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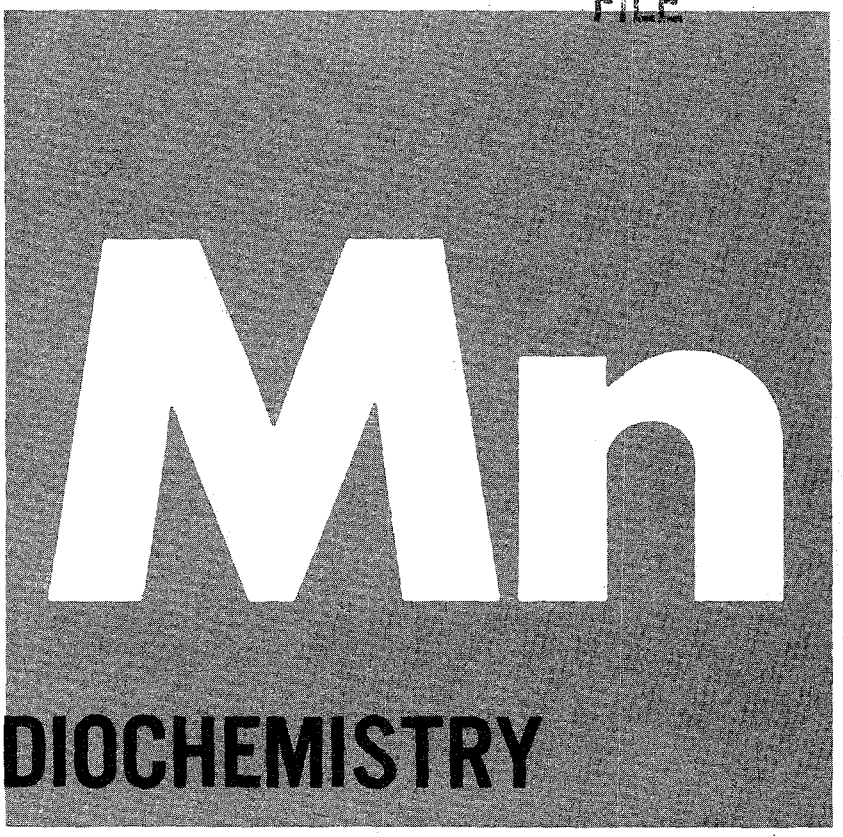


# RADIOCHEMISTRY OF MANGANESE

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# Radiochemistry of Manganese

by R. P. Schuman

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revised from the original text of G. W. LEDDICOTTE

I. GENERAL REVIEWS OF THE CHEMISTRY OF MANGANESE.

A. Inorganic Chemistry

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## II NUCLEAR PROPERTIES OF MANGANESE ISOTOPES

Natural manganese consists of one stable isotope, $^{55}Mn$, 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 $^{12}C = 12.000000$. The nuclear spin of $^{55}Mn$ is 5/2-. Very small but detectable amounts of radioactive $^{53}Mn$ and $^{54}Mn$, 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 $^{54}Mn$ 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 $^{56}Mn$ which decays by beta emission and emits abundant 847, 1811, and 2110 keV gamma rays. The half life and characteristic gamma rays make $^{56}Mn$ an ideal isotope for activation analysis. Because $^{53}Mn$ 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 $^{54}Mn$[5].

Neutron capture cross sections have been measured as a function of neutron energy for $^{55}Mn$[6]. The thermal (0.025 eV) cross section of $^{55}Mn$ is 13.3 barns and the resonance integral is 14.2 barns[7]. A capture cross section of 170 barns has been determined for $^{53}Mn$[8] using typical reactor neutrons. Fast neutrons will produce 303 day $^{54}Mn$ by an n,2n reaction on $^{55}Mn$, 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. $^{55}Cr$, and n,$\alpha$ giving 3.8 min. $^{52}V$, are possible with fast

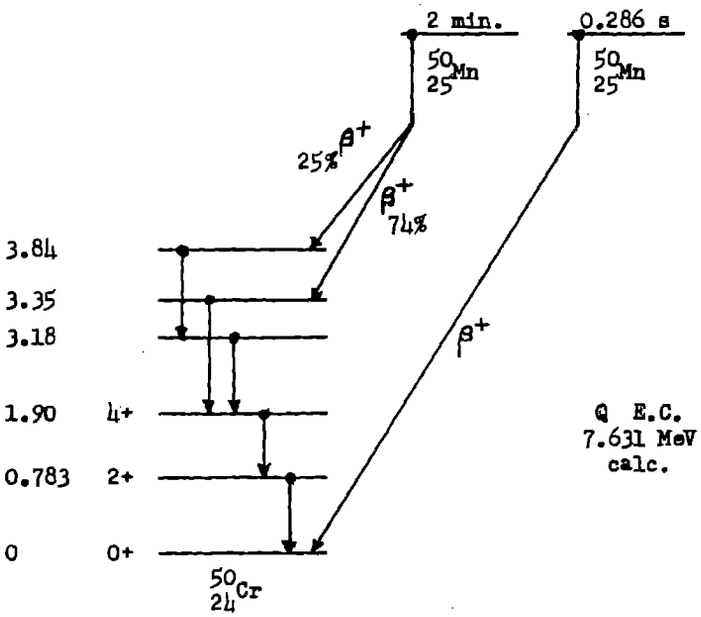
TABLE II.1

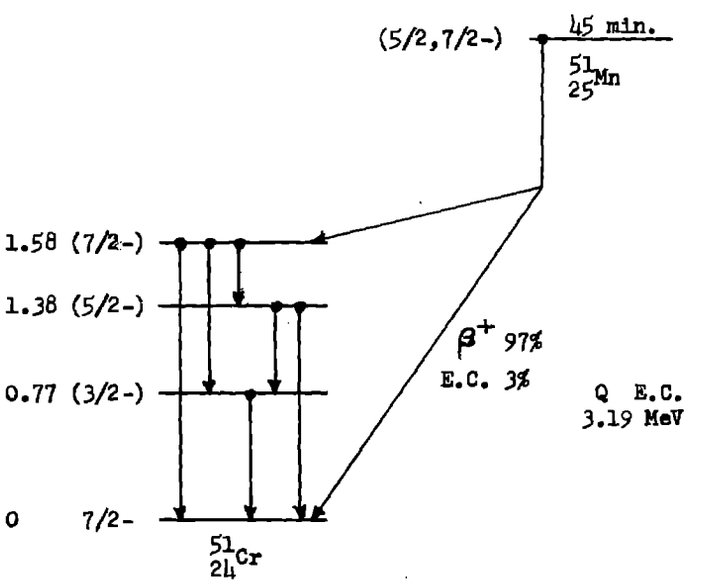
ISOTOPES OF MANGANESE[4]

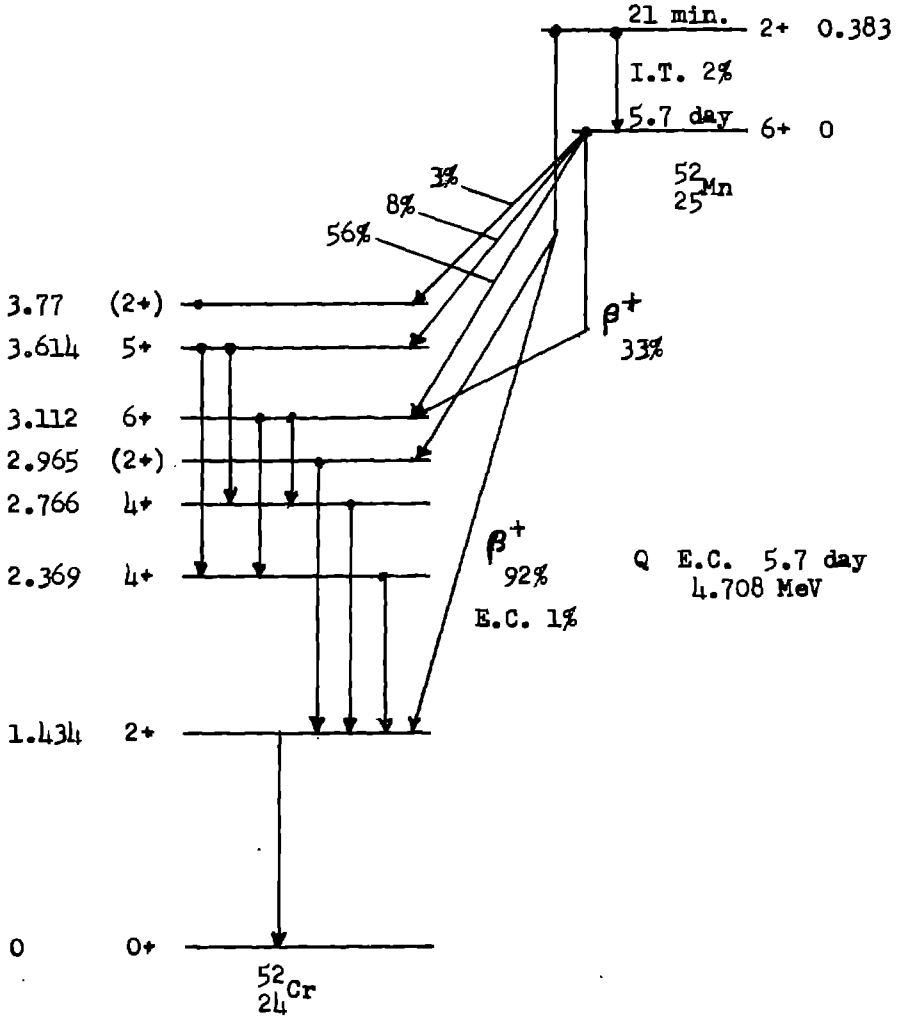
| NUCLIDE | HALF-LIFE | TYPE OF DECAY Mode | Energy MeV | GAMMA RAYS Energy MeV | Abundance % | HOW MADE | NOTES |
|---|---|---|---|---|---|---|---|
| $^{49}Mn$ | 0.4 sec. | | | | | | uncertain |
| $^{50}Mn$ | 0.286 sec. | $\beta^+$ | 6.61 max. | 0.511 $\gamma^\pm$ | 200% | $^{50}Cr(p,n)$ | probable |
| $^{50}Mn$ | 2 min. | $\beta^+$ | | 0.511 $\gamma^\pm$ | 198% | $^{50}Cr(p,n)$ | uncertain |
| | | | | 0.66 | 25 | | |
| | | | | 0.783 | 100 | | |
| | | | | 1.11 | 100 | | |
| | | | | 1.28 | 25 | | |
| | | | | 1.45 | 75 | | |
| $^{51}Mn$ | 45.2 min. | $\beta^+$ | 2.17 max. | 0.511 $\gamma^\pm$ | 194% | $^{50}Cr(d,n)$ $^{50}Cr(p,\gamma)$ | certain |
| | | | | 1.56 | | | |
| | | | | 2.03 | | | |
| $^{52}Mn$ | 5.60 day | $\beta^+$ (34%) E.C. (66%) | 0.575 max. | 0.511 $\gamma^\pm$ | 67% | $^{52}Cr(p,n)$ $^{52}Cr(d,2n)$ | certain |
| | | | | 0.744 | 82 | | |
| | | | | 0.935 | 84 | | |
| | | | | 1.434 | 100 | | |
| $^{52m}Mn$ | 21.1 min. | $\beta^+$ I.T. (2%) | 1.63 max. | 0.383 | 2% | $^{52}Fe$ decay | certain |
| | | | | 0.511 $\gamma^\pm$ | 193 | | |
| | | | | 1.434 | 100 | | |
| $^{53}Mn$ | $1.9\times10^6$ yr. | E.C. | | Cr X-rays | | $^{53}Cr(p,n)$ $^{52}Cr(d,n)$ | probable |
| $^{54}Mn$ | 303 day | E.C. | | Cr X-rays | | $^{56}Fe(d,\alpha)$ $^{54}Fe(n,p)$ | certain |
| | | | | 0.835 | 100% | | |
| $^{55}Mn$ | stable | 100% abundant | | | | | |
| $^{56}Mn$ | 2.576 hr. | $\beta^-$ | 2.85 max. | 0.847 | 99% | $^{55}Mn(n,\gamma)$ $^{56}Fe(n,p)$ | certain |
| | | | | 1.811 | 29 | | |
| | | | | 2.110 | 15 | | |
| $^{57}Mn$ | 1.7 min. | $\beta^-$ | 2.55 max. | Fe X-rays | | $^{54}Cr(\alpha,p)$ $^{57}Fe(n,p)$ | probable |
| | | | | 0.014 | conv. | | |
| | | | | 0.122 | strong | | |
| | | | | 0.136 | strong | | |
| | | | | 0.22 | | | |
| | | | | 0.353 | | | |
| | | | | 0.692 | | | |
| $^{58}Mn$ | 1.1 min. | $\beta^-$ | | 0.36, 0.41 | | $^{58}Fe(n,p)$ | probable |
| | | | | 0.52, 0.57 | | | |
| | | | | 0.82, 1.0 | | | |
| | | | | 1.25, 1.4 | | | |
| | | | | 1.6, 2.2 | | | |
| | | | | 2.8 | | | |

