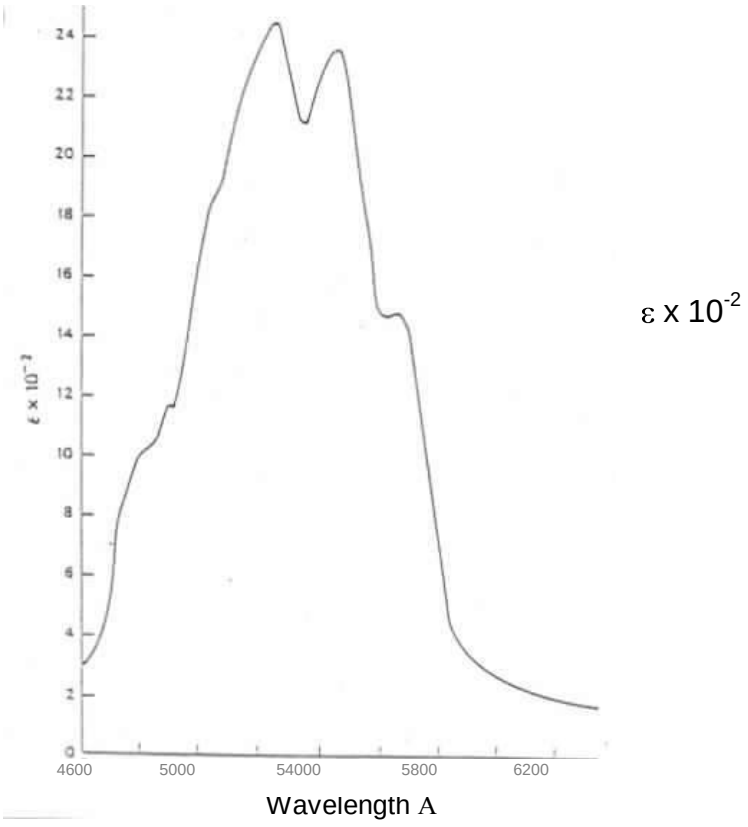

Figure 3. Absorption Spectrum of $Mn0_4^-$

Some substances, like MnO_4^-, are so intensely colored that the conversion of all the Mn in a sample to MnO_4^- can serve to tell its percentage by the amount of light it absorbs. More often, very sensitive and selective reagents are added which react with only one component in solution to form an intense color, even if the substance is in very low concentration. Once a reagent has been selected, it must be shown not to yield a competing color with some other substance that is present. If it yields a color in some other part of the spectrum that you do not plan to use, then of course this color will not interfere.

Next, you must choose the narrow wavelength band that you will use for analysis (remember Beer's Law applies only to monochromatic light .... or, in practice, to a narrow band of wavelengths). You naturally want to use a wavelength which is strongly absorbed (for which ε is very high) because this will permit you to analyze for much smaller quantities. It is advantageous to choose a wavelength where ε changes slowly with wavelength. Then if a small error is made in setting the wavelength, the value of e will not be greatly affected. For MnO_4^-, the wavelengths of the peaks near 5200 Å and 5500 Å would be ideal. You also want to choose a wavelength which is not absorbed by other components of the mixture; sometimes a less strong absorption band is chosen in order to have it more selective.

Finally, you must use an instrument which will provide reasonably monochromatic light. Such an instrument, a spectrophotometer, is described below. All instruments, simple or fancy, use absorption cells of identical light path and provide for the comparison of the colored solution with a blank solution. The instrument is adjusted so that the blank solution gives a reading of zero absorbance (or 100% transmittance); the colored solution then shows some absorption of the light (or, stated in terms of transmittance, the colored solution transmits some percentage of the light transmitted by the blank).

The function of the blank can be understood from a consideration of Eq. (4). Assume that our solution contains, in addition to the species of interest, designated s, an impurity, designated i, which absorbs light at the wavelength used. From Eq. (4) the total light absorbed is

$$A_T = A_S + A_i$$

Since the blank contains only the impurity, its absorbance will be A_i. When we adjust the instrument to zero absorbance with the blank, we are using the instrument to subtract the absorbance of the impurity. Then the absorbance indicated for the solution will be only the absorbance of the species of interest, A_S.

