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# The Radiochemistry of Silicon

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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

# INTRODUCTION

This volume which deals with the radiochemistry of silicon 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 silicon which might be included in a revised version of the monograph.

# CONTENTS

# The Radiochemistry of Silicon

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## I. GENERAL REFERENCES ON THE INORGANIC AND ANALYTICAL CHEMISTRY OF SILICON

1. Remy, H., Treatise on Inorganic Chemistry, p. 469-516, Vol. I, Elsevier, Amsterdam, 1956.

2. Kolthoff, I. M., and Sandell, E. B., Textbook of Quantitative Inorganic Analysis, 3rd Ed., New York, 1951.

3. Latimer, W. M., and Hildebrand, J. H., Reference Book of Inorganic Chemistry, 3rd Ed., New York, 1951.

4. Sidgwick, N. V., The Chemical Elements and Their Compounds, University Press, Oxford, 1951.

5. Sneed, M. C., and Maynard, J. L., General Inorganic Chemistry, pp. 700-724, Van Nostrand, Inc., New York, 1942.

## II. RADIOACTIVE NUCLIDES OF SILICON

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

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*Operated for U. S. Atomic Energy Commission by Union Carbide Nuclear Company

Table I. The Radioactive Nuclides of Silicon

| Radionuclide | Half-life | Mode of Decay | Energy of Radiation, Mev | Produced By |
|---|---|---|---|---|
| $Si^{27}$ | 4.9 sec | $\beta^+$ | $\beta^+$: 3.48 | $Mg^{24}(\alpha,n)Si^{27}$<br>$Al^{27}(p,n)Si^{27}$<br>$Si^{28}(\gamma,n)Si^{27}$ |
| $Si^{31}$ | 2.65 hr | $\beta^-,\gamma$ | $\beta^-$: 1.47<br>$\gamma$ : 0.17, 0.52 | Si-d-p, Si-n-$\gamma$<br>Si-$He^3$-2p, p-n-p<br>S-n-$\alpha$ |
| $Sc^{32}$ | ~ 710 y | $\beta^-$ | $\beta^-$: 0.10 | Si-t-p, S-$\gamma$-2p,<br>S-d-3p-n |

## III. THE CHEMISTRY OF SILICON AND ITS APPLICATION TO THE RADIOCHEMISTRY OF THE SILICON RADIONUCLIDES

Radiochemistry is probably best described as being an analysis technique used primarily either (1) to assist in obtaining a pure radionuclide in some form so that an absolute measurement of its radioactivity, radiation energies and half-life can be made, or (2) to determine the amount of radioactivity of a particular radioelement in a radionuclide mixture, or (3) to complete a radioactivation analysis being used to determine the concentration of a specific stable element in a particular sample material. In order to be an aid in accomplishing any one of the above interests, radiochemistry usually considers the isolation of the desired radionuclide by either carrier or carrier-free separation methods.

Carrier methods are used most frequently in radiochemistry. They involve the addition of a small amount of inactive stable element to a solution of the irradiated material to serve as a carrier of the radionuclide of that element through the separation method. In carrier-free separations, i.e., those radiochemical techniques used mostly for absolute radioactivity measurements, it is required that the radioelement be isolated in a manner capable of giving either no amount or a minimal amount of stable element in the final form to be used in the radioactivity measurements.

In most instances, analytical radiochemistry is dependent upon more conventional ideas in analytical chemistry involving separations by such methods as precipitation, solvent extraction, chromatography, volatilization, and/or electroanalysis and the subsequent presentation of the isolated

radioelement in a form suitable for a measurement of the radioelement's radioactivity. One major difference exists between carrier radiochemistry and more conventional techniques in that it is not always necessary to remove completely the added amount of carrier element, since a radiochemical analysis is designed to assure that the atoms of a radioactive element achieve an isotopic state with the atoms of the inactive element and any loss of the radioactive species is proportional to the "loss" of carrier during the separation process.

Colorimetric, polarographic and similar analysis techniques are seldom used in radiochemistry because they do not separate the desired radionuclide from contaminants (either radioactive or stable) in the mixture being analyzed. However, some of the developments used in these analysis techniques may be useful in radiochemistry.

The general information that follows describes the behavior of silicon and its compounds and how this behavior can be used in developing radiochemical analysis methods for the silicon radionuclides. More detailed information can be obtained either from the references given in this section or from the general references given in Section I of this monograph.

## A. The General Chemistry of Silicon

Although silicon is one of the most abundant of the elements, it never occurs free in nature. It is always in the form of its compounds, chief of which is $SiO_2$ and its derivatives. Elemental silicon, in crystalline form, can be prepared by the high temperature reduction of silicon dioxide with carbon. The product of this process is gray and lustrous. The high temperature reduction of the tetrachloride with sodium or magnesium will produce amorphous silicon, whereas, the reduction of sodium fluorosilicate with aluminum will produce a gray and lustrous product.

### 1. Metallic Silicon

Gray, very lustrous, crystalline silicon is brittle. It has a density of 2.36, and it will melt at $1413^{\circ}$. It can conduct electricity, and its con-

ductivity will increase with an increase in temperature.

Crystalline silicon is practically insoluble in all acids, including hydrofluoric acid. At room temperature, it is not chemically active toward elemental substances. However, when contacted with fluorine, it will ignite spontaneously to form the tetrafluoride. At high temperatures, it will also react with the other halogens. Silicon will not burn, but it can be brought into combination with oxygen and sulfur to form the dioxide and the disulfide. It will also combine with hydrogen when heated in an electric arc to form silicones. It will also react with nitrogen to form the nitride, $Si_3N_4$. Most metals will alloy with silicon on heating either by direct combination or by being dissolved in the molten metal to form silicides. None of the alkali metals, except lithium, will form an alloy with silicon. However, silicon will react very readily when dissolved in dilute solutions of the alkali metal hydroxides to form silicates and release hydrogen by the reaction

$$Si + 4OH^{-1} \rightleftharpoons SiO_4^{-4} + 2H_2 \qquad (1)$$

Silicon can be solubilized by boiling it with water in a glass vessel. The loss of alkali from the glass lining boiling causes this chemical action.

Silicon disulfide, $SiS_2$, can be prepared by melting amorphous silicon with an excess of sulfur. When amphorous silicon is combined with alkali sulfides, or thiosilicates, $M_2^1SiS_3$ salts are formed.

