This experiment offers the student an exhibition of solutions having some splendid colors. The photo below gives a preview of what one might expect.

Discussion

The manganese content of most steels is quite low (<1%). It is therefore difficult quantitatively to analyze for Mn in the presence of large amounts of iron by purely chemical techniques. A colorimetric method based on the characteristic purple color of the permanganate ion, MnO$_4^-$, however, yields accurate results. The method is based on the dissolution of the steel in nitric acid which also oxidizes the Mn to Mn$^{2+}$. The reaction involved is:

\[
3\text{Mn} + 2\text{NO}_3^- + 8\text{H}^+ \rightleftharpoons 3\text{Mn}^{2+} + 2\text{NO} + 4\text{H}_2\text{O}
\]

The nitric oxide produced must be removed since it would react with periodate and would thus inhibit the oxidation of the Mn$^{2+}$ to permanganate. The removal of the NO is accomplished through boiling and the addition of ammonium peroxydisulfate, (NH$_4$)$_2$S$_2$O$_8$. This compound is also known as ammonium persulfate. The reaction is:

\[
2\text{NO} + 3\text{S}_2\text{O}_8^{2-} + 4\text{H}_2\text{O} \rightleftharpoons 2\text{NO}_3^- + 6\text{SO}_4^{2-} + 8\text{H}^+
\]

The peroxydisulfate also oxidizes and removes carbon or other organic matter. The S$_2$O$_8^{2-}$ is a powerful oxidizing agent. It may oxidize some of the manganous ion to MnO$_2$, which will appear as a brown precipitate. The addition of small amounts of sodium bisulfite, NaHSO$_3$, will reduce the MnO$_2$ back down to the +2 state. Boiling will expel the SO$_2$ that is formed. The next step in the procedure is the oxidation of the Mn$^{2+}$ to MnO$_4^-$. Peroxydisulfate has a sufficiently large electrode potential to accomplish this conversion; however, the reaction rate is quite low. Potassium metaperiodate, KIO$_4$, is therefore used as the oxidizing agent. The reaction is:

\[
2\text{Mn}^{2+} + 5\text{IO}_4^- + 3\text{H}_2\text{O} \rightleftharpoons 2\text{MnO}_4^- + 5\text{IO}_3^- + 6\text{H}^+
\]
Phosphoric acid is added to the solution in order to prevent any interference from ferric ion. The latter forms a colorless complex with phosphoric acid. Most colored ions can be compensated for with a blank containing those ions, but cerium (III) and chromium (III) present problems because they also undergo oxidation in the presence of periodate, producing oxidation products which exhibit significant absorption of light at the same wavelength used to measure the absorbance of permanganate. This method cannot be used if those ions are present unless the absorbance is measured at wavelengths at which the other two oxidation products exhibit absorbance maxima. The concentrations of each species can then be found using simultaneous equations.

The procedure for the determination of the Mn content consists of two parts:

1. The preparation of a calibration curve from the measured absorbances of a number of solutions of known Mn concentrations.
2. The preparation of the unknown solution and determination of its absorbance.

A major source of error in this experiment is misuse of the Spectronic 20 spectrophotometer. Before you take any measurements on this instrument read the instructions at the end of this manual and commit them to memory. There is also a useful Web page available via the instructor's home page which gives you the same information. Be sure to make all the measurements on the same instrument and the same cuvettes. Record the number of the spectrophotometer. (This is the number on the blue plastic decal on the front of the instrument.)

**Experimentals**

Before you start this procedure obtain the following from the instructor: two spectrophotometer cuvettes and a small vial containing KIO₄. Throughout this analysis it is essential that you use the same spectrophotometer and the same two cuvettes. The first part of the analysis which establishes the required calibration curve in effect calibrates both the cuvettes and the spectrophotometer. You will be using one of the cuvettes repeatably to hold sample solutions. The other will serve as the blank. The cuvette holding samples will be refilled repeatedly with different solutions. It will have to be rinsed first with distilled water, then rinsed with a small amount of the solution to be added before adding the solution whose optical density is to be measured. Each time a separate aliquot of the same sample will be used.

