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Si

RADIOCHEMISTRY OF SILICON

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Radiochemistry of Silicon

by David R. Schink

Isotopes, A Teledyne Company
Palo Alto, California

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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 radiochemical purity of reagents, the place of radiochemistry in college and university programs, and radiochemistry in environmental science.

This series of monographs has grown out of the need for compilations of radiochemical information, procedures, and techniques. The Subcommittee has endeavored to present a series that will be of maximum use to the working scientist. Each monograph presents pertinent information required for radiochemical work with an individual element or with a specialized technique.

Experts in the particular radiochemical technique have written the monographs. The Atomic Energy Commission has sponsored the printing of the series.

The Subcommittee is confident these publications will be useful not only to radiochemists but also to research workers in other fields such as physics, biochemistry, or medicine who wish to use radiochemical techniques to solve specific problems.

Gregory R. Choppin, *Chairman*
Subcommittee on Radiochemistry

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Isotopes, A Teledyne Company
Palo Alto, California

revised from the original text of
W. T. MULLINS and G. W. LEDDICOTTE

I. REFERENCES ON THE INORGANIC AND ANALYTICAL CHEMISTRY OF SILICON

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II. NUCLIDES OF SILICON

A. Nuclear Properties

Five radioactive species of silicon are known (Table I), but of these, three are too short-lived to interest the radiochemist. Si^{25} is a rather curious isotope, apparently decaying by emission of a proton from the nucleus.[4] Si^{26} decays by positron emission to Al^{26} which has a half life longer than its precursor, ultimately decaying to Mg^{26}. Si^{31} is the only isotope commonly used for laboratory tracer studies, although its half-life is inconveniently short. Si^{32} is found in nature, always very dilute. Production of high activities of Si^{32} is not possible, but the very sensitive detection techniques — utilizing the radioactive daughter P^{32} — permit tracer experiments involving quite small amounts of this isotope.

There are three stable isotopes of silicon. The few studies of natural isotopic variations show small, but measurable, fractionation in natural silicates.[5]

TABLE I-a

SUMMARY OF SILICON ISOTOPE CHARACTERISTICS (a)

ISOTOPE	HALF LIFE	DECAY SCHEME	ENERGY (Mev)
Si^{25}	.23 sec	β^+, proton emission	5.39, 4.68, 4.08, 3.34
Si^{26}	2.1 sec(b)	β^+	β^+: 3.8 γ : 0.82
Si^{27}	4.2 sec	β^+	β^+: 3.8
Si^{28}	stable	natural abundance	92.2%
Si^{29}	stable	natural abundance	4.7%
Si^{30}	stable	natural abundance	3.1%
Si^{31}	2.62 hr	β^-	β^-: 1.48 γ : 1.26
Si^{32}	500±200 (c)	β^-	0.21 (d)

Notes

(a) Data are taken from Lederer, et al.[1]

(b) Silicon-26 decays to aluminum-26 which has a longer half life (6.4 sec).

(c) The half-life of silicon-32 has never been accurately measured. Calculations based on estimated production cross-sections have varied from 140 - 710 years. The upper value, often used, is improbable. The value cited is from Honda and Lal (1964).[2]

(d) Jantsch[3] recently measured this value to be 0.11 in reasonable agreement with Lindner's initial estimate of 0.1.

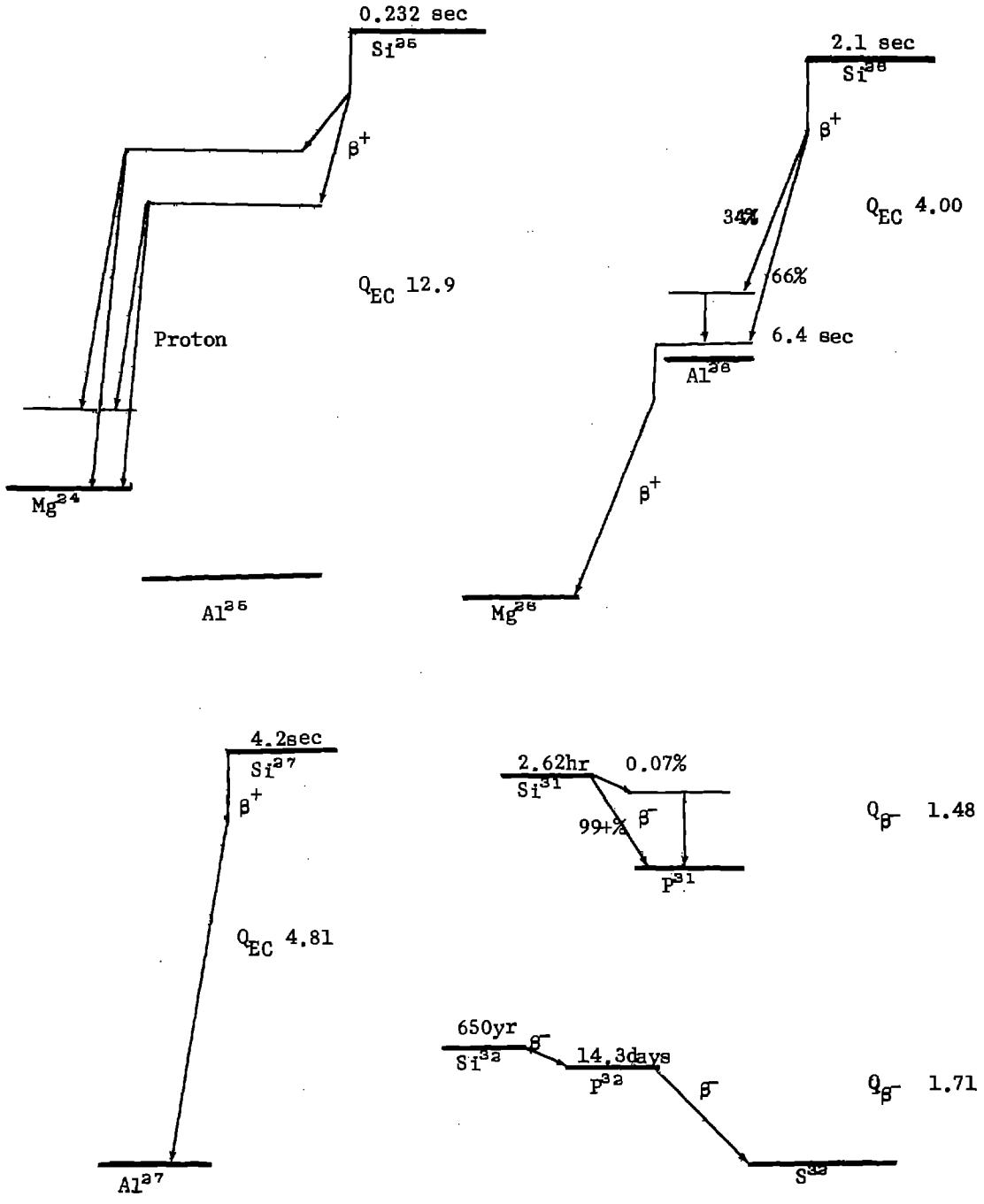


TABLE I-b

DECAY SCHEMES FOR THE SILICON RADIOISOTOPES
Q Values in Mev (from Lederer et al.[1])

B. Production

Silicon-25: Produced by proton bombardment (80-97 Mev) of Al^{27} and silicon targets $Al^{27}(p,3n)Si^{25}$ [4], $Si^{28}(p,p3n)$ [6].

Silicon-26: Produced by He^3 reaction on magnesium-24 or silicon-28: $Mg^{24}(He^3,n)Si^{26}$ [7]; $Si^{28}(He^3,\alpha n)$.

