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The Radiochemistry of Manganese

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The Radiochemistry of Manganese

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Subcommittee on Radiochemistry
National Academy of Sciences—National Research Council

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FOREWORD

The Subcommittee on Radiochemistry is one of a number of subcommittees working under the Committee on Nuclear Science within the National Academy of Sciences - National Research Council. Its members represent government, industrial, and university laboratories in the areas of nuclear chemistry and analytical chemistry

The Subcommittee has concerned itself with those areas of nuclear science which involve the chemist, such as the collection and distribution of radiochemical procedures, the establishment of specifications for radiochemically pure reagents, availability of cyclotron time for service irradiations, the place of radiochemistry in the undergraduate college program, etc.

This series of monographs has grown out of the need for up-to-date compilations of radiochemical information and procedures. The Subcommittee has endeavored to present a series which will be of maximum use to the working scientist and which contains the latest available information. Each monograph collects in one volume the pertinent information required for radiochemical work with an individual element or a group of closely related elements.

An expert in the radiochemistry of the particular element has written the monograph, following a standard format developed by the Subcommittee. The Atomic Energy Commission has sponsored the printing of the series.

The Subcommittee is confident these publications will be useful not only to the radiochemist but also to the research worker in other fields such as physics, biochemistry or medicine who wishes to use radiochemical techniques to solve a specific problem.

W. Wayne Meinke, Chairman
Subcommittee on Radiochemistry

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INTRODUCTION

This volume which deals with the radiochemistry of manganese is one of a series of monographs on radiochemistry of the elements. There is included a review of the nuclear and chemical features of particular interest to the radiochemist, a discussion of problems of dissolution of a sample and counting techniques, and finally, a collection of radiochemical procedures for the element as found in the literature.

The series of monographs will cover all elements for which radiochemical procedures are pertinent. Plans include revision of the monograph periodically as new techniques and procedures warrant. The reader is therefore encouraged to call to the attention of the author any published or unpublished material on the radiochemistry of manganese which might be included in a revised version of the monograph.

The Radiochemistry of Manganese

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Oak Ridge National Laboratory
Oak Ridge, Tennessee
October 1960

I. General References on the Inorganic and Analytical Chemistry of Manganese

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II. Radioactive Nuclides of Manganese

The radioactive nuclides of manganese that are of interest in the radiochemistry of manganese are given in Table I. This Table has been compiled from information appearing in reports by Strominger, et al.[1] and by Way and Schwartz.[2]

Table I: The Principal Radioactive Nuclides of Manganese

Radionuclide	Half-life	Mode of Decay	Energy of Radiations, Mev	Produced by
Mn^{51}	45.2 m	β^+	β^+: 2.6 γ: None	$Cr^{50}(p,\gamma)Mn^{51}$ $Cr^{50}(d,n)Mn^{51}$
Mn^{52m}	21.3 m	β^+(99%) IT(<1%)	β^+: 2.62 γ: 1.46,0.392	$Cr^{52}(p,n)Mn^{52m}$ $Cr^{52}(d,2n)Mn^{52m}$
Mn^{52}	5.6 d	EC(65%) β^+(35%)	β^+: 0.58 γ: 0.73,0.94,1.46	$Cr^{52}(p,n)Mn^{52}$ $Cr^{52}(d,2n)Mn^{52}$
Mn^{54}	291 d	EC	γ: 0.840	$Fe^{54}(n,p)Mn^{54}$ $Cr^{57}(p,n)Mn^{54}$ $Fe^{53}(p,\alpha)Mn^{54}$ $Cr^{55}(\alpha,\gamma)Mn^{54}$ $Mn^{55}(p,pn)Mn^{54}$ $Mn^{55}(\gamma,n)Mn^{54}$
Mn^{56}	2.576 h	β^-	β^-: 2.81,1.04, 0.65 γ: 0.845,1.81, 2.13	$Mn^{55}(n,\gamma)Mn^{56}$ $Fe^{56}(n,p)Mn^{56}$ $Co^{59}(n,\alpha)Mn^{56}$ $Mn^{55}(d,p)Mn^{56}$ $Cr^{54}(d,\gamma)Mn^{56}$
Mn^{57}	1.7 m	β^-	β^-: 2.6 γ: 0.117,0.134, 0.22,0.35,0.69	$Fe^{57}(n,p)Mn^{57}$ $Fe^{57}(d,2p)Mn^{57}$
Mn^{57}(?)	7 d	β^-	β^-: 1.0	

III. Review of the Chemistry of Manganese

Manganese, like iron, is one of the most abundant heavy metals to be found in the earth's crust. The ores of manganese, chief of which is pyrolusite, MnO_2, are found almost everywhere. Manganese is also found in small quantities in plant and animal tissues and is considered to be a required constituent because of its catalytic role in the chemical processes which occur in the cells of living organisms.

