RADIOCHEMISTRY
OF MANGANESE

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Radiochemistry of Manganese

by R. P. Schuman

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Bebek P.K. 8 Istanbul, Turkey

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Radiochemistry of Manganese

by R. P. Schuman

Department of Chemistry
Robert College
Bebek P.K. 8 Istanbul, Turkey

revised from the original text of G. W. LEDDICOTTE

I. GENERAL REVIEWS OF THE CHEMISTRY OF MANGANESE.

A. Inorganic Chemistry


B. Analytical Chemistry


C. Radiochemistry


II  NUCLEAR PROPERTIES OF MANGANESE ISOTOPES

Natural manganese consists of one stable isotope, $^{55}\text{Mn}$, atomic number 25. This isotope is in the region of maximum nuclear stability; its binding energy is 8.76 MeV per nucleon and its atomic weight is 54.938054 \( ^{(1)} \) based on $^{12}\text{C} = 12.000000$. The nuclear spin of $^{55}\text{Mn}$ is 5/2-. Very small but detectable amounts of radioactive $^{52}\text{Mn}$ and $^{54}\text{Mn}$, produced by cosmic ray induced spallation reactions, are found in meteorites \( ^{(2)} \). The relative abundances of these radioactive manganese isotopes have been used to determine both the age of meteorites and the time since they fell to earth. The determination of these isotopes is a challenging radiochemical problem \( ^{(3)} \).

Manganese isotopes from mass number 50 to 58 have been produced; their properties and methods of production are summarized in Table II.1 \( ^{(4)} \). The decay schemes of these manganese isotopes, as given in the Table of Isotopes \( ^{(4)} \), are given in Figure II.1. The most useful isotope for tracer studies is the 303 day $^{54}\text{Mn}$ which decays by electron capture and emits a 100% abundant 835 keV gamma ray. The major isotope of interest in activation analysis and flux monitoring is 2.576 hour $^{56}\text{Mn}$ which decays by beta emission and emits abundant 847, 1811, and 2110 keV gamma rays. The half life and characteristic gamma rays make $^{56}\text{Mn}$ an ideal isotope for activation analysis. Because $^{53}\text{Mn}$ decays solely by electron capture (emitting only Cr X-rays) and has a very long half life, it is extremely difficult to count and can be more accurately determined by activation to $^{51}\text{Mn} \( ^{(5)} \).

Neutron capture cross sections have been measured as a function of neutron energy for $^{55}\text{Mn} \( ^{(6)} \). The thermal (0.025 eV) cross section of $^{55}\text{Mn}$ is 13.3 barns and the resonance integral is 14.2 barns \( ^{(7)} \). A capture cross section of 170 barns has been determined for $^{53}\text{Mn} \( ^{(8)} \) using typical reactor neutrons. Fast neutrons will produce 303 day $^{54}\text{Mn}$ by an n,2n reaction on $^{55}\text{Mn}$, and the reaction can be used for low sensitivity activation analysis or as a fast neutron flux monitor if the sample is free of iron. Other threshold reactions, n,p giving 3.5 min. $^{55}\text{Cr}$, and n,α giving 3.8 min. $^{52}\text{V}$, are possible with fast
<table>
<thead>
<tr>
<th>Nuclide</th>
<th>Half-Life</th>
<th>Type of Decay</th>
<th>Gamma Rays</th>
<th>How Made</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{49}$Mn</td>
<td>0.4 sec.</td>
<td>$\beta^+$</td>
<td>6.61 MeV</td>
<td>$0.511 \gamma^2$</td>
<td>200%</td>
</tr>
<tr>
<td>$^{50}$Mn</td>
<td>0.286 sec.</td>
<td>$\beta^+$</td>
<td>0.511 MeV</td>
<td>198%</td>
<td>0.66</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.783</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.111</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.28</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.45</td>
<td>75</td>
<td></td>
</tr>
<tr>
<td>$^{51}$Mn</td>
<td>4.52 min.</td>
<td>$\beta^+$</td>
<td>2.17 MeV</td>
<td>$0.511 \gamma^2$</td>
<td>194%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.56</td>
<td>2.03</td>
<td></td>
</tr>
<tr>
<td>$^{52}$Mn</td>
<td>5.60 day</td>
<td>$\beta^+$</td>
<td>0.575 MeV</td>
<td>$0.511 \gamma^2$</td>
<td>67%</td>
</tr>
<tr>
<td></td>
<td>(3%)</td>
<td></td>
<td>0.711</td>
<td>82</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(6%)</td>
<td></td>
<td>0.711</td>
<td>82</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.434</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>$^{52}$Mn</td>
<td>21.1 min.</td>
<td>$\beta^+$</td>
<td>1.63 MeV</td>
<td>$0.511 \gamma^2$</td>
<td>2%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.134</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>$^{53}$Mn</td>
<td>1.9x10⁶ yr.</td>
<td>E.C.</td>
<td>Cr X-rays</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^{54}$Mn</td>
<td>303 day</td>
<td>E.C.</td>
<td>Cr X-rays</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.635</td>
<td>100%</td>
<td></td>
</tr>
<tr>
<td>$^{55}$Mn</td>
<td>stable</td>
<td>100% abundant</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^{56}$Mn</td>
<td>2.576 hr.</td>
<td>$\beta^-$</td>
<td>2.85 MeV</td>
<td>$0.887 \gamma^1$</td>
<td>99%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.811</td>
<td>29</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2.110</td>
<td>35</td>
<td></td>
</tr>
<tr>
<td>$^{57}$Mn</td>
<td>1.7 min.</td>
<td>$\beta^-$</td>
<td>2.55 MeV</td>
<td>Fe X-rays</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.031</td>
<td>Conv.</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.122</td>
<td>Strong</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.336</td>
<td>Strong</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.22</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.353</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.692</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^{58}$Mn</td>
<td>1.1 min.</td>
<td>$\beta^-$</td>
<td>0.36, 0.41</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.52, 0.57</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.83, 1.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.25, 1.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.6, 2.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2.8</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
FIGURE II.1
Decay Schemes of Manganese Isotopes

- 50Mn
- 51Mn

- 2 min.
- 0.286 s

- 25% β+
- 74% β+
- 2.5 MeV
- 7.631 MeV
- Q.E.C.

- 5% 7/2-
- 3% 5/2-
- 97% 3/2-
- 3.19 MeV

- 0.783 2+
- 1.90 1+
- 3.35
- 3.18
- 3.84

- 0 0+ 52Cr 52Cr
\( Q_{\beta^-} = 2.7 \text{ MeV} \)

\[
\begin{array}{c}
(5/2-) \\
57_{\text{Mn}}^{25} \\
1.7 \text{ min.} \\
57_{\text{Fe}}^{26}
\end{array}
\]

\[
\begin{array}{c}
5/2^- 0.7064 \\
3/2^- 0.3668 \\
5/2^- 0.13632 \\
3/2^- 0.01439 \\
1/2^- 0
\end{array}
\]
neutrons. Charged particle and photonuclear reactions, $^{55}$Mn(p,n)$^{55}$Fe (2.6 yr.), $^{55}$Mn(p,pn)$^{54}$Mn (303 d.), $^{55}$Mn(d,p)$^{56}$Mn (2.576 hr.), and $^{55}$Mn(n,n)$^{55}$Mn (303 d.), are also of possible interest for activation analysis and producing tracers.

Manganese can be determined with great sensitivity and very easily by thermal neutron activation analysis (9). With reactors as the source of neutrons, the sensitivity of the analysis is of the order of $10^{-12}$ grams. The relatively high cross section of $^{55}$Mn, coupled with the ideal half life and gamma spectrum of the $^{56}$Mn capture product combine to make activation analysis particularly attractive. A large amount of the radiochemical work on manganese has been in conjunction with activation analysis. With the development of high resolution lithium drifted germanium gamma spectrometers, manganese can be determined by activation analysis with either no chemical separation or a simple group separation (10). If highly thermalized neutrons are used, there is no interference in the analysis, but if typical reactor or radioactive source neutrons are used, iron will cause a serious interference due to the $^{56}$Fe(n,p)$^{56}$Mn reaction; cobalt can also interfere due to the $^{59}$Co(n,a)$^{56}$Mn reaction. By irradiating samples both in highly moderated and hard neutron fluxes, the interferences due to iron and cobalt can be determined and corrections made (11). If the neutron irradiation is carried over a long time, manganese activity can be produced from chromium by the reaction sequence $^{51}$Cr(n,$\gamma$)$^{55}$Cr(β$^-$)$^{55}$Mn(n,$\gamma$)$^{56}$Mn. Various portable neutron sources have been used for manganese activation analysis; $^{252}$Cf is a particularly attractive source (12). Fast, 1 MeV, neutrons have also been used (13).

A number of chemical separation procedures used in activation analysis are given in section VI. Because of the increased use of high resolution Ge(Li) gamma spectrometers in activation analysis, the interest in manganese radiochemical separations is decreasing. Activation analysis of manganese is extensively used in archaeology (14), agriculture (15), geology (16), and other fields (17), and is especially valuable when the samples must not be destroyed.
Manganese has been extensively used as a neutron flux monitor. The reaction, $^{55}\text{Mn}(n,\gamma)^{56}\text{Mn}$, has been used as a neutron flux monitor from almost the time of discovery of the neutron. For short irradiations, small samples of a dilute alloy of Mn in Al are particularly useful flux monitors since they minimize the radiation dose upon discharge from the reactor and because of the small amount of manganese there is no self shielding of neutrons. Since $2.576 \text{ hour } ^{56}\text{Mn}$ decays to stable $^{56}\text{Fe}$, and since neutron capture in $^{56}\text{Fe}$ and $^{57}\text{Fe}$ both lead to stable iron isotopes, manganese can be used as a total integral neutron flux monitor for very long irradiations in high fluxes; the total integral flux being determined by the fraction of manganese converted to iron as determined by colorimetric analysis for iron and manganese.$^{(7a)}$

A large bath of MnSO$_4$ solution is commonly used to obtain the absolute intensity of a neutron beam or source.$^{(18)}$. The hydrogen in the solution moderates the neutrons which are then largely captured by $^{55}\text{Mn}$. A very sensitive neutron monitor for weak sources and beams is a bath of KMnO$_4$ solution. The $^{56}\text{Mn}$ neutron capture product is concentrated by a Szilard Chalmers reaction in the MnO$_2$ produced by the decomposition of the MnO$_4^-$, and so, by filtering the irradiated solution, most of the activity can be concentrated on a small filter and so counted with high sensitivity.$^{(19)}$.

III REVIEW OF THE CHEMISTRY OF MANGANESE

1. Introduction

Manganese compounds have been known since prehistoric times. From the beginning, the glass industry has used manganese dioxide to remove the green tint in glass due to ferrous silicates, and in larger amounts as a color producer. Manganese metal was first produced by J. G. Gahn in 1774 by the reduction of manganese oxide by oil and charcoal.$^{(20)}$. Manganese today is used extensively in industry, especially as an alloying and deoxidizing agent for steel.

2. Occurrence in Nature

Manganese is the eleventh most abundant element in the earth's crust,
being more abundant than such common elements as sulfur, copper, carbon, and
zinc. It comprises about 0.1% of the lithosphere\(^{(21)}\). Manganese is present to
the extent of about one part per million in average river water and about one to
ten parts per billion in ocean water\(^{(22)}\). The manganese brought into the ocean
is slowly and nearly completely precipitated; the manganese nodules in the ocean
being formed in this manner. Manganese is an essential (usually at the trace
level) constituent of living tissue, both plant and animal. Its abundance
varies from a few parts per billion to over one per cent; it is usually more
abundant in plant than animal tissue. Manganese deficiency is a cause of
disease in plants. Activation analysis has been an important tool in the
determination of manganese in biological materials.

Manganese is one of the more abundant elements in meteorites where it has
a somewhat greater abundance than in the earth’s crust. Meteorites also contain
detectable amounts of \(^{53}\text{Mn}\) and \(^{54}\text{Mn}\) formed by cosmic ray bombardment, see
section II\(^{(23)}\). Manganese is quite abundant in the sun and other stars as
shown by spectroscopy\(^{(24)}\). Its abundance in the universe is estimated as \(6850\)
atoms per million atoms \(\text{Si}\)\(^{(25)}\). Its relatively large abundance is expected
since \(^{55}\text{Mn}\) is one of the nuclides in the iron region abundance peak\(^{(26)}\).

Manganese does not occur as the free element in nature, but is very wide-
spread in compounds and is an essential constituent of about \(1\%\) minerals and a
minor constituent of many more\(^{(27)}\). A few of the more important minerals are
listed in Table III.1. Although manganese minerals are widespread, high grade
ores are found in only a few localities, especially the U.S.S.R. (producing
nearly half of the world’s supply), Union of South Africa, Gabon, India, Brazil,
and China\(^{(28)}\). Low grade ores are widely distributed.

