

THIRD EDITION
**FUNDAMENTALS
OF ANALYTICAL
CHEMISTRY**

Douglas A. Skoog Donald M. West

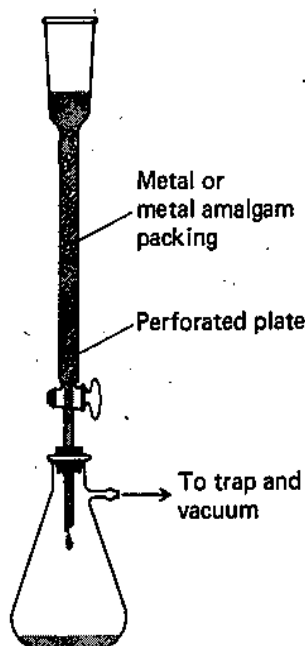


Figure 16-1 A Metal or Metal Amalgam Reductor.

Figure 16-1 illustrates a typical amalgam reductor (called a *Jones reductor*), in which amalgamated zinc acts as the reducing agent. The column is 40 to 50 cm long and has a diameter of about 2 cm. The packing is covered with liquid at all times to protect against air oxidation and the resultant formation of basic salts which tend to cause clogging.

The Jones reductor is the most widely used amalgam reductor. Table 16-1 lists its principal applications. The preparation and use of the Jones reductor is described in Chapter 31, Experiment 18.

Gaseous Reductants. Both hydrogen sulfide and sulfur dioxide are reasonably effective reducing reagents and have been used for prereduction. Excesses of these reagents can be readily eliminated by boiling the acidified solution.

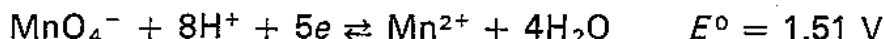
The reactions of both reagents are often slow, half an hour or more being required to complete the reduction and rid the solution of excess reagent. In addition to this time disadvantage, both gases are noxious and toxic. The employment of other reductants is much preferred.

Potassium Permanganate

Potassium permanganate, a powerful oxidant, is perhaps the most widely used of all standard oxidizing agents. The color of a permanganate solution is so intense that an indicator is not ordinarily required. The reagent is readily available at modest cost. On the other hand, the tendency of permanganate to oxidize chloride ion is a disadvantage because hydrochloric acid is such a useful solvent. The multiplicity of possible reaction products can, at times, cause uncertainty regarding the stoichiometry of a permanganate oxidation. Finally, permanganate solutions have limited stability.

REACTIONS OF PERMANGANATE ION

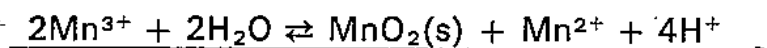
Potassium permanganate is most commonly employed with solutions that are 0.1 *N* or greater in mineral acid. Under these conditions, the product is manganese(II) ion:



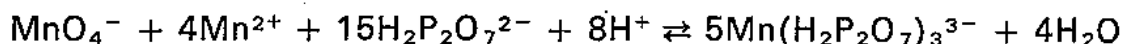
Although the mechanisms involved in the formation of manganese(II) are frequently complicated, the oxidation of most substances proceeds rapidly in acidic solution. Notable exceptions include the reaction with oxalic acid which requires elevated temperatures and with arsenic(III) oxide for which a catalyst is needed.

In solutions that are weakly acidic (above pH 4), neutral, or weakly alkaline, permanganate usually undergoes a three-electron reduction, a brown precipitate of manganese dioxide, MnO_2 , being formed. Titrations of certain species with permanganate can be carried out to advantage under these conditions. For example, cyanide is oxidized to cyanate; sulfide, sulfite, and thiosulfate are converted to sulfate; manganese(II) is oxidized to manganese dioxide; and hydrazine is oxidized to nitrogen.

Solutions of manganese(III) are not stable owing to the disproportionation reaction



However, manganese(III) ion forms several complexes that are sufficiently stable to permit existence of the +3 state in aqueous solution. Lingane has made use of this property to titrate manganese(II) with permanganate in highly concentrated solutions of pyrophosphate ion²; the reaction may be expressed as



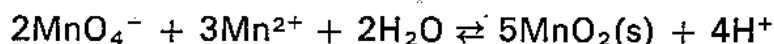
The titration is carried out in a pH range between 4 and 7.

In solutions that are greater than 1 *N* in sodium hydroxide, permanganate ion undergoes a one-electron reduction to manganate ion, MnO_4^{2-} . Alkaline oxidations with permanganate have proved useful for the determination of certain organic compounds.