When filled with identical solutions, our sample cuvettes do not produce identical absorbances from one to the next. You may want to put distilled water into two cuvettes and use one as the blank to calibrate the Spectronic 20 and the other to check the systematic error in absorbance. Alternatively, you may wish to find a pair of cuvettes which read within 0.001 absorbance units from each other so that you won't have to make any correction.

For your amusement and amazement, here are some data showing how absorbance can vary from one cuvette to the next:

**B&L cuvettes**

Wavelength = 525 nanometers

One tube. Blank reading at 0 degrees

<table>
<thead>
<tr>
<th>Orientation</th>
<th>0</th>
<th>45</th>
<th>90</th>
<th>135</th>
<th>180</th>
<th>225</th>
<th>270</th>
<th>315</th>
<th>360</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
**degrees**

<table>
<thead>
<tr>
<th>Absorbance</th>
<th>0.000</th>
<th>0.009</th>
<th>0.000</th>
<th>0.001</th>
<th>0.007</th>
<th>-0.001</th>
<th>0.001</th>
<th>0.000</th>
<th>-0.002</th>
</tr>
</thead>
</table>

Cuvette comparisons

Wavelength = 525 nanometers

<table>
<thead>
<tr>
<th>Cuvette</th>
<th>B&amp;L</th>
<th>B&amp;L</th>
<th>B&amp;L</th>
<th>B&amp;L</th>
<th>B(F)</th>
<th>Brand X</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>A</td>
<td>B</td>
<td>C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Absorbance</td>
<td>0.000</td>
<td>0.003</td>
<td>-0.002</td>
<td>0.008</td>
<td>0.002</td>
<td>-0.008</td>
</tr>
</tbody>
</table>

The large variations evident by the rotation of one cuvette or the comparison of two cuvettes holding the same solution are unacceptable. As you can see from the 0 and 360 degree readings, there is going to be some variation; plus or minus 0.002 might have to be tolerated, but the .008 and -.008 readings cry out for a "cuvette correction".

Clean two cuvettes and fill both with distilled water. Calibrate the spectrophotometer using one, then take an absorbance reading with the other. Make sure that the vertical line on the cuvette lines up opposite to the mark on the plastic cuvette holder in the spectrophotometer for both the calibration and all future readings. If the vertical line is in a different position during any reading, the absorbance will change slightly. The second cuvette will be the one in which you place your sample. It will be used as your sample cuvette. The other one will be used as your blank cuvette. We will call this absorbance A systematic error. The absorbance you measure is the systematic error between the two cuvettes, using the first cuvette as the blank. This absorbance will be subtracted from all future sample readings.

Alternatively, you may search through our collection of cuvettes until you find a pair which read to within ± 0.001 absorbance units of each other. Then you won't have to make an absorbance correction. In any case, cuvettes ought always to be placed in the cuvette holder in the same position because even a slight rotation can lead to large errors in absorbance.

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**Preparation of the Calibration Curve**

Clean a 50 mL volumetric flask, put your initials on the marking spot and give it to the instructor. The flask will be filled with 5 mL of a solution which contains 1.000 g of Mn per liter. Fill this flask with distilled water to the calibration mark. Make sure that you continually mix it while you are adding water. When filled, stopper the flask and mix the contents by inverting and shaking the flask. This ten-fold dilution will provide you with a solution that contains 0.1000 g of Mn per liter and represents the stock solution which you will use to prepare the Mn standards.

