

Determination of manganese in steel by permanganate colorimetry

Use this method if you do not have access to a colorimeter

Introduction

Steel is mainly composed of iron; however, most kinds of steel contain a small amount (up to 1%) of manganese (with chemical symbol Mn). This can be detected by oxidising it to the permanganate ion (MnO_4^-), which has an intensely purple colour. The concentration of manganese can then be determined by measuring the intensity of the purple colour, and comparing it with the colour of known permanganate solutions.

Equipment and Materials Required:

- steel sample (e.g., steel wool, paper clips, nails, etc.)
- potassium permanganate
- 6 mol L⁻¹ nitric acid
- concentrated phosphoric acid
- potassium periodate
- 10 mL and either 5 or 15 mL pipettes
- 200, 250, 500, 1000 mL volumetric flasks
- 250 mL conical flask
- 10 and 100 mL measuring cylinders
- bunsen burner, tripod and gauze mat
- at least 6 boiling tubes (or large test tubes)
- distilled water

Method

Preparation of MnO_4^- standard solutions

1. First prepare a 0.005 mol L⁻¹ standard solution of potassium permanganate by accurately weighing out about 0.79 g of solid KMnO_4 and dissolving it in 1 L of distilled water in a volumetric flask. The concentration of permanganate ions solution may be calculated as follows:

$$[\text{MnO}_4^-] \text{ (mol L}^{-1}\text{)} = \text{mass of KMnO}_4 \text{ used (g)} \div 158 \text{ (g mol}^{-1}\text{)} \div 1 \text{ (L)}$$

Pipette 10 mL of the above permanganate solution into separate 200, 250, 500 and 1000 mL volumetric flasks and make each one up to the mark with distilled water, giving you standard permanganate solutions with concentrations of 2.5, 2.0, 1.0 and 0.5×10^{-5} mol

L⁻¹ respectively. Also pipette 15 mL of your 0.005 mol L⁻¹ permanganate solution into a 1000 mL volumetric flask and make up to the mark with distilled water, giving a standard with concentration of 1.5×10^{-5} mol L⁻¹.

Label each standard solution you have prepared.

Preparation of steel sample for analysis

1. Accurately measure the mass of about 0.2 g of steel. Good steel samples to use include steel wool, paper clips, or small nails.
2. Place your sample in a 250 mL conical flask and add 20 mL of 6 mol L⁻¹ nitric acid. (Caution: Reaction of steel with nitric acid produces toxic nitrogen oxides. Do this in a fume hood. Concentrated acids are highly corrosive – wear safety glasses and rubber gloves and take care when handling.) Once the reaction has stopped, warm the flask gently over a Bunsen burner (using tripod and gauze mat) for a few minutes to drive out all remaining nitrogen oxide gases. The steel has now dissolved, mostly to form Fe^{3+} ; any manganese has been converted to Mn^{2+} ions.
3. Add 80 mL of distilled water followed by 5 mL of concentrated phosphoric acid (Take care with concentrated acid), and swirl to mix.
4. Add about 0.5 g of solid potassium periodate. This contains the IO_4^- ion which oxidises Mn^{2+} to MnO_4^- .
5. Heat the mixture over a Bunsen burner to nearly boiling for 5 minutes, and then keep heating it (without boiling) until the solution begins to develop a purple colour. Continue heating until there is no further colour change – this may take a further 15 – 30 minutes. Figures 1 – 4 illustrate the sort of colour change that you can expect to see during this time.
6. Let your solution cool for 5 minutes. Pour it carefully into a 250 mL volumetric flask, rinsing any remaining solution into the flask with distilled water. Finally, make up to the mark with distilled water and shake to mix.

Colorimetric analysis

1. Accurately measure 10 mL of your steel sample solution into a clean, dry boiling tube. This measurement is most accurately made using a 10 mL pipette; however, it is possible to do this accurately



Figures 1 – 4. Development of purple colour due to formation of MnO_4^- in steel sample solution. Figure 1 shows the nearly colourless solution containing dissolved steel, before any oxidation of manganese has occurred. As the solution is heated over a period of about 20 minutes the purple colour of MnO_4^- gradually becomes stronger and stronger, as shown in Figures 2, 3 and 4.

enough (and with less hassle) using a clean 10 mL measuring cylinder if you measure carefully.