Silicon-27: $Mg^{24}(\alpha,n)Si^{27}$; $Al^{27}(p,n)$ [8]; $Si^{28}(\gamma,n)$.

Silicon-31: This isotope may be produced in a variety of reactions. The most convenient and most common for activation analysis is the (n,γ) reaction on silicon-30 by thermal neutrons. Reactions include: $Si^{30}(n,\gamma)Si^{31}$; $Si^{30}(d,p)$; $Si^{30}(He^3,2p)$; $S^{34}(n,\alpha)$.[1]

Silicon-32: The isotope has been prepared by spallation from chlorine in a beam of protons at 340-420 Mev by a reaction of the type $Cl^{37}(p,\alpha 2p)Si^{32}$ [9].

A strong flux of neutrons acting on lithium silicide will produce tritons which in turn react with Si^{30} to produce Si^{32}. $Li^6(n,t)He^4$; $Si^{30}(t,p)Si^{32}$[10]. A few dpm of Si^{32} can be made by double neutron capture in a reactor, $Si^{30}(2n,\gamma)Si^{32}$ [11]. Jantsch has studied the reactions $Si^{31}(n,\gamma)Si^{32}$ and $^{32}P(n,p)Si^{32}$ and suggested that these reactions could never produce microcurie amounts of Si^{32}. [3]

$Ar^{40}(p,p2\alpha)Si^{32}$ [12] is the atmospheric production reaction.

C. Availability

Silicon-31 is the one silicon radioisotope readily available at present. It is most often prepared by neutron activation, but because of its short half-life, can be obtained only on special order.[13]

III. CHEMISTRY OF SILICON AS APPLICABLE TO RADIOCHEMISTRY

In most instances, radiochemistry is dependent upon more conventional ideas in analytical chemistry involving separations by such methods as precipitation, solvent extraction, chromatography, volatilization, and/or electroanalysis. Following separation and purification, the element is converted to the form most suitable for measurement of its radioactivity. With so much of analytical chemistry now done by instrument, radiochemistry remains one of the few areas where chemists can practice traditional techniques, but even here it is seldom necessary to make perfect separations, since the radiochemical determination is generally adjusted for the chemical yield of the carrier. Such an adjustment will be correct only if the carrier has the same chemical form as the radioisotope, insuring that loss of carrier is matched by a proportional loss of activity. Failure to achieve this identity of chemical species has caused many an error in radiochemical analyses.

Colorimetry, polarography, and similar instrumental techniques are seldom used in radiochemistry because they do not separate the desired radionuclide from contaminants in the mixture being analyzed. Nevertheless, they are often essential to monitor the development of radiochemical procedures.

The discussion that follows is by no means a complete treatment of the chemistry of silicon. Silicon — like its group four precursor, carbon — has an extremely complex behavior, with myriad mineral forms, and a multitude of combinations with oxygen, hydrogen, halogen, and carbon. These topics are largely beyond the scope of this treatment, as they are unlikely to be of value to the radiochemist. Most silicates are very stable chemical forms, but cannot be readily formed from solution because the rates of reaction are extremely slow. Similarly the chemistry of the silicones, while of great practical interest, is unlikely to be important in radiochemical procedures. The colloidal chemistry of silica is of great practical interest, but, the behavior of the colloids is generally to be avoided in radiochemical procedures.

The conventional textbook treatment of silicon chemistry is of surprisingly little value to the radiochemist. Such treatments usually include a lengthy discussion of silicate structure, and a mention of the

TABLE II

NOMENCLATURE OF SOME SILICON COMPOUNDS[14]

SiH_4	silane	SiH_3R	alkyl (aryl)silane
Si_2H_6	disilane	SiH_2XR	halo alkyl silane
Si_3H_8	trisilane	R_3SiOH	silicol
SiH_3^-	silyl radical	$R_3Si-O-Alk$	ether
SiH_2^{-2}	silylene radical	$R_3Si-O-CO-Alk$	ester
SiH^{-3}	silylidyne radical	$R_3Si-O-SiR_3$	silico-ether
$Si_2H_5^-$	disilanyl radical	$R_2Si = O$	silicoketone
SiR_4	silicon tetra alkyl (aryl)	$SiO_3^=$	silicate (meta)
		SiO_2	silica
$Si(OR)_4$	tetra alkyl (aryl) silicate	H_4SiO_4	silicic acid (ortho)
$H_3Si-O-SiH_3$	disiloxane(silicyl oxide)	H_2SiO_3	metasilicic acid
$H_3Si-O-SiH_2^-$	disiloxanyl radical	$H_2Si_2O_5$	disilicic acid
H_3Si-O-	siloxy radical	$H_6Si_2O_7$	pyrosilicic acid
$H_3Si-NH-$	silylamino radical	$H_2Si_2O_4$	silicoxalic acid
H_3SiOH	silanol	H_2SiF_6	fluosilicic acid
$H_3Si(OH)_2$	silanediol	SiF_6^{-2}	silicofluoride or fluosilicate
		$H_4SiMo_{12}O_{40}$	silicomolybdic acid
SiX_4	silicon tetrahalide	$R \cdot SiO \cdot OH$	siliconic or silonic acid
SiH_3X	halosilane		
SiH_2X_2	dihalosilane		

TABLE III

SOLUBILITY OF SOME SILICON COMPOUNDS

COMPOUND	FORMULA	WATER SOLUBILITY Cold	WATER SOLUBILITY Hot	OTHER SOLVENTS
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	Insoluble	Insoluble	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

* See Table V for solubilities of the fluosilicates.

TABLE III (cont'd)

Silicates	Solubility (g/100 ml water)
$CaSiO_3$	.0095
$BaSiO_3 \cdot 6H_2O$	.17
$CdSiO_3$	very slightly soluble
$ThSiO_4$	very slightly soluble
$Na_2O \cdot XSiO_2$	soluble
Na_2SiO_5	soluble
Na_2SiO_3	soluble
Na_4SiO_4	soluble
$Na_4[Si(W_3O_{10})_4] \cdot 2H_2O$	very soluble

Insoluble Silicates

$Pb_2Si_2O_7$	$MgSiO_3$
$PbSiO_3$	$KAlSi_2O_6$
Fe_2SiO_4	$Na_2O \cdot Al_2O_3 \cdot 4SiO_2$
Co_2SiO_4	$Na_2O \cdot Al_2O_3 \cdot 2SiO_2$
$2Bi_2O_3 \cdot 3SiO_2$	$SrSiO_3$
$BaSiO_3$	$2ZnO \cdot SiO_2 \cdot H_2O$
$Al_2O_3 \cdot SiO_2$	$ZnSiO_3$
Li_2SiO_3	Zn_2SiO_4
Li_4SiO_4	$ZrSiO_4$
Mg_2SiO_4	

hydrides, halides, and organo-silicon compounds. Seldom is there a worthwhile discussion of the aqueous solution chemistry of silicon compounds. Silicon solution chemistry is largely confined to the silico-fluorides, and the heteropoly acids, but it also includes the soluble silicates and silicic acid.

A. Compounds of Silicon

1. Metallic Silicon

Elemental silicon forms octahedral crystals that are lustrous, gray, and very brittle. So-called amorphous silicon is merely a conglomeration of minute crystals. Pure silicon is the starting material for a large fraction of all transistors and integrated circuits made today; for this reason it is available in extraordinary purity, and its behavior is the subject of a vast body of research. The free element is never found in nature, but may be produced by the high temperature reduction of silicon dioxide with carbon, by reduction of sodium silicofluoride with aluminum, or by the high-temperature reduction of silicon tetrachloride with sodium or magnesium.