3. **Industrial Chemistry of Manganese\(^{(29)}\)**

Activation analysis and tracer studies are widely used in industry, so it
will be useful to briefly outline the industrial uses of manganese. About 97% of
the manganese consumption is for metallurgical purposes: plain carbon steel,
high manganese steels, ferromanganese, manganese in pig iron, spiegeleisen,
TABLE III.1
IMPORTANT MANGANESE MINERALS (27)

<table>
<thead>
<tr>
<th>Name</th>
<th>Chemical Composition</th>
<th>Color</th>
<th>Use</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alabandite</td>
<td>MnS</td>
<td>iron-black</td>
<td>zinc ore</td>
</tr>
<tr>
<td>Franklinite</td>
<td>(Fe, Zn, Mn)Fe₂O₄</td>
<td>iron-black</td>
<td></td>
</tr>
<tr>
<td>Manganosite</td>
<td>MnO</td>
<td>emerald-green</td>
<td></td>
</tr>
<tr>
<td>Hausmannite</td>
<td>Mn₃O₄</td>
<td>brown-black</td>
<td>manganese ore</td>
</tr>
<tr>
<td>Braunite</td>
<td>3MnO₂·MnSiO₃</td>
<td>brown-black</td>
<td>manganese ore</td>
</tr>
<tr>
<td>Pollanite</td>
<td>MnO₂</td>
<td>steel-gray</td>
<td>manganese ore</td>
</tr>
<tr>
<td>Pyrolusite</td>
<td>MnO₂ (+ trace H₂O)</td>
<td>iron-black</td>
<td>manganese ore</td>
</tr>
<tr>
<td>Manganite</td>
<td>Mn(OH)₂</td>
<td>iron-black</td>
<td>manganese ore</td>
</tr>
<tr>
<td>Pyrochroite</td>
<td>Mn(OH)₂</td>
<td>white, darkens</td>
<td></td>
</tr>
<tr>
<td>Psilomelane, Wad</td>
<td>impure MnO₂·xH₂O</td>
<td>brown-black</td>
<td>manganese ore</td>
</tr>
<tr>
<td>Rhodochrosite</td>
<td>MnCO₃</td>
<td>rose-red</td>
<td>manganese ore</td>
</tr>
<tr>
<td>Rhodonite</td>
<td>Mn₈SiO₁₃</td>
<td>rose</td>
<td>manganese ore</td>
</tr>
<tr>
<td>Halvite</td>
<td>3(Mn, Fe)BaSiO₄·MnS</td>
<td>yellow</td>
<td>ornamental stone</td>
</tr>
<tr>
<td>Spessartite</td>
<td>Mn₃Al₂(SiO₄)₃</td>
<td>dark-red</td>
<td>semiprecious gem</td>
</tr>
<tr>
<td>Tephroite</td>
<td>Mn₃SiO₄</td>
<td>flesh-red</td>
<td></td>
</tr>
<tr>
<td>Piedmontite</td>
<td>HCa₂(Al, Mn)₃Si₃O₁₀</td>
<td>red-brown</td>
<td></td>
</tr>
<tr>
<td>Bementite</td>
<td>H₁₀Mn₆Si₇O₂₇</td>
<td>gray-yellow</td>
<td>manganese ore</td>
</tr>
<tr>
<td>Inosite</td>
<td>H₂(Mn₂Ca)₆Si₈O₁₉·3H₂O</td>
<td>rose-red</td>
<td></td>
</tr>
<tr>
<td>Columbite-Tantalite</td>
<td>(Fe, Mn)(Ta, Nb)₂O₆</td>
<td>iron-black</td>
<td>Ta and Nb ore</td>
</tr>
<tr>
<td>Lithiophilite</td>
<td>Li(Mn, Fe)PO₄</td>
<td>salmon-pink</td>
<td></td>
</tr>
<tr>
<td>Triplite</td>
<td>(Fe, Mn)F(Fe, Mn)PO₄</td>
<td>brown</td>
<td></td>
</tr>
<tr>
<td>Hübnerite</td>
<td>MnWO₄</td>
<td>brown-black</td>
<td>tungsten ore</td>
</tr>
<tr>
<td>Pyrophanite</td>
<td>MnTiO₃</td>
<td>deep red</td>
<td></td>
</tr>
</tbody>
</table>
silico-manganese, manganese in copper, aluminum, nickel, and magnesium. The remaining 3% is used in dry cells, glass making, ceramics, agriculture, and other chemical purposes (28).

The major ores of manganese are listed, along with some other manganese minerals, in Table III.1. The manganese used in iron and steel manufacture is usually in the form of a high manganese-iron alloy (ferromanganese) with up to 80% Mn, or a lower manganese-iron alloy (spiegeleisen) with 15 to 20% Mn. The alloys are produced in blast furnaces (reduction by coke). Where low carbon alloy is needed, a silicon-manganese containing about 70% Mn, 20% Si, 5% Fe, and less than 1% C is produced in an electric furnace. Fairly pure manganese metal, > 97%, is produced by reduction of the oxide with silicon or aluminum, or by electrolysis of an aqueous solution of manganese salts. The electrolytic manganese is the purest commercial product with up to 99.9% Mn excluding occluded hydrogen. Electrolytic manganese is being increasingly used for the production of high grade alloys.

Manganese is an essential constituent of many copper and bronze alloys, in most commercial aluminum alloys, in certain nickel alloys, and in almost all steels. Typical low carbon steel contains about 0.2% Mn, stainless steels up to 2.5%, and some alloys up to 12%. However, for nuclear purposes steels with a minimum of manganese content are required because of the high manganese neutron capture cross section. The major functions of manganese in steel are: to combine with the sulfur to form insoluble MnS which, unlike FeS, does not cause the steel to be brittle, to deoxidise the steel, and at times to combine with carbon. Manganese, since it is much more reactive than iron, reduces the FeS, FeO, FeSiO₃, and Fe₃C in the steel and gives the corresponding manganese compounds.

Manganese compounds are important in nonmetallic products. Methyl cyclopentadienyl manganese tricarbonyl is a gasoline additive claimed to be greatly superior to tetraethyl lead (30); the substitution of nearly nontoxic manganese for lead would greatly reduce the pollution due to automobile exhaust.
Manganese at about the 0.2% level is an activator in electroluminescent phosphors; Mn and Cu in ZnS give a yellow color, Mn in zinc silicate gives a green color. Manganese is still important in the glass industry, it is important in paints and varnishes, sometimes as a beneficial additive (drying agent), sometimes as an objectionable impurity. Manganese dioxide, which is a fairly good conductor of electricity, is an important constituent of dry cells and is also used as nonconsumable anodes for electrolysis. Manganese oxides are used as pigments. Manganese in small amounts is beneficial in fertilizers.

3. Chemical Properties of Manganese

Manganese is an element of the first (3d) transition series. The electronic configuration of the normal atomic state is 1s² 2s² 2p⁶ 3s² 3p⁶ 3d⁵ 4s², the normal state being ⁵/₂. The odd number of electrons in the 3d shell results in an electronic paramagnetism, and many studies of the paramagnetic resonance of manganese have been made. The manganese resonance frequency is split into six lines, as expected, because of its ⁵/₂ nuclear spin, and the intensity of the lines have been used for analysis.

Manganese has many optical emission lines of interest in its analysis by emission spectroscopy, flame photometry, and atomic absorption. An energy level diagram of manganese has been published. The ionisation potential of manganese is 7.41 eV for the first and 15.70 eV for the second electron.

Chemically manganese is rather similar to iron and its ions have about the same radii as the corresponding iron ions. Manganese(II) will usually isomorphously replace Fe(II) and often Mg(II). Manganese metal is considerably more reactive than iron. Trivalent manganese, although forming compounds isomorphous with those of Fe(III), is a strong oxidising agent and is, unless complexed or insoluble, unstable disproportionating into Mn(II) and MnO₂. In its most oxidized form, Mn(VII), manganese resembles chlorine in perchlorates, and Mn(VI), although disproportionating except in strongly alkaline solutions, resembles chromates(VI) and ferrates(VI).

Manganese exhibits all the valences from zero to seven. Under normal
conditions only the +2, +4, and +7 are of importance. In acid solution, the Mn(II) compounds are by far the most stable, although very strong oxidizing agents such as KBrO₃ and KClO₃ will oxidize Mn⁺⁺ to MnO₂, and other strong oxidizing agents like H₂O₂ and Ag⁺⁺ will oxidize it to MnO₄⁻⁻. In basic solutions Mn(II) is much more easily oxidized, and even such weak oxidizing agents as Fe(CN)₆³⁻ and H₂O₂ will oxidize Mn(II) to MnO₂. In basic solutions, Mn(OH)₂ is oxidized by air first to MnOOH and ultimately to hydrated MnO₂. The standard redox potentials for manganese, both in acid and basic solution, are given in Table III.2, and shown in Figure III.1.

### TABLE III.2

<table>
<thead>
<tr>
<th>Half-cell Reaction</th>
<th>Oxidation States</th>
<th>E° volts</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>In acid solution, H⁺ unit activity</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn⁺⁺ + 2e⁻ - Mn⁺</td>
<td>2 - 0</td>
<td>-1.20</td>
</tr>
<tr>
<td>Mn³⁺ + e⁻ - Mn²⁺</td>
<td>3 - 2</td>
<td>-1.5</td>
</tr>
<tr>
<td>Mn(CN)₆³⁻ + e⁻ - Mn(CN)₁⁻</td>
<td>3 - 2</td>
<td>-0.24</td>
</tr>
<tr>
<td>MnO₂ + H₂O⁺ + 2e⁻ - Mn⁺⁺ + 2H₂O</td>
<td>4 - 2</td>
<td>1.239</td>
</tr>
<tr>
<td>MnO₂⁻ + 8H⁺ + 5e⁻ - Mn⁺⁺ + 4H₂O</td>
<td>7 - 2</td>
<td>1.51</td>
</tr>
<tr>
<td>MnO₂⁻ + H₂O⁺ + e⁻ - Mn³⁺ + 2H₂O</td>
<td>4 - 3</td>
<td>1.0</td>
</tr>
<tr>
<td>MnO₄⁻ + H₂O⁺ + 2e⁻ - MnO₂ + 2H₂O</td>
<td>6 - 4</td>
<td>2.26</td>
</tr>
<tr>
<td>MnO₄²⁻ + H₂O⁺ + 3e⁻ - MnO₂ + 2H₂O</td>
<td>7 - 4</td>
<td>1.69</td>
</tr>
<tr>
<td>MnO₄²⁻ + e⁻ - MnO₄⁻⁻</td>
<td>7 - 6</td>
<td>0.558</td>
</tr>
<tr>
<td><strong>In basic solution, OH⁻ unit activity</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn(OH)₂ + 2e⁻ - Mn⁺ + 2OH⁻</td>
<td>2 - 0</td>
<td>-1.58</td>
</tr>
<tr>
<td>Mn(OH)₃ + e⁻ - Mn(OH)₂ + OH⁻</td>
<td>3 - 2</td>
<td>-0.2</td>
</tr>
<tr>
<td>MnO₂ + 2H₂O + 2e⁻ - Mn(OH)₂ + 2OH⁻</td>
<td>4 - 2</td>
<td>-0.93</td>
</tr>
<tr>
<td>MnO₄⁻ + 4H₂O + 5e⁻ - Mn(OH)₂ + 6OH⁻</td>
<td>7 - 2</td>
<td>0.34</td>
</tr>
<tr>
<td>MnO₂⁻ + 2H₂O + e⁻ - Mn(OH)₃ + OH⁻</td>
<td>4 - 3</td>
<td>-0.1</td>
</tr>
<tr>
<td>MnO₄²⁻ + 2H₂O + e⁻ - MnO₂ + 4OH⁻</td>
<td>5 - 4</td>
<td>-0.9</td>
</tr>
<tr>
<td>MnO₄⁻ + 2H₂O + 2e⁻ - MnO₂ + 4OH⁻</td>
<td>6 - 4</td>
<td>0.603</td>
</tr>
<tr>
<td>MnO₄⁻ + 2H₂O + 3e⁻ - MnO₂ + 4OH⁻</td>
<td>7 - 4</td>
<td>0.58</td>
</tr>
<tr>
<td>MnO₄⁻ + e⁻ - MnO₃⁻⁻</td>
<td>6 - 5</td>
<td>-0.3</td>
</tr>
<tr>
<td>MnO₄⁻ + e⁻ - MnO₄⁻⁻</td>
<td>7 - 6</td>
<td>0.558</td>
</tr>
</tbody>
</table>
Acid Solution, $H^+$ unit activity

\[
\begin{align*}
Mn^* & \rightarrow 1.69 \\
Mn^+ & \rightarrow 1.52 \\
Mn^{2+} & \rightarrow 1.03 \\
MnO_2 & \rightarrow 2.26 \\
MnO_4^- & \rightarrow 0.558 \\
MnO_4^{2-} & \rightarrow 1.51
\end{align*}
\]

Basic Solution, $OH^-$ unit activity

\[
\begin{align*}
Mn^* & \rightarrow -0.58 \\
Mn(OH)_2 & \rightarrow -0.2 \\
Mn(OH)_3^- & \rightarrow 0.1 \\
MnO_2 & \rightarrow 0.9 \\
MnO_4^- & \rightarrow 0.558 \\
MnO_4^{2-} & \rightarrow 0.3
\end{align*}
\]

Manganese Metal

Manganese metal, as normally formed, is a hard brittle metal that can be powdered in a mortar. It has four allotropes, alpha and beta which are hard and brittle, gamma which is soft and ductile, and delta. The properties of manganese are summarized in Table III.3. Gamma manganese can be produced at room temperature by electrodeposition, and can be rolled into foils before it slowly converts into the stable alpha form \(^{(38)}\). Manganese forms many alloys; alloys of Al, Mn, Sb, and Cu, Heusler alloys, are ferromagnetic. Alloys of manganese with uranium and plutonium form very low melting eutectics and have been studied for fast reactor applications \(^{(39,40)}\). Manganese forms many intermetallic compounds. Chemically manganese is a highly reactive metal, reacting slowly with oxygen free cold water and more rapidly with oxygen free warm water to give $Mn(OH)_2$ and hydrogen. It is very rapidly soluble in acids, even very weak ones, giving the corresponding manganous salt. The metal burns in air and oxygen and in the halogens; above 1200°C, it burns in nitrogen forming the
TABLE III.3

PROPERTIES OF MANGANESE METAL (34)

<table>
<thead>
<tr>
<th>Allotrope</th>
<th>Crystal Structure</th>
<th>Density g/cm³</th>
<th>Specific Heat cal./g °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alpha</td>
<td>Body centered cubic</td>
<td>7.44 (20°C)</td>
<td>0.114</td>
</tr>
<tr>
<td>Beta</td>
<td>Body centered cubic</td>
<td>7.29 (20°C)</td>
<td>0.154</td>
</tr>
<tr>
<td>Gamma</td>
<td>Face centered tetragonal</td>
<td>7.18 (20°C)</td>
<td>0.148</td>
</tr>
<tr>
<td>Delta</td>
<td></td>
<td></td>
<td>0.191</td>
</tr>
<tr>
<td>Liquid</td>
<td></td>
<td>6.54</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Transition</th>
<th>Temperature °C</th>
<th>Heat of Transition cal./g-atom</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alpha - Beta</td>
<td>727</td>
<td>535</td>
</tr>
<tr>
<td>Beta - Gamma</td>
<td>1100</td>
<td>545</td>
</tr>
<tr>
<td>Gamma - Delta</td>
<td>1138</td>
<td>530</td>
</tr>
<tr>
<td>Delta - Liquid</td>
<td>1245 (melting point)</td>
<td>3500</td>
</tr>
<tr>
<td>Liquid - Gas</td>
<td>2097 (760 mm boiling point)</td>
<td>53620</td>
</tr>
<tr>
<td>Alpha - Gas</td>
<td>25</td>
<td>67200</td>
</tr>
</tbody>
</table>

Manganese forms a carbide, Mn₂C, which is isomorphous with Fe₃C and is important in steel.