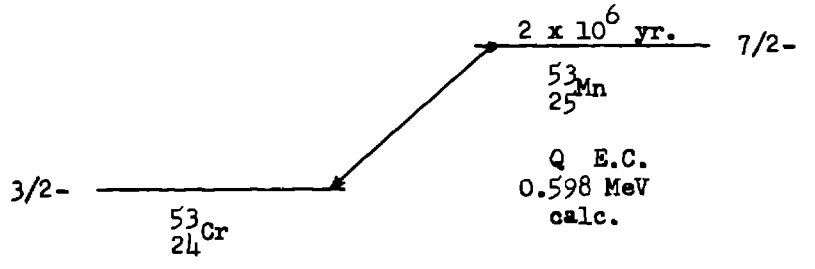
FIGURE II.1

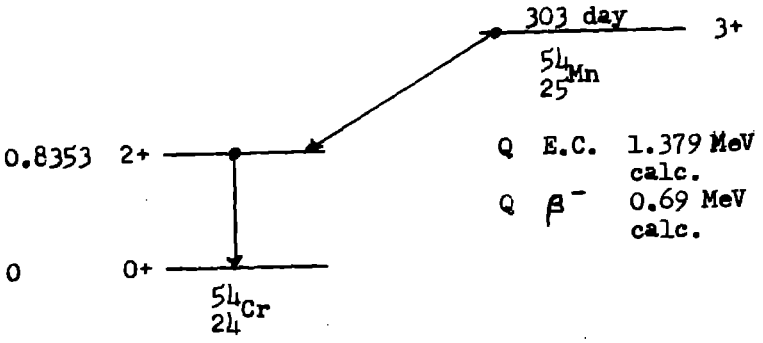
Decay Schemes of Manganese Isotopes[4]

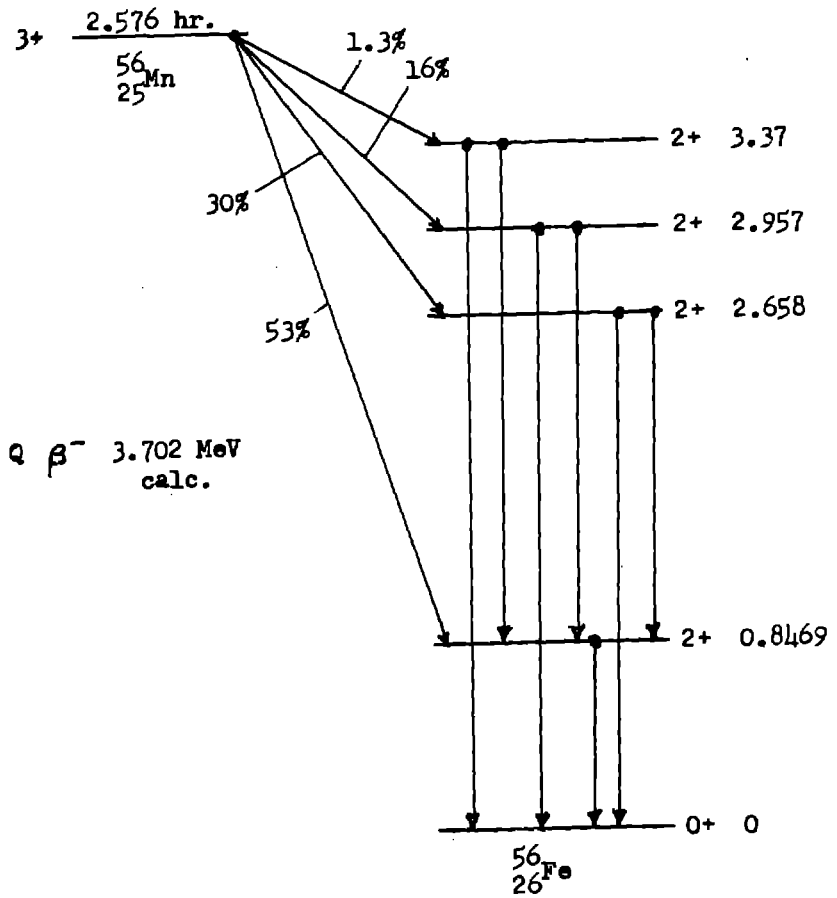


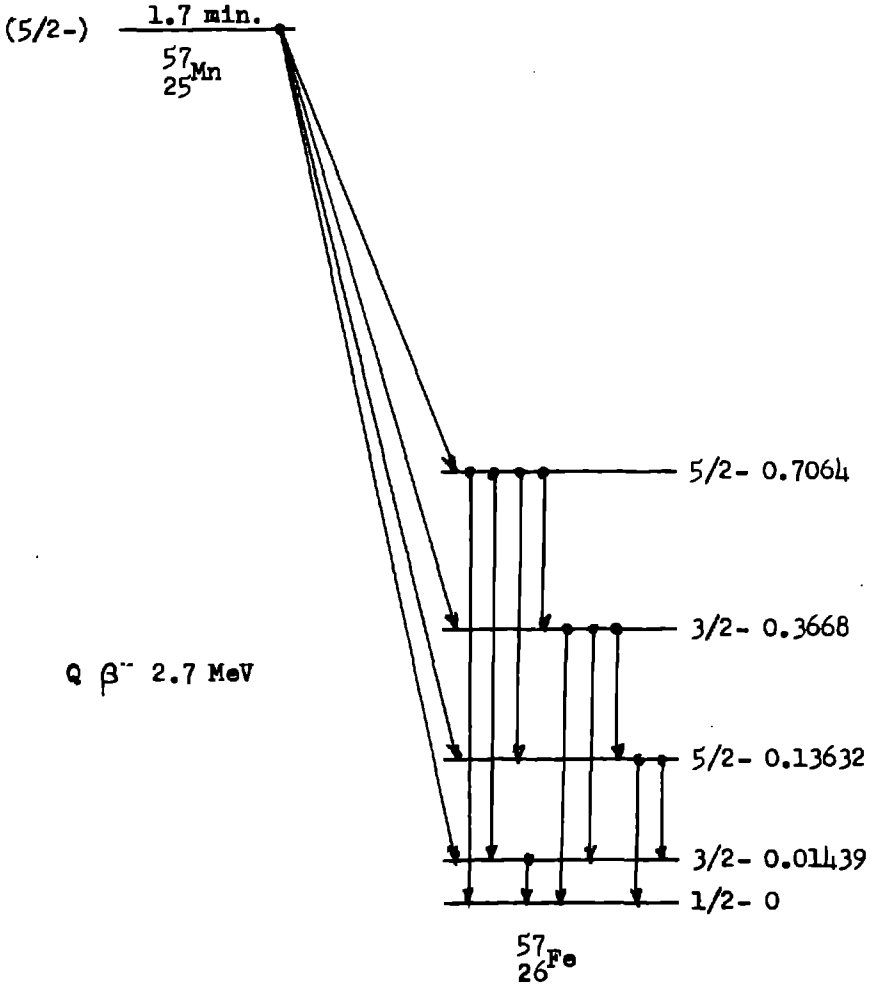




21 min.
2+
0.383
I.T. 2%
5.7 day
6+
0
$^{52}_{25}$Mn
3%
8%
56%
$\beta^+$
33%
3.77 (2+)
3.614 5+
3.112 6+
2.965 (2+)
2.766 4+
2.369 4+
$\beta^+$
92%
E.C. 1%
Q E.C. 5.7 day
4.708 MeV
1.434 2+
0 0+
$^{52}_{24}$Cr


2 x $10^6$ yr.
7/2-
$^{53}_{25}$Mn
Q E.C.
0.598 MeV
calc.
3/2-
$^{53}_{24}$Cr


303 day
3+
$^{54}_{25}Mn$
0.8353
2+
0
0+
$^{54}_{24}Cr$
Q E.C. 1.379 MeV calc.
Q $\beta^-$ 0.69 MeV calc.


3+
2.576 hr.
$^{56}_{25}Mn$
1.3%
16%
30%
53%
2+ 3.37
2+ 2.957
2+ 2.658
2+ 0.8469
0+ 0
$^{56}_{26}Fe$
Q $\beta^-$ 3.702 MeV calc.


(5/2-)
1.7 min.
57 Mn 25
Q β⁻ 2.7 MeV
5/2- 0.7064
3/2- 0.3668
5/2- 0.13632
3/2- 0.01439
1/2- 0
57 Fe 26

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 $^{55}Mn(\gamma,n)^{54}Mn$ (303 d.), are also of possible interest for activation analysis and producing tracers[9].

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 $^{59}Co(n,\alpha)^{56}Mn$ 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 $^{54}Cr(n,\gamma)^{55}Cr(\beta^-)^{55}Mn(n,\gamma)^{56}Mn$. Various portable neutron sources have been used for manganese activation analysis; $^{252}Cf$ is a particularly attractive source[12]. Fast, 14 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 archeology[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, $^{55}Mn(n,\gamma)^{56}Mn$, 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 hour $^{56}Mn$ decays to stable $^{56}Fe$, and since neutron capture in $^{56}Fe$ and $^{57}Fe$ 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[7b].