Elemental silicon is relatively inactive, and practically insoluble in all acids, including hydrofluoric. At room temperature, it is inert toward most elemental substances, but ignites spontaneously with fluorine to form the tetrafluoride. At high temperatures, it will react with the other halogens. Silicon will not burn, but can be made to combine with oxygen or sulfur to form the dioxide or the disulfide. 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 solution in the molten metal, to form silicides.

Silicon will react very readily with alkaline solutions to form the silicate, releasing hydrogen by the reaction

$$Si + 4OH^{-1} \rightarrow SiO_4^{-4} + 2H_2$$

The metal can be solubilized by boiling it with water in a glass vessel; alkali leached from the glass is sufficient to induce reaction.

2. Hydrides

Silicon, like carbon, can form covalently bonded chains, but these self-linkages diminish in stability quickly as the chain length increases. Six member chains are about the limit of stability for the hydrides. Double or triple bonds do not occur. Mixtures of silanes — SiH_4, Si_2H_6, and so on — are formed by treatment of magnesium silicide with dilute HCl, H_2SO_4 or H_3PO_4, or with ammonium ion in liquid ammonia solution. The mixtures may be separated by fractional distillation or by vapor phase chromatography.

All the silanes ignite in air yielding SiO_2 and water. In solutions that are the least bit basic, the silanes hydrolyze rapidly to form silica and hydrogen. The weakness of Si-Si and Si-H bonds, as compared to Si-O bond, makes all silanes strong reducing agents. They react explosively with halogens.

The colorless gas monosilane, SiH_4, (m.p. - 185°, b.p. - 112°) is most often prepared by the reaction of $SiCl_4$ with $LiAlH_4$ and is readily reduced to its elements upon heating. Reaction of SiH_4 with copper salts yields Cu_2Si, but with silver salts the elemental silver and silicon form. Disilane is also colorless (m.p. - 132°, b.p. - 14°), stable up to 300°, but inflammable in air. It dissolves in benzene and carbon disulfide.

The extensive family formed by the silanes and their derivatives have been reviewed by MacDiarmid[15]. The halogen derivatives are discussed briefly in this monograph. Other compounds, not treated, include silane derivatives with -CN, -NCO, -NCS, sulfur and selenium, nitrogen, phosphorus, arsenic, alkali metals, germanium, tin, boron, and iron.

3. Silicides

Most metals will alloy with silicon on heating, either by direct combination or by solution in the molten metal to form silicide. Of the alkali metals, only lithium will form an alloy with silicon. A mixture of lithium and silicon will produce Li_4Si_2 and Li_8Si_2 when heated in a vacuum.

Most silicides hydrolyze readily to yield silanes. Silicides are very powerful reducing agents. At red heat, they reduce oxides of iron, chromium and manganese to the respective metals. Commonly, the silanes are produced by treating magnesium silicide (Mg_2Si) either with HCl, or with NH_4Br in liquid ammonia, in a current of hydrogen[16].

4. Borides

The borides SiB_3 and SiB_6 are formed in an electric furnace. They are best known for their hardness.

5. Nitrogen Compounds

Silicon and nitrogen can combine in a variety of ways, but only recently have the many possibilities begun to be explored. The organo-halosilanes provide the most important starting materials. Some of the simpler compounds are listed in Table IV.

Silicon nitride, Si_3N_4, may be prepared by heating a mixture of silicon and nitrogen or ammonia above 1300°C, or by decomposing $Si(NH_3)$ at 1350°C. Si_3N_4 is very stable, only slightly attacked by concentrated HNO_3 or HF, unreactive with concentrated HCl, 50% NaOH, or hot Cl_2 [17]. $(SiH_3)_3N$ and $[(CH_3)Si]_3N$ are also known.

Wannagat[18] has recently reviewed the silicon-nitrogen compounds, but the radiochemist will be hard-pressed to find use for this class and the interested reader is referred to that review.

6. Carbides

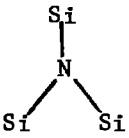
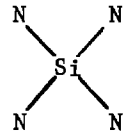
If SiO_2 is reduced with an excess of carbon in an electric furnace, silicon carbide SiC (carborundum) is formed. Silicon carbide is very hard and quite stable.

7. Sulfides

Heating a mixture of silicon and sulfur produces silicon disulfide, SiS_2. At high temperatures SiS_2 sublimes to produce colorless needles. It is easily hydrolyzed by water to yield SiO_2 and H_2S.

TABLE IV

SOME SILICON-NITROGEN STRUCTURES[18] *

SiN	Silylamine	NSi	Aminosilane
SiNSi	Bis(silyl)amine	NSiN	Bis(amino)silane
	Tris(silyl)amine		Tetrakis(amino)silane
Si(NSi)n	Polysilazane		
(- NSi -)n	Cyclosilazane		

* N. B. It is common practice to use, for structural units, abbreviated formulations which show only the arrangement of the SiN groups in the structure. In this case, just the symbols for adjacent elements are given, e. g. $(CH_3)_2Si[NHC(CH_3)_3]_2$ is shown as NSiN. Basic units are SiH_4 and NH_3, and there exists a wide variety of substituents for the hydrogens, e.g.

H_3SiNH_2	silylamine
$(CH_3)_3SiNHCH_2COOH$	trimethylsilylaminoacetic acid

Nomenclature is based on the hydrocarbon analogy, with CH_2 replacement by SiH_2 labeled by the prefix sila-, and replacement by -NH- labeled aZA.

8. Halogen Compounds

a. Tetrahalides

All of the simple (binary) tetrahalides of silicon have been made, and many mixed halides are known. The binary compounds can be made by direct combination, e.g. passing chlorine over a heated mixture of silica plus carbon or magnesium, or by reacting iodine vapor with silicon metal.

The preparation of $SiCl_4$, $SiBr_4$ and SiI_4 has been described by Schumb.[19] Silicon tetrachloride is a volatile liquid (m.p. -70°C, b.p. 56.8°C), sometimes prepared by passing carbon tetrachloride vapor over hot silica. $SiCl_4$, a colorless, pungent liquid, reacts violently with metallic potassium when heated slightly. $SiBr_4$ reacts with ammonia or other substances to create a variety of addition compounds. The crystalline SiI_4 dissolves readily in carbon disulfide, and unlike $SiCl_4$ or $SiBr_4$, silicon tetraiodide reacts with ethanol to form ethyl iodide, hydrogen iodide, and silicic acid. The tetrahalides decompose in the presence of water, due to the strong affinity of silicon for oxygen:

$$SiCl_4 + 2H_2O = SiO_2 + 4HCl.$$

Radiochemists will find silicon tetrafluoride the most useful of the tetrahalides. SiF_4 is a colorless, incombustible, strongly fuming gas. It solidifies without liquification at -97°C (1 atm.), or liquifies at 50 atmospheres pressure. Silicon tetrafluoride forms in the reaction of a silicon compound with hydrofluoric acid. Silicon metal ignites spontaneously in fluorine to give the SiF_4. Upon heating, the silicofluorides of barium or other metals in Groups Ia and IIa decompose, producing metal fluoride and SiF_4. In the laboratory, SiF_4 is most commonly prepared by heating a mixture of fluoride salt with silica and sulfuric acid.

Silicon tetrafluoride dissolves in alcohols: 33% in methanol; 36% in absolute ethanol; and 28% in isopropanol (by weight). It does not react with most of the non-metals (e.g. H_2, C, P, I) nor with Zn, Hg, H_2S, HNO_3, N_2O_4, N_2O_5, nor with anhydrous alkaline borates. However, sodium and potassium metals burn in SiF_4 to yield Si + NaF + Na_2SiF_6, etc. Heating with aluminum also reduces silicon tetrafluoride to silicon. With iron or platinum, SiF_4 is reported to form silicides.