Once the color reagent has been selected and the wavelength for analysis chosen,

there still remains the necessity of making a calibration curve. For this purpose, solutions of known concentrations (of MnO_4^-, for example) are made and colored just as they would be in the analytical procedure; as a blank, another solution is used containing everything except that for which analysis is being made. The values of absorbance, A, are found for each solution and plotted as A vs c. In addition, you can see from Eq. (3) that the slope of the straight line obtained in the plot of A vs c is εb. Thus, if you know the length of the light path in the absorption cell, your calibration curve also makes it possible to evaluate ε. As usual, the best line through a series of independent points makes a better calibration curve than one made by one point and the origin, or by several points obtained by dilution of a single sample. Your analyses cannot be better than your calibration curve. For an analysis, the unknown samples are simply run as usual, and from the observed absorbance values the concentrations in the samples are read from the calibration curve.

Spectrophotometer

A spectrophotometer makes it possible to measure the fraction (I/I_0) of light of different wavelengths transmitted by a sample; I_0 is the intensity of the light beam incident on the sample and I is the intensity of the beam which emerges from the sample. To accomplish this, the spectrophotometer must provide (a) a source of white light of steady light intensity, (b) a means of selecting a beam of desired wavelengths from the white light, (c) a stable light-sensitive detector, and (d) a convenient means for reproducibly placing samples in the light beam.

Most instruments use a simple tungsten filament lamp for the light source in the visible region of the spectrum, with stability of light intensity provided by an electronically controlled circuit. Lamp stability is important in order to avoid oscillations of the meter, or drift in light intensity from one sample to the next. By alternating each sample with the blank it is possible to check on the drift and to make a suitable corrective adjustment if necessary. A H_2 discharge lamp must be used for a continuous spectrum in the ultraviolet.

The desired wavelength band is selected from the spectrum by rotating, with a calibrated knob, a reflective diffraction grating or a refracting prism**.** The grating consists of a glass plate, containing about 15,000 parallel and uniformly grooved lines per inch, which has been rendered reflecting by aluminizing. The prism is a 30° - 60° type which is aluminized on the back side so as to reflect the beam back through the prism in the direction from which it came; this doubling-back trick gives the same degree of refraction as a 60° - 60 ° prism and greatly cuts down on the length of the instrument that would otherwise be required. In either case, the reflected beam is dispersed to produce a

continuous spectrum.

The detector, which measures the amount of light transmitted, is usually a photoelectric cell in which the electrons that are ejected by the light quanta falling on an alkali metal surface (usually cesium) are collected by a positively charged wire and passed as an electric current through a meter. The higher the light intensity, the more quanta per unit time, the greater the number of electrons ejected per unit time, and the higher the meter reading.