With a volumetric pipet, transfer 5 mL of your stock solution into a clean 125 mL Erlenmeyer flask. Add 20 mL of water and 4 mL of concentrated H3PO4. Then add 0.4 g of KIO4 and boil for 2 minutes on a small hot plate. Cool to room temperature with the aid of an ice bath. Quantitatively transfer the contents of this flask into a 50 mL volumetric flask with the aid of one of your plastic funnels and a glass rod. Use numerous small water washes to rinse the flask. Then
dilute the contents of the volumetric flask to the mark with distilled water. Invert the flask several times so that the concentration of the solution becomes uniform. Rinse and fill your sample cuvette with the solution just prepared and fill the blank cuvette with a solution of H$_3$PO$_4$ prepared by diluting 1 mL of concentrated H$_3$PO$_4$ to a total of 10 mL with distilled water. Calibrate the spectrophotometer again using your blank cuvette. Then, determine the absorbance of the MnO$_4^-$ solution in your sample cuvette at a wavelength of 525 nm. Record both absorbance and percent transmittance. Pour out the solution in the cuvette the absorbance of which was just read, refill with the same solution in the volumetric flask and read the absorbance again. Carry out the measurement of absorbance a total of three times. Use the average value of the three absorbances in the preparation of the calibration curve.

Now repeat the procedure in the paragraph above, using volumes of the 0.1000 g of Mn per liter solution, such that you obtain MnO$_4^-$ solutions whose absorbance values span the range from 0.1 to 1.0. Keep in mind that according to Beer’s Law, absorbance is directly proportional to concentration. You must have five calibration points. You are somewhat limited in the volumes that you can choose, by the fact that volumetric pipets are available only for 1, 2, 3, 5 and 10 mL but due to the high relative error for 1 mL pipets you should avoid their use. For your fifth volume you may choose any one of the following combination of pipettes: 2+2, 3+3, 5+2 or 5+3 mL. Plot the points carefully and neatly on a piece of millimeter graph paper. Place the absorbance values on the ordinate, or y-axis, and the concentrations, in units of g of Mn per mL, on the abscissa or x-axis. The five values plotted in this manner should all fall on or close to a straight line. If one or more points appear to deviate from this line, ask your instructor about which ones ought to be redone.

Additional helpful hints:

a. The “best” straight line will be found by applying linear regression analysis, not by “eyeballing” the points and drawing a line which you think is “best.”

b. Follow the instructions given for linear regression in one of the appendices or use an appropriate spread sheet program to do the same thing.

c. Your slope should come out to be somewhere between 40000 and 50000.

d. Your y-intercept should be a small negative or positive number, between -0.03 and +0.03.

e. The straight line you get will conform to $y = mx + (y\text{-intercept})$ where $m$ is the slope. The y- intercept is the value of the absorbance when concentration (plotted on x) equals zero.

f. Beer’s Law is often written as $A=abc$ where $A$ is the absorbance, $c$ is the concentration, $b$ is the path length of the cuvette and $a$ is a constant characteristic of the substance under study. In the ideal Beer’s Law, given by $A=abc$, the y-intercept is equal to zero.

g. The method of linear regression gives you absorbance, on the y-axis, $A = mc + (y\text{-intercept})$, a straight line with a y-intercept resulting from small deviations caused by your procedure and the instrument you use. “$m$” is the slope, equivalent to “$ab$” in the Beer’s Law equation. “$c$” is the concentration, plotted on the x-axis. It is the same “$c$” as in the Beer’s Law equation.

h. The “best” straight line which you draw is for the presentation of your data alone, not to be used to determine the concentration of your unknown. The concentration of your unknown will be found by applying a rearrangement of your regression formula, that is $c = (A-(y\text{-intercept}))/m$

i. If you use a spreadsheet program to get the slope “$m$” and the (y-intercept), you may draw your “best” straight line using that program.

Now repeat the procedure in the paragraph above, using volumes of the 0.1000 g of Mn per liter solution, such that you
obtain MnO₄⁻ solutions whose absorbance values span the range from 0.1 to 1.0. Keep in mind that absorbance is directly proportional to concentration, i.e. the volume of stock solution used. You must have five calibration points. You are somewhat limited in the volumes that you can choose, by the fact that volumetric pipets are available only for 2, 3, 5 and 10 mL. Due to the high relative error for 1 mL pipets you should avoid their use. For volumes between 5 and 10 mL it is therefore necessary to double pipet. Plot the points carefully and neatly on a piece of millimeter graph paper. Place the absorbance values on the ordinate and the concentrations, in units of g of Mn per mL, on the abscissa. Use the long side of the paper for the abscissa. The five values plotted in this manner should all fall on a straight line. If one or more points deviate from this line, redo that particular point. In addition to this plot you should also use the experimental values and fit them to a straight line. The method of least squares is one procedure which will calculate the parameters of the equation for the best straight line through the experimental points. The equation for this line will be of the form \( y = mx + b \) where “m” is the slope and “b” is the y-intercept. Detailed directions for the calculation of such a line are given in one of the appendices to this manual. Many calculators also have the capability to calculate the required parameters, this feature is usually called linear regression. Be sure to consult the instruction manual of your calculator to see whether it has this capability.