SiF_4 reacts with water in two ways:

$$SiF_4 + 2H_2O \rightarrow 4HF + SiO_2$$

$$3SiF_4 + m\,H_2O \rightarrow 2H_2SiF_6 + SiO_2 \cdot (m-2)H_2O$$

When the solution is sufficiently alkaline, a reaction may occur of the type

$$6NaOH + SiF_4 \rightarrow 4NaF + Na_2SiO_3 + 3H_2O$$

With gaseous ammonia, SiF_4 forms a volatile white solid $SiF_4 \cdot 2NH_3$. In the presence of CaO, MgO, Al_2O_3, MnO_2, HgO, or FeO, reactions of the type $2CaO + SiF_4 \rightarrow SiO_2 + 2CaF_2$ occur. With calcium the reaction is quite energetic. Silicon tetrafluoride reacts with HF or the alkali fluorides to form the respective silicofluorides, with ethanol to form ethyl orthosilicate and fluosilicic acid, with a number of other organic compounds (e.g. acetone, aromatic amines), or with Grignard reagents to form trialkyl or triarylsilicyl fluorides.

Silicon forms many mixed tetrahalides such as fluorochloro- (e.g. SiF_3Cl, SiF_2Cl, $SiFCl_3$), fluorobromo-, fluoroiodo-, chlorobromo-, and fluorochlorobromo- derivatives (e.g. $SiFCl_2Br$ and $SiFClBr_2$). All the mixed tetrahalides are volatile and can be hydrolyzed to give products analogous to those from the binary tetrahalides.

b. Catenated Halides

Compounds of the type Si_2X_6 can be formed with all the halogens.[20] The hexahalide compounds are unstable at ordinary temperatures, although decomposition occurs only after moderate heating. Cold water will decompose the hexahalides to form "silico-oxalic acid," $H_2Si_2O_4$. This is a white powder with no acidic properties, but it is a strong reducing agent, liberating hydrogen when dissolved in alkalis.

Binary halogens with the general formula Si_nX_{2n+2} can be prepared by a further treatment of the tetrahalides to form an homologous series of compounds having a molecular composition up to n = 10, e.g., $Si_{10}Cl_{22}$. The compound SiF_2 has also been prepared and exhibits an interesting set of chemical reactions.[21] Compounds such as the silicon monochloride $(SiCl)_x$ also exist.

c. Oxyhalides

Silicon forms oxyhalides of the type $Si_nO_{n-1}X_{2n+2}$ (X=F, Cl, Br).[22] For chlorides n may go as high as 7, and for bromides, up to 6. The oxyhalides are colorless, oily liquids, soluble in monohydroxylic solvents and miscible with CCl_4, $SiCl_4$, $CHCl_3$ or CS_2. They show various degrees of volatility, but all hydrolyze readily in the presence of moisture.

Tetramers, of the type $(SiOBr_2)_4$ and $(SiOCl_2)_4$ have similar properties.

d. Halo-monosilanes[17]

Compounds of the type SiH_nX_{4-n} have properties intermediate between monosilane and the corresponding tetrahalides, being somewhat less stable than the corresponding SiX_4. The analogs of chloroform, $SiHCl_3$ (silico-chloroform) and of bromoform, $SiHBr_3$, are of particular interest. These compounds form in the reaction of HCl or HBr with silicon at 380°C and can be separated from the reaction mixture by distillation. Silicofluoroform decomposes upon heating. $4SiHF_3 \rightarrow 3SiF_4 + Si + 2H_2$.

9. Fluosilicic Acid and the Fluosilicates[23]

When SiF_4 hydrolyzes in water, the SiO_2 and the HF which are formed react to produce fluosilicic acid*.

$$3SiF_4 + 2H_2O = SiO_2 + 2H_2SiF_6$$

Similarly, this acid is formed if HF is added to SiO_2

$$SiO_2 + 6HF = H_2SiF_6 + 2H_2O$$

Fluosilicic acid is a colorless liquid. It cannot be isolated from water, nor can dry HF and SiF_4 be made to react. The concentrated acid emits toxic, corrosive fumes. When pure, it does not attack glass, but if evaporated will decompose to SiF_4 and HF, the latter attacking silicates or a wide variety of other things. H_2SiF_6 is a strong dibasic acid. The

* H_2SiF_6, sometimes called hydrofluosilicic acid, silico-fluoric acid, hydrofluorosilicic acid, fluorosilicic acid, or hexafluorosilicic acid.

TABLE V

SOLUBILITIES OF THE FLUOSILICATES[23,25]

Formula	Mol. Wt.	Solubility (g/100 cc) 17-22°C	Ksp
$(NH_4)_2SiF_6$	178	18.6	4.6
$BaSiF_6$	279	0.025	8.0×10^{-7}
$CaSiF_6$	182	10.6	3.4×10^{-1}
Cs_2SiF_6	408	0.60	1.3×10^{-5}
$CoSiF_6 \cdot 6H_2O$	301	118.0	15.4
$CuSiF_6 \cdot 6H_2O$	313	233.0	55.4
$FeSiF_6 \cdot 6H_2O$	306	128.0	17.5
$PbSiF_6 \cdot 4H_2O$	421	69 *	3.9
$Li_2SiF_6 \cdot 2H_2O$	192	73	2.2×10^{2}
$MgSiF_6 \cdot 6H_2O$	274	23.5*	2.0
$MnSiF_6 \cdot 6H_2O$	305	141	21.4
K_2SiF_6	220	0.12	6.5×10^{-7}
Rb_2SiF_6	313	0.16	5.4×10^{-7}
Na_2SiF_6	188	0.65	2.4×10^{-5}
$SnSiF_6 \cdot 2H_2O$	265	3.22	1.5×10^{-2}
$ZnSiF_6 \cdot 2H_2O$	315	35.2*	2.9
$CdSiF_6$		slightly	
$Hg_2SiF_6 \cdot 2H_2O$		slightly	
$Fe_2(SiF_6)_3$		soluble	
$PbSiF_6$		soluble	
$N_2H_4 \cdot H_2SiF_6$		very	
$(NH_2OH)_2H_2SiF_6 \cdot 2H_2O$		very	
$Ag_2SiF_6 \cdot 4H_2O$		very	
$Tl_2SiF_6 \cdot 2H_2O$		very	
$ZnSiF_6 \cdot 6H_2O$		very	

* solubility as anhydrous salt

first proton is completely dissociated in aqueous solution; the second dissociation constant is $10^{-3.0}$. The acid is prepared industrially in rubber tanks by the action of HF on quartz. In the laboratory it can be prepared by bubbling pure SiF_4 through mercury into water.[24] Pure H_2SiF_6 is then obtained by filtering off the silica precipitate. With boric acid, fluosilicic acid forms fluoboric acid and silica:

$$3H_3BO_3 + 2H_2SiF_6 \rightarrow 3HBF_4 + 5H_2O + 2SiO_2\downarrow$$

With alumina it forms $AlF_3 + SiO_2$. The latter two reactions often serve to deactivate fluoride in solutions, when its presence becomes undesirable.

The fluosilicate ion may decompose in two ways:[28]

$$SiF_6^{=} \rightarrow SiF_4 + 2F^- \qquad K = 6 \times 10^{-7}$$

or

$$SiF_6^{=} + 2H_2O \rightarrow SiO_2 + 4H^+ + 6F^- \qquad K = 5 \times 10^{-27}$$

When reacted with most oxides, hydroxides or carbonates, the fluosilicate salt is formed. Many of these have only limited solubility: e. g. Na_2SiF_6, K_2SiF_6, Rb_2SiF_6 and $BaSiF_6$. Precipitates of cesium and rubidium fluosilicate have nearly the same index of refraction as water, hence are frequently mistaken for "gelatinous." The potassium salt has this property to a lesser extent. Usually complete precipitation requires less than 15 minutes. Table V gives the solubilities of some fluosilicates.