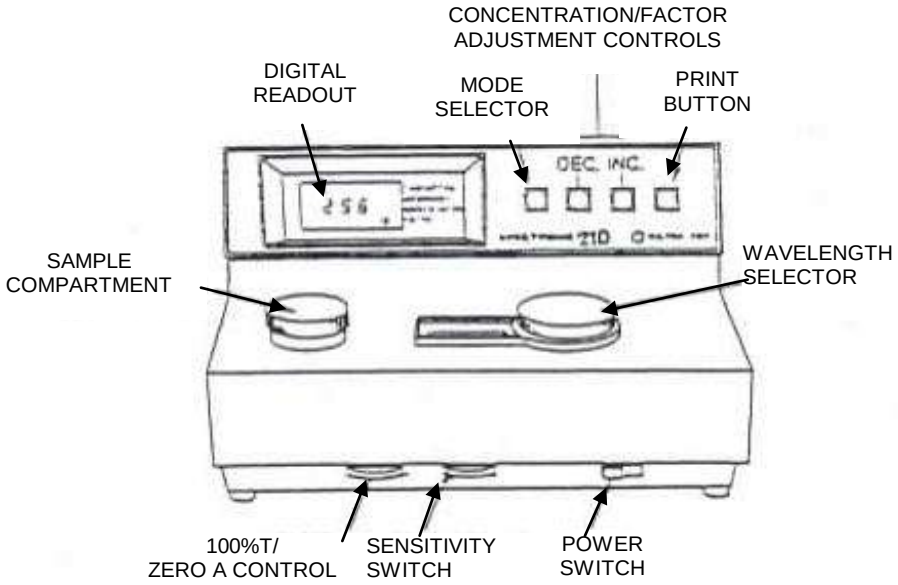

Figure 4. Spectronic 21DV Spectrophotometer

The sample cells are made as nearly identical as possible, but to insure good results, the group of cells which are used for an analysis should all be filled with the same solution and checked to see whether they all register the same percent transmission. For measurements in the ultraviolet region, all optical equipment (lens, windows, cells, etc.) must be made of quartz since Pyrex and regular glass do not transmit ultraviolet light. The cell compartment must have a cover in order to keep out room light.

In the description of the instrument that follows, a simplified schematic (Fig. 5) is shown in order to illustrate the principles. Modern instruments have sophisticated electronic circuits to insure high sensitivity and excellent stability, and rectifiers to convert alternating current to direct current so as to eliminate the use of batteries; they simply plug into a standard 115-V ac wall outlet.

Visible light is produced by a tungsten lamp and is focused by a lens, a mirror, and

slits onto the grating. The wavelength selector rotates the diffraction grating so that the desired wavelength band passes through the exit slit and sample cell. The transmitted light which passed through the exit slit is converted to an electronic signal by a photocell sensor. The signal is amplified and is routed to the final step of analogue-to-digital A/D conversion. The analogue and hence continuously variable signal is converted to a digital format which drives the digital readout and enables interfacing of the spectrophotometer via a serial port on the back.

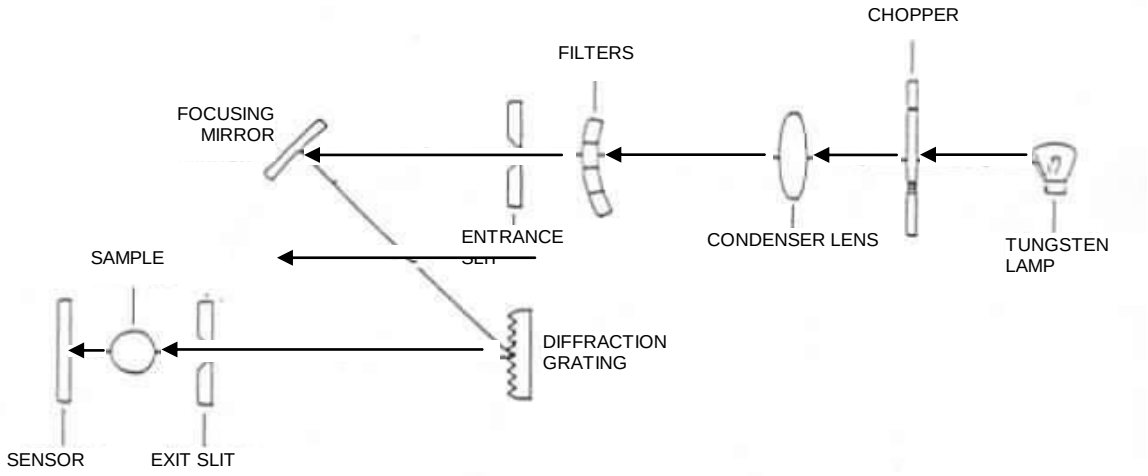

Figure 5. Schematic Diagram of a Spectrophotometer

When the cell containing the blank solution is placed in the cell holder, the 100%T/Zero A control is adjusted so that the digital readout reads zero absorbance (100% transmittance). If the blank is removed and the sample cell is placed in the cell holder, the digital readout will now read directly the absorbance of the sample so long as the wavelength selector, 100% T/ Zero A and sensitivity switch are not disturbed. If a completely opaque sample were inserted in the instrument, it would read 0%T. The zero end of the 0-100%T scale is handled automatically by the electronics.

Preparation of Sample

A solution of concentrated H_3PO_4 is used to dissolve the steel sample. In addition to the use of the acid function of H_3PO_4 to react with the metals in steel, use is made of the very strong complexing action of $HPO_4^{=}$ for Fe^{+++}. For some samples a small amount of HNO_3 is needed as an oxidizing agent to help dissolve the metals.