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 $^{55}Mn$. A very sensitive neutron monitor for weak sources and beams is a bath of $KMnO_4$ solution. The $^{56}Mn$ 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 $^{53}Mn$ and $^{54}Mn$ 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 Si[25]. Its relatively large abundance is expected since $^{55}Mn$ 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 widespread in compounds and is an essential constituent of about 140 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]

| Name | Chemical Composition | Color | Use |
|---|---|---|---|
| Alabandite | MnS | iron-black | |
| Franklinite | $(Fe,Zn,Mn)Fe_2O_4$ | iron-black | zinc ore |
| Manganosite | MnO | emerald-green | |
| Hausmannite | $Mn_3O_4$ | brown-black | manganese ore |
| Braunite | $3Mn_2O_3 \cdot MnSiO_3$ | brown-black | manganese ore |
| Polianite | $MnO_2$ | steel-gray | manganese ore |
| Pyrolusite | $MnO_2$ (+ trace $H_2O$) | iron-black | manganese ore |
| Manganite | MnOOH | iron-black | manganese ore |
| Pyrochroite | $Mn(OH)_2$ | white, darkens | |
| Psilomelane, Wad | impure $MnO_2 \cdot xH_2O$ | brown-black | manganese ore |
| Rhodochrosite | $MnCO_3$ | rose-red | manganese ore |
| Rhodonite | $MnSiO_3$ | rose | manganese ore ornamental stone |
| Helvite | $3(Mn,Fe)BeSiO_4 \cdot MnS$ | yellow | |
| Spessartite | $Mn_3Al_2(SiO_4)_3$ | dark-red | semiprecious gem |
| Tephroite | $Mn_2SiO_4$ | flesh-red | |
| Piedmontite | $HCa_2(Al,Mn)_3Si_3O_{13}$ | red-brown | |
| Bementite | $H_{10}Mn_8Si_7O_{27}$ | gray-yellow | manganese ore |
| Inesite | $H_2(Mn,Ca)_6Si_6O_{19} \cdot 3H_2O$ | rose-red | |
| Columbite-Tantalite | $(Fe,Mn)(Ta,Nb)_2O_6$ | iron-black | Ta and Nb ore |
| Lithiophilite | $Li(Mn,Fe)PO_4$ | salmon-pink | |
| Triplite | $(Fe,Mn)F(Fe,Mn)PO_4$ | brown | |
| Hübnerite | $MnWO_4$ | brown-black | tungsten ore |
| Pyrophanite | $MnTiO_3$ | deep red | |

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 silicomanganese 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 deoxidize the steel, and at times to combine with carbon. Manganese, since it is much more reactive than iron, reduces the FeS, FeO, $FeSiO_3$, and $Fe_3C$ 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[31]. 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[32]. 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.

4. Chemical Properties of Manganese[33,34]

Manganese is an element of the first (3d) transition series. The electronic configuration of the normal atomic state is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^2$, the normal state being $^6S_{5/2}$. 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[35].

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[36]. The ionization 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 oxidizing agent and is, unless complexed or insoluble, unstable disproportionating into Mn(II) and $MnO_2$. 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 oxidising agents such as $KBrO_3$ and $KClO_3$ will oxidize $Mn^{++}$ to $MnO_2$, and other strong oxidising agents like $KIO_4$ and $Ag^{++}$ will oxidize it to $MnO_4^-$. In basic solutions Mn(II) is much more easily oxidised, and even such weak oxidising agents as $Fe(CN)_6^{3-}$ and $H_2O_2$ will oxidize Mn(II) to $MnO_2$. In basic solutions, $Mn(OH)_2$ is oxidized by air first to MnOOH and ultimately to hydrated $MnO_2$. 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

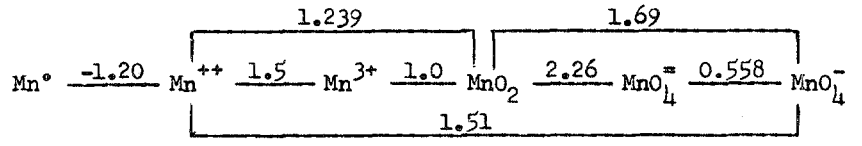
STANDARD REDUCTION POTENTIALS OF MANGANESE COUPLES[34,37]

| Half-cell Reaction | Oxidation States | E° volts |
|---|---|---|
| *In acid solution, $H^+$ unit activity* | | |
| $Mn^{++} + 2e^- \rightarrow Mn^\circ$ | 2 - 0 | - 1.20 |
| $Mn^{3+} + e^- \rightarrow Mn^{2+}$ | 3 - 2 | ~ 1.5 |
| $Mn(CN)_6^{3-} + e^- \rightarrow Mn(CN)_6^{4-}$ | 3 - 2 | - 0.24 |
| $MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{++} + 2H_2O$ | 4 - 2 | 1.239 |
| $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{++} + 4H_2O$ | 7 - 2 | 1.51 |
| $MnO_2 + 4H^+ + e^- \rightarrow Mn^{3+} + 2H_2O$ | 4 - 3 | ~ 1.0 |
| $MnO_4^- + 4H^+ + 2e^- \rightarrow MnO_2 + 2H_2O$ | 6 - 4 | 2.26 |
| $MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$ | 7 - 4 | 1.69 |
| $MnO_4^- + e^- \rightarrow MnO_4^{=}$ | 7 - 6 | 0.558 |
| *In basic solution, $OH^-$ unit activity* | | |
| $Mn(OH)_2 + 2e^- \rightarrow Mn^\circ + 2OH^-$ | 2 - 0 | - 1.58 |
| $Mn(OH)_3 + e^- \rightarrow Mn(OH)_2 + OH^-$ | 3 - 2 | ~ - 0.2 |
| $MnO_2 + 2H_2O + 2e^- \rightarrow Mn(OH)_2 + 2OH^-$ | 4 - 2 | - 0.03 |
| $MnO_4^- + 4H_2O + 5e^- \rightarrow Mn(OH)_2 + 6OH^-$ | 7 - 2 | 0.34 |
| $MnO_2 + 2H_2O + e^- \rightarrow Mn(OH)_3 + OH^-$ | 4 - 3 | ~ 0.1 |
| $MnO_4^{3-} + 2H_2O + e^- \rightarrow MnO_2 + 4OH^-$ | 5 - 4 | ~ 0.9 |
| $MnO_4^{=} + 2H_2O + 2e^- \rightarrow MnO_2 + 4OH^-$ | 6 - 4 | 0.603 |
| $MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^-$ | 7 - 4 | 0.58 |
| $MnO_4^{=} + e^- \rightarrow MnO_4^{3-}$ | 6 - 5 | ~ 0.3 |
| $MnO_4^- + e^- \rightarrow MnO_4^{=}$ | 7 - 6 | 0.558 |

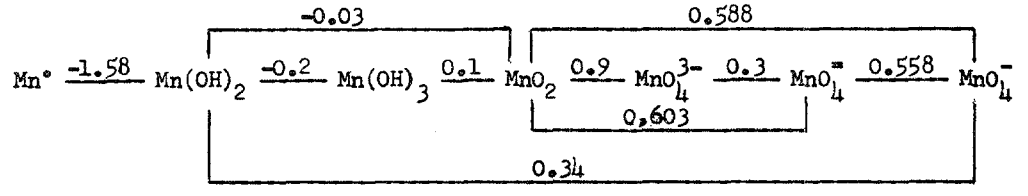
FIGURE III.1

POTENTIAL DIAGRAM FOR MANGANESE[37]

Acid Solution, $H^+$ unit activity




Basic Solution, $OH^-$ unit activity




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]

| Allotrope | Crystal Structure | Density g/cm$^3$ | Specific Heat cal./g °C |
|---|---|---|---|
| Alpha | Body centered cubic | 7.44 (20°C) | 0.114 |
| Beta | Body centered cubic | 7.29 (20°C) | 0.154 |
| Gamma | Face centered tetragonal | 7.18 (20°C) | 0.148 |
| Delta | | | 0.191 |
| Liquid | | 6.54 | |

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

nitride $Mn_3N_2$. Manganese forms a carbide, $Mn_3C$, which is isomorphous with $Fe_3C$ 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, $Mn_2(CO)_{10}$, the dicyclopentadienyl manganese complex, $(C_5H_5)_2Mn$, and the cyclopentadienyl carbonyl, $C_5H_5Mn(CO)_3$. 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 Szillard Chalmers reaction studies[41].

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 $Na_5Mn(CN)_6$, $K_5Mn(CN)_6$, etc.[42]. These compounds are extremely

strong reducing agents and liberate $H_2$ from aqueous solutions and reduce $Pb^{++}$ and $Cd^{++}$ to metal. A nitrosyl compound, $K_3Mn(CN)_5NO$ 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 $Fe^{++}$, although in many other ways it closely resembles $Fe^{++}$. The ionic radius of the $Mn^{++}$ ion is 0.80 Å, a little larger than $Fe^{++}$, and as expected $Mn^{++}$ normally forms somewhat less stable complexes than $Fe^{++}$. In acid solution almost any operation other than treatment with very strong oxidizing agents will yield 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 $MnO_2 \cdot xH_2O$. The oxide, MnO, is produced by the ignition of higher oxides in hydrogen and is stable but easily oxidized in air to $Mn_3O_4$. Some Mn(II) salts of interest are listed in Table III.4. Of special interest to the radiochemist are: $MnNH_4PO_4 \cdot H_2O$ which is precipitated from a $NH_4OH$ plus $NH_4Cl$ solution of $Mn^{++}$ by $(NH_4)_2HPO_4$, MnS which is precipitated from an alkaline solution of $Mn^{++}$, even in the presence of tartrate ion, by $(NH_4)_2S$. The solubility products of a number of slightly soluble manganous compounds are given in Table III.4. The anhydrous sulfate, $MnSO_4$, is produced by igniting almost any manganese compound with $H_2SO_4$; it is a suitable weighing form for manganese. The thermodynamic properties of some manganese compounds are given in Table III.5[37].

Divalent manganese has a weak tendency to form complexes. Cyanide complexes of the type $Mn(CN)_6^{4-}$ [42] 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.4

COMPOUNDS OF MANGANESE

SOLUBLE SALTS

| Compound | Mol. weight | How Made | Color § | Solubility g/100g $H_2O$ | Hydrates mols $H_2O$ |
|---|---|---|---|---|---|
| | | **Manganese II Compounds** | | | |
| $Mn(CH_3COO)_2$ | 173.02 | $Mn(NO_3)_2$+$(CH_3CO)_2O$ | pink(4) | 40(20°C) | 4 |
| $MnBr_2$ | 214.76 | Mn oxide + HBr | rose-red(4) | 144(18°C) | 6,4,2 |
| $MnCl_2$ | 125.84 | Mn oxide + HCl | rose(4) | 74(20°C) | 6,4,2 |
| $Mn(ClO_4)_2$ | 253.84 | $Mn(OH)_2$ + $HClO_4$ | | 136(25°C) | 6,4 |
| $MnF_2$ | 92.93 | MnO + HF | pink(0) | 1.06(25°) | 4 |
| $MnI_2$ | 308.77 | MnO + HI | rose-red(4) | sol. | 9,6,4,2,1 |
| $Mn(NO_3)_2$ | 178.94 | Mn oxide + $HNO_3$ | pink(6) | 134(18°C) | 6,4,2,1 |
| $MnSO_4$ | 151.00 | Mn comp. + $H_2SO_4$ | rose(5) | 68(25°C) | 7,5,4,2,1 |
| $K_4Mn(CN)_6$ | 367.43 | $MnCO_3$ + KCN | blue-violet | sol. | 3 |
| | | **Manganese III Compounds** | | | |
| $Mn(CH_3COO)_3$ | 232.07 | $Mn(CH_3COO)_2$ + $MnO_4^-$ | brown(2) | sol. acid | 2 |
| $K_2MnCl_5$ | 161.30 | $Mn_2O_3$ + HCl + KCl | red-violet | sol. decomp. | |
| $MnF_3$ | 111.93 | $MnI_2$ + $F_2$ | red(2) | sol. acid | 2 |
| $K_3Mn(CN)_6$ | 328.33 | $K_4Mn(CN)_6$ + air | dark red | sol. acid | |
| $K_3Mn(C_2O_4)_3$ | 436.30 | $H_2C_2O_4$ + $MnO_4^-$ + $CO_3^=$ $+K^+$ | red(3) | v. sol. | 3 |
| $CsMn(SO_4)_2$ | 379.98 | $Cs_2SO_4$ + $Mn(CH_3COO)_3$ + $H_2SO_4$ | coral red(12) | sol. acid | 12 |
| | | **Manganese IV Compounds** | | | |
| $K_2MnCl_6$ | 345.86 | $KMnO_4$ + con. HCl | dark red | sol. decomp. | |
| $K_2MnF_6$ | 247.12 | $MnO_2$ + HF | gold-yellow | sol. acid | |
| | | **Manganese VI Compound** | | | |
| $K_2MnO_4$ | 197.12 | $MnO_2$ + KOH + $KNO_3$ | dark green | sol. KOH | |
| | | **Manganese VII Compounds** | | | |
| $NH_4MnO_4$ | 136.97 | | purple | 7.9(15°C) | |
| $Ca(MnO_4)_2$ | 277.94 | | purple(9) | 250(25°C) | 9 |
| $HMnO_4$ | 119.94 | evap. frozen sol'n. | dark purple | sol. | 2 |
| $KMnO_4$ | 158.03 | $K_2MnO_4$ + $Cl_2$ + $H^+$ | dark purple | 6.34(20°C) | |
| $AgMnO_4$ | 226.81 | | dark violet | 0.92(20°C) | |
| $NaMnO_4$ | 141.93 | | purple(3) | v. sol. | 3 |