Excess oxide, hydroxide, or carbonate cause the fluosilicate reactions to proceed farther: $H_2SiF_6 + 6NaOH + nH_2O \rightarrow 6NaF + SiO_2 \cdot (n+4)H_2O$. This reaction frequently complicates preparation of the fluosilicate salts. Ammonia may also react to form soluble fluosilicate or fluoride. Aryl, Alkyl, or heterocyclic amines may form fluosilicates. Aqueous solutions of soluble salts, treated with benzidine or tolidine in hot alcohol or acetone solution, form insoluble complex salts, e.g.

$$[Cu(NH_2C_6H_4NH_2)_2]SiF^{(27)}$$

Pyridine complexes have also been described.

Insoluble fluosilicates may be solubilized by reaction with a dilute solution of the salt of a metal which forms a soluble fluosilicate (e.g. $MgSO_4$). The fluosilicates decompose when heated, liberating SiF_4. Salts of the heavy metals may decompose at temperatures as low as 100°C. Barium, potassium, and sodium are among the most stable, requiring red heat for dissociation.[24,28]

All fluosilicates decompose rapidly in hot H_2SO_4 or hot NaOH:[29]

$$MSiF_6 + H_2SO_4 \rightarrow MSO_4 + SiF_4\uparrow + 2HF\uparrow$$

$$MSiF_6 + 4NaOH \rightarrow 2NaF + 2H_2O + SiO_2\downarrow + MF_2$$

The first reaction is quantitative; the second may or may not be.

10. Oxides and Acids

In nature, the normal oxide of silicon -- SiO_2 or silica -- exists in several forms: alpha and beta quartz; tridymite; crystobolite; and amorphous silica or opal. The relationship between these various forms is of more interest to the geochemist than to the radiochemist. The most stable form, quartz, is less soluble in water than amorphous silica by about a factor of ten, but precipitation of quartz from solution is inhibited by kinetic factors. Amorphous silica is the form most commonly found in equilibrium with natural solutions. SiO_2 melts at 1700°C. It is quite stable, inert to hydrogen and all the halogens except fluoride. It does not react with any acids except HF which converts it to SiF_4 or H_2SiF_6. It can be reduced to silicon when heated with alkali or alkaline earth metals or carbon. Upon fusion, SiO_2 will combine with basic oxides or carbonates to form silicates.

Considerable confusion regarding the solution chemistry of silica has resulted from the failure to recognize the existence of true solutions of silicic acid. Earlier literature must be read with care [30] to avoid compounding the confusion. The concept of a series of silicic acids: orthosilicic, metasilicic, disilicic acid, etc., is now obsolete, but references to these acids still appear in the literature. Alexander[31] reported the true solubility of silica as monomeric silicic acid,

$Si(OH)_4$ or H_4SiO_4. At 25°C the solution reaction SiO_2(amorph.) + $2H_2O$ = $Si(OH)_4$ has a solubility constant of $10^{-2.7}$. The reaction is strongly temperature sensitive, with solubility rising rapidly as the temperature increases. Although one may frequently read in older works that $Si(OH)_4$ has never been isolated, cation exchange techniques now make such preparation routine. Orthosilicic acid is commercially available, but the water content of this material is by no means stoichiometric.

The solubility of silicic acid is independent of pH; Corren's[32] oft cited pH vs. solubility relationship is wrong.[30] The dissociation of silicic acid, as defined by the following equilibria and illustrated in Figure 1 [33] causes an apparent rise in the solubility at high pH. For acid, neutral or slightly alkaline solutions, only $Si(OH)_4$ occurs below a concentration of about 2mM. At pH>9 $SiO(OH)_3^-$ appears and at pH>12 $SiO_2(OH)_2^{-2}$ becomes important.

Data from Lagerstrom:[34]

$$Si(OH)_4 = SiO(OH)_3^- + H^+ \qquad \log K = -9.46$$

$$SiO(OH)_3^- = SiO_2(OH)_2^{-2} + H^+ \qquad = -12.56$$

$$4Si(OH)_4 = Si_4O_6(OH)_6^{-2} + 2H^+ + 4H_2O \qquad = -12.57$$

The addition of strong acid to supersaturated solution usually causes colloidal silica to precipitate, producing the illusion of a solubility decrease. A sequence of progressive condensation and hydroxylation reactions take place, leading to multinuclear species with relatively low (3 or 4) numbers of silicon atoms.[34,35] These species condense by formation of Si-O-Si bonds (polymerization and crosslinking) and by physical aggregation to a negatively charged silica hydrosol consisting of suspended particles in the size range 50 to 1000 A°. As precipitation proceeds, these particles aggregate into a gel structure containing continuous water patches amongst the intersticies; then finally, condensation results in a continuous SiO_2 structure with separate parcels of interstitial water. As the water is squeezed out, the gel becomes progressively more rigid. The polymerization can be stopped and reversed at intermediate stages by adjusting the pH or the concentration.

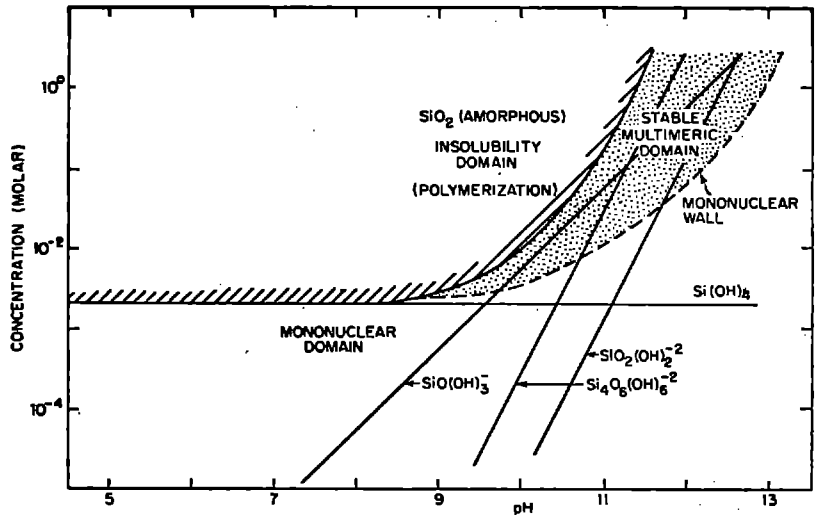


Figure 1 Species in equilibrium with amorphous silica

Diagram computed with equilibrium constants (25°C) given by Lagerstrom. Line surrounding shaded area gives maximum soluble silica. Mononuclear wall represents lower concentration limit below which multinuclear silica species are not stable. Reprinted by permission from "Environmental Science and Technology."