Metallic manganese resembles iron in both chemical and physical properties. When pure, it is silvery white like iron and is the softer of the two; it becomes hard and brittle and grey when it contains carbon. As an active metal, it displaces hydrogen slowly from water; however, it dissolves very readily in dilute acids, forming the bivalent ion Mn^{+2} and liberating hydrogen.

Sulfur dioxide and nitric oxide are evolved when manganese is dissolved in sulfuric acid and in nitric acid, respectively. Sulfur, chlorine, carbon, silicon, boron, and nitrogen react to form MnS, $MnCl_2$, Mn_3C, MnSi, Mn_2Si, Mn_3B, and Mn_3N_2. It also reacts very vigorously with fluorine, forming MnF_2 and MnF_3.

A. The Compounds of Manganese

Manganese forms compounds having valence states of from +1 to +7. The most important compounds of manganese are derived from the +2, +4, and +7 valence states. Compounds of Mn^{+3} and Mn^{+6} can be readily formed and some Mn^{+5} forms are known. The cyano salts $M^{1}_{-5}[Mn(CN)_6]$ are usually compounds of Mn^{+1}.

The Oxide and Hydroxide Compounds of Manganese. MnO, Mn_2O_3, MnO_2, Mn_2O_7 are the more important of the manganese compounds. MnO and Mn_2O_3 are basic in character; MnO_2 is amphoteric and Mn_2O_7 is strongly acidic since it is derived from permanganic acid, $HMnO_3$, which is one of the strongest acids known. Manganese trioxide, MnO_3, is not known to exist in the free state; the manganate compounds, $M^{1}_{2}[MnO_4]$, are derived from the oxide. In these salts, the manganese is present within the acid radical. An intermediate oxide, Mn_3O_4, red in color, is also known.

MnO is obtained by reducing at very high temperatures the higher oxides of manganese with hydrogen or carbon monoxide, or by igniting manganese carbonate in hydrogen or nitrogen. Manganese(II) salt solutions treated with alkali hydroxides will produce $Mn(OH)_2$. It is incompletely precipitated in ammonium hydroxide or with ammonium salts.

Mn_2O_3 is produced by treating MnO_2 in air at temperatures in the range of from 530-940°; or by igniting manganese(II) salts in the air or oxygen. Mn_2O_3 can be converted to Mn_3O_4 to lose oxygen by igniting it above 940° in air or above 1090° in oxygen. This particular reaction is of importance in any gravimetric determination of manganese employing as a finally product manganese oxide. Mn_2O_3 will reduce to the intermediate compound, Mn_3O_4, and finally to MnO if it is heated in hydrogen

in the temperature range of from 200° to 350°. When Mn_2O_3 is dissolved in acids, manganese(III) salts will be produced. Depending upon the acid and the temperature, manganese(II) salts and MnO_2 can be formed. The precipitates of manganese(III) salts from solution will produce a hydrated manganese(III) oxide, $Mn_2O_3 \cdot H_2O$.

MnO_2, is the chief constituent of the most important ore of manganese, pyrolusite. It can be prepared artificially in the anhydrous state by such chemical reactions as the mild ignition of manganese(II) nitrate. It has an extremely low solubility, but it can be readily attacked by strong reducing agents in the presence of dilute acids. It forms manganese(II) dithionate, MnS_2O_6 with sulfurous acid and when it interacts with hydrogen peroxide and sulfuric acid, $MnSO_4$ and O_2 are produced. When a mixture of MnO_2 and concentrated hydrochloric acid are warmed, manganese tetrachloride, $MnCl_4$, is produced. $MnCl_4$ readily decomposes into manganese trichloride, $MnCl_3$ and free chlorine. The oxidation of manganese salts, or the reduction of manganates or permanganates in alkaline solution will produce a manganese dioxide hydrate. The salts of the hydrate reactions with basic oxides are known as manganites. It will also form salts with very strong acids; however, these are rather unstable because manganese tends to become bivalent in acid solutions. These reaction capabilities suggest that manganese dioxide is amphoteric although it is extremely insoluble.

The manganese heptoxide, Mn_2O_7 is usually obtained by treating potassium permanganate with concentrated sulfuric acid. It appears as a heavy, greenish-brown oil that is quite stable in air and at ordinary temperatures. It will decompose explosively when warmed into MnO_2 and O_2. It can also be decomposed in water and will completely dissolve in cold water or in acetic anhydride to form a violet solution. This indicates that permanganate ions, MnO_4^- are formed and that permanganic acid, $HMnO_4$, exists in the solution. The solution can only be concentrated up to a content of about 20% $HMnO_4$. Beyond that concentration, decomposition will occur.

Derivatives of the Manganese Oxide Compounds. Table II lists some of the other compounds containing manganese that can be derived by chemical actions upon the different manganese oxide compounds. Characteristic reactions and the solubility of these derivations in different solvents are also given as part of the table.