§ Color of hydrate with ( ) moles of $H_2O$

## INSOLUBLE SALTS

| Compound | Mol. weight | How Made | Color | Solubility product |
|---|---|---|---|---|
| | | **Manganese II Compounds** | | |
| $MnCO_3$ | 114.94 | neutral $Mn^{++} + CO_3^{=}$ | pink | $8.8 \times 10^{-11}$ (25°C) |
| $Mn_2Fe(CN)_6 \cdot 7H_2O$ | 447.93 | $Mn^{++} + Fe(CN)_6^{4-}$ | green-white | $7.9 \times 10^{-13}$ (25°C) |
| $Mn(OH)_2$ | 88.95 | $Mn^{++} + OH^-$ | white, turns brown | $1.6 \times 10^{-13}$ (22°C) |
| $Mn(IO_3)_2$ | 404.77 | $Mn^{++} + IO_3^-$ | | $4.8 \times 10^{-7}$ (25°C) |
| $MnC_2O_4 \cdot 2H_2O$ | 178.98 | $Mn^{++} + C_2O_4^{=}$ | pink | $\sim 10^{-13}$ |
| $MnO$ | 70.93 | $Mn_3O_4 + H_2$ heated | green | |
| $Mn_3(PO_4)_2 \cdot 7H_2O$ | 480.86 | neutral $Mn^{++} + HPO_4^{=}$ | pink | $\sim 10^{-22}$ |
| $MnNH_4PO_4 \cdot H_2O$ | 185.97 | $Mn^{++} + NH_4OH + HPO_4^{=}$ | pink | |
| $Mn_2P_2O_7$ | 283.82 | ignite $MnNH_4PO_4 \cdot H_2O$ | pink | |
| $MnSiO_3$ | 130.99 | $MnO + SiO_2$ fused | red | |
| $Mn_2SiO_4$ | 201.92 | $2MnO + SiO_2$ fused | pink | |
| $MnS$ | 87.00 | $Mn^{++} + (NH_4)_2S$ | flesh | $2 \times 10^{-13}$ (25°C) |
| | | **Manganese III Compounds** | | |
| $MnOOH$ | 87.94 | $Mn(OH)_2 + O_2$ | brown | $\sim 10^{-42}$ |
| $Mn_3O_4$ | 228.79 | ignite oxides at 1000°C | red | |
| $Mn_2O_3$ | 157.86 | ignite oxides at 700°C | black | |
| $MnPO_4 \cdot H_2O$ | 167.93 | $Mn(CH_3COO)_3 + H_3PO_4$ | gray-green | |
| | | **Manganese IV Compounds** | | |
| $MnO_2 \cdot xH_2O$ | | $Mn^{++} + BrO_3^-$ or $ClO_3^-$ | brown-black | very insoluble |
| $MnO_2$ | 86.93 | decomp. $Mn(NO_3)_2$ 250°C | black | |
| | | **Manganese VI Compound** | | |
| $BaMnO_4$ | 256.29 | basic $Ba^{++} + MnO_4^{=}$ | gray-green | $1.5 \times 10^{-10}$ |
| | | **Manganese VII Compound** | | |
| $CsMnO_4$ | 251.84 | $Cs^+ + MnO_4^-$ | purple | $1.5 \times 10^{-5}$ |

VOLATILE COMPOUNDS

| Compound | Mol. weight | How made | Color | Melting point °C | Boiling point °C |
|---|---|---|---|---|---|
| $Mn_2O_7$ | 221.86 | $KMnO_4$ + con. $H_2SO_4$ | red | -33° | 70° explodes |
| $Mn(C_5H_7O_2)_3$ | 352.25 | acetylacetone + $Mn(CH_3COO)_3$ | green-black | 172° | volatile |
| $Mn_2(CO)_{10}$ | 389.96 | | gold | 154° | |
| $C_5H_5Mn(CO)_3$ | 204.05 | | yellow | 77° | volatile |
| $(C_5H_5)_2Mn$ | 185.11 | | amber | 172° | 245° |

TABLE III.5

THERMODYNAMIC DATA FOR MANGANESE COMPOUNDS[37]
298°K

| Compound | ΔH kcal/mol. | ΔG kcal/mol. | ΔS cal/mol.,°C |
|---|---|---|---|
| Mn(c,α) | 0 | 0 | 7.64 |
| Mn(g) | 67.2 | 57.1 | 41.49 |
| $Mn^{++}(H_2O)$ | -53.2 | -55.1 | -17 |
| MnO(c) | -92.0 | -86.7 | 14.3 |
| $Mn_3O_4$(c) | -331.3 | -306.2 | 36.8 |
| $Mn_2O_3$(c) | -228.7 | -210.1 | 26.4 |
| $MnO_2$(c) | -124.4 | -111.3 | 12.68 |
| $Mn(OH)_2$(c) | -167 | -148 | 23 |
| $MnF_2$(c) | -190 | -179 | 22.25 |
| $MnCl_2$(c) | -115.6 | -105.9 | 28.26 |
| $MnBr_2$(c) | -92.6 | -89 | 33 |
| $MnI_2$(c) | -64.2 | -65 | 37 |
| MnS(c) | -49.5 | -50.5 | 18.7 |
| $MnSO_4$(c) | -254.9 | -229.1 | 26.8 |
| $MnCO_3$(c) | -214 | -196 | 20.5 |
| $KMnO_4$(c) | -200.6 | -176.8 | 41.0 |
| $Mn_2(CO)_{10}$(c) | -400.9 | | |

chloride complexes are known, $MnCl_3^-$, $MnCl_4^=$, and $MnCl_6^{4-}$, 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. $Mn(NH_3)_6^{++}$, but the complexes are not stable in aqueous solution.

TABLE III.6

STABILITY CONSTANTS OF MANGANESE COMPLEXES[34,37]

| Reaction | $Log_{10}$ Equilibrium constant |
|---|---|
| $Mn^{++} + H_2O(l) \rightarrow MnOH^+ + H^+$ | -10.59 |
| $Mn^{++} + F^- \rightarrow MnF^+$ | 0.79 |
| $Mn^{++} + Cl^- \rightarrow MnCl^+$ | 0.59 |
| $Mn^{++} + SO_4^= \rightarrow MnSO_4$ | 2.26 |
| $Mn^{++} + C_2O_4^= \rightarrow MnC_2O_4$ | 3.89 |
| $Mn^{++}$ + malonate $\rightarrow Mn(OOCCH_2COO)$ | 3.29 |
| $Mn^{++}$ + 2 acetylacetone $\rightarrow Mn(CH_3COCHCOCH_3)_2$ | 9.96 |
| $Mn^{++} + EDTA^{4-} \rightarrow MnEDTA^=$ | 13.4 |
| $Mn^{3+} + H_2O(l) \rightarrow MnOH^{++} + H^+$ | -0.056 |
| $Mn^{3+} + F^- \rightarrow MnF^{++}$ | 2.48 |
| $Mn^{3+} + Cl^- \rightarrow MnCl^{++}$ | 0.96 |
| $Mn^{3+} + C_2O_4^= \rightarrow MnC_2O_4^+$ | 9.98 |
| $Mn^{3+} + 2C_2O_4^= \rightarrow Mn(C_2O_4)_2^-$ | 16.6 |
| $Mn^{3+} + 3C_2O_4^= \rightarrow Mn(C_2O_4)_3^{3-}$ | 19.42 |

Trivalent Manganese

Simple, uncomplexed $Mn^{3+}$ in solution disproportionates into $Mn^{++}$ 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, $Mn_2O_3$, and the "ous-ic" oxide, $Mn_3O_4$, are stable, the latter compound being the usual, but somewhat uncertain, weighing form for manganese. Mn(III) forms a moderately stable manganicyanide, $Mn(CN)_6^{3-}$ (42), which is much more difficult to reduce than $Fe(CN)_6^{3-}$ and also shows a tendency to hydrolyze in water. A phosphate complex, $Mn(H_2P_2O_7)_3^{3-}$, 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 oxidizing 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 $KClO_3$ to a nitric acid solution of $Mn^{++}$. The dioxide is also precipitated as a scavenger during the processing of irradiated uranium fuel by the addition of first $Mn^{++}$, 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 $Mn^{++}$ and $Cl_2$. Mn(IV) forms some fluoro and chloro complexes such as $K_2MnF_6$ and $K_2MnCl_6$, and also some iodate complexes of the anion $Mn(IO_3)_6^{=}$. Hydrated $MnO_2$ reacts with strong alkalies to form insoluble manganites such as $K_2Mn_2O_5$.

Pentavalent Manganese

Manganese forms a few compounds in which it exhibits a valence of five. The recently synthesized $MnOCl_3$[43] and $KMnO_3$ are examples.

Hexavalent Manganese

Manganates, e.g. $K_2MnO_4$, can be prepared by fusing $MnO_2$ with KOH and $KNO_3$. They are stable in strongly alkaline solutions, but disproportionate to $MnO_2$ and $MnO_4^-$ in weakly alkaline, neutral, or acidic solutions. The $MnO_4^=$ ion is green. A manganyl chloride, $MnO_2Cl_2$, has been recently prepared[43].

Heptavalent Manganese

Seven is the group valence of manganese. Mn(VII) forms the strongly oxidizing but stable $MnO_4^-$ ion which is of great importance in radiochemistry and analytical chemistry. $KMnO_4$ is usually prepared by fusing $MnO_2$ with KOH in air or with KOH and $KNO_3$, then treating the resulting manganate with $H_2SO_4$ plus at times oxidation with $Cl_2$. Permanganates are deep purple and strong oxidizing agents. The acid, $HMnO_4$, is a strong acid like $HClO_4$ and has recently been prepared as a solid crystalline compound by the vacuum evaporation of a frozen solution[44]. The oxide, $Mn_2O_7$, has been isolated and can be distilled, usually with considerable decomposition. The distillation of $Mn_2O_7$ is the basis of a radiochemical separation for manganese.