Zerovalent Manganese

Manganese forms a few covalent compounds in which it is considered as exhibiting the valence of zero, the best characterized being the carbonyl, Mn₂(CO)₁₀, the dicyclopentadienyl manganese complex, (C₅H₅)₂Mn, and the cyclopentadienyl carbonyl, C₅H₅Mn(CO)₃. These compounds are too difficult to prepare to be of interest in radiochemical separations, but they are of interest in isotope exchange studies and in Skillard Chalmers reaction studies (11).

Univalent Manganese

A few cyanide complexes of Mn(I) have been prepared by electrolytic reduction or the action of very strong reducing agents on manganocyanides giving Mn₅Mn(CN)₆, E₅Mn(CN)₆, etc. (12). These compounds are extremely...
strong reducing agents and liberate \( \text{H}_2 \) from aqueous solutions and reduce \( \text{Pb}^{++} \) and \( \text{Cd}^{++} \) to metal. A nitrosyl compound, \( K_3\text{Mn} \text{(CN)}_6 \text{NO} \) is also known.

**Divalent Manganese**

Divalent manganese has a half-filled 3d electron shell and so is particularly stable. It is both much more difficult to oxidize and reduce than \( \text{Fe}^{++} \), although in many other ways it closely resembles \( \text{Fe}^{++} \). The ionic radius of the \( \text{Mn}^{++} \) ion is 0.80 \( \text{\AA} \), a little larger than \( \text{Fe}^{++} \), and as expected \( \text{Mn}^{++} \) normally forms somewhat less stable complexes than \( \text{Fe}^{++} \). In acid solution almost any operation other than treatment with very strong oxidizing agents will yield \( \text{Mn(II)} \). Manganese (II) salts are, in general, stable and usually have a pale pink color which has given the name to the minerals rhodochrosite, MnCO\(_3\), and rhodonite, MnSiO\(_3\). The hydroxide, Mn(OH)\(_2\), is oxidized in air to the Mn(III) hydroxide and ultimately to hydrated Mn(IV) oxide; Mn(OH)\(_2\), however, is much more stable than Fe(OH)\(_2\), and is found in nature as the mineral pyrochroite.

Manganous salts show a very slight tendency to hydrolyze; however in air, the hydrolysis of acid free manganous salts continues because the Mn(OH)\(_2\) produced is oxidized to extremely insoluble MnOOH and MnO\(_2\)·xH\(_2\)O. The oxide, MnO\(_2\), is produced by the ignition of higher oxides in hydrogen and is stable but easily oxidized in air to Mn\(_3\)O\(_4\). Some Mn(II) salts of interest are listed in Table III. A. Of special interest to the radiochemist are: Mn\(_4\)NH\(_4\)PO\(_4\)·H\(_2\)O which is precipitated from a NH\(_4\)OH plus NH\(_4\)Cl solution of Mn\(^{++}\) by (NH\(_4\))\(_2\)HPO\(_4\), MnS which is precipitated from an alkaline solution of Mn\(^{++}\), even in the presence of tartrate ion, by (NH\(_4\))\(_2\)S. The solubility products of a number of slightly soluble manganous compounds are given in Table III. A. The anhydrous sulfate, MnSO\(_4\), is produced by igniting almost any manganese compound with H\(_2\)SO\(_4\); it is a suitable weighing form for manganese. The thermodynamic properties of some manganese compounds are given in Table III. A (37).

Divalent manganese has a weak tendency to form complexes. Cyanide complexes of the type Mn(CN)\(_6\)\(^{1-}\) \( (\text{CN})_2 \) are well known but are far less stable than ferrocyanide and are very easily oxidized, even in air, to Mn(CN)\(_6\)\(^{3-}\). Very weak
### TABLE III.h

**COMPOUNDS OF MANGANESE**

#### SOLUBLE SALTS

<table>
<thead>
<tr>
<th>Compound</th>
<th>Mol. weight</th>
<th>How Made</th>
<th>Color</th>
<th>Solubility g/100g H₂O</th>
<th>Hydrates mol H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Manganese II Compounds</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn(CH₃COO)₂</td>
<td>173.02</td>
<td>Mn(NO₃)₂+(CH₃COO)₂O</td>
<td>pink(h)</td>
<td>40(20°C)</td>
<td>4</td>
</tr>
<tr>
<td>MnBr₂</td>
<td>214.76</td>
<td>Mn oxide + HBr</td>
<td>rose-red(h)</td>
<td>114(18°C)</td>
<td>6,4,2</td>
</tr>
<tr>
<td>MnCl₂</td>
<td>125.84</td>
<td>Mn oxide + HCl</td>
<td>rose(h)</td>
<td>7I(20°C)</td>
<td>6,4,2</td>
</tr>
<tr>
<td>Mn(CIO₄)₂</td>
<td>253.84</td>
<td>Mn(OH)₂ + HClO₄</td>
<td>136(25°C)</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>MnF₂</td>
<td>92.93</td>
<td>MnO + HF</td>
<td>pink(0)</td>
<td>1.06(25°)</td>
<td>4</td>
</tr>
<tr>
<td>MnI₂</td>
<td>306.77</td>
<td>MnO + Hl</td>
<td>rose-red(h)</td>
<td>sol.</td>
<td>9,6,4,2,1</td>
</tr>
<tr>
<td>Mn(NO₃)₂</td>
<td>178.94</td>
<td>Mn oxide + HNO₃</td>
<td>pink(0)</td>
<td>134(18°C)</td>
<td>6,4,2</td>
</tr>
<tr>
<td>MnSO₄</td>
<td>151.00</td>
<td>Mn comp. + H₂SO₄</td>
<td>rose(5)</td>
<td>68(25°C)</td>
<td>7,5,4,2,1</td>
</tr>
<tr>
<td>K₂Mn(CN)₆</td>
<td>367.13</td>
<td>MnCO₃ + KCN</td>
<td>blue-violet</td>
<td>sol.</td>
<td>3</td>
</tr>
<tr>
<td><strong>Manganese III Compounds</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn(CH₃COO)₃</td>
<td>232.07</td>
<td>Mn(CH₃COO)₂ + MnO₄⁻</td>
<td>brown(2)</td>
<td>sol. acid</td>
<td>2</td>
</tr>
<tr>
<td>K₂MnCl₅</td>
<td>161.30</td>
<td>Mn₂O₃ + HCl + KCl</td>
<td>red-violet</td>
<td>sol. decomp.</td>
<td></td>
</tr>
<tr>
<td>MnF₃</td>
<td>111.93</td>
<td>MnI₂ + F₂</td>
<td>red(2)</td>
<td>sol. acid</td>
<td>2</td>
</tr>
<tr>
<td>K₂Mn(CN)₆</td>
<td>328.33</td>
<td>K₂Mn(CN)₆ + air</td>
<td>dark red</td>
<td>sol. acid</td>
<td></td>
</tr>
<tr>
<td>K₃Mn(C₂O₄)₃</td>
<td>436.30</td>
<td>H₂C₂O₄ + MnO₄⁻ + CO₃⁻</td>
<td>red(3)</td>
<td>v. sol.</td>
<td>3</td>
</tr>
<tr>
<td>Ca₂Mn(SO₄)₃</td>
<td>379.98</td>
<td>Ca₂SO₄ + Mn(CH₃COO)₃</td>
<td>cereb red(12)</td>
<td>sol. acid</td>
<td>12</td>
</tr>
<tr>
<td><strong>Manganese IV Compounds</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K₂MnCl₆</td>
<td>315.86</td>
<td>KMnO₄ + con. HCl</td>
<td>dark red</td>
<td>sol. decomp.</td>
<td></td>
</tr>
<tr>
<td>K₂MnF₆</td>
<td>247.12</td>
<td>MnO₂ + HF</td>
<td>gold-yellow</td>
<td>sol. acid</td>
<td></td>
</tr>
<tr>
<td><strong>Manganese VI Compound</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K₂MnO₄</td>
<td>197.12</td>
<td>MnO₂ + KOH + KNO₃</td>
<td>dark green</td>
<td>sol. KOH</td>
<td></td>
</tr>
<tr>
<td><strong>Manganese VII Compounds</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH₄MnO₄</td>
<td>136.97</td>
<td>purple</td>
<td>7.9(15°C)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca₂(MnO₄)₂</td>
<td>277.94</td>
<td>purple(9)</td>
<td>250(25°C)</td>
<td></td>
<td>9</td>
</tr>
<tr>
<td>H₂MnO₄</td>
<td>119.94</td>
<td>evap. frozen sol'n.</td>
<td>dark purple</td>
<td>sol.</td>
<td>2</td>
</tr>
<tr>
<td>KMnO₄</td>
<td>158.03</td>
<td>K₂MnO₄ + Cl₂ + H⁺</td>
<td>dark purple</td>
<td>6.3I(20°C)</td>
<td></td>
</tr>
<tr>
<td>Ag₂MnO₄</td>
<td>226.81</td>
<td>dark violet</td>
<td>0.92(20°C)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na₂MnO₄</td>
<td>141.93</td>
<td>purple(3)</td>
<td>v. sol.</td>
<td></td>
<td>3</td>
</tr>
</tbody>
</table>

§ Color of hydrate with ( ) moles of H₂O

18
### Manganese II Compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>Mol. weight</th>
<th>How Made</th>
<th>Color</th>
<th>Solubility product</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnCO₃</td>
<td>114.94</td>
<td>neutral Mn⁺⁺ + CO₃⁻</td>
<td>pink</td>
<td>8.8x10⁻¹¹(25°C)</td>
</tr>
<tr>
<td>Mn₂Fe(CN)₆•7H₂O</td>
<td>147.93</td>
<td>Mn⁺⁺ + Fe(CN)₆⁻</td>
<td>green-white</td>
<td>7.9x10⁻¹³(25°C)</td>
</tr>
<tr>
<td>Mn(OH)₂</td>
<td>88.95</td>
<td>Mn⁺⁺ + OH⁻</td>
<td>white, turns brown</td>
<td>1.6x10⁻¹³(22°C)</td>
</tr>
<tr>
<td>Mn(IO₃)₂</td>
<td>140.77</td>
<td>Mn⁺⁺ + IO⁻</td>
<td></td>
<td>1.8x10⁻⁷(25°C)</td>
</tr>
<tr>
<td>Mn₂O₄•2H₂O</td>
<td>178.98</td>
<td>Mn⁺⁺ + C₂O₄²⁻</td>
<td>pink</td>
<td>-10⁻¹³</td>
</tr>
<tr>
<td>MnO</td>
<td>70.93</td>
<td>Mn₃O₄ + H₂ heated</td>
<td>green</td>
<td>-10⁻²²</td>
</tr>
<tr>
<td>Mn₂(PO₄)₆•7H₂O</td>
<td>480.86</td>
<td>neutral Mn⁺⁺ + HP⁴⁻</td>
<td>pink</td>
<td>-10⁻¹³</td>
</tr>
<tr>
<td>Mn₂(OH)₂•4H₂O</td>
<td>185.97</td>
<td>Mn⁺⁺ + MnOH + HPO⁴⁻</td>
<td>pink</td>
<td>-10⁻³³</td>
</tr>
<tr>
<td>Mn₂P₂O₇</td>
<td>283.82</td>
<td>ignite MnNH₄PO₄•H₂O</td>
<td>pink</td>
<td></td>
</tr>
<tr>
<td>MnSiO₃</td>
<td>130.99</td>
<td>MnO + SiO₂ fused</td>
<td>red</td>
<td></td>
</tr>
<tr>
<td>Mn₂SiO₄</td>
<td>201.92</td>
<td>2MnO + SiO₂ fused</td>
<td>pink</td>
<td></td>
</tr>
<tr>
<td>MnS</td>
<td>87.00</td>
<td>Mn⁺⁺ + (NH₄)₂S</td>
<td>flesh</td>
<td>2x10⁻¹³(25°C)</td>
</tr>
</tbody>
</table>

### Manganese III Compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>Mol. weight</th>
<th>How Made</th>
<th>Color</th>
<th>Solubility product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn(OH)₂</td>
<td>87.94</td>
<td>Mn(OH)₂ + O₂</td>
<td>brown</td>
<td>-10⁻³²</td>
</tr>
<tr>
<td>Mn₂O₃</td>
<td>228.79</td>
<td>ignite oxides at 1000°C</td>
<td>red</td>
<td></td>
</tr>
<tr>
<td>Mn₂O₅</td>
<td>157.86</td>
<td>ignite oxides at 700°C</td>
<td>black</td>
<td></td>
</tr>
<tr>
<td>MnPO₄•H₂O</td>
<td>167.93</td>
<td>Mn(CH₃COO)₃ + H₃PO₄</td>
<td>gray-green</td>
<td></td>
</tr>
</tbody>
</table>

### Manganese IV Compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>Mol. weight</th>
<th>How Made</th>
<th>Color</th>
<th>Solubility product</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnO₂•H₂O</td>
<td>85.93</td>
<td>Mn⁺⁺ + BrO⁻ or ClO⁻₃</td>
<td>brown-black</td>
<td>very insoluble</td>
</tr>
<tr>
<td>MnO₂</td>
<td>86.93</td>
<td>decompos. Mn(NO₃)₂ 250°C</td>
<td>black</td>
<td></td>
</tr>
</tbody>
</table>

### Manganese VI Compound

<table>
<thead>
<tr>
<th>Compound</th>
<th>Mol. weight</th>
<th>How Made</th>
<th>Color</th>
<th>Solubility product</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaMnO₄</td>
<td>256.29</td>
<td>basic Ba⁺⁺ + MnO₄⁺</td>
<td>gray-green</td>
<td>1.5x10⁻¹⁰</td>
</tr>
</tbody>
</table>

### Manganese VII Compound

<table>
<thead>
<tr>
<th>Compound</th>
<th>Mol. weight</th>
<th>How Made</th>
<th>Color</th>
<th>Solubility product</th>
</tr>
</thead>
<tbody>
<tr>
<td>CsMnO₄</td>
<td>251.84</td>
<td>Cs⁺ + MnO₄⁻</td>
<td>purple</td>
<td>1.5x10⁻⁵</td>
</tr>
</tbody>
</table>