2. The Compounds of Silicon

The formation of compounds of silicon with other elements usually results from the reactivity of complex silicon-oxygen anions, i.e., a linkage of silicon atoms to other silicon atoms through oxygen atoms. The following information generally describes these compound formations and gives some details about their chemical reactivity. Table II reports on the solubility of many silicon compounds in water and in other solvents.

a. The Oxygen Compounds of Silicon

$SiO_2$, silica or silicon dioxide, is the normal oxide compound of silicon. It has a melting point of $1700^{\circ}$ and is not easily fused with other materials. It exists in nature in three crystalline modifications: as quartz, as tridymite,

Table II. Solubility of Silicon Compounds

| Compound | Formula | Water Solubility | | Other Solvents |
|---|---|---|---|---|
| | | Cold | Hot | |
| Bromides | $Si_2Br_6$ | Decomposes | Decomposes | Decomposes in KOH; soluble in $CS_2$ |
| | $SiSBr_2$ | Decomposes | Decomposes | Soluble in benzene and $CS_2$ |
| | $SiBr_4$ | Decomposes | Decomposes | Decomposes in $H_2SO_4$ |
| Carbides | SiC | Insoluble | Insoluble | Decomposes in fused KOH; insoluble in acid |
| | $Si_2C$ | Decomposes | | Soluble in $HNO_3$, $H_2SO_4$; insoluble in alcohol and ether |
| Chlorides | $Si_2Cl_6$ | Decomposes | Decomposes | Decomposes in alcohol |
| | $SiSCl_2$ | Decomposes | Decomposes | Soluble in $CCl_4$ and $CS_2$ |
| | $SiCl_4$ | Decomposes | Decomposes | Decomposes in alcohol |
| | $SiCl_3HS$ | Decomposes | Decomposes | Decomposes in alcohol |
| Fluorides | $SiF_4$ | Decomposes | Decomposes | Soluble in absolute alcohol, ether, HF |
| | $Si_2F_6$ | Decomposes | Decomposes | |
| Hydrides | $SiH_4$ | Insoluble | | Decomposes in KOH |
| | $Si_2H_6$ | Slowly Decomposes; Slightly Soluble | | Soluble in benzene, alcohol and $CS_2$ |
| Nitride | $Si_3N_4$ | | | Soluble in HF |
| Oxides | $SiO_2$ | Insoluble | Insoluble | Soluble in HF; very slightly soluble in alkali |
| | $SiO_2(+XH_2O)$ | Insoluble | Insoluble | Soluble in HF and hot alkali |
| Oxy-Salts | $Si_2OCl_6$ | Decomposes | Decomposes | Decomposes in alcohol; soluble in all portions in $CS_2$, $CCl_4$, chloroform and ether |
| Sulfides | SiS | Decomposes | Decomposes | Decomposes in alkali and alcohol |
| | $SiS_2$ | Decomposes | | Decomposes in alcohol; soluble in dilute alkali; insoluble in benzene |
| Thiocyanate | $Si(SCN)_4$ | | | Soluble in benzene; slightly soluble in $CS_2$ and chloroform |

and as crystobalite.[3] It is also found in a hydrated form as opal and in earthy form as kiselguhr or diatomaceous earth.[3] These silicon dioxide forms are common to two tetrahedra. The great strength of the Si-O bonds and the polymeric nature of the substance accounts for the extreme chemical stability of silicon dioxide.

$SiO_2$ is inert to hydrogen and to all of the halogens, except fluorine. It will not react with any acid except hydrofluoric acid, which converts it to the volatile tetrafluoride, $SiF_4$. When heated to an elevated temperature in the presence of either alkali or alkaline earth metals, or carbon, $SiO_2$ can be reduced.

Upon fusion, silicon dioxide will combine with basic oxides or carbonates to form silicates having a wide variety of compositions. The simplest silicate forms are the meta- or orthosilicates that have compositions of $M_2^1SiO_3$ and $M_4^1SiO_4$, respectively. Polysilicates, such as the di-, or trisilicates, which contain 2 or more $SiO_2$ ions for each $M_2^1O$ group are also known.

Since silicon dioxide is an acidic oxide, it should be the anhydride of a series of silicic acids.[4] However, free silicic acids have not been isolated. The preparation of metasilicic acid, $H_2SiO_3$, and disilicic acid, $H_2Si_2O_5$, has been reported.[5] They are considered to be extremely weak acids and are electrolytically dissociated only to a very slight extent. The silicic acids usually have low solubilities and can be readily displaced from soluble silicates by even the weakest acids. Attempts to prepare solid silicic acids by treating soluble silicates yield only a silicon dioxide hydrate, or gel.

The alkali silicates are the only water-soluble silicate compounds, and they are strongly alkaline in reaction. The other metal silicate compounds are insoluble in water and will decompose in strong acids to produce silica gel. Many of the silicates will react with hydrofluoric acid to form silicon fluoride. Fusions of the silicates in alkali carbonates results in a double decomposition process that yields an alkali silicate and carbon dioxide. When silicate solutions are acidified, a monomolecular, water-soluble form of silicic acid will be formed. Upon a loss of water, a higher molecular and an insoluble polymeric aggregate, sometimes dispersed as a colloid, will be produced.

Some silicates form well-defined addition compounds with $H_2O_2$. For example, sodium metasilicate di-peroxyhydrate, $Na_2SiO_3 \cdot 2H_2O_2$ can be formed by the vacuum evaporation of a solution of sodium metasilicate that has been treated with $H_2O_2$. The alkali silicate peroxyhydrates are readily soluble in water and are quite stable in the absence of moisture. The alkaline earth silicate peroxyhydrates and silicon peroxyhydrate, $SiO_2 \cdot H_2O_2$, are not very soluble in water and are very unstable.

b. Silicon Carbide

As pointed out above, silicon dioxide, $SiO_2$, can be reduced by carbon in an electric furnace. If excess carbon is present in this reaction, silicon carbide, SiC, can be produced. SiC is a very stable compound, and it reacts with only a few agents. For example, fused sodium hydroxide attacks it only slightly.

c. The Silicon Hydrides

At least four (4) forms of silicon hydride (silane or silicomethane) exist in the pure states: monosilane, $SiH_4$, disilane, $Si_2H_6$, trisilane, $Si_3H_8$, and tetrasilane, $Si_4H_{10}$. Pentasilane, $Si_5H_{12}$, and hexasilane, $Si_6H_{14}$, are synthesized by chemical reactions upon the pure silanes. Since silicon and hydrogen will not combine directly under ordinary temperatures, the pure silanes are usually produced by the hydrolysis of magnesium silicide, $Mg_2Si$, with 20% hydrochloric acid and are separated from each other by fractionation.