The fine particles of carbon or iron carbide which are often associated with steel are normally not susceptible to the attack of the acids just mentioned. If they linger on in the solution until after the MnO_4^- is formed, an error will be introduced, partly because they will reduce some of the MnO_4^- and partly because they will scatter some of the light, an effect which will be interpreted as light absorption. An excellent reagent for the oxidation of carbon to CO_2 in solution is ammonium peroxydisulfate.

$$2S_2O_8^{=} + C + 2H_2O \xrightarrow{\Delta} CO_2 \uparrow + 4HSO_4^-$$

Finally, in order to oxidize the Mn^{++} ions to the intensely colored MnO_4^- ions, the very strong oxidizing agent, $KI0_4$, is used.

$$5IO_4^- + 2Mn^{++} + 3H_20 \xrightarrow{\Delta} 2MnO_4^- + 5IO_3^- + 6H^+$$

In the process of using these strong oxidizing agents, some of the possible components of steel, such as Cr and V, may be partially or completely converted to such colored forms as $Cr_20_7^{=}$ and $V(OH)^+$. In addition, the common colored ions of Co^{++}, Ni^{++}, and Cu^{++} may be present in the solution. To some degree these colored ions may absorb the same light (5250Å) as that used for the analysis of MnO_4^-. These interferences may be corrected for exactly if part of the solution for which analysis will be made is treated with a reagent that decolorizes only the MnO_4^- and does not interact with the interferences; this decolorized solution can then be used for the blank in color comparison. KNO_2, if not used in excess of the amount needed only for the decolorization of MnO_4^-, is a satisfactory reducing agent for this purpose.

$$5N0_2^- + 2MnO_4^- + 6H^+ \longrightarrow 5N0_3^- + 2Mn^{++} + 3H_20$$

It should be noted that the concentrated H_3P0_4 used initially not only aids the solution of the sample, but once in solution, the iron is kept in the form of a colorless

phosphate complex, $FeHPO_4^+$, instead of a yellow iron complex. This is very helpful in the color comparison. The H_3P0_4 also prevents the undesirable precipitation of periodates and iodates of manganese by forming phosphate complexes of manganese.

EXPERIMENTAL PROCEDURE

1. Weighing the Steel Samples. Obtain a sample of unknown alloy from the side shelf and record its number in your notebook. Using a weighing paper, weigh an approximately 0.3-g sample of the alloy to the nearest 0.1 mg. Transfer it to a clean (but not necessarily dry) 400-ml beaker numbered on its frosted spot for identification.

Similarly, weigh an approximately 0.3 g sample to the nearest 0.1 mg of the Mn standard which is stored in small bottles located near the analytical balances and transfer it to another numbered beaker Record in your notebook the percentage of Mn in the standard.

2. **Dissolving the Steel Samples.** To each weighed sample add 20 ml of 15 M H_3P0_4 and warm *gently* UNDER A HOOD, using an electric hotplate. If after 10-15 minutes of heating below the boiling point, the sample proves to be particularly resistant to dissolving or if a fine gray suspension appears, carefully add about 0.5 - 1.0 ml of 6M $HN0_3$ to the hot solution by pouring it down the beaker wall; swirl to mix.

> *[Safety notes: this step should be done entirely under the hood. Never tilt a hot acid solution toward your face—tilt the solution away from your face when trying to observe if it has all dissolved. If you must add nitric acid, do so slowly and carefully; cool slightly first and add dropwise to avoid splattering. NO_x fumes will be given off, so again make sure you're under the hood!]*

Continue with gentle heating until the sample is completely dissolved. (Avoid overheating as the samples will form an irretrievable gel if too much solution evaporates. Ask the instructor for help if your volume gets very low or if you notice a "thickening" of the solution.)