---

19
### VOLATILE COMPOUNDS

<table>
<thead>
<tr>
<th>Compound</th>
<th>Mol. weight</th>
<th>How made</th>
<th>Color</th>
<th>Melting point °C</th>
<th>Boiling point °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn₂O₇</td>
<td>221.86</td>
<td>MnO₄ + conc. H₂SO₄</td>
<td>red</td>
<td>-33°</td>
<td>70° explodes</td>
</tr>
<tr>
<td>Mn(C₅H₇O₂)₃</td>
<td>352.25</td>
<td>acetylacetone + Mn(CH₃COO)₃</td>
<td>green-black</td>
<td>172°</td>
<td>volatile</td>
</tr>
<tr>
<td>Mn₂(CO)₁₀</td>
<td>389.96</td>
<td>gold</td>
<td></td>
<td>151°</td>
<td></td>
</tr>
<tr>
<td>C₅H₇Mn(CO)₃</td>
<td>201.05</td>
<td>yellow</td>
<td>77°</td>
<td></td>
<td>volatile</td>
</tr>
<tr>
<td>(C₅H₇)₂Mn</td>
<td>185.11</td>
<td>amber</td>
<td>172°</td>
<td>245°</td>
<td></td>
</tr>
</tbody>
</table>

### TABLE III.5

#### THERMODYNAMIC DATA FOR MANGANESE COMPOUNDS (37)

<table>
<thead>
<tr>
<th>Compound</th>
<th>ΔH kcal/mol.</th>
<th>ΔS kcal/mol.</th>
<th>ΔS cal/mol., °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn(s,a)</td>
<td>0</td>
<td>0</td>
<td>7.64</td>
</tr>
<tr>
<td>Mn(g)</td>
<td>67.2</td>
<td>57.1</td>
<td>11.69</td>
</tr>
<tr>
<td>Mn**(H₂O)</td>
<td>-53.2</td>
<td>-55.1</td>
<td>-17</td>
</tr>
<tr>
<td>MnO(a)</td>
<td>-92.0</td>
<td>-86.7</td>
<td>11.3</td>
</tr>
<tr>
<td>Mn₃O₄(a)</td>
<td>-331.3</td>
<td>-306.2</td>
<td>36.8</td>
</tr>
<tr>
<td>Mn₂O₃(a)</td>
<td>-228.7</td>
<td>-210.1</td>
<td>26.4</td>
</tr>
<tr>
<td>MnO₂(a)</td>
<td>-124.4</td>
<td>-111.3</td>
<td>12.68</td>
</tr>
<tr>
<td>Mn(CH₃COO)₂(a)</td>
<td>-167</td>
<td>-118</td>
<td>23</td>
</tr>
<tr>
<td>MnF₂(a)</td>
<td>-190</td>
<td>-179</td>
<td>22.25</td>
</tr>
<tr>
<td>MnCl₂(a)</td>
<td>-115.6</td>
<td>-105.9</td>
<td>28.26</td>
</tr>
<tr>
<td>MnBr₂(a)</td>
<td>-92.6</td>
<td>-89</td>
<td>33</td>
</tr>
<tr>
<td>MnI₂(a)</td>
<td>-64.2</td>
<td>-65</td>
<td>37</td>
</tr>
<tr>
<td>MnS(a)</td>
<td>-49.5</td>
<td>-50.5</td>
<td>18.7</td>
</tr>
<tr>
<td>MnSO₄(a)</td>
<td>-254.9</td>
<td>-229.1</td>
<td>26.8</td>
</tr>
<tr>
<td>MnCO₃(a)</td>
<td>-214</td>
<td>-196</td>
<td>20.5</td>
</tr>
<tr>
<td>Mn₂O₄(a)</td>
<td>-200.6</td>
<td>-176.8</td>
<td>41.0</td>
</tr>
<tr>
<td>Mn₂(CO)₁₀(a)</td>
<td>-600.9</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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chloride complexes are known, \( \text{MnCl}_3 \), \( \text{MnCl}_4^- \), and \( \text{MnCl}_6^{3-} \), the latter being stable enough to be weakly absorbed on anion resins from very strong HCl. Mn(II) forms a number of chelate complexes, see Table III.6, for example, the Mn(II) chelate with ethylenediaminetetraacetic acid which is of importance in analytical chemistry. Divalent manganese forms complexes with acetylacetone and oxalic acid. Manganese (II) forms double sulfates, nitrates, and halides with a number of metals; these compounds are very weak complexes if they are true complexes at all. Mn(II) can form amine complexes, e.g. \( \text{Mn(NH}_3)_6^{4+} \), but the complexes are not stable in aqueous solution.

### TABLE III.6

STABILITY CONSTANTS OF MANGANESE COMPLEXES\(^{(34, 37)}\)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>( \log_{10} ) Equilibrium constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Mn}^{2+} + \text{H}_2\text{O}(1) \rightarrow \text{MnOH}^+ + \text{H}^+ )</td>
<td>-10.59</td>
</tr>
<tr>
<td>( \text{Mn}^{2+} + \text{F}^- \rightarrow \text{MnF}^+ )</td>
<td>0.79</td>
</tr>
<tr>
<td>( \text{Mn}^{2+} + \text{Cl}^- \rightarrow \text{MnCl}^+ )</td>
<td>0.59</td>
</tr>
<tr>
<td>( \text{Mn}^{2+} + \text{SO}_4^{2-} \rightarrow \text{MnSO}_4 )</td>
<td>2.26</td>
</tr>
<tr>
<td>( \text{Mn}^{2+} + \text{C}_2\text{O}_4^{2-} \rightarrow \text{MnC}_2\text{O}_4 )</td>
<td>3.89</td>
</tr>
<tr>
<td>( \text{Mn}^{2+} + \text{malonate} \rightarrow \text{Mn(OOCCH}_2\text{COO)} )</td>
<td>3.29</td>
</tr>
<tr>
<td>( \text{Mn}^{2+} + 2 \text{acetylacetone} \rightarrow \text{Mn(CH}_3\text{COCHCOCH}_3)_2 )</td>
<td>9.96</td>
</tr>
<tr>
<td>( \text{Mn}^{2+} + \text{EDTA}^{4-} \rightarrow \text{MnEDTA}^{2-} )</td>
<td>13.4</td>
</tr>
<tr>
<td>( \text{Mn}^{3+} + \text{H}_2\text{O}(1) \rightarrow \text{MnOH}^{2+} + \text{H}^+ )</td>
<td>-0.056</td>
</tr>
<tr>
<td>( \text{Mn}^{3+} + \text{F}^- \rightarrow \text{MnF}^{2+} )</td>
<td>2.18</td>
</tr>
<tr>
<td>( \text{Mn}^{3+} + \text{Cl}^- \rightarrow \text{MnCl}^{2+} )</td>
<td>0.96</td>
</tr>
<tr>
<td>( \text{Mn}^{3+} + \text{C}_2\text{O}_4^{2-} \rightarrow \text{MnC}_2\text{O}_4 )</td>
<td>9.98</td>
</tr>
<tr>
<td>( \text{Mn}^{3+} + 2\text{C}_2\text{O}_4^{2-} \rightarrow \text{Mn(C}_2\text{O}_4)_2 )</td>
<td>16.6</td>
</tr>
<tr>
<td>( \text{Mn}^{3+} + 3\text{C}_2\text{O}_4^{2-} \rightarrow \text{Mn(C}_2\text{O}_4)_3 )</td>
<td>19.42</td>
</tr>
</tbody>
</table>
Trivalent Manganese

Simple, uncomplexed Mn$^{3+}$ in solution disproportionates into Mn$^{2+}$ and MnO$_2$; however, Mn(III) forms a number of complexes and insoluble compounds that are stable. Some compounds of Mn(III) are listed in Table III.4. The oxide, Mn$_2$O$_3$, and the "ous-ic" oxide, Mn$_3$O$_4$, are stable, the latter compound being the usual, but somewhat uncertain, weighing form for manganese. Mn(III) forms a moderately stable manganicyanide, Mn(CN)$_3$- (I2), which is much more difficult to reduce than Fe(CN)$_3$- and also shows a tendency to hydrolyze in water. A phosphate complex, Mn(H$_2$P$_2$O$_7$)$_3$-, is important in analytical chemistry. Mn(III) forms fluoro, chloro, and sulfato (alum) complexes. It forms a number of organic complexes, see Table III.6. Mn(III) complexes are normally red to violet, and even the complexes tend to hydrolyze and disproportionate and are usually strong oxidising agents. The ion, Mn$^{3+}$, is considered to have the greatest tendency to hydrolyze of any trivalent cation$^{(37)}$.

Tetravalent Manganese

The only readily obtainable compound of Mn(IV) is the extremely insoluble dioxide which is insoluble in almost any aqueous medium which does not reduce it. The hydrated dioxide is the form in which manganese is precipitated in many radiochemical separations by the addition of a strong oxidizing agent such as KBrO$_3$ or KCIO$_3$ to a nitric acid solution of Mn$^{2+}$. The dioxide is also precipitated as a scavenger during the processing of irradiated uranium fuel by the addition of first Mn$^{2+}$, then MnO$_4^-$. Anhydrous MnO$_2$, formed by the thermal decomposition of Mn(NO$_3$)$_2$, is stable to above 500°C; hydrated MnO$_2$, however, may start to decompose at a temperature as low as 200 - 300°C. MnO$_2$ dissolves in strong HCl to give a dark colored Mn(IV) chloro complex which gradually decomposes to Mn$^{2+}$ and Cl$_2$. Mn(IV) forms some fluoro and chloro complexes such as K$_2$MnF$_6$ and K$_2$MnCl$_6$, and also some iodate complexes of the anion Mn(IO$_3$)$_5$$^+$.

Hydrated MnO$_2$ reacts with strong alkalies to form insoluble managanites such as K$_2$MnO$_7$. 

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Pentavalent Manganese

Manganese forms a few compounds in which it exhibits a valence of five. The recently synthesized MnOCl₃ (h₃) and K₂MnO₃ are examples.

Hexavalent Manganese

Manganates, e.g. K₂MnO₄, can be prepared by fusing MnO₂ with KOH and KNO₃. They are stable in strongly alkaline solutions, but disproportionate to MnO₂ and MnO₄⁻ in weakly alkaline, neutral, or acidic solutions. The MnO₄⁻ ion is green. A mangany chloride, MnO₂Cl₂, has been recently prepared (h₃).

Heptavalent Manganese

Seven is the group valence of manganese. Mn(VII) forms the strongly oxidizing but stable MnO₄⁻ ion which is of great importance in radiochemistry and analytical chemistry. K₂MnO₄ is usually prepared by fusing MnO₂ with KOH in air or with KOH and KNO₃, then treating the resulting manganate with H₂SO₄ plus at times oxidation with Cl₂. Permanganates are deep purple and strong oxidizing agents. The acid, H₂MnO₄, is a strong acid like HClO₄ and has recently been prepared as a solid crystalline compound by the vacuum evaporation of a frozen solution (h₃). The oxide, Mn₂O₇, has been isolated and can be distilled, usually with considerable decomposition. The distillation of Mn₂O₇ is the basis of a radiochemical separation for manganese.

Permanganyl chloride, MnO₃Cl, has been synthesized (h₃). Permanganates can be produced from Mn²⁺ in acid solution by oxidation with periodate, persulfate plus Ag⁺ catalyst, Ag⁺, PbO₂, and sodium bismuthate. Permanganate can be extracted with alkaline pyridine and alkaline (C₅H₅)₄AsCl in CHCl₃.

Data on some common permanganates are included in Table III. Permanganates are isomorphous with perchlorates, perhenates, and pertechnetates. Permanganate solutions are relatively stable, especially if free of MnO₂, and are used extensively as standard oxidizing solutions in analytical chemistry.

When heated, K₂MnO₄ is first decomposed at about 200°C to K₂MnO₄ and MnO₂, then at higher temperatures to Mn₂O₃ and Mn₂O₄.
5. **Analytical Chemistry of Manganese**

Manganese is a member of the third group in the standard qualitative analysis scheme and is characterized by a sulfide, MnS, insoluble in basic solutions, and a hydroxide, Mn(OH)$_2$, which, while insoluble in NH$_4$OH alone, is soluble in NH$_4$OH plus excess NH$_4^+$ salts and which is slowly oxidized in air to an insoluble hydrated oxide of Mn(III) or Mn(IV). The final test for manganese is usually its oxidation to purple permanganate.

Emission spectroscopy is an excellent method for detecting and making semiquantitative determinations of manganese.$^{(45)}$ X-ray fluorescence can also be used. Permanganate ion has a strong infrared absorption band in the eleven micron region and infrared has been used for the identification of the ion. Many extremely sensitive spot tests are known for detecting microgram or smaller quantities of manganese.$^{(46)}$ The most common test is based upon the oxidation to MnO$_4^-$ by various oxidizing agents. An extremely sensitive, although not very specific test, is based upon the oxidation of bensidine to a blue color by the MnO$_2$ produced by air oxidation of alkaline Mn(OH)$_2$. Another sensitive test (0.001 µg Mn in one drop) is based upon the oxidation of "tetrabase" (tetramethyl p-diaminodiphenylmethane) to a blue oxidation product by periodate with manganese serving as a catalyst. A third sensitive (0.05 mg/liter) and fairly specific test has been developed in which manganese produces an intense red-violet color with an alkaline solution of formaldehyde.

Manganese can be determined quantitatively by a number of methods. The most convenient method is a photometric method based upon the oxidation of manganese to MnO$_4^-$ with KI$_2$O$_4$ or some other oxidizing agent. If a narrow band spectrophotometer is used to measure the absorbance, a precision of 0.5% standard deviation over a wide range of manganese concentration can be obtained and as little as 2 µg Mn in 50 ml can be detected.$^{(47)}$ The method is virtually free of interferences. Because the method is commonly used to determine manganese yields in radiochemical separations, it is included with the radiochemical separation procedures in section VI. A number of other photometric
methods have been developed based upon either the color of Mn(III) complexes or on the colors produced in organic reagents due to oxidation by manganese compounds. Activation analysis is also widely used to determine manganese, and several separation schemes are included in section VI.