Monosilane, $SiH_4$, is a colorless gas. It is spontaneously inflammable in air, and it will react vigorously with water to form hydrogen and silicon dioxide. $SiH_4$ will not react readily with carbon tetrachloride or chloroform. Disilane, $Si_2H_6$, behaves similarly to $SiH_4$, and it will react with carbon tetrachloride and chloroform. The higher silanes are more unstable. The halogenosilanes have characteristics similar to those exhibited by the silane compounds.

d. The Halide Compounds of Silicon

Silicon forms both simple and mixed tetrahalides. The simple halides are obtained by a direct or indirect combination of the elemental species. For example, the tetrachloride, $SiCl_4$, can be prepared by passing chlorine

over a heated mixture of silica and carbon. The tetrafluoride, $SiF_4$, can also be prepared by treating $SiO_2$ with HF. The simple tetrahalide compounds are quite stable; however, they can be decomposed by water (for example, $SiCl_4 + 3H_2O \longrightarrow H_2SiO_3 + 4HCl$) at ordinary temperatures. This decomposition process is caused by the great affinity of silicon for oxygen. All of the tetrahalides are volatile and exhibit increased boiling points with the increase in the atomic weight of the halogen.

The silicon ions in the tetrahalides function as electron pair acceptors and use available d orbitals to become readily hydrolyzed and to act as acceptor molecules in the formation of coordination compounds.(6) The hydrolytic reaction is complete and irreversible and proceeds in the following manner for the chlorides, bromides, and iodides:

$$SiS_4 + (y+2)\ H_2O \longrightarrow SiO_2 \cdot y\ H_2O + 4H + 4X^- \qquad (2)$$

A secondary reaction occurs between silicon tetrafluoride and the hydrofluoric acid formed initially. This reaction is

$$SiF_4 + 2HF \longrightarrow H_2SiF_6 \qquad (3)$$

Silicon fluoride, $SiF_4$, formed as the product of the treatment of a silicon compound with hydrofluoric acid, is used more often in analytical chemistry than is any of the other simple silicon halide compounds. It is volatile and is colorless. It has a pungent odor and will form dense fumes in moist air. $SiF_4$ can pass directly at a sublimation temperature of $-95^{\circ}$ from the gaseous to the solid state when strongly cooled under ordinary pressures. It can also be liquified under 50 atm. pressure.

$SiF_4$ is a very stable compound (heat of formation = 360 Kcal per mol.). It will not decompose in an electric spark. However, water hydrolyzes $SiF_4$ to form white hydrated $SiO_2$ or silica gel.

$$SiF_4 + 2H_2O \longrightarrow SiO_2 + 4HF \qquad (4)$$

The hydrofluoric acid formed will unite with any unhydrolyzed silicon fluoride to produce fluorosilicic acid, $H_2SiF_6$, as in equation (3) above. Fluorisilicic acid is a much stronger and more stable acid than hydro-

fluoric acid, and its salts are only slightly hydrolyzed. It will neutralize oxides and hydroxides to form fluorosilicates.

$$2M^{O}OH + H_2SiF_6 \longrightarrow M_2^{I}SiF_6 + 2H_2O \qquad (5)$$

Fluorosilicates can also be formed by decomposing carbonate compounds with $H_2SiF_6$ or by mixing solutions of the respective compounds.

Many water-soluble metal fluorosilicates have been prepared; the alkali metal salts, $Na_2(SiF_6)$, $K_2(SiF_6)$, $Rb_2(SiF_6)$, and $Cs_2(SiF_6)$ are not very soluble in water. Their solubility increases when heat is applied to the mixture. The alkali salts are also insoluble in alcohol. Barium fluorosilicate, $Ba_2(SiF_6)$ is more insoluble than the alkali metal fluorosilicates. Yttrium and the rare earth fluorosilicates exhibit similar characteristics.

The preparation of the other simple halide compounds of silicon, i.e., $SiCl_4$, $SiBr_4$, and $SiI_4$, is generally described by Remy.[7] $SiCl_4$ is a colorless, pungent liquid which can be easily hydrolyzed by water. $SiBr_4$ is also a colorless liquid which forms rapidly in air. It reacts violently with metallic potassium when heated slightly. It will react with ammonia and other substances to form additional compounds. $SiI_4$ is crystalline and is extremely soluble in carbon disulfide. When treated with alcohol, it will react to form ethyl iodide, hydrogen iodide, and silicic acid. $SiCl_4$ and $SiBr_4$ have no characteristic reactions with alcohol. Halide compounds, such as the silicon monochloride, $(SiCl)_x$, and the silicon monoiodide, $(SiI)_x$, also exist. $(SiCl)_x$ is prepared by the thermal decomposition of $Si_{10}Cl_{22}$. It is a yellow solid which is insoluble in inert solvents. Caustic potash will dissolve it causing a vigorous evolution of hydrogen. A silicon hydroxy compound, $Si_4(OH)_6$ can be formed if $(SiCl)_x$ is hydrolyzed in an acid solution at a low temperature. $(SiI)_x$, when hydrolyzed, will form an oxidizable compound, $(Si_2O_3H_4)_x$. This is an ivory-colored solid which will decompose to a mixture of $SiO_2$ or Si when treated in a vacuum.

Binary silicon halide compounds also have been prepared by a series of reactions upon the tetraiodide, $SiI_4$. When heated to 290-300°, in the presence of finely divided silver, $SiI_4$ is transformed to $Si_2I_6$, a solid crystalline compound composed of colorless, six-sided prisms which form when

$Si_2I_6$ is recrystallized from a hot carbon disulfide solution. When $Si_2I_6$ is treated with bromine or chlorine, solid silicon hexabromide, $Si_2Br_6$ , or liquid silicon hexachloride, $Si_2Cl_6$, is formed. The hexahalide compounds are unstable at ordinary temperatures; decomposition occurs only after a moderate heat treatment. Cold water will decompose the hexahalides to form silico-oxyacid, $(H_2Si_2O_4)_x$. This is a white mass and a strong reducing agent. Hydrogen will be evolved when it is dissolved in alkalis. Other binary forms having the general formula $Si_nX_{2n+2}$ can be prepared by a further treatment of the tetrahalides to a homologous series of compounds having a molecular composition up to n = 10, e.g., $Si_{10}Cl_{22}$.