Table II: Manganese Oxide Compounds and Their Derivatives

Compound	Formed By	Color	Solubility
	A. The Manganese(II) Salts		
$MnCl_2$	Dry HCl upon MnO, $MnCO_3$ on Mn^{+2}	Pale pink	Very soluble in H_2O
$MnCl_2$ hydrates	Crystallized from aqueous solutions	Rose	Very soluble in H_2O
$MnCl_2 \cdot 2NH_2OH$	$MnCl_2$ + hydroxlamine	Pink	Soluble in acids
Alkali Metal Chlorides ($M^{I}Cl \cdot MnCl_2$ or $2M^{I}Cl \cdot MnCl_2$)	$MnCl_2$ + alkali metals chlorides	Pink	Decomposes in water
$MnBr_2$) MnI_2)	Form the same hydrates, ammoniates, etc.,as $MnCl_2$		
MnF_2	HF upon MnO, $MnCO_3$, or Mn^{+2}	Pink	Slightly soluble in water
$MnSO_4$	All manganese compounds + sulfuric acid	White to red	Soluble in water
$MnCO_3$	Soluble manganese(II) salts + soluble carbonates	Pink	Slightly soluble in cold water; soluble in dilute acids
$Mn(NO_3)_2$	$MnCO_3$ + dilute HNO_3 crystallization	Rose-white	Very soluble in water and alcohol
$Mn(NO_3)_2 \cdot 6H_2O$	Evaporation of $MnCO_3$ + dilute HNO_3 solution	Rose-white	Very soluble in water and alcohol
$Mn(NO_3)_2 \cdot 3H_2O$	$MnCO_3$ + conc. HNO_3	Colorless	Soluble in water
$Mn(C_2H_3O_2)_2 \cdot 4H_2O$	$MnCO_3$ + acetic acid crystallization	Red	Soluble in cold water
$Mn_3(PO_4)_2 \cdot 7H_2O$	Neutral manganese(II) salts + disodium phosphate	White to red	Very slightly soluble in water; soluble in acids and acetic acid

Table II (Continued)

Compound	Formed By	Color	Solubility
$Mn(NH)_4PO_4 \cdot H_2O$	Mn(II) salt solutions + ammonium chloride, ammonium phosphate and ammonia	White to	Soluble in acids
$Mn_2P_2O_7$	Ignition of $Mn(NH_4)PO_4 \cdot H_2O$	Pink	Insoluble in water; slightly soluble in acids
MnS_7	Mn(II) salts + ammonium or alkali sulfides	Flesh pink	Soluble in dilute acids
$MnSO_3$	$MnCO_3$ + aq. solution of sulfur dioxide	Pink	Soluble in acids
MnB	Double decomposition of Mn(II) salts and borax	White	Soluble in acids
$MnC_2O_4 \cdot 2H_2O$	Hot oxalic acid + hot solution of a Mn(II) salt or + hot $MnCO_3$	White-red	Slightly soluble in water
MnC_2O_4	$MnC_2O_4 \cdot 2H_2O$ heated above 100°	Pale pink	Insoluble in water; soluble in acids and NH_4Cl
$Mn(CN)_2$	Cyanide ions + Mn(II) salt solutions	Greenish-white	Slightly soluble in water; soluble in HCl
$Mn(SCN)_2$	Evaporation of a solution of $MnCO_3$ in thiocyanic acid	White	Soluble in water and alcohols
	B. The Manganese III Salts		
$MnCl_3$	Concentrated HCl + MnO_2	Dark red	Soluble in water and alcohol
MnF_3	Free fluorine + MnI_2	Reddish-brown	Decomposes in water, soluble in acids
$MnF_3 \cdot 2H_2O$	Crystals caused by evaporation of HF solution of MnF_3	Ruby	Soluble in Acids
$Mn_2(SO_4)_3 \cdot H_2SO_4 \cdot H_2O$	Concentrated H_2SO_4 + Mn_2O_3	Red	Decomposes in water, soluble in HCl and dilute H_2SO_4
$MnPO_4 \cdot H_2O$	Mn(III) salts + disodium phosphates	Green	Insoluble in water

Table II (Continued)

Compound	Formed By	Color	Solubility
$Mn(PO_3)_3$	Mn(III) salts + disodium phosphates	Red	Insoluble in water
$Mn(C_2H_3O_2)_3 \cdot H_2O$	Oxidation of $Mn(C_2H_3O_2)_2 \cdot 4H_2O$ with glacial acetic acid and permanganate or chlorine	Cinnamon-brown	Soluble in water
	C. The Manganese(IV) Compounds		
$MnCl_4$	MnO_2 + HCl		Decomposes
Chloromanganate (IV) Salts ($4KCl \cdot MnCl_2$, etc.)	$MnCl_4$ + alkali chlorides	Varied	Soluble in water
$Mn(SO_4)_2$	$MnSO_4$ oxidized in H_2O_4 with permanganate	Black	Soluble in water
Metal Manganites	MnO_2 + metallic oxides	Varied	Soluble in acids
	D. The Manganate VII Compounds		
$KMnO_4$	Electrolytic oxidation of Manganate(VI) salts	Purple	Soluble in H_2O
Other alkali permanganates	Formed by crystalization; violet in color, very soluble in water		

A limited number of compounds of the manganate(V) and manganate(VI) salt types have originated from the reactions of alkali metal compounds upon manganese dioxide systems. Most of these are produced as impure salts and they are very soluble in dilute caustic alkalis, giving the solution a green color. They will hydrolyze in water or dilute acids to form MnO_2 + permanganate.