Several titrimetric methods, based upon oxidation-reduction, are widely used for manganese. A widely used method is based upon the titration of Mn(II) with standard permanganate in a neutral pyrophosphate solution. The reaction is:

\[ \text{Mn}^{2+} + \text{MnO}_4^- + 8\text{H}^+ + 15(\text{H}_2\text{P}_2\text{O}_7)^{2-} \rightarrow 5(\text{Mn(H}_2\text{P}_2\text{O}_7)_3)^{3-} + 16\text{H}_2\text{O} \]

Since the Mn(III) complex is intensely colored, the endpoint is determined potentiometrically. The method is virtually free of interference. Manganese (II) can also be titrated with MnO₄⁻ in a nearly neutral solution (Volhard method) according to the reaction:

\[ 3\text{Mn}^{2+} + 2\text{MnO}_4^- + 8\text{H}^+ \rightarrow 5\text{MnO}_2 + 2\text{H}_2\text{O} \]

The endpoint is determined by observing the appearance of purple MnO₄⁻. The reaction is not quite stoichiometric and the end point is difficult to observe visually because of the precipitate of MnO₂. The classical titrimetric method is based upon the oxidation of Mn⁺⁺ to MnO₄⁻ with sodium bismuthate, then removal of the excess bismuthate by filtration and reduction of the permanganate with standard ferrous ammonium sulfate. The reactions are:

\[ 2\text{Mn}^{2+} + 5\text{NaBiO}_3 + 14\text{H}^+ \rightarrow 2\text{MnO}_4^- + 5\text{Bi}^{3+} + 7\text{H}_2\text{O} + 5\text{Na}^+ \]
\[ \text{MnO}_4^- + 5\text{Fe}^{2+} + 8\text{H}^+ \rightarrow \text{Mn}^{2+} + 5\text{Fe}^{3+} + 4\text{H}_2\text{O} \]

Most commonly an excess of standard Fe⁺⁺ is added and the excess titrated with standard permanganate, ferrous o-phenanthroline or the appearance of the purple of MnO₄⁻ being the indicator. A large number of materials including cerium, cobalt, chromium, nitrous acid, fluoride, and chloride interfere. As an alternate procedure, the permanganate can be treated with standard arsenite. Another titrimetric method is based upon the oxidation of the Mn⁺⁺ in boiling H₂SO₄ - H₃PO₄ solution with (NH₄)₂S₂O₈ and Ag⁺ catalyst, then titration of the MnO₄⁻ with standard arsenite. The reactions are:
The endpoint can be determined by the disappearance of the purple MnO₄⁻ color or potentiometrically. Fewer elements interfere than with the Fe⁺⁺ titration. Manganese can be determined by titration with ethylenediaminetetraacetic acid using Erichrome Black T as the indicator. Complexing with cyanide will prevent interference by Mg, Gd, Co, Zn, Cu, Ni, and Fe.

Manganese is determined quantitatively by emission spectroscopy, flame photometry, atomic absorption, and X-ray fluorescence. It can be determined polarographically. A number of gravimetric methods have been developed but are seldom used because other methods are much faster and less subject to interference. The gravimetric methods make use of the precipitation of manganese as MnNH₄PO₄·H₂O, MnS, and Mn₂O₃ and ignition to Mn₂P₂O₇, MnSO₄, or Mn₃O₄; all of these precipitation methods have been used in radiochemical separations.

6. **Dissolution of Manganese Samples**

**Inorganic Materials**

The dissolution of manganese minerals and ores can often be accomplished by acid attack followed by H₂SO₄ or Na₂CO₃ fusion of the insoluble residue. The dissolution of MnO₂ is greatly facilitated by the addition of a reducing agent such as H₂O₂ or SO₂. The dissolution method is often dictated by what other elements are present in the sample and what elements in addition to manganese are being determined.

Manganese metal is very readily soluble in dilute acids. Most steels and cast irons can be dissolved in HNO₃, HCl, H₂SO₄, or aqua regia. Tungsten steels may require H₃PO₄. Some high temperature alloys containing major amounts of Ni, Co, Cr, W, and Nb are very difficult to dissolve and may require fusion with Na₂O₂ or anodic electrolytic attack. An interesting dissolution technique for analyzing inclusions in steel is the solution of the metal in cold Fe₃O₄ solution which leaves the oxide inclusions, FeO, MnO, SiO₂, Al₂O₃, etc. unattacked.©1978
Organic Materials

Biological samples are usually either wet or dry ashed before analyzing for manganese. Ignition of dried plant material, grain, feeds, fruit, etc., at about 525°C in a porcelain or platinum crucible and digestion of fertilizers with H₂SO₄ and HNO₃ is recommended by the Association of Official Agricultural Chemists (52). Wet oxidation is becoming more popular for destroying organic matter. Biological materials, grasses, feces, body tissues, etc., are boiled with HNO₃ in a Kjeldahl flask then finally fumed with HNO₃ plus HClO₄; dye intermediates and rubber chemicals are treated with H₂SO₄, HNO₃, and H₂O₂. Petroleum and petroleum distillates are wet ashed preparatory to analysis for manganese and other trace metals; HNO₃ + H₂SO₄ digestion is used for analyzing paint driers for manganese. Manganese organometallic compounds, e.g. gasoline additives, are decomposed by ultraviolet radiation, bromine oxidation, and sometimes by water alone.

7. Separation of Manganese (34)

Precipitation Methods

The most generally used and quite specific method for separating manganese is its precipitation as hydrated MnO₂ from a boiling HNO₃ solution of Mn⁺⁺ by adding bromate, chlorate, or persulfate oxidizing agent. The MnO₂ so formed carries Si, W, Ta, Nb, and Pa nearly quantitatively and often is also contaminated with Zr, Fe, Sb, and other elements which hydrolyze easily. The MnO₂ precipitation is usually not quite quantitative. Precipitation of MnO₂ may be made from nearly neutral solutions by oxidation with Br₂. Manganese, even at trace level, can be electrodeposited on the anode as MnO₂ (53).

Iron (III), aluminum, zirconium, and other elements with very insoluble hydroxides can be precipitated with NH₄OH in the presence of excess ammonium salts, leaving Mn(II) in solution. Some manganese is usually precipitated since the Mn(II) is air oxidized to very insoluble Mn(OH)₃; however, the air oxidation can be prevented by the addition of hydroxylamine hydrochloride to the solution. After filtering or centrifuging out the insoluble hydroxides,
manganese can be precipitated from the same solution by the addition of an oxidizing agent, e.g., $\text{H}_2\text{O}_2$.

The precipitation of manganese as $\text{MnS}$ from a slightly basic solution of $\text{Mn}^{2+} + \text{NH}_4^+$ with $\text{H}_2\text{S}$ or $(\text{NH}_4)_2\text{S}$ will separate manganese from alkaline earths. The acid insoluble sulfides, including $\text{ZnS}$, can be first precipitated from a weak acetic acid solution. The precipitation of $\text{MnO}_2$ with $\text{NaOH}$ plus $\text{H}_2\text{O}_2$ will separate manganese from $\text{Al}$, $\text{Cr}$, $\text{Mo}$, $\text{V}$, and other amphoteric elements which form alkali soluble salts. Many elements, $\text{Fe}$, $\text{Ni}$, $\text{Cu}$, $\text{Zn}$, $\text{Cr}$, etc., can be separated from Mn by quantitative deposition in a mercury cathode; under properly controlled conditions, Mn can also be quantitatively deposited.

Other precipitation separations are sometimes used: $\text{Fe(III)}$, $\text{Ti}$, $\text{Zr}$, and $\text{V}$ can be precipitated with cupferron leaving Mn in solution; $\text{MnNH}_4\text{PO}_4\cdot\text{H}_2\text{O}$ can be precipitated from citrate solutions leaving Co in solution, $\text{CoS}$ and NiS can be precipitated in the presence of pyridine leaving Mn in solution, $\text{Fe(III)}$ can be precipitated as a basic formate using urea with Mn remaining in solution. Complexing with EDTA and other chelates prevents the precipitation of Mn during the hydrolytic precipitation of $\text{Nb}$ and $\text{Ta}$. $\text{Fe(III)}$ can be precipitated with pyridine leaving Mn in solution.

Manganese(VII) can be separated by precipitation as tetraphenylarsonium permanganate. Perchlorate, perrhenate, etc., can be precipitated before the manganese is oxidized to $\text{MnO}_4^{-}$.

**Volatilization Methods**

Manganese, as $\text{Mn}_2\text{O}_7$, can be slowly distilled from 10 M $\text{H}_2\text{SO}_4$ containing $\text{HIO}_4^{-}$.

**Solvent Extraction**

Solvent extraction has been extensively studied as a method for separating manganese. Manganese does not form very many extractable complexes, and often other elements are extracted away from the manganese, e.g., $\text{Fe(III)}$ from $\text{HCl}$ with ether. Since manganese exists in several valences, it is often possible to adjust the valence so manganese will or will not extract. Several solvent
extraction separations for manganese are given below:

a. Pyridine\(^{(56)}\)

Add pyridine to a solution containing MnO\(_4\)^{-}, shake, add 4 N NaOH, shake a few seconds and centrifuge. MnO\(_4\)^{-} extracts. Speed is essential since pyridine slowly reduces MnO\(_4\)^{-} to nonextractable MnO\(_4\)^{-}. ReO\(_4\)^{-} and TeO\(_4\)^{-} also extract.

b. 8-Quinolinol (8-hydroxyquinoline)\(^{(56)}\)

Take 50 ml of solution with up to 0.2 mg Mn and 10 ml 10% NaK tartrate, adjust to pH 7.5 - 12.5. Shake 1 min with 10 ml 1% 8-quinolinol in CHCl\(_3\). Mn(II) complex extracts; Fe and Cu interfere.

c. Tetraphenylarsonium Chloride\(^{(56,57)}\)

Make the solution alkaline with NaOH. Oxidize Mn to MnO\(_4\)^{-} with K\(_2\)S\(_2\)O\(_8\). Add 1% (C\(_6\)H\(_5\))\(_4\)AsCl solution to make solution about 5 x 10\(^{-5}\)M. Extract 5 min. with an equal volume of CHCl\(_3\); Mn extracts quantitatively as (C\(_6\)H\(_5\))\(_4\)AsMnO\(_4\). ReO\(_4\)^{-}, TeO\(_4\)^{-}, ClO\(_4\)^{-} also extract, but can be removed by extraction before the manganese is oxidized.

d. Diethylthiocarbamate\(^{(58)}\)

Use 175 ml of solution with some citric acid, adjust the pH to about 5.3, add 0.4 g Na diethylthiocarbamate (DECA), adjust pH again to 5.4, and extract with 25 ml CHCl\(_3\) readjusting the pH by adding HCl.

e. Thienyl trifluoroacetone\(^{(59)}\)

Manganese(II) TTA complex can be extracted from fairly high pH solutions. Buffer the solution with NH\(_4\)C\(_2\)H\(_2\)O\(_2\) plus NaOH to give a pH of 8.0 - 8.5. Add a little hydroxylamino hydrochloride to prevent air oxidation of Mn(II). Add a little TTA (0.1 M in alcohol) and extract with ethyl acetate for 2 to 3 minutes.

Many other solvent extraction systems have been used for extracting manganese and separating unwanted elements from manganese. The separation of Fe and Mn by thiocyanate extraction with tributylphosphate has been studied\(^{(60)}\); 1-phenyl-3-methyl-4-hexyl-pyrazole-5 has been used to complex Mn (depending upon pH) so that it will extract into methylisobutyl ketone\(^{(61)}\). Octyl-\(\alpha\)-anilinonexyolphosphonate in ligroin has been used to extract Mn from H\(_2\)SO\(_4\).
solution (62). The long chain amine, alamine 336, has been used to extract manganese from solutions highly salted with LiCl, etc. (63). Cupferron has been used to extract manganese (64). Dithizone has been used to quantitatively extract trace Mn from seawater (65). Manganese has been extracted from a pH 2.7 solution by di-(2-ethylhexyl) phosphoric acid in hexane (66).

**Ion Exchange**

Divalent manganese in strong HCl is weakly absorbed on strong base anion exchange resin, and manganese can thus be separated from those ions that are not absorbed at all (Cr³⁺, Al³⁺, Tl⁺, Ni²⁺, and trivalent rare earths) and those ions that are strongly absorbed (Fe³⁺, UO₂²⁺, WO₄³⁻, Co⁴⁺, Tl³⁺, and noble metals) (67). Anion exchange separations have been worked out in other media, oxalic acid (68), acetone plus HCl in water (69), ethanol plus HCl in water (70). Because Mn²⁺ is normally so weakly absorbed, the separations are not very useful for concentrating manganese. A weakly basic anion resin has been used to concentrate Mn²⁺ in natural waters prior to analysis (71).

Divalent manganese is quite strongly adsorbed on cation exchange resins. Cation resins (sulfonic acid type) have been used to concentrate manganese from dilute NH₄Cl plus (NH₄)₂HPO₄ solutions (72). In general, cation resins have not been widely used to separate and concentrate manganese.

A chelating resin, Chelex 100, has been used to concentrate manganese and many other trace elements from seawater (73).

**Other Chromatographic Separations**

A number of other chromatographic separation methods have been used for manganese. Paper chromatography (74) has been used to separate manganese and other elements for both radiochemical and analytical purposes. The manganese is detected by the formation of insoluble Mn₃(PO₄)₂ (containing ³²P) in the paper (75). Metal TTA complexes have been used with solvents containing CH₃OH, C₆H₆, and glacial CH₃COOH (76) to separate Mn from Fe, Co, Ni, and Cu; 80% methyl-n-propyl ketone, 10% acetone, and 10% HCl, also, acetone plus 5% H₂O and 8% HCl have been used as solvents (77).
Partition chromatography has been rather more extensively studied. A column made up of $\text{CCl}_4$-dithizone solution supported on cellulose acetate has been used to separate manganese from natural waters (77). The manganese is eluted with $1 \text{M HCl}$. Kel F supported tri-n-octylphosphine oxide (78) and teflon supported tri-n-octylamine (79) have also been used.

8. Szilard Chalmers Reactions with Manganese

Because of the use of permanganate solutions and the Szilard Chalmers concentration of the $^{54}\text{Mn}$ on $\text{MnO}_2$ for the standardization of weak neutron sources, many studies have been made of the partition of manganese activity between the $\text{MnO}_2$ decomposition product and the unaltered $\text{MnO}_4^-$ (80). The activity is almost all collected on the $\text{MnO}_2$ if the pH of the solution is less than about 11. Even when solid $\text{MnO}_4^-$ is irradiated, only about 35% of the activity is retained with the $\text{MnO}_2^-$. If the salt is dissolved in a solution with a pH of less than 11, Szilard Chalmers reactions have been recently studied in dilute solutions of $\text{Mn}_2(\text{CO})_10$ and $\text{C}_5\text{H}_5\text{Mn}(\text{CO})_3$ (81), and on crystalline $\text{C}_5\text{H}_5\text{Mn}(\text{CO})_3$ (82).