COOL to room temperature, then add 5-10 ml distilled water, mix by swirling, then add about 1 g $(NH_4)_2S_2O_8$; again mix by swirling. After the initial major evolution of gas has subsided, heat the solution at near its boiling point for about 10 minutes in order to decompose the excess $S_2O_8^=$. COOL the solution, then dilute it with distilled water to approximately 50 ml and mix by swirling. If at this point there is a bit of brown

precipitate (probably MnO_2) or if any pink color has appeared (MnO_4^-), add a few crystals of Na_2SO_3 with swirling until the precipitate and/or color have disappeared. Other colors (such as green) are caused by harmless constituents (such as Ni) in the alloy and should be ignored. Heat to near boiling for several minutes to drive off the excess $SO_3^=$ as SO_2 gas . The solutions can be stored conveniently at this point. The rest of the experiment should be done on one day.

3. **Preparation of the Unknown MnO_4^- Solution and Blank.** Dilute the cool solution of unknown from Section (2) above to about 100 ml, then add about 0.5 g KIO_4 very carefully and in small portions; avoid vigorous gas evolution and possible loss by spattering. Heat the solution to near boiling for about 5 min during which time the MnO_4^- color will develop. Cool and quantitatively transfer the solution to a clean 250-ml volumetric flask, dilute to the mark with distilled water (see page 17 for these techniques), and **mix thoroughly**.

To make a "blank," pour about 50 mL from the volumetric flask into a clean dry container, then add 0.1 M KNO_2 dropwise and with stirring until the MnO_4^- color just disappears. Pour the remainder of the colored solution into a separate clean dry flask so that you can use your 250 mL volumetric flask in the next step.

4. **Preparation of Standard MnO_4^- Solutions.** Treat the standard solution prepared in Section (2) above exactly as was done for the unknown, ending finally with the MnO_4^- solution thoroughly mixed and diluted to exactly 250 ml in the clean volumetric flask. After dilution to the mark and thorough mixing, pour this solution into a clean dry glass container.

5. **Dilution of the Standard and Preparation of Blanks.** Select three clean, dry glass vessels and by means of a clean, well-rinsed 25-ml pipet, add 75.0 ml of the solution prepared in step four to one of them, 50.0 ml to the second, and 25.0 ml to the third. The pipet should be well rinsed with small portions of the solution to be pipetted before a transfer is made (pour about 25 mL of your solution into a separate flask for use in rinsing the pipet in order to avoid contaminating or diluting your stock solution); other techniques of pipetting (see pp. 18-19) should be reviewed. After rinsing the pipet thoroughly with distilled water, additional 25-ml portions of water should be added to each vessel to give a total volume of 100 ml in each; stir each to give uniform composition.

You now have four colored solutions of your standard: the original and three made

by dilution. Part of each of these solutions must be converted to a blank for color comparison. For each colored solution, pour about 20 mL of the colored solution into a clean dry glass container and add 0.1 M KNO_2 dropwise and with stirring until the MnO_4^- color just disappears. This forms the blank solution for that dilution.

6. Measurement of the Absorption Spectrum of the MnO_4^- Anion. In order to obtain maximum sensitivity, the wavelength of the spectrometer should be set at the value where the extinction coefficient of permanganate has a maximum value. Rather than read the value from the spectrum in figure 3, you will measure the full spectrum on a Cary 300 recording spectrophotometer located in Room 10. The instrument contains two cells, one filled with blank and the other with the colored solution, and automatically measures the ratio of the light passing through the two cells as the wavelength is varied.. The instrument will be configured by the instructor to scan in the range 400 to 700 nm. Two 1 cm x 1 cm square cuvettes will be found with the instrument. Rinse one with your blank solution, fill it *ca*. 75% full, and load in the back (away from you) position of the sample compartment. Rinse the other cuvette with your unknown solution, fill it ca. 75% full, and load it in the front (towards you) position of the sample compartment. Close the door of the sample compartment and initiate the measurement by clicking on the GREEN stoplight on the window of the Cary Scan software. You will be asked to provide a file name (use the Chem51 folder) and a file name. The instrument will automatically record the spectrum. The instructor will show you how to autoscale the spectrum and measure of the positions of its peaks. You need the wavelength where the absorbance is the greatest. When the spectrum has been recorded, remove and rinse the two cuvettes. Plot the spectrum by loading a page in the Epson printer and clicking in succession on the Clear Report and Print buttons in the panel on the left.