11. Silicates[36]

Amongst the silicates, only the alkali forms are appreciably soluble. Their solubility derives from the dissociation of the silicic acid species in strong alkaline solution. A great deal of industrial research has been devoted to the soluble silicates and their uses in modern technology are legion. The silica:alkali ratio is generally regarded as the key to soluble silicate behavior, mainly because this ratio expresses the number of hydroxide ions tied up by silicic acid. In a solution containing only NaOH and $Si(OH)_4$ electrical neutrality requires that:

$$[Na^+] + [H^+] - [OH^-] = [SiO(OH)_3^-] + 2[SiO_2(OH)_2^{-2}] + 2[Si_4O_8(OH)_6^{-2}] + \text{etc.}$$

$Si(OH)_4$ does not appear on the right side of the equation, but is a part of total silicate in solution (Si_T). Thus the relative extent of OH^- uptake by silicic acid is represented by $\tilde{n}$ (called the ligand number or the formation function).

$$\tilde{n} = \frac{[Na^+] + [H^+] - [OH^-]}{[Si_T]}$$

which is approximately equal to $[Na^+] / [Si_T]$

since $[H^+] - [OH^-]$ will usually be much smaller than $[Na^+]$. If the approximation applies, then $\tilde{n} \simeq 2/R$, where R is the molar ratio (or approximately the ratio of weights) of $SiO_2:Na_2O$. Commercial soluble silicate solutions are generally in the range 2.2 to 3.5. Figure 2 shows the stability relations for log concentrations in solution vs. R.[33]

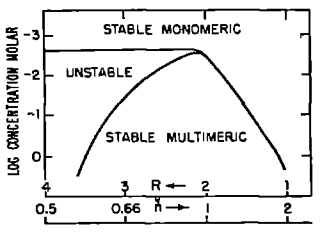


Figure 2

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The soluble silicates are prepared by the action of hydroxide on silica, or less often, on silicon. The sodium, potassium, and lithium silicates are common. Cesium and rubidium have aroused less interest, and ammonium silicate has been, until recently, unknown. The soluble silicates are precipitated by heavy metal ions, such as Cu, Zn, Mn, Cd, Pb, Ni, Ag, Mg, and Ca, in order of decreasing ease of precipitation.[37] These precipitates are seldom stoichiometric in composition, but rather seem to contain varying ratios of colloidal SiO_2, the basic salt, the hydroxide of the metal or a colloidal floc.

Crystals of soluble heavy metal salts, placed in concentrated solutions of silicate, become encased in a gel-like covering. Osmotic effects soon cause the gel to burst, exposing a fresh bit of the heavy metal salt solution. This too becomes encased, bursts, and so on, forming streamers or growths of various shapes. Copper, nickel, cobalt, manganese, iron, and uranium form such silicate gardens.

Alcohol, glycerine, acetone, strong ammonia, and salt brine will precipitate silicates. Solid ZnO, CaO, amorphous $CaCO_3$, and some clays will react with silicate solutions to form insolubles. Because of their alkalinity, silicate solutions react with metallic Al or Zn to liberate hydrogen, but the metal soon becomes coated with silicate, stopping the reaction.

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 silica peroxyhydrate, $SiO_2 \cdot H_2O_2$, are not very soluble in water and are very unstable.

12. Minerals

Silicon -- second only to oxygen as the most abundant element in the earth's crust — is the key element in a vast number of minerals and structures. The SiO_4 tetrahedron is the building block from which silicates build by various combination of shared oxygen corners. Most minerals form

at temperatures and pressures outside the range normally available in the radiochemical laboratory; those which form at earth-surface conditions do so very slowly. Thus, the vast silicate mineral chemistry is of little value to the radiochemist and is not covered here. The interested reader is referred to Barth.[38]

13. Phosphorus Compounds

The silicon-phosphorus compounds may someday prove of particular interest since Si^{32} has the phosphorus-32 daughter. Monosilyl phosphine, SiH_3PH_2, forms when a mixture of silane and phosphine are heated. This compound boils at 13°C and is thermally stable up to 400°C. It reacts with NH_4OH to produce SiH_4, PH_3 and H_2.

Reaction of R_3SiCl with alkali metal phosphides or their derivatives will produce triorganosilyl compounds.

$$2(CH_3)_3\ SiCl + Li_2PH \rightarrow [(CH_3)_3Si]_2\ PH + 2LiCl$$

Although such alkylsilyl phosphines have good thermal stability, they are extremely sensitive to air and water, often igniting spontaneously. These compounds are generally colorless liquids or low melting solids.[13]

Upon heating of SiO_2 with phosphoric acid, a clear solution of $H_2Si(PO_4)_2$ forms. At higher temperatures this converts to $3SiO_2 \cdot 2P_2O_5$ or several polymorphs of $SiO_2 \cdot P_2O_5$.[39]

14. Heteropoly Acids and Their Salts[40]

Silicon often serves as the central atom for the large and complex group known as heteropoly acids. The chemistry of the heteropoly acids is important to both the solution chemistry and the analytical chemistry of silicon. In the silicon heteropoly forms, a silicon central atom is linked -- through four oxygen atoms -- to complex surrounding groups. The silicon heteropoly acids and their anions are of particular interest, since they are involved in most colorimetric analyses of silicon, are often quite soluble, are extractable into organic solvents, or can readily be precipitated or decomposed, yet their behavior is rarely discussed in chemistry text books. Silicomolybdates are the best known of the group.

Silicon is by no means the only element which can serve as the central atom for an heteropoly acid. Phosphorus, arsenic, and germanium often follow very similar chemical paths, and at least twenty-nine other elements have been reported in similar roles. Nor is the molybdate group the only one which might surround the silicon central atom. Tungstates and vanadates do so readily, and combinations of surrounding groups have been formed such as silicovanado tungstic acid (a hetero-hetero-poly acid). Vanadosilicates and tungstosilicates are less studied, but surely present a variety of chemical and analytical possibilities. Because silicomolybdates are most often used, we will focus the discussion on these species. The name silicomolybdate is commonly applied to the anion ($SiMo_{12}O_{40}^{-4}$) but the more proper name is 12-molybdosilicate. The anion is formed around a central SiO_4 tetrahedron. Each oxygen of the tetrahedron forms one corner of a group of three MoO_6 octahedra, and is shared by all three. Four oxygens from each molybdenum atom are shared between pairs of tetrahedra and the sixth oxygen of each Mo atom, unshared, forms the outer surface of the anion. Crystallization of this large anion leaves many open spaces for water of hydration; twenty-four or thirty-one waters per molecule are common in heteropoly-molybdate crystals.

Silicomolybdate occurs in at least two forms, alpha and beta.[41] A variety of other forms has been reported, and it is not yet clear whether this variety of forms derives from the complexity of heteropoly and chemistry, or from the difficulties in chemical analysis of such high molecular weight compounds.

Silicomolybdate is formed by reaction of silicic acid with molybdic acid (or ammonium molybdate). At pH <1, the reaction proceeds very slowly, the optimum pH for rapid reaction is 1.5 - 2.0. Molybdate will react with SiF_6^{-2} to form silicomolybdate, but not in the presence of excess fluoride; silicomolybdate in the presence of excess fluoride ion decomposes slowly.

The beta form of silicomolybdate is more easily made, and is generally sought for its greater light absorption (approximately double at 4000 A). The ratio of the alpha/beta form produced is highly pH dependent, alpha predominating above pH 5 and beta below pH 3, but the alpha form is more stable. The beta form spontaneously converts to alpha over a period of many hours, or more rapidly if boiled above pH 2 for 60 minutes. Beta

silicomolybdate is much more susceptible to fading upon the addition of strong acid than is alpha[42] (possibly from α to β conversion). The best way to distinguish alpha from beta is by reduction to the silicomolybdous form form (alpha or beta) where the ratio of light absorbance at 7420 and 8100 Å is quite different.

The yellow, silicomolybdate anion is a fairly effective oxidizing agent, on a par with chromic acid. It is readily reduced to the dark blue, silicomolybdous form by ferrous salts, sulfites, urea, metal, and a variety of other agents. Strong reduction -- e.g. with metallic zinc + HCl -- will destroy the complex. Oxidation back to the yellow form can be caused by bromine water, peroxide, nitric acid in strong acid solution, and sometimes even by air.