Mixed tetrahalides of silicon such as fluorochloro (e.g., $SiF_3Cl$, $SiF_2Cl_2$, $SiFCl_3$), fluorobromo, fluoroiodo, and chlorobromo derivatives, (e.g., $SiFCl_2Br$ and $SiFClBr_2$), also exist. Booth and Swinehart[8] report that all of the fluorochlorides and $SiF_4$ can be prepared from the reaction of $SiCl_4$ and $SbF_3$ in the presence of $Sb_2F_5$ or chlorine gas as a catalyst. The products of these reactions are separated by fractionation techniques. The fluorobromides can be prepared by the exchange reaction between $SiBr_4$ and $SbF_3$ at 100° and without the presence of a catalyst.[9] Anderson[9] also reports that the fluoroiodide and the chlorobromide can be obtained by a redistribution reaction between equal volumes of the appropriate tetrahalides and a fractionation process to separate the products. The mixed tetrahalides are volatile and can be hydrolyzed to give the same products as the parent tetrahalides.

Silicon also forms oxyhalides;[10,11] the characteristic formula is $Si_7O_7\text{-}_1X_{2n+2}$. Members in the homologous chloro and the bromo series have been isolated to N = 7 and 6, respectively. Fluoro compounds have also been isolated. The oxyhalides are oily liquids which are soluble in monohydroxylic solvents. They show varied degrees of volatility and they can be easily hydrolyzed. Silicic acid esters, $Si(OR_4)$, are formed by the reaction of silicon halides with alcohols or phenols. Silicon thiocyanate, $Si(SCN)_4$, can be prepared by a double decomposition reaction between $SiCl_4$ and $Pb(SCN)_2$ in a benzene solution. It is a white needle-like solid that is stable in dry air. Water, acids and alkali will hydrolyze $Si(SCN)_4$, to produce silica gel, or to form silicates.

e. The Organosilicon Compounds

Many organosilicon compounds in which at least one organic group is attached to silicon directly through the carbon atoms of the molecule are known. Eaborn,[12] and Post[13] report on the synthesis of these compounds, their nomenclature, their physical properties, and their uses. Thus, since most organosilicon compounds are used in industry no information will be presented in this monograph on this particular group of silicon compounds.

f. Silicon Disulfide

The heating of a mixture of silicon and sulfur produces silicon disulfide, $SiS_2$. At high temperatures $SiS_2$ sublimes to produce colorless needles that can be easily hydrolyzed by water to yield $SiO_2$ and $H_2S$.

g. Silicon Nitride

When heated to temperatures in excess of 1300° C, a mixture of silicon and nitrogen will produce silicon nitride, $Si_3N_4$. $Si_3N_4$ is a very stable gray-colored compound which sublimes at about 1900° C and at high pressures.

h. Reactions with Metals

Silicon, like carbon, reacts with a number of metals to form metal silicides having the general composition, $M_2Si$. Most silicides, e.g., $Mg_2Si$, are readily hydrolyzed to produce silanes.

## B. The Analytical Chemistry of Silicon

Silicon, following its separation from other elements, is most frequently determined gravimetrically by precipitating and dehydrating silicon dioxide, $SiO_2$.[14,15] The dehydration is usually carried out in a hydrochloric acid solution; however, sulfuric acid, percholoric acid, and nitric acid solutions have also been used with good results.[15,16] For example, Willard and Cake[17] have shown that less time is required to decompose and to dehydrate the sample if 60-70% perchloric acid solutions are used.

The insoluble $SiO_2$ obtained in these precipitations and dehydrations is collodial in form. The addition of a warm gelatine solution to the acid solution will cause the colloid to flocculate so that it can be more easily filtered for calcination.[18-22]

The $SiO_2$ obtained by precipitation and dehydration techniques is almost always impure.[23,24] Aluminum, titanium, iron, and other metals, and the sulfates of calcium, barium, and sodium are frequently found in the precipitate. Usually, the amount of $SiO_2$ in the precipitate is determined by removing it as the volatile tetrafluoride by a treatment with hydrofluric and sulfuric acids and then weighing the residue. The loss in weight represents the amount of pure $SiO_2$ in the dehydrated product.

In a recent study, using a radioactivation analysis method[25,26] to determine trace stable silicon in metals and alloys, Mullins and Leddicotte[27] report that a pure $SiO_2$ precipitate was obtained by a dehydration in concentrated $H_2SO_4$ following a volatilization of the radioactive $Si^{31}$ (2.6 h) and inactive silicon carrier as silicon tetrafluoride. Large amounts of inactive and radioactive iron, strontium, barium, antimony, selenium, tungsten, and many other elements did not interfere in this method.

Silicon can also be determined as potassium fluosilicate, $K_2SiF_6$.[28] Oxine,[29-31] hexamine,[32] pyramidone,[33,34] or pyridine[35] have also been used in the gravimetric determination of silicon as $SiO_2 \cdot 12MoO_3$. Duval[32] reports that a constant weight on the molybdosilicate compound can be obtained by heating the precipitate at temperatures between 593° and 813°.

More specific information about analytical methods used to isolate and separate silicon from other elements follows. Precipitation, volatilization, solvent extraction, and chromatography methods have been used to effect these separations.

1. Separations By Precipitation

Hillebrand, et al,[15] report that a complete separation of silicon from other elements is rarely necessary, since its amount is usually determined by the loss of weight that occurs when the weighed and impure silica is treated with hydrofluoric and sulfuric acids, ignited, and again weighed. Boron, tungsten, iron, tin, lead, niobium, and tantalum can accompany silicon in a precipitation-dehydration method[14-17] and whenever necessary can be removed before the dehydration of the $SiO_2$.

Boron is best removed by volatilizing the boron as the trimethyl compound,

$B(OCH_3)_3$, from a solution containing little or no water.[36] Fluorine can be removed as $BF_3$ by a fusion of the silica with either a mixture of sodium carbonate and borax or boric acid.[36] Tungsten can be separated from silicon by making the dehydration in dilute hydrochloric acid[37] or by dissolving the precipitated tungstic acid in ammonia.[38] A sulfuric acid dehydration of silica will assist in separating it from iron.[39] Tin is best separated from silica by an HCl dehydration.[40] Dehydrations in sulfuric acid or perchloric acid could yield insoluble compounds of tin upon dilution. Lead can be separated by dehydrating with sulfuric acid and then extracting the lead sulfate formed with ammonium acetate or ammonium chloride.[40] Besides the use of methods of direct volatilization of silicon in $HF-H_2SO_4$ acid mixtures to separate it from niobium and tantalum, it has been reported[41] that niobium and tantalum can be separated from silica by an extraction of their pyrosulfate salts with oxalic or tartaric acid following a fusion with potassium pyrosulfate.