Permanganyl chloride, $MnO_3Cl$, has been synthesized[43]. Permanganates can be produced from $Mn^{++}$ in acid solution by oxidation with periodate, persulfate plus $Ag^+$ catalyst, $Ag^{++}$, $PbO_2$, and sodium bismuthate. Permanganate can be extracted with alkaline pyridine and alkaline $(C_6H_5)_4AsCl$ in $CHCl_3$. Data on some common permanganates are included in Table III.4. Permanganates are isomorphous with perchlorates, perrhenates, and pertechnetates. Permanganate solutions are relatively stable, especially if free of $MnO_2$, and are used extensively as standard oxidizing solutions in analytical chemistry.

When heated, $KMnO_4$ is first decomposed at about 200°C to $K_2MnO_4$ and $MnO_2$, then at higher temperatures to $Mn_2O_3$ and $Mn_3O_4$.

5. Analytical Chemistry of Manganese[34]

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 $NH_4OH$ alone, is soluble in $NH_4OH$ 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 benzidine 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 formaldoxime.

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 $KIO_4$ 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[48]. The reaction is:

$$4Mn^{++} + MnO_4^- + 8H^+ + 15(H_2P_2O_7)^{2-} \rightarrow 5(Mn(H_2P_2O_7)_3)^{3-} + 4H_2O$$

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 $MnO_4^-$ in a nearly neutral solution (Volhard method) according to the reaction:

$$3Mn^{++} + 2MnO_4^- + 4OH^- \rightarrow 5MnO_2 + 2H_2O$$

The endpoint is determined by observing the appearence of purple $MnO_4^-$. The reaction is not quite stoichiometric and the end point is difficult to observe visually because of the precipitate of $MnO_2$. The classical titrimetric method is based upon the oxidation of $Mn^{++}$ to $MnO_4^-$ with sodium bismuthate, then removal of the excess bismuthate by filtration and reduction of the permanganate with standard ferrous ammonium sulfate[49]. The reactions are:

$$2Mn^{++} + 5NaBiO_3 + 14H^+ \rightarrow 2MnO_4^- + 5Bi^{3+} + 7H_2O + 5Na^+$$

$$MnO_4^- + 5Fe^{++} + 8H^+ \rightarrow Mn^{++} + 5Fe^{3+} + 4H_2O$$

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 $MnO_4^-$ 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 $H_2SO_4$ - $H_3PO_4$ solution with $(NH_4)_2S_2O_8$ and $Ag^+$ catalyst, then titration of the $MnO_4^-$ with standard arsenite. The reactions are:

$$2Mn^{++} + 5S_2O_8^{=} + 8H_2O \rightarrow 2MnO_4^{-} + 10SO_4^{=} + 16H^{+}$$

$$2MnO_4^{-} + 5AsO_2^{-} + 6H^{+} \rightarrow 2Mn^{++} + 5AsO_3^{=} + 3H_2O$$

The end point can be determined by the disappearance of the purple $MnO_4^{-}$ color or potentiometrically. Fewer elements interfere than with the $Fe^{++}$ titration. Manganese can be determined by titration with ethylenediaminetetraacetic acid using Eriochrome Black T as the indicator. Complexing with cyanide will prevent interference by Hg, Cd, Co, Zn, Cu, Ni, and Fe.

Manganese is determined quantitatively by emission spectroscopy, flame photometry, atomic absorption, and X-ray fluorescence(51). 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 $MnNH_4PO_4 \cdot H_2O$, MnS, and $MnO_2$ and ignition to $Mn_2P_2O_7$, $MnSO_4$, or $Mn_3O_4$; all of these precipitation methods have been used in radiochemical separations.

6. Dissolution of Manganese Samples(34)

Inorganic Materials

The dissolution of manganese minerals and ores can often be accomplished by acid attack followed by $KHSO_4$ or $Na_2CO_3$ fusion of the insoluble residue. The dissolution of $MnO_2$ is greatly facilitated by the addition of a reducing agent such as $H_2O_2$ or $SO_2$. 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 $HNO_3$, HCl, $H_2SO_4$, or aqua regia. Tungsten steels may require $H_3PO_4$. Some high temperature alloys containing major amounts of Ni, Co, Cr, W, and Nb are very difficult to dissolve and may require fusion with $Na_2O_2$ or anodic electrolytic attack. An interesting dissolution technique for analyzing inclusions in steel is the solution of the metal in cold $FeI_2$ solution which leaves the oxide inclusions, FeO, MnO, $SiO_2$, $Al_2O_3$, etc. unattacked(50).

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 $H_2SO_4$ and $HNO_3$ 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 $HNO_3$ in a Kjeldahl flask then finally fumed with $HNO_3$ plus $HClO_4$; dye intermediates and rubber chemicals are treated with $H_2SO_4$, $HNO_3$, and $H_2O_2$. Petroleum and petroleum distillates are wet ashed preparatory to analysis for manganese and other trace metals; $HNO_3$ + $H_2SO_4$ 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 $MnO_2$ from a boiling $HNO_3$ solution of $Mn^{++}$ by adding bromate, chlorate, or persulfate oxidizing agent. The $MnO_2$ 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 $MnO_2$ precipitation is usually not quite quantitative. Precipitation of $MnO_2$ may be made from nearly neutral solutions by oxidation with $Br_2$. Manganese, even at trace level, can be electrodeposited on the anode as $MnO_2$[53].

Iron (III), aluminum, zirconium, and other elements with very insoluble hydroxides can be precipitated with $NH_4OH$ 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. $H_2O_2$.

The precipitation of manganese as MnS from a slightly basic solution of $Mn^{++}$ + $NH_4^+$ with $H_2S$ or $(NH_4)_2S$ will separate manganese from alkaline earths. The acid insoluble sulfides, including ZnS, can be first precipitated from a weak acetic acid solution. The precipitation of $MnO_2$ with NaOH plus $H_2O_2$ will separate manganese from Al, Cr, Mo, V, and other amphoteric elements which form alkali soluble salts. Many elements, Fe, Ni, Cu, Zn, 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: Fe(III), Ti, Zr, and V can be precipitated with cupferron leaving Mn in solution, $MnNH_4PO_4 \cdot H_2O$ can be precipitated from citrate solutions leaving Co in solution, CoS and NiS can be precipitated in the presence of pyridine leaving Mn in solution, 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 Nb and Ta. 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 $MnO_4^-$.

Volatilization Methods

Manganese, as $Mn_2O_7$, can be slowly distilled from 10 M $H_2SO_4$ containing $HIO_4$ (55).

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. Fe(III) from 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 $TcO_4^-$ 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 $K_2S_2O_8$. Add 1% $(C_6H_5)_4AsCl$ solution to make solution about $5 \times 10^{-5}$ M. Extract 5 min. with an equal volume of $CHCl_3$; Mn extracts quantitatively as $(C_6H_5)_4AsMnO_4$. $ReO_4^-$, $TcO_4^-$, $ClO_4^-$ also extract, but can be removed by extraction before the manganese is oxidized.

d. Diethyldithiocarbamate[58]

Use 175 ml of solution with some citric acid, adjust the pH to about 5.3, add 0.4 g Na diethyldithiocarbamate (DIECA), adjust pH again to 5.4, and extract with 25 ml $CHCl_3$ readjusting the pH by adding HCl.

e. Thenoyltrifluoroacetone[59]

Manganese(II) TTA complex can be extracted from fairly high pH solutions. Buffer the solution with $NH_4C_2H_3O_2$ plus NaOH to give a pH of 8.0 - 8.5. Add a little hydroxylamine 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-pyrazolone-5 has been used to complex Mn (depending upon pH) so that it will extract into methylisobutyl ketone[61]. Octyl-α-analinobenzylphosphonate in ligroin has been used to extract Mn from $H_2SO_4$

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 ($Cr^{3+}$, $Al^{3+}$, $Tl^{+}$, $Ni^{++}$, and trivalent rare earths) and those ions that are strongly absorbed ($Fe^{3+}$, $UO_2^{++}$, $WO_4^{=}$, $Co^{++}$, $Tl^{3+}$, 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 $Mn^{++}$ is normally so weakly absorbed, the separations are not very useful for concentrating manganese. A weakly basic anion resin has been used to concentrate $Mn^{++}$ 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 $NH_4Cl$ plus $(NH_4)_2HPO_4$ 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 $Mn_3(PO_4)_2$ (containing $^{32}P$) in the paper[75]. Metal TTA complexes have been used with solvents containing $CH_3OH$, $C_6H_6$, and glacial $CH_3COOH$[76] to separate Mn from Fe, Co, Ni, and Cu; 80% methyl-n-propyl ketone, 10% acetone, and 10% HCl, also, acetone plus 5% $H_2O$ and 8% HCl have been used as solvents[74].

Partition chromatography has been rather more extensively studied. A column made up of $CCl_4$ -dithizone solution supported on cellulose acetate has been used to separate manganese from natural waters[77]. The manganese is eluted with 1 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 $^{56}Mn$ on $MnO_2$ for the standardization of weak neutron sources, many studies have been made of the partition of manganese activity between the $MnO_2$ decomposition product and the unaltered $MnO_4^-$[80]. The activity is almost all collected on the $MnO_2$ if the pH of the solution is less than about 11. Even when solid $KMnO_4$ is irradiated, only about 35% of the activity is retained with the $MnO_4^-$ 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 $Mn_2(CO)_{10}$ and $C_5H_5Mn(CO)_3$[81], and on crystalline $C_5H_5Mn(CO)_3$[82].

Radioisotope exchange has been used to study the structure of $Mn(CN)_5NO^{3-}$ [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 contents 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. $Mn_2O_7$ and $NH_4MnO_4$, are explosive.

A major hazard in the radiochemical studies of manganese is the radiation due to $^{56}Mn$. Since manganese has a relatively high cross section and $^{56}Mn$ 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 $^{56}Mn$ are difficult to shield. A sample of about 50 mg. Mn irradiated for 2 1/2 hours in a flux of $10^{13}$ $n/cm^2 sec.$ will give a gamma dose, unshielded, of about 1 R/hr. at one foot (30 cm.).

As ingestion hazards, $^{52}Mn$, $^{54}Mn$, and $^{56}Mn$ 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[86]

| Isotope | | Body Burden μCi | 40hr. week in $H_2O$ μCi/cm³ | 40hr. week in air μCi/cm³ | 168hr. week in $H_2O$ μCi/cm³ | 168hr. week in air μCi/cm³ |
|---|---|---|---|---|---|---|
| $^{52}Mn$ | sol. | 5 | $10^{-3}$ | $2\times10^{-7}$ | $3\times10^{-4}$ | $7\times10^{-8}$ |
| 5.6 d. | insol. | | $9\times10^{-4}$ | $10^{-7}$ | $3\times10^{-4}$ | $5\times10^{-8}$ |
| $^{54}Mn$ | sol. | 20 | $4\times10^{-3}$ | $4\times10^{-7}$ | $10^{-3}$ | $10^{-7}$ |
| 303 d. | insol. | | $3\times10^{-3}$ | $4\times10^{-8}$ | $10^{-3}$ | $10^{-8}$ |
| $^{56}Mn$ | sol. | 2 | $4\times10^{-3}$ | $8\times10^{-7}$ | $10^{-3}$ | $3\times10^{-7}$ |
| 2.6hr. | insol. | | $3\times10^{-3}$ | $5\times10^{-7}$ | $10^{-3}$ | $2\times10^{-7}$ |

## V COUNTING TECHNIQUES

All of the radioactive isotopes of manganese except $1.9 \times 10^6$ year $^{53}Mn$ decay by the emission of gamma rays of high abundance, so gamma counting, either with NaI(Tl) crystals or Ge(Li) dectectors 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, Eichler, and O'Kelley[90].