B. Analytical Chemistry of Manganese

Methods of Determination. Hillebrand[3] reports that most of the analytical methods for determining manganese are based upon volumetric methods in which the manganese is first oxidized to permanganic acid followed by a subsequent reduction by some reducing agent. Colormetric methods are also available in which the manganese is first oxidized to

permanganic acid by such agents as periodate, persulfate, bismuthate, or lead dioxide. However, these methods, as well as any other analagous analytical method, are not easily applied for use in an analytical technique having as a basis of measurement the radioactivity of a radionuclide. Thus, gravimetric methods in which some precipitible compound of the radionuclide sought after is produced is desirable.

Suitable methods for the gravimetric determination of a radiomanganese compound are those based upon a precipitation of the manganese, either as the sulfide, or the hydrated dioxide, or as manganese ammonium phosphate, or as the sulfate. The sulfide may be weighed directly; however, it must be first ignited to the oxide and then converted to the sulfide by covering it with sulfur and igniting to 900°C. The sulfide can be converted to the $MnSO_4$ for weighing by dissolving in dilute sulfuric acid and then evaporating off the acid. The hydrated dioxide can be converted to Mn_3O_4 by ignition. Although Mn_3O_4 is the form most frequently obtained in the radiochemical procedures reported in Section VII, it is unsatisfactory since the composition of the weighed oxide depends upon the temperature of the ignition and the nature of the atmosphere surrounding the precipitate.[4]

The most satisfactory weighable precipitate is the pyrophosphate, $Mn_2P_2O_7$, resulting from the ignition of manganese ammonium phosphate, $MnNH_4PO_4 \cdot H_2O$. The method is based upon the precipitation of manganese ammonium phosphate in a slightly ammonical solution containing an excess of ammonium salts.[5,6,7] The method requires a preliminary separation of manganese from other elements that can be precipitated under similar conditions.

Separation by Precipitation. Hillebrand[8] points out that one of the best methods of separating manganese from other elements is in its precipitation as the dioxide by boiling with nitric acid and potassium chlorate. The dioxide can be purified in a number of ways. Iron, aluminum and other hydroxide precipitible elements can be removed from a solution

of the dioxide by a precipitation with ammonium hydroxide in a boiling solution.[9] Iron, aluminum and chromium can also be removed by a barium carbonate precipitation.[10] A cupferron precipitation will quantitatively separate iron, titanium, zirconium and vanadium from manganese.[11] Electralytic decomposition with a mercury cathode in dilute sulfuric acid or concentrated nitric acid solutions[12] often provides a separation of such elements as iron, chromium, nickel, or molybdenum.

Manganese can be separated from the hydrogen sulfide group elements by precipitation with hydrogen sulfide group elements by precipitation with hydrogen sulfide in solutions containing mineral acids[13] and zinc can be separated by a sulfide precipitation in acetic or formic acid solution.[14] The alkaline earths are satisfactorily separated by a precipitation of MnS with ammonium sulfide.[15] A sodium hydroxide precipitation following a sodium peroxide oxidation will remove molybdenum, vanadium and chromium.[16]

Besides these separations by precipitations, manganese can be separated from other elements by solvent extraction, ion exchange and complex or chelate ions. However, it would appear to be necessary that a precipitation step should be incorporated into any radiochemical procedure following such separation techniques in order to concentrate the manganese radioactivity for its measurement.

Separation by Solvent Extraction. In addition to the precipitation techniques, solvent extraction can be used to separate manganese from other elements. For example iron, molybdenum, gallium, gold, antimony, and thallium can be removed from a manganese solution by extracting with ether from a hydrochloric acid solution of the chlorides.[17] Morrison and Freiser[18] present other data on ion association systems and acknowledge reports on complexes that might be of interest to a radiochemist in separating radiomanganese isotopes. Some of these reports include (1) the non-extraction of Mn from Sn(II) and Sn(IV), As(III), Sb(III), Se(IV) and Mo(VI) in Hf systems of varying concentrations to ethyl ether,[19] (2) the

non-extraction of Mn(II) from Fe(III) in a methyl isobutyl ketone-HBr system,[20] (3) the non-extraction of Mn from Sb(III), Hg(II), Cd, Au, and Sn(II) in HI solutions extracted with ethyl ether,[21] (4) the extraction of Mn in a butyric acid-benzene system,[22] (5) the non-extraction of Mn(II) in alkyl phosphine oxide - 1M HCl systems[23] and the extraction of Mn(VII) with chloroform from a basic medium after a formation of an insoluble salt of MnO_4^- with tetraphenylarsonium chloride.[24] The chelate systems described in the following sections can be used in solvent extraction with considerable success to determine manganese.