Specific separations of silicon from aluminum alloys,[20,39,43-44] steels,[23,45-48] uranium,[47] vanadium,[47] nickel,[47] iron ore,[23] iron,[23] and organosilicon compounds[49] have been reported in the literature. However, each one of these methods uses a precipitation-hydration technique followed either by a volatilization of $SiF_4$ or a colorimetric method of determination to determine silicon.

2. Separation By Volatilization

One of the best methods to separate silicon from other elements in that based upon its volatilization as $SiF_4$ or $H_2SiF_6$.[15,50] However, this technique is most frequently used to expel $SiO_2$ from the impure precipitation-dehydration produced oxides[14-17] so that the loss of weight in these products corresponds to the weight of $SiO_2$ originally present.

An adaptation of this technique was used by Mullins and Leddicotte[27] in the radiochemical analysis procedure of their radioactivation analysis method for the determination of trace silicon in metals and alloys. This volatility separation method gave a complete separation of inactive silicon and radioactive silicon-31 (2.6 h) from metal and alloy specimens containing

radioactive and inactive iron, strontium, cobalt, selenium, chromium, barium, zirconium, niobium, zinc, antimony, silver, ruthenium, cesium, manganese, scandium, tantalum, and tungsten.

A distillation of the volatile silicon tetrafluoride from a perchloric acid solution has been used to determine silicon in uranium alloys, steels, and phosphoric acid.[51] The distillate is adsorbed in a solution of boric and molybdic acids and the molybdenum blue color of the silicon complex determined colorimetrically.

3. Separations By Solvent Extraction

Bock and Herrmann[52] have shown that less than 0.1% $Si^{+4}$ is extracted from a 20 M HF aqueous solution with ethyl ether while $Nb^{+5}$, $Ta^{+5}$, and $Re^{+7}$ are extracted greater than 50%; $Sn^{+2}$, $Sn^{+4}$, $As^{+3}$, $As^{+5}$, $Te^{+4}$, $Ge^{+4}$, $P^{+5}$, $Se^{+4}$, $V^{+3}$, $V^{+5}$, $Mo^{+6}$, and $Sb^{+3}$ partially extract.

Silicon (as well as $Sn^{+4}$, $Ti^{+4}$, $Mn^{+2}$, $Zr^{+4}$, and $Hf^{+4}$) do not extract with diisopropylketone from a mineral acid-hydroflouric aqueous solution (6 M HCl - 0.4 m HF).[53]

Silicon (like W, Mo, As, P, and V) forms heteropoly acids which can be extracted into such organic solvents as esters, ketones, aldehydes, and others.[54-56] Such systems serve to separate silicon from other metals, or from W, Mo, As, P, and V. For instance, silicon, as molybdosilicic acid, can be separated from molybdophosphoric acid by removing the molybdophosphoric acid by extracting with either ethyl acetoacetate,[54] ethyl acetate,[55] or butyl acetate.[56] Silicon (and As) heteropoly acids can be separated from molybdophosphoric acid by extracting with a mixture of 1-butanol and chloroform.[57,58] Molybdoarsenic acid can be removed from this mixture by extracting with a mixture of 1-butanol-ethyl ether and finally extracting the molydosilicic acid with 1-butanol.[59,60]

4. Chromatography Separations

Silicates have been separated from borates and molybdates in an atmosphere saturated with 5% HCl in 2-butanone[61] by use of 5% conc. HCl in acetone as a solvent. The silicate ions did not move whereas the moly-

bdate and borate ions were eluted in that order. Isopropanol-water-acetic acid solvents have been used to separate oligosilicic acids.[62]

## IV. DISSOLUTION OF SAMPLES CONTAINING SILICON

The use of acids to solubilize silicon-containing materials usually results in the precipitation of insoluble silica.[20,42-44,46] Possible losses of silicon, as $SiH_4$, can occur depending upon the types of materials being put into solution. Silicon, silicon alloys, and silicides usually can be solubilized in an acid mixture of either $HNO_3$-HF, or $HClO_4$-HF. In such an acid attack of this kind, the solution should be both dilute in HF and at room temperature in order to prevent the loss of fluosilicic acid by distillation.

Alkaline fusions, either with mixed sodium and potassium carbonates, or with sodium and potassium carbonates and boric acid, or with caustic soda, can bring most silicon-containing materials into solution as well as separate certain interfering elements from silicon.[63] It is recommended that sodium peroxide be present in fusions of silicon materials in order to convert all of the silicon into a silicate.[45]

Either of these dissolution methods can be used in the radiochemistry of silicon; however, the addition of silicon carrier to the mixture before the dissolution begins will assist in achieving an isotopic exchange of the radioactive and inactive silicon atoms during the processing of the radioactive material.

## V. SAFETY PRACTICES

Most of the nonradioactive sample materials that are submitted to an analyst can be safely handled under normal laboratory procedures. However, it is to be recommended that a good safety manual be consulted before any new analytical task is undertaken. A very suitable manual for use in determining the toxicology of most elemental compounds is that by Pieters and Creyghton.[64] It, as well as any other safety manual, should be consulted before laboratory work on a sample material begins.

All radioactive sample materials must be handled and processed safely. The discharge of radioactivity into a laboratory area by explosion or

spillage can be hazardous to personnel as well as cause wide-spread radioactive contamination throughout a laboratory area. Thus, it is essential that sources of information concerned with safe-handling practices for processing radioactive materials should be reviewed before a radiochemical analysis is started. Typical of these information sources are those to be found in the Oak Ridge National Laboratory's Master Analytical Manual[65] and in the International Atomic Energy Agency's publication on the "Safe-Handling of Radioisotopes."[66] Similar sources of information are also usually available from any laboratory engaged in work with radioactive materials. It is highly important that such information sources be consulted in order to establish an operational procedure for handling radioactivity safely.