R. L. Heath[91] gives scintillation gamma ray spectra of most of the radioactive nuclides including 5.6 day $^{52}Mn$, 303 day $^{54}Mn$, and 2.576 hour $^{56}Mn$. His scintillation spectra of $^{52}Mn$ and $^{54}Mn$ are included in this monograph as Figures V.1 and V.2. A scintillation spectrum of $^{56}Mn$, 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]

| Isotope | Gamma Ray Energy MeV | Peak to Total Ratio | Gamma Counting Efficiency |
|---|---|---|---|
| Positron Emitters | 0.511 | 0.641 | 0.0217 |
| 2 min. $^{50}Mn$ | 0.783(100%)<br>1.11 (100%) | 0.492<br>0.395 | 0.0192<br>0.0174 |
| 5.60 day $^{52}Mn$ | 0.744(82%)<br>0.935(84%)<br>1.434(100%) | 0.506<br>0.440<br>0.335 | 0.0195<br>0.0183<br>0.0161 |
| 303 day $^{54}Mn$ | 0.835(100%) | 0.474 | 0.0189 |
| 2.576 hour $^{56}Mn$ | 0.848(99%)<br>1.811(29%)<br>2.110(15%) | 0.470<br>0.290<br>0.262 | 0.0188<br>0.0152<br>0.0146 |

FIGURE V.1

GAMMA SPECTRUM OF $^{52}Mn$ (91)

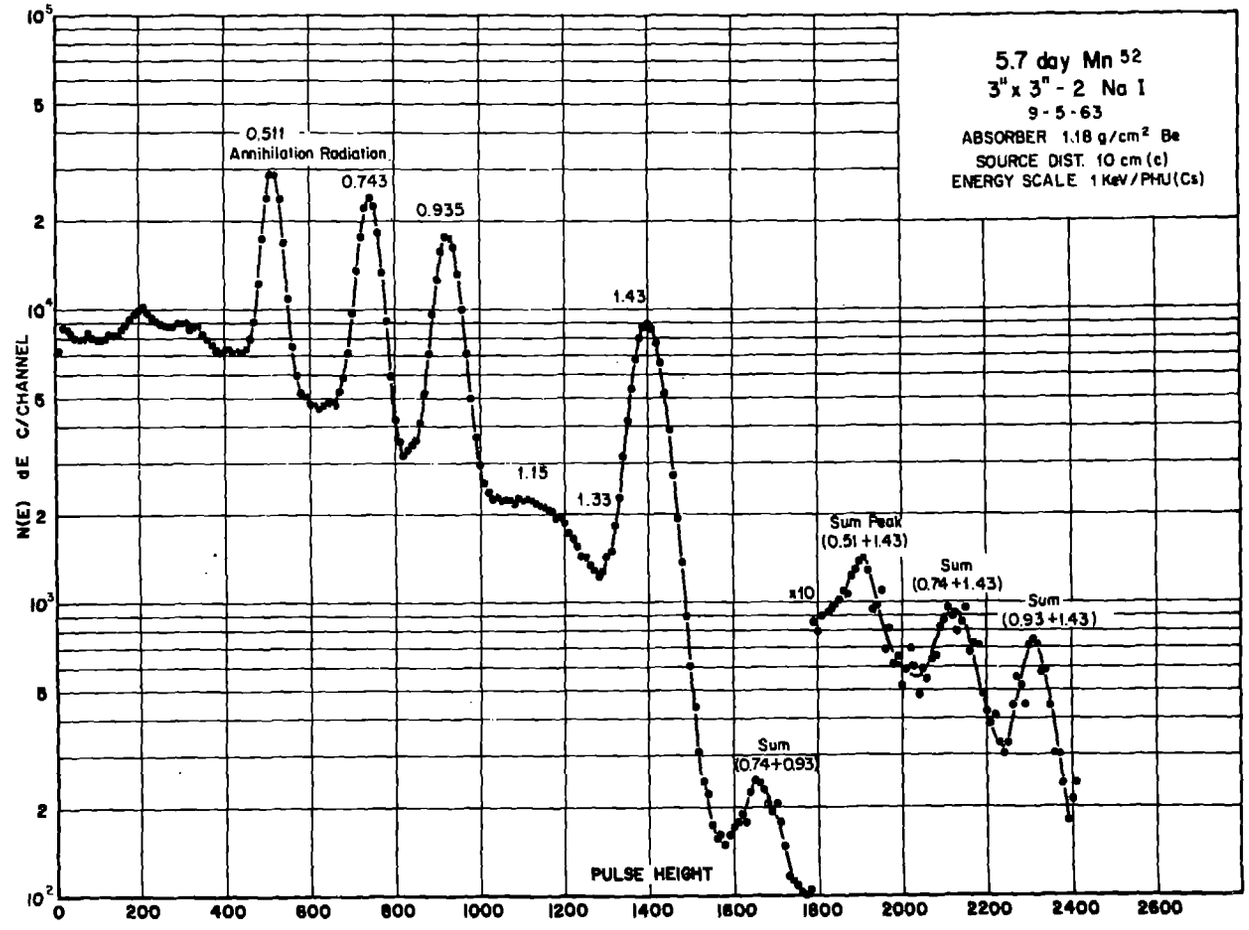


FIGURE V.2

GAMMA SPECTRUM OF $^{54}Mn$ (91)

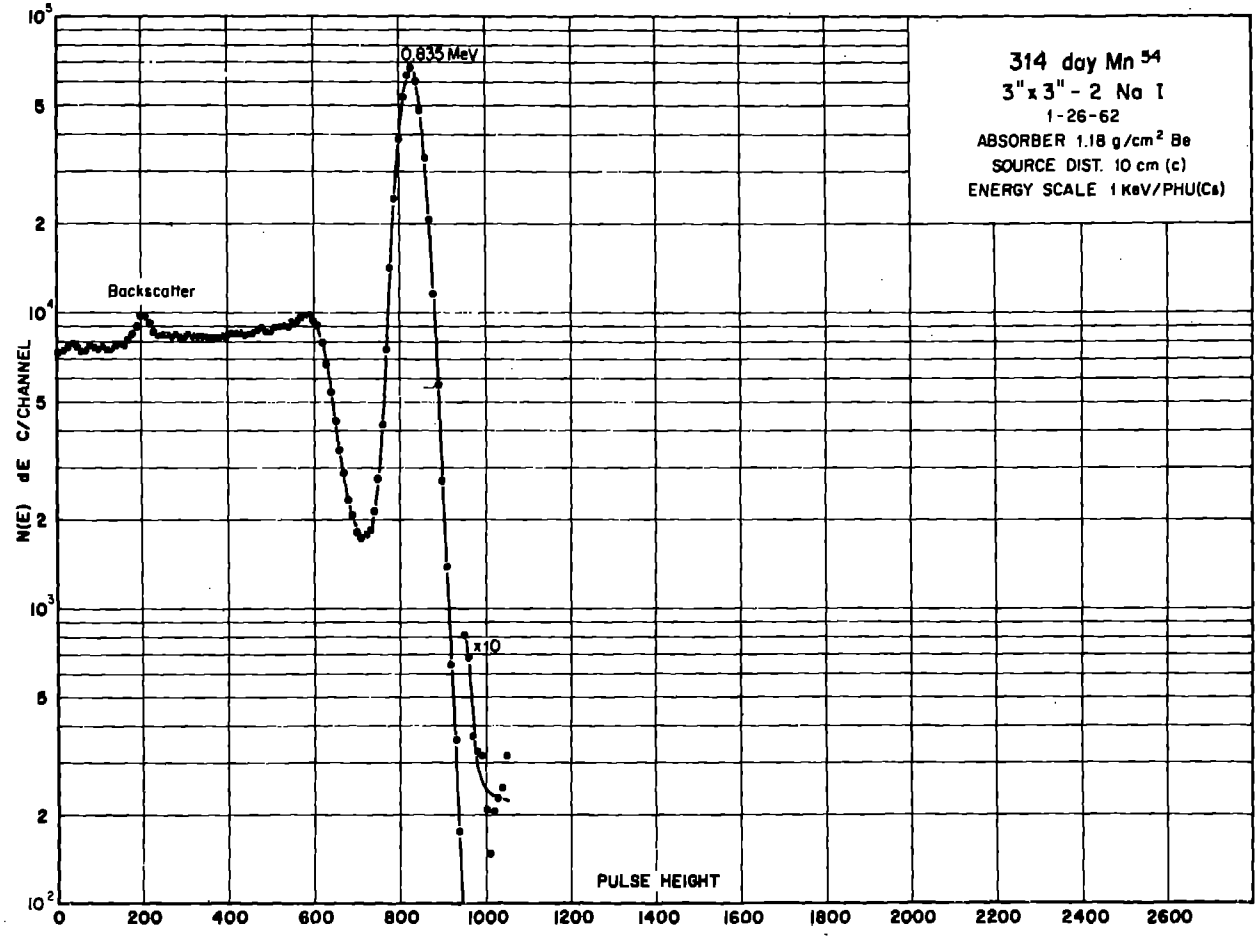
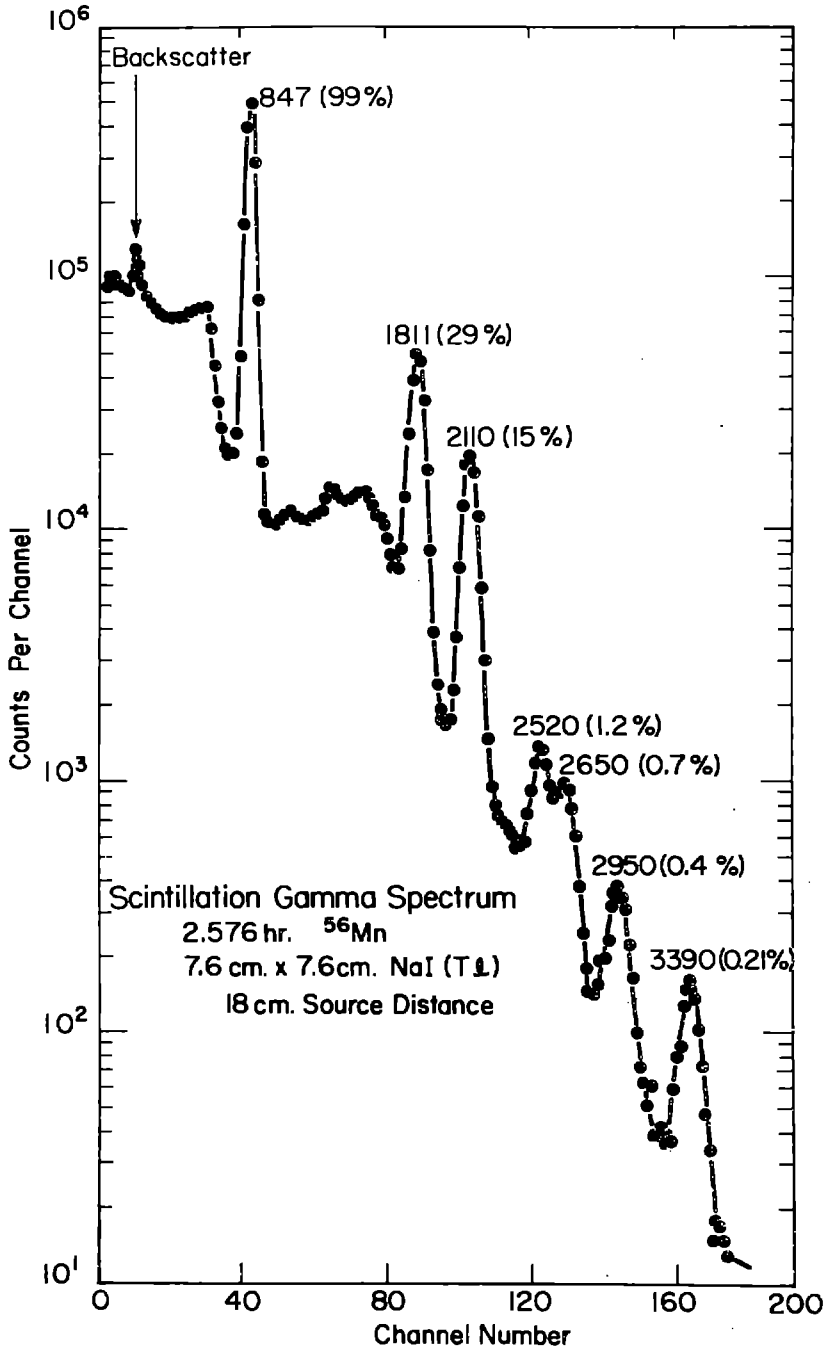