The reduction of alpha silicomolybdate proceeds stepwise, first forming a green compound (+4 electrons), then the familiar blue (+1 more electron) α-silico molybdous ion. Upon reduction, the beta form goes directly to the blue (+4 electron) β-silicomolybdous anion. The structural difference between the alpha and beta forms is not known, nor is the location of the extra 4 or 5 electrons in the silicomolybdous species. In general, the reduced silicomolybdous forms show the same chemical behavior as the silicomolybdates.

Silicomolybdic acid is a fairly strong acid. Sillen[26] does not list the ionization constants, but K_1 is probably between 10^0 and 10^{-3}. The several replacable protons are fairly equal. Most of the metal salts are soluble in water (up to 70% by weight) but rubidium, cesium, mercurous and thallous salts are insoluble. Silicomolybdate anion precipitates many heavy metal cations in the presence of various chelating agents (e.g. Cu, Ag, Cd, Zn, Sn, Cr, Ni, and Co, with EDTA, thiourea and hexamethylenetriamine). A number of organic bases such as 8-hydroxy quinoline will precipitate silicomolybdates.[43]

All of the heteropolymolybdate anions are decomposed by strong base to form simple molybdate ions and some anionic species of the central atoms, e.g. $22OH^- + SiMo_{12}O_{40}^{-4} \rightarrow 12MoO_4^{-2} + H_2SiO_4^{-2} + 10H_2O$.

Solvent extraction is utilized in the preparation of pure silicomolybdic acid,[44] and in the separation of phosphorus and silicon.[45] The heteropoly acids extract into various oxygen containing organic solvents. Phosphorus is generally considered the most readily extracted,[46] but by making the

aqueous phase ~3M with acid the silicon will extract readily (Figure 3).[47]

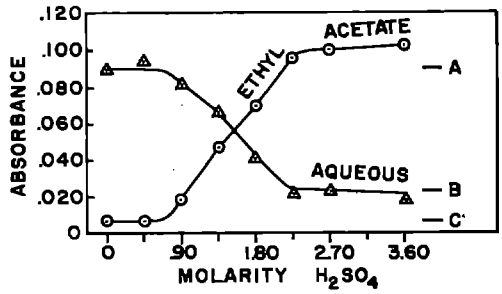
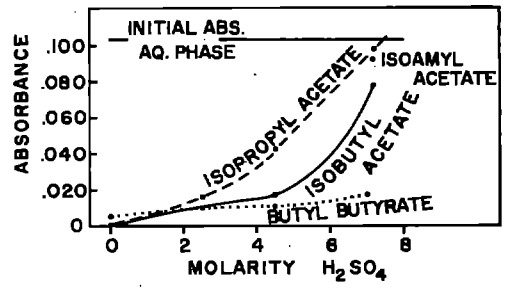


Figure 3 Silicomolybdate absorbance (adjusted to equal volumes) in ethyl acetate and aqueous phases after extraction from various concentrations of H_2SO_4 solutions

A. Absorbance of aqueous phase before extraction
B. Absorbance of aqueous blank after extraction
C. Absorbance of blank in ethyl acetate after extraction. Concentration of silicomolybdate 14 μM. Absorbance measured at 3600 A.



Silicomolybdate absorbance (adjusted to equal volumes) in various esters after extraction from various concentrations of H_2SO_4 solutions

Concentration of silicomolybdate is 14 μM. Absorbance measured at 3600 A.

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Alcohol has been used[48] as an extractant, but ether and ethyl acetate are the best solvents for silicomolybdic acid. Formation of an oxonium type complex is credited for the extractability; non-oxygenated solvents will not take heteropoly acids. Strong acid conditions are not the only means for driving the complex into the organic phase. High concentrations of NaCl, LiCl, $LiNO_3$, or $LiSO_4$, without acid, have been used to force silicotungstic acid into ethyl acetate.[49]

In the colorimetric determination of silica by silicomolybdate, the molybdic acid reagent absorbance and the phosphomolybdate absorbance are both in the same region as the silicomolybdate peak. For this reason, many analysts prefer reduction to the molybdous form where the blank is low. Colorimetry on the reduced form has the further advantage of nearly threefold increase in sensitivity. Many erroneous analyses have resulted, however, from the variety of reactions that may occur during reduction: formation of either of two alpha forms; formation of the beta form; or reduction of molybdic acid to molybdenum blue. By solvent extraction of the yellow

silicomolybdate, the high reagent blank is left behind, the phosphomolybdate destroyed, and measurement becomes possible at 3350 A, where the alpha and beta forms have the same absorbance.[41] Thus, any errors due to alpha-beta conversion are eliminated.[47]

The preparation and some of the behavior of silicotungstic acid has been studied by Scroggie.[49] Silicotungstate is more stable than silicomolybdate against degradation by alkalis; silicovanadate is less stable. Further investigation of these compounds will surely yield interesting new colorimetric techniques.

15. Organic Compounds of Silicon

Silicon, the second member of the carbon group, might be expected to have a complicated chemistry, and it does -- but the analogy to carbon is only poorly developed. The silanes illustrate the very limited stability of Si-Si bonding, resulting in little tendency to form great varieties of silicon chain compounds. The Si-O-Si linkage, however, is very strong, as evidenced by the multitudes of silicate minerals found on the earth's crust. The Si-C linkage is of intermediate strength and a wide variety of compounds incorporate this bond, to form silicon-organic compounds. The variety of these compounds is great and they represent an area of active investigation by many chemists. Liquid scintillation counting of Si^{32} has been done on silicon tetraethyl, and further work of this sort may be done in the future, but organic-silicon compounds, for the most part, are of limited interest to the radiochemist; only a brief outline of their chemistry is included here. Sidgwick[50] presents a useful summary of this subject.

A wide variety of compounds can be made by starting from the silanes, and replacing some or all of the hydrogens with alkyls or aryls, or with partial halogen replacement followed by alkyl or aryl groups. The tetra-alkyls and aryls are quite stable, unaffected by air, water, or boiling. The alkyls are unaffected by concentrated KOH, H_2SO_4, or halogens. These compounds are most easily made by the action of Grignard reagent on silicon tetrachloride. Using only limited amounts of Grignard reagent, compounds of the type Me_2SiCl_2 can be formed.

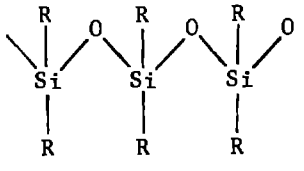
Using dichlorosilane, etc., the partial replacement compounds can be prepared, e.g. SiH_2Me_2 (a gas). When the hydrogens are only partially replaced, they are easily attacked by oxygen or halogens, causing a marked reduction in stability of the compound.

Alkyl chloro-silanes (e.g. Me_3SiCl) react with NH_3 and amines -- as do chlorosilanes -- to give amines [e.g. $(Me_3Si)_2NH$ or $Me_3Si{\cdot}NHMe$]. Hydrolysis of the alkyl chloro-silane produces a silicol type compound.

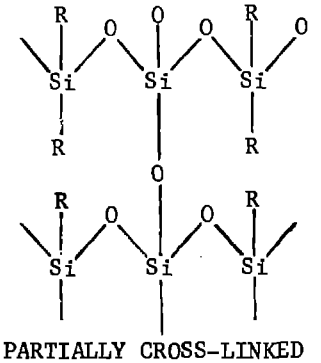
$$(CH_3)_2\ SiCl_2 \rightarrow (CH_3)_2\ Si(OH)_2 + 2HCl$$

The simple silicols (R_3SiOH) are colorless liquids which can be distilled without decomposition. They lose water to form the silico ethers $R_3Si\text{-}O\text{-}SiR_3$ or, with alkali, the R_3SiONa. These ethers are resistant to hydrolysis and most other forms of attack, but will form esters with acids such as acetic ($Et_3Si{\cdot}O{\cdot}CO{\cdot}CH_3$) or covalent sulfates $(Me_3Si)_2SO_4$ with sulfuric acid. The esters are saponified even by atmospheric moisture.