Radioisotope exchange has been used to study the structure of $\text{Mn(OCN)}_3\text{NO}_3$ (83).

IV HAZARDS AND PRECAUTIONS

Manganese is relatively nontoxic in most of its compounds, and very few cases of manganese poisoning are known (84). However, workers exposed to large concentrations of manganese containing dust have been known to be poisoned. Manganism in its earliest stages results in muscular incoordination, general lassitude and sleepiness, and certain emotional disturbances such as uncontrollable laughter or crying. If the exposure to the manganese dust is continued, the poisoning will cause permanent crippling but apparently does not shorten the life span. An average concentration of 6 mg. of manganese per cubic meter of air is considered safe for an eight hour work day. Relatively large doses of manganese compounds taken orally are required to cause poisoning.
Manganese is an important trace constituent of food and the normal daily intake is about 10 mg. Activation analysis has been used to compare the manganese content of different body fluids in normal people and people suffering from manganese poisoning (85). Since manganism results from exposures to large quantities of dust, the handling of normal laboratory amounts of manganese is essentially without chemical hazard. Certain manganese compounds, e.g., Mn₂O₇ and NH₄MnO₄, are explosive.

A major hazard in the radiochemical studies of manganese is the radiation due to ⁵⁶Mn. Since manganese has a relatively high cross section and ⁵⁶Mn has a fairly short half life and many abundant gamma rays, quite large activities which give off large gamma doses are easily produced. Any sample containing manganese and irradiated in a moderate neutron flux should be very carefully surveyed before any work is started. The gamma rays from ⁵⁶Mn are difficult to shield. A sample of about 50 mg. Mn irradiated for 2 1/2 hours in a flux of 10¹³ n/cm² sec. will give a gamma dose, unshielded, of about 1 R/hr. at one foot (30 cm.).

As ingestion hazards, ⁵²Mn, ⁵⁴Mn, and ⁵⁶Mn are roughly equal. The recommended maximum permissible concentration of both soluble and insoluble forms in air and water are given in Table IV.1(86). Some recent studies of the biological half life of radiomanganese in man show two half lives, one of about four days (30% of the Mn) and one of about 39 days (70% of the Mn)(87).

Any work with radioactive substances should be carefully planned and proper safety precautions taken. Samples should be adequately monitored and care taken to prevent the spread of contamination. A good reference on safety procedures is included in the Oak Ridge Master Analytical Manual(88).
TABLE IV.1
MAXIMUM PERMISSIBLE CONCENTRATIONS OF MANGANESE ISOTOPES

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Body Burden</th>
<th>1 hr. week</th>
<th>168 hr. week</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>µCi</td>
<td>in H₂O</td>
<td>µCi/cm³</td>
</tr>
<tr>
<td>⁵²Mn sol.</td>
<td>5</td>
<td>10⁻³</td>
<td>2x10⁻⁷</td>
</tr>
<tr>
<td>⁵₂Mn insol.</td>
<td>9x10⁻⁴</td>
<td>10⁻⁷</td>
<td>3x10⁻⁴</td>
</tr>
<tr>
<td>⁵₄Mn sol.</td>
<td>20</td>
<td>1x10⁻³</td>
<td>1x10⁻⁷</td>
</tr>
<tr>
<td>³⁰³Mn insol.</td>
<td>3x10⁻³</td>
<td>1x10⁻⁷</td>
<td>10⁻³</td>
</tr>
<tr>
<td>⁵⁶Mn sol.</td>
<td>2</td>
<td>3x10⁻³</td>
<td>5x10⁻⁷</td>
</tr>
<tr>
<td>²,₆hr. insol.</td>
<td>3x10⁻³</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

V COUNTING TECHNIQUES

All of the radioactive isotopes of manganese except 1.9 x 10⁶ year ⁵³Mn decay by the emission of gamma rays of high abundance, so gamma counting, either with NaI(Tl) crystals or Ge(Li) detectors, is the most commonly used method of determination. The isotopes can also be counted using Geiger Müller or flow proportional counters. An excellent discussion of counting techniques is given in the monograph by O'Kelley (89) and the book by Johnson, Richler, and O'Kelley (90).

R. L. Heath (91) gives scintillation gamma ray spectra of most of the radioactive nuclides including 5.6 day ⁵²Mn, 303 day ⁵₄Mn, and 2,576 hour ⁵⁶Mn. His scintillation spectra of ⁵²Mn and ⁵₄Mn are included in this monograph as Figures V.1 and V.2. A scintillation spectrum of ⁵⁶Mn, taken at a somewhat greater source to detector distance in order to minimize sum peaks, is given as Figure V.3. Heath also describes methods of absolute counting using scintillation counters and gives counting efficiencies, peak to total ratios, and absorption corrections for gamma rays of different energies and for different counter geometries. The total gamma emission rate (photons per unit time) is determined by dividing the integrated area of the photopeak (counts) by the...
counting time, the counting efficiency at the known geometry, and the peak to total ratio. Corrections also need to be made for the fraction of the gamma ray transmitted through all absorbing material such as added beta absorber, crystal housing, and if the sample is thick, the sample itself. By using Heath's efficiency curves, absolute gamma emission rates can be determined to better than 5% standard deviation. Since 7.6 cm x 7.6 cm (3" x 3") cylindrical crystals and 10 cm source to detector distances are rather standard, Heath's values of the overall counting efficiency and the peak to total ratios for some of the manganese gamma rays are given in Table V.1. Heath gives the values for other size crystals and source to detector distances(91).

### Table V.1

**Counting Efficiencies for Manganese Gamma Rays Using a 7.6 cm x 7.6 cm Cylindrical NaI(Tl) Crystal and a 10 cm Source to Crystal Distance(91)**

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Gamma Ray Energy MeV</th>
<th>Peak to Total Ratio</th>
<th>Gamma Counting Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>Positron Emitters</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 min. $^{50}$Mn</td>
<td>0.511</td>
<td>0.641</td>
<td>0.0217</td>
</tr>
<tr>
<td>5.60 day $^{52}$Mn</td>
<td>0.783 (100%)</td>
<td>0.892</td>
<td>0.0192</td>
</tr>
<tr>
<td></td>
<td>1.11 (100%)</td>
<td>0.395</td>
<td>0.0174</td>
</tr>
<tr>
<td>303 day $^{54}$Mn</td>
<td>0.746 (82%)</td>
<td>0.506</td>
<td>0.0195</td>
</tr>
<tr>
<td></td>
<td>0.395 (100%)</td>
<td>0.335</td>
<td>0.0161</td>
</tr>
<tr>
<td>2.576 hour $^{56}$Mn</td>
<td>0.848 (99%)</td>
<td>0.470</td>
<td>0.0188</td>
</tr>
<tr>
<td></td>
<td>1.831 (29%)</td>
<td>0.290</td>
<td>0.0152</td>
</tr>
<tr>
<td></td>
<td>2.110 (15%)</td>
<td>0.262</td>
<td>0.0116</td>
</tr>
</tbody>
</table>
FIGURE V.1
GAMMA SPECTRUM OF $^{52}\text{Mn}$

5.7 day Mn $^{52}$
3" x 3" - 2 Na I
9-5-63
ABSORBER 1.18 g/cm$^2$ Be
SOURCE DIST. 10 cm (s)
ENERGY SCALE 1 keV/PHU(Ca)
FIGURE V.2
GAMMA SPECTRUM OF $^{54}_{\text{Mn}}(91)$

314 day Mn $^{54}$
3" x 3" - 2 No 1
1-26-62
ABSORBER 1.18 g/cm$^2$ Be
SOURCE DIST 10 cm (c)
ENERGY SCALE 1 keV/PNU(Ca)
FIGURE V.3
GAMMA SPECTRUM OF $^{56}\text{Mn}$

Backscatter
847 (99%)

1811 (29%)
2110 (15%)
2520 (1.2%)
2650 (0.7%)
2950 (0.4%)
3390 (0.2%)

Scintillation Gamma Spectrum
2.576 hr. $^{56}\text{Mn}$
7.6 cm. x 7.6 cm. NaI (TI)
18 cm. Source Distance

Counts Per Channel

Channel Number

37
The most accurate method of determining the amount of an isotope by gamma counting is by comparison with a standard; relative gamma activities can be determined to better than 1%. The most accurate determinations also require radiochemically pure samples. However, by using scintillation counting it is often possible to resolve the composite spectrum of several nuclides into those of the individual components; thus, it is often possible to determine $^{56}\text{Mn}$ accurately in impure samples. Computer resolution of composite scintillation spectra is commonly done especially for routine analysis.$^{92}$

The use of high resolution lithium drifted germanium detectors has made the accurate determination of gamma emitters in impure samples much easier and more accurate.$^{93}$ Typical Ge(Li) detectors are much smaller than NaI(Tl) crystals and thus have much smaller counting efficiencies. Also, germanium has a lower atomic number than iodine so that the ratio of the photoelectric process to the Compton process is smaller. However, the much higher resolution of the Ge(Li) counters makes the gamma ray photo peaks stand up much more clearly above the general background due to the Compton effect. Thus gamma rays with relatively minor abundances can be easily detected and often have their absolute counting rates determined with fair precision. The peak counting efficiency (integrated counting rate in the photo peak divided by the gamma emission rate) at a particular reproducible geometry can be determined by counting gamma standards, and a curve of peak counting efficiency vs. gamma energy for a particular detector obtained. Absolute gamma disintegration rates can be determined with a precision of about 5% from such a curve. Since for activation analysis a standard is commonly irradiated with the unknown, greater precision can usually be obtained. Lithium drifted germanium gamma detectors will easily resolve gamma rays that differ in energy by 5 or 10 keV and allow the intensities of each ray to be measured.

A lithium drifted germanium gamma spectrum of $^{56}\text{Mn}$ is shown in Figure V.4. The spectrum was taken with a 2 cm$^3$ planar detector using a 1024 channel analyzer. It clearly shows the single escape (SE) and double escape (DE) peaks
FIGURE V.4
Ge(Li) GAMMA SPECTRUM OF $^{56}\text{Mn}$
from the higher energy gamma rays. The spectrum can be compared with the NaI(Tl) spectrum shown in Figure V.3 which was taken on the same sample.

If Ge(Li) counters are used, the major gamma rays of $^{56}$Mn can usually be seen without chemical separation on most neutron irradiated rocks and much biological material. A major interference is often sodium (15 hr. $^{24}$Na) and a single precipitation of MnO$_2$ from a nitric acid solution plus KBrO$_3$ or KClO$_3$ will usually be adequate to remove Na and some other interferences. Lithium drifted germanium gamma spectra, because of the excellent energy resolution, lend themselves to computer processing and analysis of the data. Even though germanium detectors have very high resolution, it is essential to check that there are no interfering gamma rays, especially if computer data processing is being used. Thus if manganese is being determined on a new type of sample, it would be well to check by following the decay of the gamma peaks and by doing radiochemical separations to be sure there are no interferences.

Beta particle counting can also be used, especially for $^{56}$Mn, and has the advantage that it requires a minimum of equipment. The most commonly encountered nuclide, $^{56}$Mn, emits mainly energetic beta rays: 2.81 MeV (17%), 1.03 MeV (3%), and 0.72 MeV (18%). Two other nuclides, 45 min $^{51}$Mn (emitting 2.17 MeV positrons 97% abundant) and 21 min $^{52}$Mn (emitting 2.63 MeV positrons 92% abundant) emit high energy particles. These three nuclides could, therefore, be counted and sample self absorption corrections made fairly easily. The nuclide, 5.7 day $^{52}$Mn decays about 2/3 of the time by electron capture but does emit positrons, 0.575 MeV (33%). Both 1.9 x 10$^6$ year $^{53}$Mn and 303 day $^{54}$Mn decay entirely by electron capture ($^{54}$Mn does have a 100% 835 keV gamma), but can be counted with fair efficiency with an argon beryllium window flow or G.M. counter. Self absorption corrections are very difficult to make for the weak 5.4 keV Cr K X-rays from manganese electron capture and also corrections need to be made for the ratio of K to L capture. Special equipment has been developed to count weak X-rays in the presence of a high energy gamma ray background (94). High resolution lithium drifted silicon photon counters with
beryllium windows are particularly valuable for counting low energy X-rays. Those manganese isotopes emitting both particles and gamma rays can be advantageously determined by \( ^{137} \) beta-gamma coincidence counting\(^{(95)}\).

The nuclide \(^{56} \text{Mn}\) emits some high energy gamma rays, 2.110 MeV (15\%), 2.520 MeV (1.2\%), 2.950 MeV (0.4\%), and 3.390 MeV (0.21\%) which have sufficient energy to produce photoneutrons from beryllium and, except for the first, deuterium. The counting of photoneutrons produced in \( ^2 \text{H}_2\text{O} \) has been used to determine \(^{56} \text{Mn}\) in activation analysis\(^{(96)}\).

VI MANGANESE SEPARATION PROCEDURES

A number of methods have been used to separate and purify radioactive manganese for activation analysis, tracer production, reaction yield determinations, and analysis of radioactive contamination. Standardized manganese solutions to be used as carrier can be prepared by dissolving a known amount of manganese, either high purity electrolytic manganese metal or manganese sulfate ignited to 500\(^{\circ}\)C, in dilute nitric acid and making up to volume. If the purified manganese from the radiochemical separation is \( \text{MnO}_2 \), it is best to standardize the carrier by precipitation and weighing of \( \text{MnO}_2 \) since the dioxide is not quite stoichiometric and still contains a little water when dried at 110\(^{\circ}\)C. Manganese carrier can also be standardized by titrimetric or colorimetric methods, see Section 3.

The methods that are included here have not necessarily been checked by the author. Procedure 1 is a general procedure which is fast and easy to carry out but which gives a relatively poor separation from a number of other elements. The additional steps in procedure 2 have been included to separate these contaminants. Procedure 3 is essentially procedure 1 applied for activation analysis. Procedures 4, 5, and 6 are brief outlines of some solvent extraction separations used for activation analysis. Procedures 7, 8, and 9 are taken from the previous edition of this monograph. Procedure 10 is the standard colorimetric analysis procedure for manganese and will be useful for
determining chemical yields.