Separation by Solvent Extraction of Chelate Systems. Manganese forms well defined chelates with acetylacetone,[18] oxine,[25] cupferron,[17] and sodium diethyldithiocarbamate.[26] The solvents and the extraction conditions used in these separations are indicated in the reference cited. In addition to this information, Morrison and Freiser[27] report that EDTA can be used to inhibit the extraction of Mn in oxine extractions systems so that it can be separated from other elements.

Separation by Ion Exchange. Manganese(II) is not readily adsorbed on Dowex-1 or Dowex-2 anion exchange resins using moderate or strong concentrations of hydrochloric acid,[28] and such a system could be used for its separation from other elements. Riches[29] has shown manganese in low concentrations can be separated and determined in decinormal ammonium chloride or ammonium phosphate solutions adsorbed upon a sulfuric acid resin. The elutriant was 1N HCl and at least 87% of the adsorbed manganese was recovered. Maxia[30] has used an anion exchange separation for determining manganese in molybdenum-manganese alloys. After the separation, manganese was determined by activation analysis. In addition to these applications, the information and references given by Kraus and Nelson[31] in their review on radiochemical separations by ion exchange suggests, although very little work has been done, that manganese can be separated from other elements by ion exchange techniques.

IV. Decomposition of Materials Containing Manganese

Many materials, such as metals and alloys, in which manganese might be found are soluble in mineral acids. Manganese-containing minerals can be brought into solution either with single or mixed acids or by fusion with sodium carbonate or potassium pyrosulfate[32] or by alkaline peroxide.[33] Meteoritic materials can be brought into solution with acids[34] or by alkaline peroxide fusion.[35] Biological materials, such as plant and animal tissues, and petrochemicals can most often be brought into solution by a wet oxidation method using sulfuric, perchloric and nitric acid mixtures.[36]

V. Safety Practices

No matter what method is used for decomposing a sample, adequate safety precautions should be used. This is particularly significant, if an analyst is working with radioactive sample materials. The discharge of radioactivity by explosion or evolution into a laboratory area can be hazardous and can result in widespread contamination. Thus, some source of information on safe handling practices in processing radioactive samples should be consulted before a radiochemical analysis is undertaken. One such source is that which is given in the Oak Ridge National Laboratory's Master Analytical Manual.[37] Many other similar sources of information exist and should be consulted.

VI. Radioassay Techniques for Manganese

The analysis of samples containing radionuclides of manganese may be accomplished either by nondestructive or destructive techniques. Each technique is dependent upon the measurement of the radioactivity of each manganese radionuclide. In these measurements, such factors as radionuclide half-life, type of radiation and energy of radiation must be considered. The nuclear characteristics of the radioactive isotopes of manganese are shown in Table I of this monograph.

The chief radioisotopes of manganese usually encountered by the radiochemist are Mn^{54}(291d) and Mn^{56}(2.576h). As pointed out in Table I, these

isotopes are produced as a result of a number of nuclear reactions upon manganese-55 or on the stable isotopes of other elements. The radioactivity of both Mn^{54} and Mn^{56} can be analyzed and measured by standard Geiger-Mueller scintillation and proportional counting techniques.[38,39] The 0.846, 1.81 and 2.13 Mev emitted by the 2.576 hour manganese-56 are favorable for use in gamma scintillation spectrometry methods of measurement[39,40] and have been used most frequently to determine trace manganese in sample materials by neutron radioactivation analysis.[41,42] The 0.84 Mev gamma radiation of 291d Mn^{54}, produced usually as a radioisotope for tracer studies, can also be measured conveniently by gamma spectrometry. In either measurement, the nondestructive, or direct, analysis technique can be used to measure the radioactivity of the radionuclide appearing either as a radioactive tracer in solution or as a radioactivity in an nuclear particle irradiated sample material. In the latter instance, Brooksbank, et al.,[43,44] and Kusaka[45] have shown that small concentrations of manganese in aluminum, aluminum base alloys, and other metal alloys can be determined by a nondestructive analysis method following a neutron irradiation in a nuclear reactor.

As far as the destructive, or radiochemical, analysis methods are concerned, the ideas and techniques expressed in Section III B of this monograph have been used alone or in complement with each other to create radiochemical procedures suitable for use in the production of manganese tracers at Berkeley[46] or in the use of neutron radioactivation analysis in analytical chemistry.[42] The use of a precipitation method in analysis in which a "carrier", i.e. a known amount of an inactive manganese salt, to carry the radioactive manganese through a chemical processing is profitable in that it permits a concentration of the radionuclide for the measurement of its radioactivity and also provides a means of easily determining, by a weighing operation, the yield of the experiment.[38] The choice of a final precipitate form for manganese has been arbitrarily based on information appearing elsewhere in this work and upon criteria extablished in

Duval's studies.[47] The radioactivity of the separated material can be determined by either of the methods cited above.[38,39]

VII. Collection of Detailed Radiochemical Procedures for Manganese

A very few radiochemical procedures exist for the determination of the radionuclides of manganese. The origin of these have been in laboratories engaged in work on the preparation and use of radioactive tracers[46] or in the laboratories concerned with radioactivation analysis methods.[48-55]

Each researcher has attempted to evaluate each procedure with regard to contamination by other radioactive species. Special information regarding bombardment, type of material analyzed, separation time, etc., appear as part of each procedure.