END POINT

One of the most obvious properties of potassium permanganate is its intense purple color, which commonly serves as the indicator for titrations. As little as 0.01 to 0.02 ml of a 0.02-*F* (0.1-*N*) solution is sufficient to impart a perceptible color to 100 ml of water. For very dilute permanganate solutions, diphenylamine sulfonic acid or the orthophenanthroline-iron(II) complex (Chapter 15) will give a sharper end point.

△ The permanganate end point is not permanent and gradually fades. Decolorization results from the reaction of the excess permanganate with the relatively large concentration of manganese(II) ion that is present at the end point.



² J. J. Lingane and R. Karplus, *Ind. Eng. Chem., Anal. Ed.*, **18**, 191 (1946).

The equilibrium constant for this reaction, which is readily calculated from the standard potentials for the two half-reactions, has a numerical value of about 10^{47} . Thus, even in a highly acidic solution, the concentration of permanganate in equilibrium with manganese(II) ion is small. Fortunately, the rate at which this equilibrium is attained is slow, with the result that the end point fades only gradually.

The intense color of a permanganate solution complicates the measurement of reagent volumes in a buret. It is frequently more practical to use the surface of the liquid rather than the bottom of the meniscus as the point of reference.

STABILITY OF PERMANGANATE SOLUTIONS

Aqueous solutions of permanganate are not completely stable because of the tendency of that ion to oxidize water. The process may be depicted by the equation



Although the constant for this equilibrium indicates that the products are favored in neutral solution, the reaction is so slow that a permanganate solution that has been properly prepared is moderately stable. The decomposition has been shown to be catalyzed by light, heat, acids, bases, manganese(II) ion, and manganese dioxide. In order to obtain a stable reagent for analysis, it is necessary to minimize the influence of these effects.

The decomposition of permanganate solutions is greatly accelerated in the presence of manganese dioxide. Since it is also a product of the decomposition, this solid has an *autocatalytic* effect upon the process.

Photochemical catalysis of the decomposition is often observed when a permanganate solution is allowed to stand in a buret for an extended period. Manganese dioxide forms as a brown stain and serves to show that the concentration of the reagent has undergone change.

In general, the heating of acidic solutions containing an excess of permanganate should be avoided because of the decomposition error that cannot adequately be compensated for with a blank. At the same time, it is perfectly acceptable to titrate hot, acidic solutions of reductants directly with the reagent, since at no time during the titration is the oxidant concentration large enough to cause a measurable uncertainty.

PREPARATION, STANDARDIZATION, AND STORAGE OF PERMANGANATE SOLUTIONS

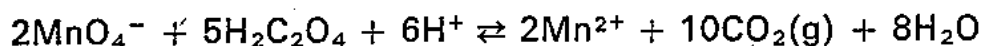
Solid potassium permanganate, which is ordinarily used for the preparation of permanganate solutions, is inevitably contaminated with manganese dioxide to some extent; as a result, preparation of standard permanganate solutions directly by weight is not possible.

A permanganate solution possessing reasonable stability can be obtained provided a number of precautions are observed. Perhaps the most important variable affecting stability is the catalytic influence of manganese dioxide. This

contaminant occurs in the starting material and is also produced when permanganate oxidizes organic matter in the water used to prepare the solution. Removal of manganese dioxide by filtration markedly enhances the stability of standard permanganate solutions. Sufficient time must be allowed for complete oxidation of contaminants in the water before filtration; the solution may be boiled to hasten the oxidation. Paper cannot be used for the filtration since it reacts with the permanganate to form the undesirable dioxide.

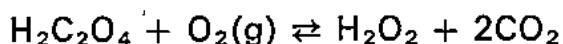
Standardized solutions should be stored in the dark. If any solid is detected in the solution, filtration and restandardization are necessary. In any event, restandardization every one to two weeks is a good precautionary measure.

Standardization against Sodium Oxalate. In acidic solution, permanganate oxidizes oxalic acid to carbon dioxide and water.



This reaction is complex and proceeds slowly at room temperature; even at elevated temperatures it is not rapid unless catalyzed by manganese(II) ion. Thus, several seconds are required to decolorize a hot oxalic acid solution at the outset of a permanganate titration. Later, when the concentration of manganese(II) ion has become appreciable, decolorization becomes rapid as a consequence of the autocatalysis.

The stoichiometry of the reaction between permanganate ion and oxalic acid has been investigated in great detail by McBride³ and more recently by Fowler and Bright.⁴ The former devised a procedure in which the oxalic acid is titrated slowly at a temperature between 60 and 90°C until the faint pink color of the permanganate persists. Fowler and Bright have demonstrated, however, that this titration consumes 0.1 to 0.4% too little permanganate, due perhaps to air oxidation of a small part of the oxalic acid



In the hot solution, the peroxide is postulated to decompose spontaneously to oxygen and water.