**Procedure 1**

**Introduction:**

The precipitation of hydrated MnO₂ from a HNO₃ solution of Mn⁺⁺ by oxidation with KBrO₃ or NaClO₃ is the most widely used separation method for manganese. It will separate manganese from most other elements; however, Si, W, Ta, Nb, and Pa are almost quantitatively carried and the precipitate will carry appreciable amounts of Fe, Zr, Ni, Co, V, and Sb. The precipitation is usually not quite quantitative. However, it is a very fast and useful step to concentrate manganese and separate it from most contaminants, and it will probably be the only step necessary if the activity is being counted with a lithium drifted germanium counter.

**Source:**

Step common to most procedures, see Laddicote (97).

**Material Analysis:**

- ⁵⁸Mn or ⁵⁶Mn for activation analysis or analysis of contamination.

**Reagents:**

- Mn carrier, 10 mg/ml Mn as nitrate (Note 1)
- HNO₃ conc.
- KBrO₃ solid
- Hold back carriers, about 10 mg/ml
- HNO₃ 6N
- H₂O₂ 30%
- Ethyl alcohol, 95%

**Procedure:**

Step 1. Dissolve sample in 6N to conc. HNO₃ (Note 2). Add about 20 mg Mn carrier. Add Fe(III) and Zr(IV) holdback carriers. Dilute to about 20 ml with 6N HNO₃.

Step 2. Add about 100 mg solid KBrO₃ and heat to boiling. MnO₂ will precipitate and be coagulated by the heat. Cool. (Note 3).
Step 3. Centrifuge and discard supernate. Wash precipitate several times with 6N HNO₃. Go to step 4 or 5 depending upon purity desired.

Step 4. Dissolve MnO₂ in 6N HNO₃ plus minimum H₂O₂. Boil to destroy excess H₂O₂. Repeat steps 1 through 3. Go to step 5 when sufficiently pure.

Step 5. Slurry MnO₂ with 0.1N HNO₃ and filter onto weighed filter paper disk about 2 cm diam. Use a Hirsch funnel or a sintered glass filtering apparatus. Wash precipitate with water and alcohol, dry at 100°C and weigh as MnO₂.

Notes:

1. Standard Mn carrier can be made by dissolving an accurately weighed amount of 99.9% electrolytic Mn metal or MnSO₄ heated to 500°C in a little dilute HNO₃ and making up to volume. For best accuracy standardise as MnO₂ dried at 100°C.

2. Avoid excess chloride or sulfate since they tend to complex Mn and the chloride also reduces Mn(IV).

3. NaClO₃ can be used instead of KBrO₃ as the oxidant. It oxidizes the Mn more slowly but gives a more filterable precipitate.

Procedure 2

Introduction:

In this procedure for the separation of manganese from fission-product solutions, manganese is finally precipitated as MnNH₄PO₄·H₂O after standard decontamination steps. No detectable contamination was found in the manganese separated from 2.5 x 10¹¹ fissions one hour old.

Source:

This procedure is taken from B. P. Bayhurst and R. J. Prestwood in the Collected Los Alamos Radiochemical Procedures (98).

Reagents:

Mn carrier, 10 mg/ml Mn as MnCl₂ in H₂O, standardised. (Note 1).

W carrier, 10 mg/ml W as Na₂WO₄·2H₂O in H₂O.

Fe carrier, 10 mg/ml Fe as FeCl₃ in 1M HCl.
Pd carrier, 10 mg/ml Pd as PdCl$_2$·2H$_2$O in 1M HCl.
Zr carrier, 10 mg/ml Zr as ZrOCl$_2$·8H$_2$O in 1M HCl.
HCl, conc. and 6M.
HNO$_3$, conc.
CH$_3$COOH glacial.
NE$_4$OH, conc.
NaOH, 10M.
H$_2$S gas.
NaBrO$_3$, saturated solution.
(NH$_4$)$_3$S 20% solution.
(NH$_4$)$_2$HPO$_4$, 1.9M.
Aerosol, 0.1% in H$_2$O.
Dowex A0 50-X8, 100-200 mesh cation resin.
Dowex A0 1-X8, 50-100 mesh anion resin.
Ethanol, absolute.

Procedure:

Step 1. Add the sample to 2 ml Mn carrier in a 40 ml conical centrifuge tube and adjust the volume to about 20 ml with conc. HNO$_3$.

Step 2. Add 5 drops W carrier and heat on a steam bath for 5-10 min. Centrifuge, transfer the supernate to a clean centrifuge tube, and repeat the W scavenge.

Step 3. To the supernate from the second W scavenge add 3 ml satd. NaBrO$_3$ and heat on a steam bath. MnO$_2$ begins to precipitate and the solution fizzes. Carefully add another 3 ml NaBrO$_3$ and heat on steam bath for a total of about 10 min. Cool, add H$_2$O to fill tube, centrifuge. Discard supernate, wash precipitate twice with H$_2$O discarding washings.

Step 4. To the precipitate add 2 drops Fe carrier and 6 ml conc. HCl and boil down to a volume of about 3 ml. Dilute to 20 ml with H$_2$O, add conc. NH$_4$OH dropwise until Fe(OH)$_3$ precipitates, and then 1-2 drops in excess. Heat on a steam bath for about 2 min and centrifuge. Transfer supernate to a clean
tube and repeat the Fe scavenge. Centrifuge and transfer second supernate to a clean tube.

Step 5. Add 2 ml of 20% (NH₄)₂S, heat for 1-2 min on a steam bath and centrifuge saving MnS precipitate.

Step 6. To the precipitate add 5 ml glacial CH₃COOH and boil over a flame. Add 5 drops Pd carrier, dilute to 20 ml with H₂O, place on a steam bath and bubble in H₂S. Centrifuge and save supernate in a clean tube. Repeat the scavenge with 5 more drops Pd carrier and again save supernate.

Step 7. To the supernate add 3 ml of 1.5M (NH₄)₂HPO₄ and about 5 drops conc HCl and boil. Add 2 drops Zr carrier, centrifuge, and save supernate. Repeat Zr scavenge and again save supernate.

Step 8. To the supernate add conc. NH₄OH dropwise until MnNH₄PO₄·2H₂O precipitates and then heat on a steam bath for 3-5 min. Cool, centrifuge, and discard supernate. Wash precipitate with water.

Step 9. Dissolve the precipitate in 2-3 drops conc. HCl, dilute to 5-7 ml with H₂O, and place on a Dowex AG 50-X1, 100-200 mesh cation resin column (6 mm diam, 3 cm. long). Rinse tube with H₂O and add rinsings to column. Wash column with 2-3 ml portions of H₂O and discard washings. Place the cation column on top of an anion column (Dowex AG 1-X8, 50-100 mesh, 8 mm diam, 4-5 cm. long) and elute with 6-9 ml 6M HCl letting eluate from cation column drip through anion column. The Mn is in the eluate from the anion column. Collect the eluate in a clean centrifuge tube, add 10M NaOH dropwise to precipitate Mn(OH)₂. Centrifuge.

Step 10. Dissolve the precipitate in 10 ml conc HNO₃, boil solution until no color left, then repeat W scavenge, step 2.

Step 11. Repeat step 3.

Step 12. Repeat Fe scavenge, step 4.

Step 13. Repeat MnS precipitation, step 5.


Step 15. Repeat Zr phosphate scavenge, step 7.
Step 16. To the supernate add conc NH₄OH dropwise until Mn⁴⁺₄·4H₂O precipitates and then heat on a steam bath for 3-5 min. Centrifuge, discard supernate. Dissolve precipitate in 1-5 drops conc HCl. Dilute to 20 ml with H₂O, add a few drops aerosol and centrifuge. Save the supernate in a clean tube and reprecipitate Mn⁴⁺₄·4H₂O by adding (NH₄)₂HPO₄ then NH₄OH. Filter onto a weighed No. 047 Whatman 7/8" (about 2 cm.) filter circle using a ground off Hirsch funnel and a filter chimney. Wash the precipitate first with 0.1 M NH₄OH and then ethanol. Dry at 110°C, cool, weigh, and mount.

Notes:

Manganese carrier is made by dissolving 22.9 grams MnCl₂ in H₂O and diluting to 1 liter. To standardize, a 2.00 ml aliquot is pipetted into a 40 ml centrifuge tube, 5 drops conc HCl added, then 3 ml 1.5M (NH₄)₂HPO₄, then NH₄OH added to make the solution basic. The solution is heated to boiling, then let standing for 10 min. The precipitate is then filtered quantitatively into a weighed sintered glass crucible, washed with 0.1 M NH₄OH, then alcohol, then dried at 110°C and weighed as Mn⁴⁺₄·4H₂O.

Procedure 3

Introduction:

Even with fairly low power reactors, flux around 5 x 10¹¹ n/cm² sec, manganese can be determined at the nanogram level. Manganese is determined by comparing the ⁵⁶Mn activity produced in the unknown with that produced in a dilute Mn in Al alloy comparator sample. Iron and cobalt can interfere due to the fast neutron reactions: ⁵⁶Fe(n,p)⁵⁶Mn and ⁵⁹Co(n,α)⁵⁶Mn. Since these reactions, unlike the ⁵⁵Mn(n,γ)⁵⁶Mn reaction, do not occur with thermal neutrons, the interference can be minimized by irradiating the samples in a highly thermalized flux. Also, the ⁵⁶Mn produced from iron and cobalt can be determined by irradiating the samples in a hard (large fast neutron component) flux and a highly thermalized flux.

Sources:

W. T. Mullins and G. W. Leddicotte, "Activation Analysis of Manganese -
Reactor Irradiation Source*, Oak Ridge Master Analytical Manual, 5 llh80{99}.

Reagents:

NH₄OH 15N, stock 28% NH₂OH
Coagulant No. 78. Slurry 1 g of No. 78 ore flocculant vegetable colloid
(Burtonite Company, Nutley, New Jersey) in 1 liter H₂O.

(C₂H₅)₂O, anhydrous.

Holdback carriers, about 10 mg/ml.

6N HCl, 500 ml conc. HCl per liter solution.

30% H₂O₂.

Dilute (typically about 1.1%) Mn in Al alloy, spectrographically pure,

Comparator sample.

3M HNO₃, 195 ml conc. HNO₃ per liter solution.

KClO₃, solid.

Samples:

Unknowns, weigh out to better than 1%, 100 to 200 mg samples of solid or
take to better than 1%, 5 to 25 ml samples of liquids. Comparator samples,

weigh 25 to 30 mg samples to ± 0.1 mg.

Irradiation:

Irradiate samples in polyethylene or quartz ampoules. Irradiate for about

2.5 hours (less if ultimate sensitivity not needed).

Procedure:

A. Comparator samples: Transfer quantitatively to a 10 ml volumetric flask.

Dissolve in minimum conc. HCl, dilute to volume, mix well (watch radiation
dose). Take 1.00 ml aliquote in 50 ml centrifuge tubes, add 2.00 ml standard-
ized Mn carrier plus about 1 ml each Cu⁺⁺, Ni⁺⁺, and Na⁺ holdback carriers.

Dilute to 20 ml with H₂O, mix, make alkaline with NH₄OH and continue as in

part C.

B. Unknowns: If solid, transfer quantitatively to a 50 ml centrifuge tube,

add 2.00 ml standardized Mn carrier and about 1 ml each Cu⁺⁺, Ni⁺⁺, and Na⁺
holdback. Add sufficient mineral acid to dissolve sample, heating if necessary.
Dilute to 20 ml, make basic with NH₄OH, and continue as in part C. If liquid unknown, pipet a known aliquot into a 50 ml centrifuge tube, add 2.00 ml standardized Mn carrier and about 1 ml each Cu⁺⁺, Ni⁺⁺, and Na⁺ holdback, dilute to 20 ml, make basic with NH₄OH, and continue as in part C.

C. Radiochemical separation:

Step 1. To NH₄OH solution add 5 drops 30% H₂O₂, heat to boiling and centrifuge, saving the MnO₂ precipitate. Wash precipitate first with 20 ml 1M NH₄OH then with 20 ml 3 M HNO₃ (Note 1).

Step 2. Dissolve MnO₂ in 2 ml 6N HCl and dilute to 10 ml with conc. HNO₃. Heat and boil 30 sec. Add solid KClO₃ in 0.5 g increments, heating to 75°C after each addition (Note 2) until MnO₂ precipitation is complete. Centrifuge, wash MnO₂ precipitate with 25 ml 3 M HNO₃.

Step 3. Slurry MnO₂ with a little H₂O plus coagulant No. 78. Filter MnO₂ through a weighed filter paper circle held in a Hirsch funnel. Wash three times with 5 ml portions each of H₂O, 95% C₂H₅OH, then ethyl ether. Dry at 100°C and weigh to determine manganese yield, then mount for counting. The chemical yield should be well over 50%.

D. Counting:

The $^{56}$Mn can be determined by either beta or gamma counting. Gamma counting with a scintillation spectrometer, or even better a lithium drifted germanium spectrometer, is preferable since the $^{56}$Mn activity can usually be accurately determined in the presence of radioactive impurities. Since the manganese activity of the unknown is being measured against a known comparator sample, it is only necessary to mount and count the unknown and known samples in exactly the same way and to correct for decay and chemical yield.

Beta Counting:

Mount the unknown and known comparator samples in the same way, usually on a cardboard mounting card, covering them with a thin layer of cellophane or Scotch tape to contain the samples. Using a Geiger-Müller counter or a flow proportional counter determine the background and the counting rates (at the
same geometry and with the same added absorber) of the known and unknown. Correct the counts to the same decay time and for chemical yields and calculate the manganese content of the unknown. If the MnO₂ samples are of considerably different size, errors will be introduced because of sample self absorption and backscattering. Empirical corrections can be applied.

If the radiochemical purity of the unknown sample is questionable, follow the decay of the sample or take an aluminum absorption curve.

**Gamma Counting**

Mount the unknown and known comparator samples in the same way and count at the same counter geometry and with the same added absorber. Use a scintillation spectrometer or a Ge(Li) spectrometer. Determine the peak counting rate of the 847 keV photopeak by integrating under the peak and subtracting off the extrapolated Compton background from the higher energy gamma rays. If the sample is radiochemically pure it is sufficient to integrate over the peak and subtract the counter background in the same channels. If there is an interfering impurity, integrate the 1811 or 2110 keV photopeaks. Correct for the difference in decay times and chemical yields and calculate the manganese in the unknown. It may be convenient to count the sample first (e.g. still in the centrifuge tube) and determine the manganese yield colorimetrically later.