## VI COUNTING TECHNIQUES FOR THE RADIOACTIVE SILICON ISOTOPES

Silicon-31 (2.65 h) is usually the only silicon radioisotope considered in the radiochemistry of silicon. Produced as the product of nuclear reactions of thermal neutrons and deuterons upon stable silicon, $Si^{31}$ decays mostly by the emission of beta radiations (1.47 Mev), and its radioactivity is usually measured by standard beta radiation measurement techniques.[67,68] The less intense gamma radiations (of 0.17 and 0.52 Mev, respectively) are never measured unless large amounts of $Si^{31}$ exists in the sample material being analyzed. Gamma scintillation spectrometry can be used in such requirements.[69]

In most of the recorded investigations concerned with the determination of radioactive silicon, radiochemical separation methods have been used to isolate and determine $Si^{31}$. However, certain studies[70,71] have shown that nondestructive radioactivation analysis methods based upon the use of fast-neutron-induced radionuclides (other than $Si^{31}$) are feasible for the determination of stable silicon.

## VII. RADIOCHEMICAL PROCEDURES FOR SILICON-31

The procedures employed in the solvent extraction and chromatography methods cited earlier in this monograph, suggest that it would be practical to determine radioactive $Si^{31}$ by carrier-free methods. However, all of the

known radiochemical methods for the determination of $Si^{31}$ follow procedures based upon carrier chemistry. For example, Rudstam, et al,[72] have used a radiochemical procedure (see Procedure 1) to determine $Si^{31}$ formed as a radioactive spallation product in the bombardment of iron with 340-Mev protons from an 184-inch synchrocyclotron. The silicon radioactivity was determined by a Geiger-Mueller counter. Other radiochemical methods (see Procedures 2 and 3) have been used in the radioactivation analysis determination of stable silicon in titanium,[73] zirconium,[74] niobium,[75] aluminum,[75] beryllium,[75] tungsten,[75] and ammonium paratungstate.[75] Similar procedures have been used by Chaudron[76] and Riezler[77] in determining trace silicon in aluminum.

Each of these procedures contain information about its usage, interefernces, chemical yield, etc., in order to assist other analysts in their evaluation of its usefulness in particular analysis problems.

## PROCEDURE 1

Procedure Used In: Radioactive tracer studies

Method: Precipitation

Element Separated: Silicon-31 (2.65 h)

Type of Material Analyzed: Iron[72]

Type Nuclear Bombardment: 340-Mev deuterons (184" synchrocyclotron)

Procedure By: Rudstam, et al.[72]

Chemical Yield: Quantitative

Time of Separation: Short

Decontamination: Excellent from all other spallation products

Equipment Required: Standard

Procedure:

1. Add $SiF^{--}$ carrier to solution, then add sufficient $H_3BO_4$ solution

to complex $F^{--}$ ions. Precipitate $SiO_2$ by adding conc. $H_2SO_4$ to the solution.

2. Dissolve the $SiO_2$ in KOH; then add a few milligrams of $Ti^{+4}$ and conc. $NH_4OH$ dropwise to precipitate $Ti(OH)_4$ (Note a).

3. Add holdback carriers (Note a); then digest with HCl to precipitate hydrated $SiO_2$.

4. Collect $SiO_2$ precipitate on a filter paper. Place it in a muffle furnace; then ignite to $SiO_2$.

5. Transfer the $SiO_2$, after a suitable cooling period, to a tared mount. Weigh to determine chemical yield; then measure the $Si^{32}$ radioactivity by means of a Geiger-Mueller counter.

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Note:

a. Serves to scavenge contaminant radionuclides from the solution.

## PROCEDURE 2

Procedure Used In: Radioactivation analysis

Method: Precipitation

Element Separated: Silicon and $Si^{31}$ (2.65 h)

Type of Material Analyzed: Titanium,[73] zirconium,[74] and other related metals and alloys[75]

Type of Nuclear Bombardment: $Si^{30}(n,\gamma)Si^{31}$ ($Si^{31}$ 2.6 hr.)

Procedure By: Mullins and Leddicotte[78]

Chemical Yield: 55-60%

Time of Separation: 4 hours

Degree of Purification: Studies with radioactive tracers of manganese and indium show that complete decontamination is possible.

Equipment Required: Neutron source and standard laboratory equipment

Procedure:

A. Irradiation of Sample Material

1. Irradiate known amounts of test (Note 1) and comparator (Note 2) sample in a neutron flux of at least $1 \times 10^{13}$ n/sec/cm$^2$ for 2.5 hours (Note 3). Test and comparator samples are individually wrapped in aluminum foil.

B. Preparation of Irradiated Test Portion and Analysis

I. The Comparator Sample

1. After the irradiation, quantitatively transfer the comparator sample (Note 2) to a 50-ml volumetric flask and dissolve in 25 ml of water. Add 5 ml of saturated $Al(NO_3)_3$ to complex the $F^-$ ion and dilute to 50-ml volume with water. Mix well, using safe-handling practices for radioactive materials.

2. Pipet a 1.0 ml aliquot of this solution into a second 50-ml volumetric flask; dilute to volume with water. Mix well.

3. Pipet a 1.0-ml aliquot of this solution into a 50-ml glass centrifuge tube. By means of a volumetric pipet, add to the same tube 1.0 ml of standard silicon carrier of known concentration (Note 4). Mix well, dilute to 5 ml with water and add 15 ml of 18 M $H_2SO_4$ and continue with Step 7 in part II, "The Test Samples."

II. The Test Samples

1. Add the titanium sample to a lusteroid tube.

2. Pipet silicon carrier into the same tube (Note 5) and dissolve the sample by adding 5 ml of $H_2O$, 0.2 ml of 19 M NaOH (Note 6), 0.5 ml of 18 N $H_2SO_4$, and 0.2 ml of 27 M HF. Add 0.1 ml of 27 M HF every 15 to 20 minutes until dissolution is complete. Approximately 0.5 ml of 27 M HF is sufficient to dissolve 100 mgs of titanium metal. This usually takes from one and one half to two hours. (Note 7)

3. After dissolution, add 10 milliquivalents in excess of saturated $Al(NO_3)_3$ to complex the $F^-$ ion and transfer the sample to a 50-ml glass centrifuge tube.

4. Cautiously add, with stirring, 15 ml of 18 M $H_2SO_4$ and precipitate $SiO_2$ by bringing to a boil for 30 seconds over a flame. Cool and centrifuge. Discard supernate.