7. Determination of the Absorbance of the MnO_4^- Solutions. You should now have a total of 10 solutions—5 colored solutions including 4 dilutions of the standard and your one unknown, and 5 blank solutions corresponding to each colored solution. Color comparison should be made in accord with the following directions based on the use of a Bausch & Lomb Spectronic 21 spectrophotometer shown in Fig. 4. It has been assumed that the spectrophotometer has been plugged in and warmed up for some time, and that the lid on the sample tube holder is closed.

(a) Set the wavelength dial of the Spectronic 21 to the value determined in the

previous step. In changing the wavelength, always move it from long wavelength to small wavelength. For example, if the target wavelength is 525 nm and the present position of the monochromator is 400 nm, one should turn it past 525 nm, perhaps to 550 nm, and turn it to the desired 525 nm.

(b) Record the number of the spectrophotometer used for these measurements since the same spectrophotometer should be used for the standard solutions.

(c) Place the digital readout in the ABSORBANCE mode by pressing the MODE SELECTOR button. The sensitivity switch should be on the medium setting.

(d) Rinse a spectrophotometer sample tube with two or three portions of your first decolorized solution, then fill it about two-thirds full.

(e) Rinse another spectrophotometer sample tube with two or three portions of the corresponding colored solution, then fill it about two-thirds full.

(f) Wipe both tubes carefully with soft, lintless paper to remove fingerprints and gently tap the tubes to dislodge any air bubbles that may be clinging to the walls.

(g) Insert the tube with the blank solution into the sample holder and rotate the tube so that the positioning mark is aligned with the mark on the holder. Close the lid. Adjust the 100%T/Zero A control so that the digital readout registers zero absorbance.

(h) Insert the tube with the colored solution into the sample holder and rotate the tube so that the positioning mark is aligned. Close the lid. Read both the absorbance and the % transmittance and record them in your notebook**.**

(i) All subsequent steps must be repeated whenever the wavelength control is adjusted. For best results steps (g) and (h) should be repeated several times for each solution to be measured so that any instrument drift during a single measurement is averaged out.

DATA ANALYSIS

1. Refer to the section: "Curve Fitting and the Method of Least Squares," for a general discussion, examples, and problems dealing with the data analysis techniques needed for this experiment.

2. **Calibration Curve**. According to Beer's Law, a plot of the absorbance A (A=log(l00/%T)) versus concentration C should yield a straight line with a <u>fixed</u> intercept of 0. Use Excel to calculate the concentration of each of the standard

solutions in moles/L. These results should be in a column of the spreadsheet. Enter the corresponding absorbances in another column. Use the regression tool in Excel to fit absorbance versus concentration to a line, selecting the "Constant is Zero" option to force a zero intercept. This is the calibration "curve" from which you will determine the concentration of your unknown solution.

3. **Determination of Unknown Quantities**. Using the slope obtained from your calibration curve, calculate the molar absorptivity of MnO_4^- and the percent manganese in your unknown. The length of the light path of our sample cells is 1.16 cm.

4. **Experimental Report.** Record the values requested on the experimental report sheet. In addition to your report sheet, turn in your excel spreadsheet outputs including the regression analysis and the calibration graph.

colorimetric51.doc, WES, 13 August 2003

NAME_____**Lab Section** _____

Meter Number_____ **Sample No.** _____

Date report submitted_____

COLORIMETRIC DETERMINATION OF MANGANESE

1. Wavelength Used _____

2. Calibration Curve

Weight of standard _____

Percentage of Mn in standard _____

Slope of calibration curve _____

Standard deviation of the slope _____

95% confidence interval of the slope _____

Correlation coefficient (Multiple R) _____

Standard error _____

Molar absorptivity _____

2. Percentage of Manganese in Alloy

Weight of sample _____

Absorbance of sample _____

Percentage of Mn in alloy _____

3. Write down the net-ionic chemical equation for the oxidation of Mn^{++} to MnO_4^- used in this experiment. Identify the oxidizing agent and the reducing agent.

4. Show calculations for (2) on back. Include the absorption spectrum recorded on

the Cary 300 with the report.