FIGURE V.3

GAMMA SPECTRUM OF $^{56}Mn$



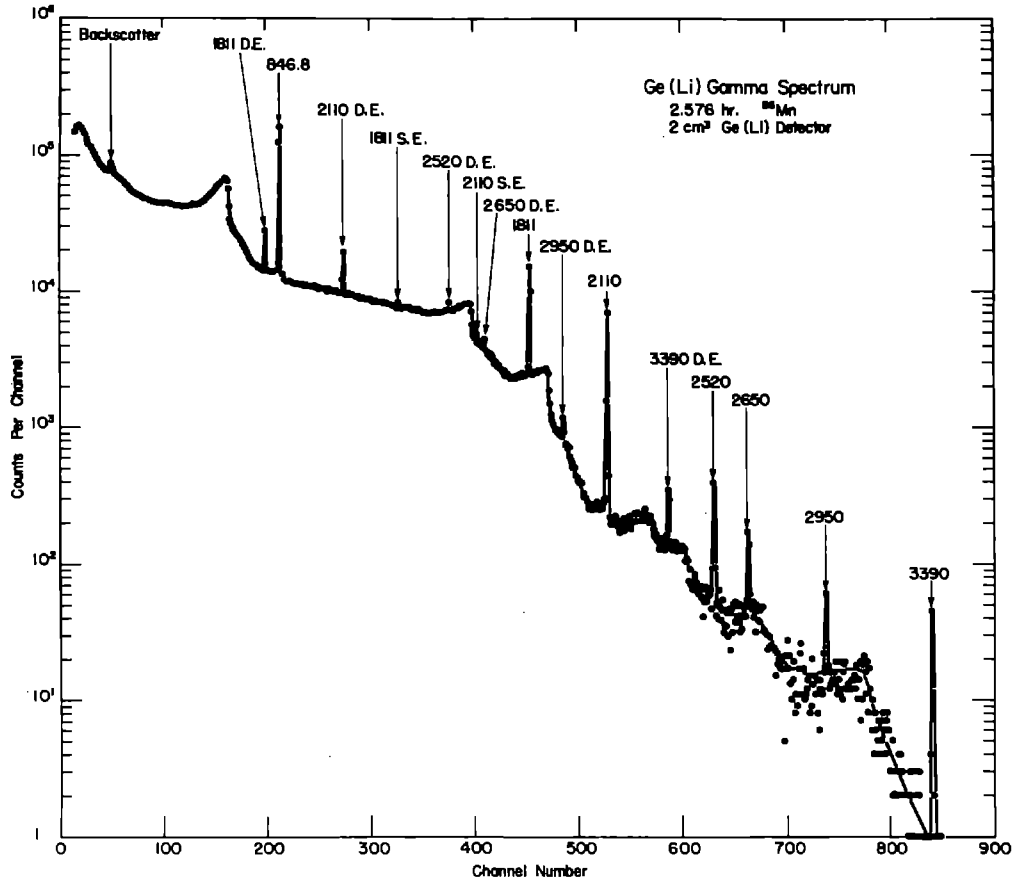
The most accurate method of determining the amount of an isotope by gamma counting is by comparison with a standard; relative gamma activities can be determined to better than 1%. The most accurate determinations also require radiochemically pure samples. However, by using scintillation counting it is often possible to resolve the composite spectrum of several nuclides into those of the individual components; thus, it is often possible to determine $^{56}Mn$ 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 $^{56}Mn$ 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 $^{56}Mn$



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: 2.84 MeV (47%), 1.03 MeV (34%), and 0.72 MeV (18%). Two other nuclides, 45 min $^{51}Mn$ (emitting 2.17 MeV positrons 97% abundant) and 21 min $^{52m}Mn$ (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 $1.9 \times 10^6$ 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 $4\pi$ beta-gamma coincidence counting[95].

The nuclide $^{56}Mn$ 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 $D_2O$ has been used to determine $^{56}Mn$ 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°C, in dilute nitric acid and making up to volume. If the purified manganese from the radiochemical separation is $MnO_2$, it is best to standardize the carrier by precipitation and weighing of $MnO_2$ since the dioxide is not quite stoichiometric and still contains a little water when dried at 110°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 $MnO_2$ from a $HNO_3$ solution of $Mn^{++}$ by oxidation with $KBrO_3$ or $NaClO_3$ 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 Leddicotte[97].

Material Analyzed:

$^{54}Mn$ or $^{56}Mn$ for activation analysis or analysis of contamination.

Reagents:

Mn carrier, 10 mg/ml Mn as nitrate (Note 1.)

$HNO_3$ conc.

$KBrO_3$ solid

Hold back carriers, about 10 mg/ml

$HNO_3$ 6N

$H_2O_2$ 30%

Ethyl alcohol, 95%

Procedure:

Step 1. Dissolve sample in 6N to conc. $HNO_3$ (Note 2). Add about 20 mg Mn carrier. Add Fe(III) and Zr(IV) holdback carriers. Dilute to about 20 ml with 6N $HNO_3$.

Step 2. Add about 100 mg solid $KBrO_3$ and heat to boiling. $MnO_2$ will precipitate and be coagulated by the heat. Cool. (Note 3).

Step 3. Centrifuge and discard supernate. Wash precipitate several times with 6N $HNO_3$. Go to step 4 or 5 depending upon purity desired.

Step 4. Dissolve $MnO_2$ in 6N $HNO_3$ plus minimum $H_2O_2$. Boil to destroy excess $H_2O_2$. Repeat steps 1 through 3. Go to step 5 when sufficiently pure.

Step 5. Slurry $MnO_2$ with 0.1N $HNO_3$ 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 $MnO_2$.

Notes:

1. Standard Mn carrier can be made by dissolving an accurately weighed amount of 99.9% electrolytic Mn metal or $MnSO_4$ heated to 500°C in a little dilute $HNO_3$ and making up to volume. For best accuracy standardize as $MnO_2$ dried at 100°C.

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

3. $NaClO_3$ can be used instead of $KBrO_3$ 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 $MnNH_4PO_4 \cdot H_2O$ after standard decontamination steps. No detectable contamination was found in the manganese separated from $2.5 \times 10^{14}$ 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 $MnCl_2$ in $H_2O$, standardized. (Note 1).

W carrier, 10 mg/ml W as $Na_2WO_4 \cdot 2H_2O$ in $H_2O$.

Fe carrier, 10 mg/ml Fe as $FeCl_3$ in 1M HCl.

Pd carrier, 10 mg/ml Pd as $PdCl_2 \cdot 2H_2O$ in 1M HCl.

Zr carrier, 10 mg/ml Zr as $ZrOCl_2 \cdot 8H_2O$ in 1M HCl.

HCl, conc. and 6M.

$HNO_3$, conc.

$CH_3COOH$ glacial.

$NH_4OH$, conc.

NaOH, 10M.

$H_2S$ gas.

$NaBrO_3$, saturated solution.

$(NH_4)_2S$ 20% solution.

$(NH_4)_2HPO_4$, 1.5M.

Aerosol, 0.1% in $H_2O$.

Dowex AG 50-X4, 100-200 mesh cation resin.

Dowex AG 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 $H_2O$ to fill tube, centrifuge. Discard supernate, wash precipitate twice with $H_2O$ 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 $H_2O$, add conc. $NH_4OH$ 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% $(NH_4)_2S$, heat for 1-2 min on a steam bath and centrifuge saving MnS precipitate.

Step 6. To the precipitate add 5 ml glacial $CH_3COOH$ and boil over a flame. Add 5 drops Pd carrier, dilute to 20 ml with $H_2O$, place on a steam bath and bubble in $H_2S$. 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 $(NH_4)_2HPO_4$ 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. $NH_4OH$ dropwise until $MnNH_4PO_4 \cdot H_2O$ 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 $H_2O$, and place on a Dowex AG 50-X4, 100-200 mesh cation resin column (6 mm diam, 3 cm. long). Rinse tube with $H_2O$ and add rinsings to column. Wash column with 2-3 ml portions of $H_2O$ 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 $HNO_3$, 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 14. Repeat PdS scavenge, step 6.

Step 15. Repeat Zr phosphate scavenge, step 7.

Step 16. To the supernate add conc $NH_4OH$ dropwise until $MnNH_4PO_4 \cdot H_2O$ precipitates and then heat on a steam bath for 3-5 min. Centrifuge, discard supernate. Dissolve precipitate in 4-5 drops conc HCl. Dilute to 20 ml with $H_2O$, add a few drops aerosol and centrifuge. Save the supernate in a clean tube and reprecipitate $MnNH_4PO_4 \cdot H_2O$ by adding $(NH_4)_2HPO_4$ then $NH_4OH$. Filter onto a weighed No. 42 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 $NH_4OH$ and then ethanol. Dry at 110°C, cool, weigh, and mount.

Notes:

Manganese carrier is made by dissolving 22.9 grams $MnCl_2$ in $H_2O$ and diluting to 1 liter. To standardize, a 2.00 ml aliquot is pipeted into a 40 ml centrifuge tube, 5 drops conc HCl added, then 3 ml 1.5M $(NH_4)_2HPO_4$, then $NH_4OH$ 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 $NH_4OH$, then alcohol, then dried at 110°C and weighed as $MnNH_4PO_4 \cdot H_2O$.

## Procedure 3

Introduction:

Even with fairly low power reactors, flux around $5 \times 10^{11}$ $n/cm^2 sec$, manganese can be determined at the nanogram level. Manganese is determined by comparing the $^{56}Mn$ 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: $^{56}Fe(n,p)^{56}Mn$ and $^{59}Co(n,\alpha)^{56}Mn$. Since these reactions, unlike the $^{55}Mn(n,\gamma)^{56}Mn$ reaction, do not occur with thermal neutrons, the interference can be minimized by irradiating the samples in a highly thermalized flux. Also, the $^{56}Mn$ 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.

Source:

W. T. Mullins and G. W. Leddicotte, "Activation Analysis of Manganese -

Reactor Irradiation Source", Oak Ridge Master Analytical Manual, 5 11480(99).

Reagents:

$NH_4OH$ 15N, stock 28% $NH_3$.

Coagulant No. 78. Slurry 1 g of No. 78 ore flocculant vegetable colloid (Burtonite Company, Nutley, New Jersey) in 1 liter $H_2O$.