Procedure 1

Type Material Analyzed: Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Br, Rb or Sr

Type of Nuclear Bombardment: 190 Mev deuterons

Procedure By: W.C. Orr (Reported in Meinke[46])

Chemical Yield of Carrier: 60-80%

Separation Time: 2 hours

Decontamination: Adequate for determining Mn^{52} and Mn^{56} yields. Increased purification upon recycling.

Equipment Needed: As indicated in procedure

Procedure:

1. Target is dissolved in ~30 ml conc. HNO_3. (HCl used for Cr).
2. 25 to 50 mg of standardized Mn carrier is added, i.e., a measured vol. of solution of known concentration.
3. Several mg of hold-back carriers added, all elements except Mn from $Z + 1$ to $Z - 12$ (Z = target at. no.).
4. Boil to expel oxides of nitrogen.
5. Solid $KClO_3$ is added SLOWLY! Wait after adding each increment for the evolution of ClO_2, etc. Continue until ppt'n of MnO_2 is complete. Boil continuously.
6. Filter through a medium sintered glass filter on which a layer of "Supercel" has been laid down. Wash with conc. HNO_3.
7. MnO_2 is dissolved directly on the filter by conc. HNO_3 to which 30% H_2O_2 is added dropwise. Solution may be drawn through the filter into a clean filtering flask and transferred to a clean 100 ml beaker.
8. The carriers of step (3) are again added.

Procedure 1 (Cont.)

9. The solution is boiled to decompose H_2O_2. Conc. HNO_3 is added to restore vol. to ~30 ml.
10. Repeat steps (5) through (9) two or more times (see remarks, following).
11. Repeat steps (5), (6), and (7).
12. Boil to decompose H_2O_2; i.e., solution becomes colorless and vol. is less than 50 ml.
13. Transfer to 50 ml vol. flask and dilute to mark. Samples of 25λ and 100λ should be suitable for counting Mn^{56} (2.59 hrs.) decaying into Mn^{52} (6 days) half-life.

Remarks: The repetition of steps indicated in (10) should give increased purification. The whole procedure should include not less than three precipitations of MnO_2.

In cases where step (9) preceded step (8) good separation was not always achieved, presumably because the active impurity was not in the same oxidation state as the added carrier at the beginning of MnO_2 precipitation.

Presence of sulfate is to be avoided because soluble sulfate complexes of Mn(III) render precipitation incomplete.

According to Scott (Std. Meth. Chem. Anal.) oxides of W, Si, Cb, and Ta are also ppt'd by $KClO_4$ as in this procedure.

Procedure 2

Type Material Analyzed: Arsenic

Type of Nuclear Bombardment: 190 Mev deuterons

Procedure By: H. Hopkins, Jr. (Reported in Meinke[46])

Chemical Yield of Carrier: ~60%

Separation Time: 1 hour

Decontamination: Approximately a factor of 50 from other radioactivities

Equipment Needed: As indicated in Procedure

Procedure:

1. Dissolve As in minimum HNO_3 and HCl, add 5 mg Mn and 1 mg other carriers.
2. Make alkaline with NH_4OH, pass in H_2S for 1 minute, centrifuge, wash with H_2O.
3. Dissolve with hot fuming nitric acid and add solid $KClO_3$ to boiling solution to ppt. MnO_2, add fuming HNO_3 and $HClO_3$ until pptn is complete.
4. Centrifuge and wash with H_2O. Dissolve with 1 dp dilute HCl and 1 dp H_2O_2.
5. Make to 5 ml volume, 3 N HCl and add 5 mg As.
6. Pass H_2S into hot solution to ppt As_2S_3.
7. Repeat pptn of As_2S_3. Make supnt alkaline, pass in H_2S to precipitate MnS. Dissolve as before and ppt. MnO_2 from a solution containing additional holdback carriers.