Fowler and Bright devised a scheme for standardization in which 90 to 95% of the required permanganate is added rapidly to the cool oxalic acid solution. After all of this reagent has reacted, the solution is heated to 55 to 60°C and titrated as before. While it minimizes the air oxidation of oxalic acid and gives data that appear to be in exact accord with the theoretical stoichiometry, this method suffers from the disadvantage of requiring a knowledge of the approximate normality of the permanganate solution to make the proper initial addition of the reagent. In this respect, the Fowler-Bright procedure is not as convenient as the McBride method.

For many purposes, the method of McBride will give perfectly adequate data (usually 0.2 to 0.3% too high). If a more accurate standardization is required, it is convenient to perform one titration by this procedure to obtain the

³ R. S. McBride, *J. Amer. Chem. Soc.*, **34**, 393 (1912).

⁴ R. M. Fowler and H. A. Bright, *J. Res. Nat. Bur. Stand.*, **15**, 493 (1935).

approximate normality of the solution. Then a pair of titrations employing the Fowler and Bright method can be made. Directions for both procedures are found in Chapter 31, Experiment 19.

Other Primary Standards. Several other primary standards can be employed to establish the normality of permanganate solutions. These include arsenic(III) oxide, potassium iodide, and metallic iron. Detailed procedures for the use of these standards are described by Kolthoff and Belcher.⁵

APPLICATIONS OF PERMANGANATE TITRATIONS TO ACIDIC SOLUTIONS

Table 16-2 indicates the multiplicity of analyses that make use of standard permanganate solutions in acidic media. Most of these reactions are rapid enough for direct titrations. Two typical applications, the determination of iron and the determination of calcium, are discussed in the paragraphs that follow.

Determination of Iron in an Ore. The common iron ores are hematite (Fe_2O_3), magnetite (Fe_3O_4), and limonite ($3\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$). Volumetric methods for analysis of iron samples containing these substances consist of three steps: (1) solution of the sample, (2) reduction of the iron to the divalent state, and (3) titration with a standard oxidant.

Iron ores are often completely decomposed in concentrated hydrochloric acid. The rate of attack by this reagent is increased by the presence of a small amount of tin(II) chloride, which probably acts by reducing slightly soluble iron(III) oxides on the surface of the particles to more soluble iron(II) species. Because iron(III) tends to form stable chloride complexes, hydrochloric acid is a much more efficient solvent than either sulfuric or nitric acid.

Most iron ores contain silicates that, in some instances, are not decomposed by treatment with hydrochloric acid. Where decomposition is complete, the white residue of hydrated silica that remains behind in no way interferes with the analysis. Incomplete decomposition is indicated by a dark residue remaining after prolonged treatment with the acid. Since this solid residue may contain iron, it must be broken down by more drastic treatment. The usual procedure entails filtration and ignition of the solid, followed by fusion with sodium carbonate. This process converts the cationic components of the residue into carbonates, which can then be dissolved in acid and combined with the solution containing the bulk of the sample.

Part or all of the iron will exist in the trivalent state after solution is complete. Prereduction of the sample must, therefore, precede titration with the oxidant. Any of the methods described earlier may be used—the Jones reductor, for example. Zinc amalgam, however, will also reduce other elements commonly associated with iron, including titanium, niobium, vanadium, chromium, uranium, tungsten, molybdenum, and arsenic. In their lower oxidation states,

⁵ I. M. Kolthoff and R. Belcher. *Volumetric Analysis*, vol. 3, pp. 41–59. New York: Interscience Publishers, Inc., 1957.

1. 16 / APPLICATIONS OF OXIDATION-REDUCTION TITRATIONS

4

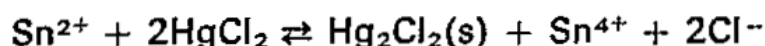
TABLE 16-2 Applications of Potassium Permanganate in Acidic Solution