**Notes:**

1. It is imperative that all the H₂O₂ be washed out before the MnO₂ is washed with 3N HNO₃; otherwise it will dissolve.

2. KBrO₃ can be used instead of KClO₃ to precipitate MnO₂. It reacts more rapidly but gives a less easily filterable precipitate. Step 2 of the procedure can be repeated for greater purity.

**Procedure 4**

**Introduction:**

Tetraphenylarsonium permanganate is extracted by CHCl₃, relatively few other elements extract; it is therefore a good purification step for Mn. In this procedure a substoichiometric amount of tetraphenylarsonium chloride is
used so that the yields for the unknown and comparator samples will be essentially the same.

Source:
A. Zeman, J. Prasilova and J. Ruzicka

Reagents:
1N and conc. H₂SO₄
Mn carrier, 1.8x10⁻² M MnSO₄
H₃PO₄, 85%
AgNO₃, 1% solution
(NH₄)₂S₂O₈
NH₄OH solution
tetraphenylarsonium chloride, 2x10⁻³ M
CHCl₃

Procedure:

Step 1. Irradiate unknown and comparator samples. Dissolve samples in 10 ml 1N H₂SO₄ (samples were chalk) (Note 1). Add 0.60 ml Mn carrier, 2 drops 85% H₃PO₄, and dilute to 50 ml with water (Note 2). Now add 1 ml conc. H₂SO₄, 1 ml 1% AgNO₃ and 1 g (NH₄)₂S₂O₈ and heat to oxidize manganese to MnO₂⁻. Boil to destroy excess persulfate.

Step 2. Cool, adjust pH to 8-9 with NH₄OH (Note 3). Transfer to a separatory funnel, add 2.00 ml 2x10⁻³ M tetraphenylarsonium chloride then add 5.00 ml CHCl₃ and extract permanganate for 3 minutes (Note 4).

Step 3. Either measure activity in 3.00 ml of the CHCl₃ extract or evaporate to dryness and take up in 2 ml hot conc. HCl. Proceed in the same way with both known and unknown samples and assume yields the same for both.

Notes:
1. H₂SO₄ is the best acid for dissolution since SO₄²⁻ is not extracted. With HCl, Fe(III), Sn(IV), Pd(II), etc. can interfere. Nitrate extracts.

2. If Au, Re, or Tc are present, add a purification step by extracting manganese diethyldithiocarbamate complex. To the sample in H₂SO₄ with Mn
carrier added and pH adjusted to 8 add 5 to 10 fold excess Na diethyldithiocarbamate and extract precipitate with 10 ml CHCl₃. The Mn(II) is air oxidised to Mn(III) and extracts as the Mn(III) complex.  

3. At pH 8, Mo⁴⁺ and Cr⁴⁺ do not extract.  

4. A substoichiometric amount of tetraphenylarsonium chloride is used.  

Manganese in the unknown is equal to the manganese in the comparator sample times the ratio of the activities in the unknown to the comparator sample (corrected for decay).  

Procedure 5  

Introductions  

This procedure was developed to separate and concentrate manganese prior to colorimetric analysis. It is based upon solvent extraction and could be adapted for activation analysis.  

Source:  

Reagents:  
citric acid  
NH₄OH, 6M, 1M  
sodium diethyldithiocarbamate  
CHCl₃  
HCl, 3M  
H₂SO₄  
HNO₃  
HClO₄  

Procedure:  
Step 1. Ash bone, teeth, milk, etc. unknowns. Irradiate with known comparator samples. Add 2 g citric acid per gram ash and dilute to about 175 ml.  

Step 2. Adjust pH to about 5.2 by adding 6M NH₄OH using a glass electrode and a pH meter to monitor the pH. Add 0.4 g sodium diethyldithiocarbamate (DITCA). Adjust pH to 5.3 with 1 M NH₄OH and dilute to 200 ml.

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Step 3. Extract with 25 ml CHCl₃. Extraction causes pH to rise to about 5.8, readjust to 5.3 with about 1 ml 3 M HCl. About 90% of Mn in extract.

Step 4. Add 0.1 g more DIBEA and reextract; about 90% of remaining Mn extracts. Ca phosphate only very slowly precipitates.


Procedure 6

Introduction:

TTA will complex Mn(II) at a fairly high pH. The extraction of the TTA complex has been used to purify manganese for activation analysis. The samples, if biological, are ashed and irradiated in a neutron flux of about 7.5 x 10¹² n/cm² sec.

Source:
F. Kukula, B. Mudrova and M. Krivanek (59).

Reagents:

Mn carrier, MnSO₄ in H₂O, 1 mg/ml
Buffer, CH₃COONH₄ plus NH₄OH
sodium tartrate, 10%
KF, 20%
thenoyltrifluoroacetone (TTA) in ethanol, 0.11 M
TTA in ethyl acetate, 0.2 M
hydroxylamine hydrochloride
HCl

Procedure:

Step 1. Dissolve irradiated ash, etc., in HCl (use HNO₃ - HF for Zr-Al alloy). Add 2 ml Mn carrier, 3 ml 10% tartrate, 3 ml 20% KF (Note 1), 10 mg hydroxylamine hydrochloride, and adjust pH to 8 - 8.5 with the NH₄OH - CH₃COONH₄ buffer (Note 2). Add 0.5 ml TTA in ethanol (complexes about 70% of Mn).

Step 2. Extract 2 to 3 min with 10 ml TTA in ethyl acetate. Measure gamma spectrum of extract. Determine yields colorimetrically.
Notes:

1. Zr, Hf, Nb, Th, Fe, Sc, and Sb are prevented from extracting by the fluoride and tartrate, \( \text{Cu} \) and \( \text{Co} \) by the \( \text{NH}_4\text{OH} \).

2. \( \text{Mn(OH)}_2 \) does not precipitate at pH 8-8.5. Hydroxylamine hydrochloride is added to prevent the air oxidation of \( \text{Mn(II)} \).

Introduction:

This procedure was developed for the neutron activation analysis of manganese in biological material (blood). It gives a manganese yield of 60 - 90\% and takes about 2.5 hours for eight samples. The fraction of \( ^{24}\text{Na} \) left is about \( 5 \times 10^{-9}\% \) and \( ^{32}\text{P} \), \( 2.2 \times 10^{-3}\% \).

Source:

H. J. Bowen(101) as reported by Leddicotte(97).

Reagents:

- Fuming \( \text{HNO}_3 \)
- Standardized Mn carrier
- Holdback carriers, about 10 mg/ml, of Br, Cl, Co, Cr, Cu, Fe, Ni, Na, K, Y, and Zn.
- \( \text{H}_2\text{O}_2 \), 30\%
- \( \text{Na}_2\text{CO}_3 \) solution
- 6M HCl
- \( (\text{NH}_4)\text{HPO}_4 \) solution
- \( \text{CH}_3\text{COONH}_4 \) solution
- 2M \( \text{HNO}_3 \)
- \( \text{NaBrO}_3 \) solution, saturated acetone

Procedure:

Step 1. Dissolve the irradiated blood in hot fuming nitric acid containing 50 mg manganese carrier and the holdback carriers listed under reagents. Precipitate manganese dioxide by adding \( \text{NaClO}_3 \) solution and heating. Centrifuge,
Step 2. Wash MnO₂ twice with water, centrifuge and discard washes.

Step 3. Dissolve MnO₂ in acidified H₂O₂, then precipitate MnCO₃ by adding Na₂CO₃ solution. Centrifuge, discard supernate.

Step 4. Wash precipitate with water. Dissolve precipitate in dil HCl and add FeCl₃, ammonium phosphate, and ammonium acetate solutions. Precipitate Fe(OH)₃ with NH₄OH. Centrifuge and save solution. Repeat scavenging by adding more Fe carrier, centrifuge, and save solution.

Step 5. To solution add enough Na₂CO₃ to precipitate MnCO₃. Centrifuge and save precipitate.

Step 6. Dissolve the MnCO₃ in 2N HNO₃ and precipitate MnO₂ by adding saturated NaBrO₃ to the solution and heating. Centrifuge, save precipitate.

Step 7. Wash the MnO₂ three times with water and once with acetone. Centrifuge, discard washes. Transfer MnO₂ to a weighed counting tray, dry under an infrared lamp, and weigh to determine chemical yield.

Step 8. Cover tray with Scotch tape and beta or gamma count ⁵⁶Mn.

**Procedure 8**

**Introduction:**

This procedure was developed for the neutron activation analysis of manganese in biological materials (tomato seeds). It gives good decontamination from P and Na and takes about 2.5 hours. Chemical yield should be 60 - 90%.

**Source:**

H. J. M. Bowen and P. A. Cawse(102) as reported by Leddicotte(97).

**Reagents:**

- HNO₃, conc.
- Standardized Mn carrier
- Cu, Y, PO₄³⁻ holdback carriers, about 10 mg/ml.
- NaClO₃, saturated solution
- 2N HCl
- 30% H₂O₂
Step 1. Transfer the irradiated tissue from the irradiation container to a 50 ml centrifuge tube. Add 10 ml conc HNO₃, 10 mg label carrier and holdback carrier of Cu, Y, and PO₃ -. Boil the mixture until the tissue dissolves. Add 1 ml NaClO₃, heat, centrifuge and save MnO₂ precipitate.

Step 2. Wash the MnO₂ twice with 5 ml ~0. Centrifuge, discard wash. Dissolve MnO₂ in 3 ml 2N HCl and min. ~0₂ and then add NH₃OH and CH₃COONH₄. Be sure all ~0₂ is boiled out first. To this mixture add 5 drops of Fe(NO₃)₃ and one drop H₂O₂. Centrifuge, discard precipitate.

Step 3. Acidify the supernate with 2N HCl, add 3 drops Cu(NO₃)₂ and boil. Centrifuge, saving supernate. Wash CuS twice with ~0. Centrifuge. Dissolve CuS in 10 ml of conc HNO₃ and add 1 ml NaClO₃, boil (caution!), centrifuge and discard supernate.

Step 4. Make the solution alkaline with 3 ml NH₃OH and NH₂OH, boil. Save NH₃ precipitate. Wash MnS twice with ~0. Centrifuge. Dissolve MnS in 10 ml of conc HNO₃ and add 1 nil NaClO₃, boil (caution!), centrifuge and discard supernate.

Step 5. Wash the HNO₃ precipitate with three 10 ml portions of hot water. Dry under an infrared lamp, cool, weigh to determine yield.

Step 6. Cover the tray with Scotch tape and beta or gamma count 5 min.

Step 7. Wash the HNO₃ precipitate with water into a weighed counting tray. Dry under an infrared lamp, cool, weigh to determine yield.
Procedure 2

Introduction:

This procedure was developed to determine manganese isotopes in cyclotron irradiated copper. The separation time is 30 min. and a decontamination of greater than $10^3$ from other elements is reported. Chemical yield about 75%.

Source:

Batsel as reported by W. W. Meinke\(^{(103)}\). Several other manganese procedures are given by Meinke. They are similar to this procedure except a different step is included to remove the target material.

Reagents:

\begin{itemize}
  \item $\text{HNO}_3$, conc.
  \item Standardized Mn carrier
  \item Holdback carriers, Zn, Ni, Co, Fe, Cr, V, Ti, Sc, Ca, and K. About 10 mg/Al
  \item $\text{H}_2\text{S}$ gas
  \item $\text{HCl}$, 6M
  \item $\text{NH}_4\text{OH}$, conc.
  \item $\text{KClO}_3$ solid
  \item $\text{H}_2\text{O}_2$, 30%
\end{itemize}

Procedure:

Step 1. Dissolve the copper in the minimum amount of conc $\text{HNO}_3$. Boil almost to dryness, add carriers, Zn and below, including 5 mg of standardized Mn. Make about 1M in HCl.

Step 2. Precipitate CuS by bubbling in $\text{H}_2\text{S}$. Centrifuge, save supernate. Make supernate alkaline with $\text{NH}_4\text{OH}$ and bubble in more $\text{H}_2\text{S}$ to precipitate sulfides including MnS. Centrifuge and wash.

Step 3. Dissolve sulfides in 1 ml fuming $\text{HNO}_3$. Add 2 or 3 crystals of $\text{KClO}_3$ and boil gently for 2 minutes to precipitate $\text{MnO}_2$.

Step 4. Wash precipitate with $\text{H}_2\text{O}$, then dissolve in minimum $\text{HNO}_3$ and $\text{H}_2\text{O}_2$. Again add holdback carriers and make 16N in $\text{HNO}_3$. Heat and precipitate $\text{MnO}_2$ with $\text{KClO}_3$ as in step 3.
Step 5. Wash, filter, dry, weigh, and mount MnO₂ precipitate. Beta or gamma count.

Procedure 10

Introduction:

The manganese yield from a radiochemical separation can often be more conveniently determined by colorimetric analysis than by weighing. If the concentration of manganese is in the optimum region, a precision of 0.5% standard deviation can be obtained, considerably better than that obtained by weighing MnO₂ or MnNH₄PO₄·H₂O.

Source:


Reagents:

6M HNO₃
H₂O₂, 30%
H₂SO₄, conc.
H₃PO₄, 85%
KIO₄, solid

Procedure:

Step 1. After counting is completed analyze the sample. If the sample is solid, dissolve it in 6M HNO₃ (plus a little H₂O₂ in the case of MnO₂) and make up to a convenient volume (10.0 ml) in a volumetric flask, and take an aliquot estimated to contain 0.5 to 1.0 mg Mn. If the sample is liquid, take a same sized aliquot.

Step 2. Add the aliquot to about 10 ml 6M HNO₃, boil to remove H₂O₂ and oxidize Fe(II) and other reducing agents. If the solution contains much HCl, the aliquot should be added to conc. H₂SO₄ and the solution evaporated to fumes of SO₃. Then, after the solution is cold, carefully add about 10 ml 6M HNO₃.

Step 3. Dilute the solution to about 20 ml with H₂O and add about 5 ml 85% H₃PO₄ (decolorizes Fe(III)), then about 0.1 g KIO₄. Heat to boiling and boil very gently for about 1 min., then add 0.1 g KIO₄ more and again boil
gently for 1 min.

Step 4. Cool solution, transfer to a 100 ml volumetric flask, make up to volume, take samples and determine the transmittance at 525 millimicrons using a spectrophotometer.

Step 5. Take a series of known manganese samples, oxidize, and establish a working curve. For a narrow band spectrophotometer, Beer's law holds.
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