Procedure 3

Type Material Analyzed: Copper

Type of Nuclear Bombardment: 60" or 184" cyclotron deuterons

Procedure By: Stewart-Softky (Reported in Meinke[46])

Chemical Yield of Carrier: 90-100%

Separation Time: 1-2 hours for 12 samples

Decontamination: 10^6 for other radioactivities

Equipment Needed: As indicated in Procedures

Procedure:

1. Dissolve copper in minimum 6 N HNO_3. Add 1 mg Mn carrier as nitrate.
2. Dilute to 1-2 N HNO_3 add about 100 mg of $KBrO_3$ and boil for 5-10 minutes, or until MnO_2 is well coagulated.
3. Filter through Whatman #42 filter paper. Wash precipitate with 6 N HNO_3 until no Cu blue shows in final wash.
4. Dissolve MnO_2 through filter paper into a 40 ml centrifuge cone, with conc. HCl. Add 2 mg Cu carrier. Make solution strongly ammonical.
5. Add a few crystals of $(NH_4)_2S_2O_8$ and boil off excess persulfate in a hot water bath. MnO_2 precipitates almost immediately.
6. Centrifuge, decant supernatant, and wahs precipitate with dilute NH_4OH.

Procedure 4

Type Material Analyzed: Copper

Type of Nuclear Bombardment: 60" and 184" cyclotron bombardment

Procedure By: Batzel (Reported by Meinke[46])

Chemical Yield of Carrier: 75%

Separation Time: 30 minutes

Decontamination: At least 10^3 from all other radioactivities

Equipment Needed: As indicated in Procedure

Procedure:

1. Dissolve the copper in the minimum amount of concentrated HNO_3. Boil almost to dryness, add carriers (Zn and below) including 5 mg of Mn and make 1 N in HCl.
2. Precipitate the copper sulfate. Make the supernate alkaline with NH_4OH and precipitate the sulfides including Mn with H_2S.
3. To the sulfides add concentrated 16 N HNO_3 carefully, to dissolve and make the volume up to 4 cc with fuming HNO_3. Add 2 or 3 crystals of $KClO_3$ and boil gently for 2 minutes to precipitate MnO_2.
4. Wash the precipitate with H_2O and dissolve in one drop of HNO_3 and H_2O_2.
5. Again add holdback carriers and make 16 N in HNO_3. Precipitate the MnO_2 with $KClO_3$ as in step 4.
6. The precipitate may be weighed as MnO_2 and counted.

Procedure 5

Type Material Analyzed: Hi purity aluminum

Type of Nuclear Bombardment: $Mn^{55}(n,\gamma)Mn^{56}$

Procedure By: Albert,[48] Albert, et al.,[49] Talbot, et al.[52]

Chemical Yield of Carrier: ~ 70%

Separation Time: Several hours

Decontamination: Complete decontamination from aluminum, copper, gallium, iron, sodium, silicon, arsenic, nickel and cobalt

Equipment Needed: Not described

Procedure

1. Dissolve irradiated material in HCl, then make solution 3N in HCl. Precipitate the acid sulfides of Cu and Sb by saturating solution with H_2S. Remove sulfide precipitates by filtering.
2. Saturate filtrate with chlorine gas to precipitate $AlCl_3 \cdot 6H_2O$. Filter to remove precipitate.
3. Concentrate solution, then extract with ether to remove gallium. Separate aqueous and organic fractions.
4. Process aqueous solution by precipitating the rare earth oxalates from an HCl solution by use of ammonium oxalate. Filter.
5. Concentrate filtrate by boiling to about 5 ml. Then precipitate $Mn(OH)_3$ by adding ammonium hydroxide. Filter.
6. Filter, then count the hydroxide precipitate for Mn^{56} (2.576h) radioactivity.

Procedure 6

Type Material Analyzed: Blood

Type of Nuclear Bombardment: $Mn^{55}(n,\gamma)Mn^{56}$

Procedure By: Bowen[50]

Chemical Yield of Carrier: 60-90%

Separation Time: 2.5 hours (for 8 samples)

Decontamination: Complete decontamination from K, Cl, Br, and I; Sodium-24 left: 5×10^{-9}%; P left: 0.0022%

Equipment Needed: Indicated in procedures

Procedure

1. Dissolve the irradiated blood in hot fuming nitric acid containing 50 milligrams of manganese carrier and "holdback" carrier of bromide, chloride, cobalt, chromium, copper, iron, nickel, sodium, potassium, yttrium and zinc. Precipitate manganese dioxide by adding conc. sodium chlorate. Centrifuge, discard supernatant liquid.
2. Wash manganese dioxide twice with water, centrifuge after each wash and discard washes.
3. Dissolve the manganese dioxide in acidified hydrogen peroxide, then precipitate $MnCO_3$ with the addition of sodium carbonate solution. Centrifuge, discard supernatant liquid.
4. Wash the precipitate with water; centrifuge and discard washes. Dissolve precipitate in dilute HCl and add $FeCl_3$, ammonium phosphate and ammonium acetate. Precipitate ferric hydroxide from the solution with ammonium hydroxide. Repeat hydroxide scavenging by adding additional iron "holdback" carrier to the solution. Centrifuge, discard the precipitate.
5. Add to the supernatant liquid enough sodium carbonate to precipitate $MnCo_3$. Centrifuge and discard the supernatant liquid.
6. Dissolve the $MnCO_3$ in 2N nitric acid and precipitate manganese dioxide by adding saturated sodium bromate solution to the solution. Centrifuge and discard supernatant liquid.
7. Wash the manganese dioxide 3 times with water and once with acetone. Centrifuge; discard washes. Transfer dioxide to a weighed counting tray, dry under an infrared lamp and weigh to determine the chemical yield.
8. Cover the tray with scotch tape and count the Mn^{56} with an end-window Geiger Counter.