**Determination of the Mn Content of a Steel Sample**

Weigh out two steel samples of about 0.8 g each, to an accuracy of ±0.1 mg, directly into two 125 mL Erlenmeyer flasks. In the fumehood add 40 mL of 6 M HNO₃ and heat to boiling. Continue heating for about five minutes. Be very careful not to let the solution go to dryness. Severe spattering will result and loss of some unknown will almost certainly occur. Cool to room temperature, with an ice bath if necessary, and then cautiously add 1 g of ammonium peroxydisulfate. Boil gently for 5 minutes. Again cool to room temperature and then add 0.1 g of sodium hydrogen sulfite and then boil for another 5 minutes. Again cool the solution to room temperature. If the solution at this point is completely clear, i.e. there is no precipitate, you can then transfer it quantitatively into a 100 mL volumetric flask. On the other hand if there is a fine black precipitate you must filter it into the 100 mL volumetric flask. Use your plastic narrow-stem funnel and #1 filter paper. Use numerous, small distilled water washes to insure the you get a quantitative transfer. Add water to bring the volume of the flask up to the calibration mark. Mix the solution well while adding the water. After the volume has been made up to the index mark, stopper the flask, invert it and then shake it a few times so as to properly mix the solution.

Pipet 25 mL aliquots from one of your dissolved steel samples into two 125 mL Erlenmeyer flasks. To each flask add 4 mL of concentrated H₃PO₄. To one of the Erlenmeyer flasks add 0.40 g of KIO₄ and gently boil for 2 minutes. The second aliquot serves as a blank and is not treated with KIO₄. Cool the boiled sample to room temperature in an ice bath, then transfer both samples, with adequate water washes, into two different 50 mL volumetric flasks and then fill them up to the mark with distilled water. Determine the absorbance of the periodate treated sample at a wavelength of 525 nm. Use the solution that was not treated with periodate as a blank. As before, repeat all steps of the absorbance determination procedure three times. If the absorbance value exceeds 1.00, discard both the periodate treated sample and the blank. Pipet 10 mL aliquots of the same unknown solution into two 125 mL Erlenmeyer flasks. Then proceed in the same manner as before except use only one half the amount of periodate. Obtain and record the absorbance and percent transmittance of this more dilute solution. Repeat the procedure with the other steel sample. From the data obtained in this manner, using either the calibration curve or the linear regression line, calculate the percentage of Mn in the steel sample.
Report

On the report sheet provided, give the following information

1. Steel sample number
2. Spectrophotometer number
3. Values of each volume and absorbance for the points used in your calibration curve.
4. Values of the linear regression parameters "m" and "b"
5. Grams of steel used for each sample
6. Measured absorbance for each sample
7. Aliquot volume of unknown solution (10 or 25 mL).
8. The percentage of Mn for each sample
9. The average percentage
10. Pages in the laboratory notebook containing the original data

Attach the original or a copy of your calibration curve to your report sheet.

Questions on Mn in Steel Analysis

1. Why is ammonium peroxydisulfate added to the solution containing the dissolved steel?
2. Why is sodium bisulfite added?
3. What is the formula of the brown oxide of manganese referred to in the procedure?
4. How many centimeters are there in 525 nm?
5. Why is phosphoric acid added to the dissolved steel aliquot?
6. Why is this method not applicable to steel samples with a high chromium or cerium content?
7. The slope of the calibration line corresponds to which symbol(s) in the relationship $A = abc$?
8. What is the name and formula of the compound used to oxidize Mn$^{2+}$ to MnO$_4^{-}$?

Contributors and Attributions

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