5. Wash the $SiO_2$ twice with hot water and dissolve the $SiO_2$ with 0.5 ml of saturated NaOH. Dilute to 10 ml with $H_2O$ and add 5 mgs of Fe holdback carrier, stir well, and centrifuge.

6. Transfer the supernate to another 50-ml glass centrifuge tube. Discard the $Fe(OH)_3$ precipitate.

7. Cautiously add 25 ml of 18 M $H_2SO_4$ and precipitate $SiO_2$ by boiling for 1 minute over a flame. Cool and centrifuge, wash the $SiO_2$ twice with hot 6 M HCl and filter, using Whatman #40 filter paper. Ignite the $SiO_2 \cdot XH_2O$ to $SiO_2$ in a muffle furnace at 1000° C for 30 minutes. Weigh the $SiO_2$ (Note 8) on an analytical balance. Then mount the precipitate for radioactivity measurements.

C. Measurement of the Radioactivity and Calculation of Inactive Silicon Content of the Original Sample

1. Since the gamma energy, $Si^{31}$, is so small, the analyst must resort to the use of the 1.47-Mev Beta energy. The measurement can be made by means of a Geiger-Mueller counter. The sample is measured every half-hour for 2 hours to establish the decay rate in order to determine if the sample is pure $Si^{31}$.

2. Following the radioactivity measurements, the observed radioactivity is corrected for loss of "carrier" during the experiment, half-life of the silicon-31, and the sample weights of both the test and the comparator sample. A comparison of these corrected radioactivities become a measure of the stable silicon content of the test sample:

$$\text{Percent stable Si in test sample} = \frac{\text{Corrected radioactivity of Si in test sample}}{\text{Corrected radioactivity of Si in comparator sample}} \times 100$$

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Notes:

1. At least 0.10 gram portion of solid samples should be used.

2. Use $(NH_4)_2SiF_6$ for silicon comparator; approximately 100 mgs.

3. The Low Intensity Test Reactor was used for this irradiation. The sensitivity of the method is such that $2 \times 10^{-7}$ grams of silicon can be determined. The sensitivity can be improved by use of higher neutron fluxes.

4. As sodium silicate $Na_2SiO_3$. Standardized to concentrations of 40 mgs/ml of $SiO_2$.

5. If possible, the sample should be dissolved in the presence of the silicon carrier. If HF is used in the dissolution of the sample, use a polystyrene stirring rod until after the HF has been complexed with saturated $Al(NO_3)_3$. If HF is not used, dissolve the sample in a 50-ml glass centrifuge tube.

6. The NaOH complexes the $SiF_4$ and prevents it from escaping as a gas.

7. Zirconium metal can be dissolved in the same manner; most other materials can be put into solution with mineral acids or by fusions with alkali carbonates.

8. By comparing the final weight of the $SiO_2$ precipitate obtained here with the theoretical yield expected from the amount of silicon carrier added, it is possible to determine the chemical yield of the experiment. The chemical yield correction is then used to determine the amount of $Si^{31}$ recovered during the separation process.

## PROCEDURE 3

Procedure Used In: Radioactivation analysis

Method: Distillation

Element Separated: Silicon and $Si^{31}$ (2.65 h)

Type of Material Analyzed: Zirconium, niobium, beryllium, aluminum, tungsten, and ammonium paratungstate(75)

Type of Nuclear Bombardment: $Si^{30}(n,\gamma)Si^{31}$ (Si 2.6 h)

Procedure By: Mullins and Leddicotte(79)

Chemical Yield: 55-60%

Time of Separation: 2.5 hours

Degree of Purification: Studies with radioactive tracers of Fe, Sr, Co, Se, Cr, Ba, Zr, Nb, Zn, Sb, Ag, Ru, Ce, Mn, Sc, Ta, and W show that decontamination is better than $10^6$ for each.

Equipment Required: Neutron source and standard laboratory equipment

Procedure:

A. Irradiation of Sample Material

1. Irradiate known amounts of test (Note 1) and comparator (Note 2) samples in a neutron flux of at least $1 \times 10^{13}$ n/sec/cm$^2$ for 2.5 hours (Note 3). Test and comparator samples are individually wrapped in aluminum foil.

B. Preparation of Irradiated Test Portion and Analysis

I. The Comparator Sample

1. After the irradiation, quantitatively transfer the comparator sample (Note 2) to a 50-ml volumetric flask and dissolve it in 25 ml of water. Add 5 ml of saturated $Al(NO_3)_3$ to complex the $F^-$ ion and dilute to 50-ml volume with water. Mix well, using safe-handling practices for radioactive materials.

2. Pipet a 1.0-ml aliquot of this solution into a second 50-ml volumetric flask; dilute to volume with water and mix well.

3. Pipet a 1.0-ml aliquot of this solution into a 50-ml glass centrifuge tube. By means of a volumetric pipet, add to the same tube 1 ml of standard silicon carrier of known concentration (Note 4). Mix well, dilute to 5 ml with water and add 15 ml of 18 M $H_2SO_4$ and continue with step 7 in part II, "The Test Sample."

II. The Test Sample

1. Add the niobium sample to the distillation flask (Note 5) as shown in Figure 1. Pipet 1.0 ml of standardized silicon carrier (Note 7) and add 5 ml of 16 M $HNO_3$ and 2 ml of 27 M HF.

2. Connect the condenser (Note 6) to the distillation flask and the other end into 10 ml of water in a 50-ml lusteriod tube. Connect the distillation flask to an air flow and begin bubbling air through the mixture. Place the $H_2SO_4$ dispenser in place as shown in Figure 1. Lower the distillation assembly into a bath of boiling water and allow 5 minutes for dissolution of the sample.