Substance Sought	Half-Reaction	Condition
I	$I^- + HCN \rightleftharpoons ICN + H^+ + 2e$	In 0.1-F HCN with ferroin indicator
Br	$2Br^- \rightleftharpoons Br_2 + 2e$	Boiling H_2SO_4 solution
As	$H_3AsO_3 + H_2O \rightleftharpoons H_3AsO_4 + 2H^+ + 2e$	KI, or ICl catalyst in HCl solution
Sb	$H_3SbO_3 + H_2O \rightleftharpoons H_3SbO_4 + 2H^+ + 2e$	HCl solution
Sn	$Sn^{2+} \rightleftharpoons Sn^{4+} + 2e$	Prereduction with Zn
H_2O_2	$H_2O_2 \rightleftharpoons O_2(g) + 2H^+ + 2e$	Prereduction with $SnCl_2$ or with Jones or Walden reductor ¹
Fe	$Fe^{2+} \rightleftharpoons Fe^{3+} + e$	
$Fe(CN)_6^{4-}$	$Fe(CN)_6^{4-} \rightleftharpoons Fe(CN)_6^{3-} + e$	Prereduction with Bi amalgam or SO_2
V	$VO^{2+} + 3H_2O \rightleftharpoons V(OH)_4^+ + 2H^+ + e$	
Mo	$Mo^{3+} + 4H_2O \rightleftharpoons MoO_4^{2-} + 8H^+ + 3e$	Prereduction with Jones reductor
W	$W^{3+} + 4H_2O \rightleftharpoons WO_4^{2-} + 8H^+ + 3e$	Prereduction with Zn or Cd
U	$U^{4+} + 2H_2O \rightleftharpoons UO_2^{2+} + 4H^+ + 2e$	Prereduction with Jones reductor
Ti	$Ti^{3+} + H_2O \rightleftharpoons TiO^{2+} + 2H^+ + e$	Prereduction with Jones reductor
Nb	$Nb^{3+} + H_2O \rightleftharpoons NbO^{3+} + 2H^+ + 2e$	Prereduction with Jones reductor
$H_2C_2O_4$ Mg, Ca, Zn, Co, La, Th, Ba, Sr, Ce, Ag, Pb	$H_2C_2O_4 \rightleftharpoons 2CO_2 + 2H^+ + 2e$ $H_2C_2O_4 \rightleftharpoons 2CO_2 + 2H^+ + 2e$	Sparingly soluble metal oxalates filtered, washed, and dissolved in acid; liberated oxalic acid titrated
HNO_2	$HNO_2 + H_2O \rightleftharpoons NO_3^- + 3H^+ + 2e$	
K	$K_2NaCo(NO_2)_6 + 6H_2O \rightleftharpoons Co^{2+} + 6NO_3^- + 12H^+ + 2K^+ + Na^+ + 11e$	15-min reaction time; excess $KMnO_4$ back-titrated
Na	$U^{4+} + 2H_2O \rightleftharpoons UO_2^{2+} + 4H^+ + 2e$	Precipitated as $NaZn(UO_2)_3(OAc)_9$; filtered, washed, dissolved; U determined as above

these too react with permanganate; their presence, if undetected, will cause high results for iron.

The Walden reductor has the advantage of being inert with respect to titanium and trivalent chromium, both of which are likely to occur in significant amounts. Vanadium continues to interfere.

Perhaps the most satisfactory of all prereductants for iron is tin(II) chloride. The only other common elements reduced by this reagent are vanadium, copper, molybdenum, tungsten, and arsenic. The excess reducing agent is removed from solution by the addition of mercury(II) chloride:



The slightly soluble mercury(I) chloride produced will not consume permanganate, nor will the excess mercury(II) chloride reoxidize divalent iron. Care must be exerted, however, to prevent occurrence of the alternative reaction,



Metallic mercury reacts with permanganate and causes a high result for iron. Formation of mercury is favored by an appreciable excess of tin(II); it is prevented by careful control of this excess and the rapid addition of excess mercury(II) chloride. A proper reduction is indicated by the appearance of a slight, white precipitate after addition of this reagent. A gray precipitate indicates the presence of mercury; the total absence of precipitate indicates that an insufficient amount of tin(II) chloride was added. In either event, the sample must be discarded.

The reaction of iron(II) with permanganate proceeds smoothly and rapidly to completion. In the presence of hydrochloric acid, however, high results are obtained owing to the oxidation of chloride ion by permanganate. This reaction, which normally does not proceed rapidly enough to cause serious errors, is induced by the presence of divalent iron. Its effects are avoided by preliminary removal of chloride by evaporation with sulfuric acid or by use of the *Zimmermann-Reinhardt reagent*. The latter is a solution of manganese(II) in fairly concentrated sulfuric and phosphoric acids. Manganese(II) inhibits the oxidation of chloride ion, while phosphoric acid forms complexes with the iron(III) produced in the titration and prevents the intense yellow color of iron(III) chloride complexes from interfering with the end point.

Determination of Calcium. Calcium is conveniently precipitated as calcium oxalate. After being filtered and washed, the precipitate is redissolved in dilute acid; the liberated oxalic acid is then titrated with a standard solution of permanganate or some other oxidizing agent. This method is applicable to samples that contain magnesium and the alkali metals. Most other cations must be absent, however, as they either precipitate or coprecipitate as oxalates and cause positive errors in the analysis.

To obtain satisfactory results from this procedure, the mole ratio of calcium to oxalate must be exactly 1 in the precipitate and thus in the solution at the time of titration. Several precautions are necessary to assure this condition.