Procedure 7

Type Material Analyzed: Biological Tissue (Tomato Seeds)

Type of Bombardment: $Mn^{55}(n,\gamma)Mn^{56}$

Procedure By: Bowen and Cowse[55]

Chemical Yield: 60-90%

Separation Time: 2.5 hours (8 samples)

Decontamination: Minimum interference from P^{32} and Sodium-24

Equipment Needed: Indicated in procedure

Procedure

1. Transfer the irradiated tissue from the irradiation container to a 50 ml centrifuge tube. Add 10 ml 24N HNO_3, 10 mg of manganese carrier and holdback carrier of Cu, Y and $Po_4^{=}$. Boil the mixture until the tissue dissolves. Add 1 ml of $NaClO_3$. Centrifuge. Discard the supernatant liquid.
2. Wash the MnO_2 precipitate twice with 5 ml of H_2O. Centrifuge, discard the washes. Dissolve the precipitate in 3 ml 2N HCl and 1 ml of H_2O_2 and then add ammonia and $CH_3CO_2NH_4$. To this mixture add 5 drops of $Fe(NO_3)_3$ and 1 drop of $NH_4H_2PO_4$. Centrifuge, discard the precipitate.
3. Acidify the supernatant liquid with 2N HCl, add 3 drops of $Cu(NO_3)_2$ and enough NH_4HS to precipitate CuS. Centrifuge, transfer the supernatant liquid to a new tube. Wash the CuS precipitate once with 2N HCl and add the wash to the supernatant liquid.
4. Make the solution alkaline with 3 ml NH_4HS and ammonia; boil and then centrifuge. Discard the supernatant liquid.
5. Wash the MnS precipitate twice with water. Centrifuge; discard the washes. Dissolve the precipitate in 10 ml of 24N HNO_3 and add 1 ml of $NaClO_3$. Boil (cautiously!!), centrifuge and discard the supernatant liquid.
6. Wash the MnO_2 precipitate with three 10 ml portions of hot water. Centrifuge after each wash and discard the wash.

Procedure 7 (Cont.)

7. Slurry the MnO_2 precipitate with water into a weighed counting tray. Dry under an infrared lamp, cool and then weigh.
8. Cover the weighing tray with Scotch tape and then count in an end-window Geiger Counter.

Procedure 8

Type Material Analyzed: Aluminum, aluminum base alloys, other metals and alloys

Type of Nuclear Bombardment: $Mn^{55}(n,\gamma)Mn^{56}$

Procedure By: Blanchard, et al.,[53] Brooksbank, et al.,[49] Leddicotte[53]

Chemical Yield of Carrier: 65-90%

Separation Time: 1.5 hours (sample in duplicate)

Decontamination: At least 10^6 for most elements; W, Si, Nb, and Ta radioactivities will interfere since these oxides are precipitated $KClO_4$

Equipment Needed: Given in procedure

Procedure

1. Sample is dissolved in conc. HNO_3(HCl is used if Cr is present). Add 1-5 mgs of following carriers (holdback): Fe, Zn, Cr, Ca, Ni, Co, and Na. Also, add 10 mgs of standardized Mn carrier.
2. Boil to expel oxides of nitrogen. Solid $KClO_3$ is added slowly. (Do not add chlorate to HNO_3SO_1 while it is boiling, a serious explosion may result, but boil after the addition of each portion of chlorate). Continue $KClO_3$ addition until ppt is complete. Centrifuge, discard supernate. Wash ppt with conc. HNO_3.
3. Dissolve ppt of MnO_2 in 2 ml of hot 6 N HCl and 5-10 drops of H_2O_2. Add 1-5 mgs each of Bi or Cu, holdback carrier and of the holdback carriers listed in Step (1). Evaporate to near dryness, add 10 ml of conc. HNO_3 and solid $KClO_3$ until precipitation of MnO_2 is complete. Centrifuge, discard supernates. Wash ppt with conc. HNO_3.

Procedure 8 (Cont.)

4. Repeat Step #3.
5. After washing ppt (obtained in step 4) with conc. HNO_3, MnO_2 may be transferred to tared filter paper, wash with H_2O and dried using C_2H_5OH and ether. Mounted and counted. Or, it can be heated to 900°C in muffle furnace and converted to Mn_3O_4 for weighing, mounting and counting. (See Note 1)

Note:

1. MnO_2 may be dissolved by an acid step and then treated with diammonium phosphate to precipitate manganese ammonium phosphate. The ammonium phosphate compound is then converted to $Mn_2P_2O_7$ by ignition at 1000°C for 1 hour.

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