3. Add 20 ml of 18 M $H_2SO_4$ from the $H_2SO_4$ dispenser into the distillation flask. Remove the distillation flask from the water bath (being careful not to remove the end of the condenser from the distillate trap) and swirl

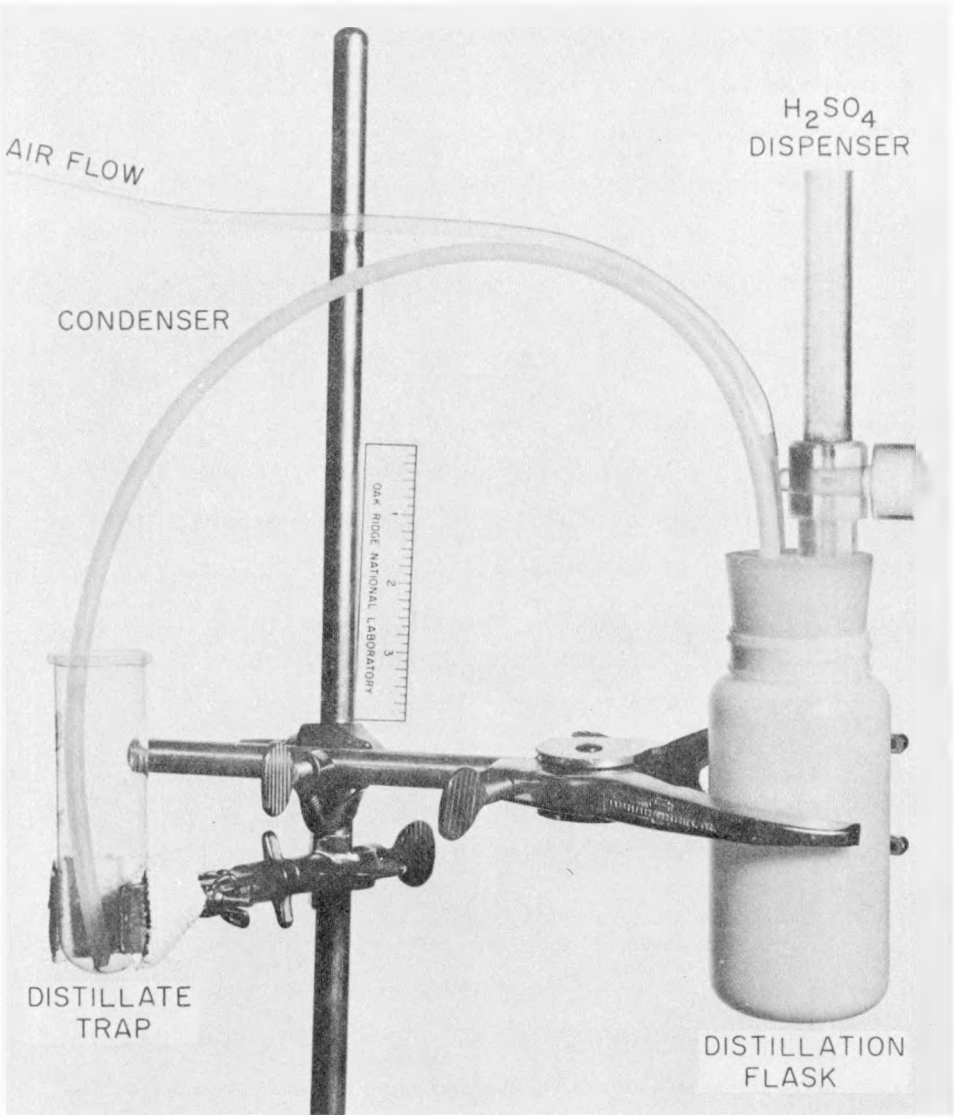


Fig. 1--Silicon distillation apparatus.

in order to mix the concentrated $H_2SO_4$ into the solution. Again lower the distillation flask into the boiling water bath and allow ten minutes for distillation of $SiF_4$ into the distillate trap.

4. After distillation is complete, remove the 50-ml lusteriod tube containing the distillate fraction and pour its contents into a 150-ml glass beaker. Add 30 ml of saturated solution of $Al(NO_3)_3$ to complex the HF that

passed over, mix well, and add 30 ml of 18 M $H_2SO_4$ to the same beaker. Mix well and bring to boil on hot plate in order to precipitate $SiO_2$. Transfer the contents equally into two 50-ml glass centrifuge tubes and centrifuge. Discard the supernate and wash twice with hot water.

5. Dissolve the $SiO_2$ with 0.5 ml of saturated NaOH. Dilute to 10-ml with $H_2O$ and add 5 mgs of Fe holdback carrier, stir well, and centrifuge.

6. Transfer the supernate to another 50-ml glass centrifuge tube. Discard the $Fe(OH)_3$ precipitate.

7. Cautiously add 25 ml of 18 M $H_2SO_4$ and precipitate $SiO_2$ by boiling for 1 minute over a flame. Cool and centrifuge. Wash the $SiO_2$ twice with hot 6 M HCl and filter on Whatman #40 filter paper. Ignite the $SiO_2 \cdot XH_2O$ to $SiO_2$ in a muffle furnace at 1000° C for 30 minutes. Weigh the $SiO_2$ (Note 8).

C. Measurement of the Radioactivity and Calculation of Inactive Silicon Content of the Original Sample

1. Since the gamma energy of $Si^{31}$ is so small, the analyst must resort to the use of the 1.5-Mev beta energy. The measurement can be made by means of a Geiger-Mueller counter. The sample is measured every half-hour for 2 hours to establish the decay rate in order to determine if the sample is pure $Si^{31}$.

2. Following the radioactivity measurements, the observed radioactivity is corrected for loss of "carrier" during the experiment, half-life of the silicon-31, and the sample weights of both the test and the comparator sample. A simple ratio of these corrected radioactivities becomes a measure of the stable silicon of the test sample:

$$\text{Percent stable Si in test sample} = \frac{\text{Corrected radioactivity of Si in the test sample}}{\text{Corrected radioactivity of Si in the comparator sample}} \times 100$$

Notes

1. At least 0.10 gram portion of solid samples should be used.
2. Use $(NH_4)_2SiF_6$ for silicon comparator, approximately 100 mgs.
3. The Low Intensity Test Reactor was used for this irradiation.

The sensitivity of the method is such that $2 \times 10^{-7}$ grams of silicon can be determined. The sensitivity can be improved by use of higher neutron fluxes.

4. As sodium silicate, $Na_2SiO_3$. Standardized to concentrations of 40 mg/ml of $SiO_2$.

5. The distillation flask is an eight ounce, high density polyethylene wide mouth bottle, that will withstand temperatures to $250^{\circ}$ F.

6. The condenser is a 1/4" diameter polyethylene tubing approximately 18" long.

7. If possible, the sample should be dissolved in the presence of the carrier in order to insure ion exchange between the active silicon in the sample and the inactive silicon in the carrier.

8. By comparing the final weight of the $SiO_2$ precipitate obtained here, with the theoretical yield expected from the amount of silicon carrier added, it is possible to determine the amount of $Si^{31}$ recovered during the separation process.

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