$(C_2H_5)_2O$, anhydrous.

Holdback carriers, about 10 mg/ml.

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

30% $H_2O_2$.

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

3M $HNO_3$, 195 ml conc. $HNO_3$ per liter solution.

$KClO_3$, 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 aliquots in 50 ml centrifuge tubes, add 2.00 ml standardized Mn carrier plus about 1 ml each $Cu^{++}$, $Ni^{++}$, and $Na^{+}$ holdback carriers. Dilute to 20 ml with $H_2O$, mix, make alkaline with $NH_4OH$ 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 $NH_4OH$, 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 $NH_4OH$, and continue as in part C.

C. Radiochemical separation:

Step 1. To $NH_4OH$ solution add 5 drops 30% $H_2O_2$, heat to boiling and centrifuge, saving the $MnO_2$ precipitate. Wash precipitate first with 20 ml 1M $NH_4OH$ then with 20 ml 3M $HNO_3$ (Note 1).

Step 2. Dissolve $MnO_2$ in 2 ml 6N HCl and dilute to 10 ml with conc. $HNO_3$. Heat and boil 30 sec. Add solid $KClO_3$ in 0.5 g increments, heating to 75°C after each addition (Note 2) until $MnO_2$ precipitation is complete. Centrifuge, wash $MnO_2$ precipitate with 25 ml 3M $HNO_3$.

Step 3. Slurry $MnO_2$ with a little $H_2O$ plus coagulant No. 78. Filter $MnO_2$ through a weighed filter paper circle held in a Hirsch funnel. Wash three times with 5 ml portions each of $H_2O$, 95% $C_2H_5OH$, 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 $MnO_2$ 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 $H_2O_2$ be washed out before the $MnO_2$ is washed with 3M $HNO_3$, otherwise it will dissolve.

2. $KBrO_3$ can be used instead of $KClO_3$ to precipitate $MnO_2$. 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 $CHCl_3$, 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[100]

Reagents:

1N and conc. $H_2SO_4$

Mn carrier, $1.8 \times 10^{-2}$ M $MnSO_4$

$H_3PO_4$, 85%

$AgNO_3$, 1% solution

$(NH_4)_2S_2O_8$

$NH_4OH$ solution

tetraphenylarsonium chloride, $2 \times 10^{-3}$M

$CHCl_3$

Procedure:

Step 1. Irradiate unknown and comparator samples. Dissolve samples in 10 ml 1N $H_2SO_4$ (samples were chalk) (Note 1). Add 0.60 ml Mn carrier, 2 drops 85% $H_3PO_4$, and dilute to 50 ml with water (Note 2). Now add 1 ml conc. $H_2SO_4$, 1 ml 1% $AgNO_3$ and 1 g $(NH_4)_2S_2O_8$ and heat to oxidize manganese to $MnO_4^-$. Boil to destroy excess persulfate.

Step 2. Cool, adjust pH to 8-9 with $NH_4OH$ (Note 3). Transfer to a separatory funnel, add 2.00 ml $2 \times 10^{-3}$M tetraphenylarsonium chloride then add 5.00 ml $CHCl_3$ and extract permanganate for 3 minutes (Note 4).

Step 3. Either measure activity in 3.00 ml of the $CHCl_3$ 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. $H_2SO_4$ is the best acid for dissolution since $SO_4^=$ 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 $H_2SO_4$ with Mn

carrier added and pH adjusted to 8 add 5 to 10 fold excess Na diethyldithiocarbamate and extract precipitate with 10 ml $CHCl_3$. The Mn(II) is air oxidized to Mn(III) and extracts as the Mn(III) complex[100b].

3. At pH 8, $MoO_4^=$ and $CrO_4^=$ 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

Introduction:

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:

W. B. Healy, Anal. Chim. Acta. 34, 228, (1966)[58a]

Reagents:

citric acid

$NH_4OH$, 6M, 1M

sodium diethyldithiocarbamate

$CHCl_3$

HCl, 3M

$H_2SO_4$

$HNO_3$

$HClO_4$

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 $NH_4OH$ using a glass electrode and a pH meter to monitor the pH. Add 0.4 g sodium diethyldithiocarbamate (DIECA). Adjust pH to 5.3 with 1 M $NH_4OH$ and dilute to 200 ml.

Step 3. Extract with 25 ml $CHCl_3$. 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 0.4 g more DIECA and reextract; about 90% of remaining Mn extracts. Ca phosphate only very slowly precipitates.

Step 5. Evaporate $CHCl_3$ extracts, digest with $H_2SO_4$ - $HNO_3$ - $HClO_4$. Count and determine Mn colorimetrically.

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 $7.5 \times 10^{12}$ $n/cm^2 sec$.

Source:

F. Kukula, B. Mudrova and M. Krivanek[59].

Reagents:

Mn carrier, $MnSO_4$ in $H_2O$, 1 mg/ml

Buffer, $CH_3COONH_4$ plus $NH_4OH$

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 $HNO_3$ - 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 $NH_4OH$ - $CH_3COONH_4$ 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, Cu and Co by the $NH_4OH$.

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

## Procedure 7

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 $^{24}Na$ left is about $5 \times 10^{-9}$% and $^{32}P$, $2.2 \times 10^{-3}$%.

Source:

H. J. Bowen[101] as reported by Leddicotte[97].

Reagents:

fuming $HNO_3$

standardized Mn carrier

holdback carriers, about 10 mg/ml, of Br, Cl, Co, Cr, Cu, Fe, Ni, Na, K, Y, and Zn.

$H_2O_2$, 30%

$Na_2CO_3$ solution

6M HCl

$(NH_4)_2HPO_4$ solution

$CH_3COONH_4$ solution

2M $HNO_3$

$NaBrO_3$ 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 $NaClO_3$ solution and heating. Centrifuge,

discard supernate.

Step 2. Wash $MnO_2$ twice with water, centrifuge and discard washes.

Step 3. Dissolve $MnO_2$ in acidified $H_2O_2$, then precipitate $MnCO_3$ by adding $Na_2CO_3$ solution. Centrifuge, discard supernate.

Step 4. Wash precipitate with water. Dissolve precipitate in dil HCl and add $FeCl_3$, ammonium phosphate, and ammonium acetate solutions. Precipitate $Fe(OH)_3$ with $NH_4OH$. Centrifuge and save solution. Repeat scavenge by adding more Fe carrier, centrifuge, and save solution.

Step 5. To solution add enough $Na_2CO_3$ to precipitate $MnCO_3$. Centrifuge and save precipitate.

Step 6. Dissolve the $MnCO_3$ in 2N $HNO_3$ and precipitate $MnO_2$ by adding saturated $NaBrO_3$ to the solution and heating. Centrifuge, save precipitate.

Step 7. Wash the $MnO_2$ three times with water and once with acetone. Centrifuge, discard washes. Transfer $MnO_2$ 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 $^{56}Mn$.

## 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:

$HNO_3$, conc.

standardized Mn carrier

Cu, Y, $PO_4^{3-}$ holdback carriers, about 10 mg/ml.

$NaClO_3$, saturated solution

2M HCl

30% $H_2O_2$

$NH_4OH$, conc.

$CH_3COONH_4$ solution

$Fe(NO_3)_3$ in dil $HNO_3$ about 10 mg/ml Fe

$NH_4H_2PO_4$

$Cu(NO_3)_2$, about 10 mg/ml Cu

ammonium sulfide solution

Procedure:

Step 1. Transfer the irradiated tissue from the irradiation container to a 50 ml centrifuge tube. Add 10 ml conc $HNO_3$, 10 mg Mn carrier and holdback carrier of Cu, Y, and $PO_4^{3-}$. Boil the mixture until the tissue dissolves. Add 1 ml $NaClO_3$, heat, centrifuge and save $MnO_2$ precipitate.

Step 2. Wash the $MnO_2$ twice with 5 ml $H_2O$. Centrifuge, discard wash. Dissolve $MnO_2$ in 3 ml 2N HCl and min. $H_2O_2$ and then add $NH_4OH$ and $CH_3COONH_4$. Be sure all $H_2O_2$ is boiled out first. To this mixture add 5 drops of $Fe(NO_3)_3$ and one drop $NH_4H_2PO_4$. Centrifuge, discard precipitate.

Step 3. Acidify the supernate with 2N HCl, add 3 drops $Cu(NO_3)_2$ and enough $NH_4HS$ to precipitate CuS. Centrifuge, saving supernate. Wash CuS once with 2N HCl and add wash to supernate.

Step 4. Make the solution alkaline with 3 ml $NH_4HS$ and $NH_4OH$, boil, then centrifuge. Save MnS precipitate.

Step 5. Wash MnS twice with $H_2O$. Centrifuge. Dissolve MnS in 10 ml of conc $HNO_3$ and add 1 ml $NaClO_3$. Boil (caution!), centrifuge and discard supernate.

Step 6. Wash the $MnO_2$ precipitate with three 10 ml portions of hot water. Discard washes.

Step 7. Slurry the $MnO_2$ precipitate with water into a weighed counting tray. Dry under an infrared lamp, cool, weigh to determine yield.

Step 8. Cover the tray with Scotch tape and beta or gamma count $^{56}Mn$.

## Procedure 9

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:

Batzel 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:

$HNO_3$, conc.

Standardized Mn carrier

Holdback carriers, Zn, Ni, Co, Fe, Cr, V, Ti, Sc, Ca, and K. About 10 mg/ml

$H_2S$ gas

HCl, 6M

$NH_4OH$, conc.

$KClO_3$ solid

$H_2O_2$, 30%

Procedure:

Step 1. Dissolve the copper in the minimum amount of conc $HNO_3$. 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 $H_2S$. Centrifuge, save supernate. Make supernate alkaline with $NH_4OH$ and bubble in more $H_2S$ to precipitate sulfides including MnS. Centrifuge and wash.

Step 3. Dissolve sulfides in 4 ml fuming $HNO_3$. Add 2 or 3 crystals of $KClO_3$ and boil gently for 2 minutes to precipitate $MnO_2$.

Step 4. Wash precipitate with $H_2O$, then dissolve in minimum $HNO_3$ and $H_2O_2$. Again add holdback carriers and make 16N in $HNO_3$. Heat and precipitate $MnO_2$ with $KClO_3$ as in step 3.

Step 5. Wash, filter, dry, weigh, and mount $MnO_2$ 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 $MnO_2$ or $MnNH_4PO_4 \cdot H_2O$.

Source:

I. M. Kolthoff and P. J. Elving, "Treatise on Analytical Chemistry"(34).

Reagents:

6M $HNO_3$

$H_2O_2$, 30%

$H_2SO_4$, conc.

$H_3PO_4$, 85%

$KIO_4$, solid

Procedure:

Step 1. After counting is completed analyze the sample. If the sample is solid, dissolve it in 6M $HNO_3$ (plus a little $H_2O_2$ in the case of $MnO_2$) 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 $HNO_3$, boil to remove $H_2O_2$ and oxidize Fe(II) and other reducing agents. If the solution contains much HCl, the aliquot should be added to conc. $H_2SO_4$ and the solution evaporated to fumes of $SO_3$. Then, after the solution is cold, carefully add about 10 ml 6M $HNO_3$.

Step 3. Dilute the solution to about 20 ml with $H_2O$ and add about 5 ml 85% $H_3PO_4$ (decolorizes Fe(III)), then about 0.1 g $KIO_4$. Heat to boiling and boil very gently for about 1 min., then add 0.1 g $KIO_4$ 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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