- Next, measure 10 mL of each MnO_4^- standard solution into separate boiling tubes (one standard per tube) in order of increasing concentration, beginning with the $0.5 \times 10^{-4} \text{ mol L}^{-1}$ standard. It is a good idea to first rinse your pipette or measuring cylinder with a few mLs of the $0.5 \times 10^{-4} \text{ mol L}^{-1}$ standard. NB: Make sure you label each boiling tube appropriately with the name of the sample or standard it contains. A test tube rack is very useful for holding your tubes (see Figure 5). Alternatively you can use a large beaker to hold them.
- Estimate the concentration of Fe^{3+} ions in your iron sample by identifying which of your MnO_4^- standards matches its colour the closest. Figure 5 illustrates the range of colour intensities that you can expect from your set of MnO_4^- standards. Tip: If you are using boiling/test tubes all of identical sizes, the best way to compare colours is by looking at your solutions from above – looking down into the tubes (see Figure 6).
- If the colour of your unknown steel solution is stronger than the colour of your highest concentration MnO_4^- standard you will need to modify the above procedure. Try diluting your purple steel sample solution so that its colour lies within the range of your standards. (NB: Any dilution must be taken into account in your calculations.)



Figure 5. Purple coloured permanganate standard solutions, corresponding to the following MnO_4^- concentrations: $0.5, 1.0, 1.5, 2.0, 2.5 \times 10^{-4} \text{ mol L}^{-1}$.



Figure 6. The same boiling tubes as in Figure 5 (MnO_4^- standard solutions with concentrations of $0.5 - 2.5 \times 10^{-4} \text{ mol L}^{-1}$) viewed from above, looking directly down the length of the tube. This view provides the most accurate "eyeball" comparison of the solutions' colour intensities.

Calculations

- Assume that the concentration of MnO_4^- in your unknown steel solution is approximately equal to that of the MnO_4^- standard whose colour was the closest

match.

- Use this concentration to calculate the mass of manganese (in g) in your original steel sample, remembering that the number of moles of MnO_4^- produced is equal to the original number of moles of Mn in the sample. The molecular weight of Mn is 54.9 g mol^{-1}).
- Using the mass of your original steel sample calculate the percentage of manganese in the steel.

Additional Notes

- The phosphoric acid added to the dissolved steel solution, forms a colourless complex with Fe^{3+} . This makes the permanganate colour easier to see.
- If you are using a colorimeter instrument, it is not critical to have identical boiling/test tubes for each permanganate solution – any small vessels (e.g., small beakers or glass vials) will do. However, if you are analysing the colour intensities by eye, as above, it is important to have identical vessels in order to make an accurate comparison – a set of identical boiling/test tubes is ideal.
- You may notice that even the standard giving the closest colour match to your sample is still quite different – meaning that your estimated MnO_4^- concentration is not very accurate. In order to obtain a more accurate result you may wish to try the following procedure:
 - Identify which two MnO_4^- standards are the closest colour matches to your unknown solution: one must be slightly darker in colour and the other slightly lighter than your unknown. The concentration of your unknown solution must lie somewhere between the concentrations of these two standards. For this example, let us pretend that the two closest standards are 1.0×10^{-4} and $1.5 \times 10^{-4} \text{ mol L}^{-1}$.
 - Take 5 clean, dry boiling tubes. To the first tube we add 10 mL of the $1.0 \times 10^{-4} \text{ mol L}^{-1}$ standard and 10 mL of the $1.5 \times 10^{-4} \text{ mol L}^{-1}$ standard. We now have a new standard that is $1.25 \times 10^{-4} \text{ mol L}^{-1}$.
 - Next, we measure 5 mL of this $1.25 \times 10^{-4} \text{ mol L}^{-1}$ standard into a new tube and also add 5 mL of the $1.0 \times 10^{-4} \text{ mol L}^{-1}$ standard. We now have another new standard that is $1.125 \times 10^{-4} \text{ mol L}^{-1}$.
 - If we measure 5 mL of the $1.25 \times 10^{-4} \text{ mol L}^{-1}$ standard into another new tube and add 5 mL of $1.5 \times 10^{-4} \text{ mol L}^{-1}$, we will make another new standard that is $1.375 \times 10^{-4} \text{ mol L}^{-1}$.
 - We finish by measuring 10 mL of the $1.0 \times 10^{-4} \text{ mol L}^{-1}$

L⁻¹ standard into one boiling tube, and 10 mL of the 1.5×10^{-4} mol L⁻¹ standard into a different tube.

- We now have a set of five boiling tubes, each containing exactly 10 mL of a different MnO₄⁻ standard solution, with concentrations of 1.0, 1.125, 1.25, 1.375 and 1.5×10^{-5} mol L⁻¹. If we now repeat the colorimetric analysis of our unknown iron solution using these new standards instead of the original ones, we should obtain a much more accurate value for MnO₄⁻ concentration.

Contact Us

If you have any questions or comments relating to this experiment, please contact us:

Outreach
College of Science
University of Canterbury
Private Bag 4800
Christchurch
New Zealand

Phone: +64 3 364 2178

Fax: +64 3 364 2490

Email: outreach@canterbury.ac.nz

www.outreach.canterbury.ac.nz