Among the disilicols, only the aryl compounds are found in the unpolymerized form. The disilicols lose water easily to form the polymers known as silicones. This important class of compounds ranges from oils, fluid at very low temperature, to rubber-like solids. They are very stable, resisting oxidation, thermal decomposition, or attack by nearly all chemical reagents. They are also water repellent and have high dielectric strength. Their physical characteristics are largely determined by the amount of cross-linking and the nature of the organic group.



SIMPLE CHAIN SILICONE



PARTIALLY CROSS-LINKED SILICONE

FIGURE 4

The triols are similarly formed by hydrolysis of alkyl trihalides but lose water at once to form polymers of siliconic acids (R·SiO·OH).

Various organic esters of ortho silicic acid can be prepared by reaction of $SiCl_4$ with alcohols or phenols to yield the tetra alkyl (or aryl) silicates (e.g. $Si(OEt)_4$). These are volatile liquids, easily hydrolyzed. Several chlorosilicates are also known (e.g. $MeOSiCl_3$).

Silicon chelate compounds may form in chloroform from the interaction of $SiCl_4$ and various beta diketones (e.g. acetylacetone). A solid salt of composition $(A_3Si)Cl$, HCl is formed. These are quickly hydrolyzed in water.

Silicon thiocyanate, $Si(SCN)_4$, can be prepared by double decomposition of $SiCl_4$ with $Pb(SCN)_2$ in benzene. The thiocyanate is stable in dry air but decomposes in the presence of water to form silica.

B. Separation Techniques

1. Precipitation [61,62]

Silicon, when present in large amounts, is most often precipitated from solution by acid dehydration. The precipitation results from the coagulation of silica sols following neutralization of the various silicate species which were kept in solution by high pH. Hydrochloric, perchloric, nitric, and sulfuric acids will cause the dehydration and precipitation. HCl is most commonly used. Throughout all SiO_2 precipitation procedures, the solubility of amorphous silica in aqueous solutions must be borne in mind. This solubility has not always been remembered or understood by those who designed the procedure.

The SiO_2 precipitate is rarely pure. Boron, tungsten, iron, tin, lead, niobium, aluminum, titanium, andor tantalum, plus sulfates of calcium, barium, andor sodium may accompany the silica precipitate.[63] In gravimetric analysis, the final determination of silicon is based on weight loss during volatilization by HF in the presence of H_2SO_4. Boron represents a particular nuisance in this procedure. Borates and boron compounds tend to coprecipitate or to become entrapped with silica. Any included boron would be weighed with the precipitate, then form BF_3 and distill out during

the HF treatment. The resultant loss in weight is liable to be attributed to SiF_4. Boron may be removed from the precipitate before the HF treatment by conversion to trimethoxyborane, $(CH_3O)_3B$, using HCl saturated methanol. The boron may then be driven off by volatilization at 80-85°C.

During silica dehydration, coprecipitation of boron may be avoided by adding glycerol followed by coagulation with gelatin.[54] Glycerol dehydration or gelatin coagulation may also be used when boron is not a problem. Addition of glycerol obviates the evaporation to total dryness. Dehydration with perchloric acid also eliminates the evaporation to final dryness, but the problems of the occasional perchlorate explosion are well known.

Separation of silica from mixtures containing fluorine requires care lest SiF_4 be lost; hot acid solutions should be avoided. Berzelius[55] first separated silica from fluoride by precipitation of zinc silicate from alkaline solution, then converted the precipitate to SiO_2 by HCl dehydration. Shell and Craig[56] have simplified this procedure. Precipitation of mercuric silicate also has been used, but represents no improvement.[57] The fluoride may be complexed with Al^{3+}, Mg^{2+}, or boric acid to prevent formation of SiF_4. Simply adding sufficient aluminum chloride to the solution before acid dehydration will allow SiO_2 to precipitate without fluoride interference.[58]

Silicon may be precipitated as the silico-fluoride — commonly K_2SiF_6. Some analytical procedures are based on the titration of this precipitate with alkaline solution.[59] Barium has also been used to precipitate the silicofluoride but barium fluoride is almost always included in the precipitate.

Silicon has been precipitated from dilute alkaline solution (pH 10) as CaH_2SiO_4.[60] Other precipitation separations are based on the conversion of silica to silicomolybdate and precipitation by oxine,[43] quinoline,[61] pyridine,[62] pyramidone,[63] or hexamine.[64] These precipitations must be performed with close attention to details of procedure if yield is to be determined by weighing. The precipitates are liable to suffer from phosphate, vanadate, or arsenate contamination, and may also carry down some molybdenum. Proper drying is critical for heteropolymolybdates because of the high degrees of hydration. The advantage of these precipitates

lies in the very large molecular weight per silicon atom; impurities tend to be swamped out by the mass of the precipitate.

Tungsten can be separated from silicon by making the SiO_2 dehydration in dilute hydrochloric acid or by dissolving the precipitated tungstic acid in ammonia.[65] A sulfuric acid dehydration of silica will assist in separating SiO_2 from iron.[66] Tin is best separated from silica by an HCl dehydration, since sulfuric acid or perchloric acid form insoluble compounds of tin. Lead can be separated by dehydrating with sulfuric acid and then extracting the lead sulfate with ammonium acetate or ammonium chloride. 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.[67]

Specific separations of silicon from aluminum alloys,[68,68] steels,[69,70] uranium, vanadium, nickel,[71] iron ore, iron,[69] and organosilicon compounds[72] have been reported in the literature. Each one of these methods uses a precipitation-dehydration technique followed either by volatilization of SiF_4 or by colorimetric determination of silicon.

2. Scavenging

Silica can be removed from solution by hydroxide scavenge, but it carries many other elements along with it. This treatment has long been used in water treatment systems: ferric ion added to water will precipitate — especially if followed by a small amount of base — carrying down many impurities. Ferric hydroxide will not scavenge silica effectively at pH less than 4. Above pH 6, the ferric hydroxide precipitate scavenges well and settles fairly quickly. At pH less than 3, silica will slowly desorb from ferric hydroxide but the precipitate does not redissolve appreciably above pH 2. At a Fe:Si mole ratio of 2:1 or less, an orange colloid forms, making the separation ineffective. At mole ratios greater than 4:1, the scavenge is essentially complete.

Aluminum hydroxide is similarly effective as a scavenger. Many other oxide or hydroxide precipitates also work, but Al and Fe are most common.

Filtering off the voluminous hydroxide precipitate is quite inconvenient, while waiting for it to settle can be prohibitively slow. The Honda Column[73] avoids these disadvantages. Honda first loaded cation

exchange resin with ferric ion, then passed ammonium hydroxide through the resin to precipitate ferric hydroxide in a monomolecular dispersion, carried on and in the beads of resin. Extraction of silica by this column is quantitative only during the first 10-20 column volumes; after that, extraction efficiency becomes sensitive to flow rate and total solution volume. In extraction of silica from natural waters, complete recovery is usually unnecessary; the collection of 20-100 g SiO_2 is satisfactory, provided that the extraction efficiency is known or that only the specific activity is determined.

The silica may subsequently be eluted by repeated recycling of dilute acid of pH ~2 through the column,[69] or by rinsing with ammonium molybdate solution at about pH 5.[74] Details of the latter procedure are yet to be worked out.

Substances other than cation exchange resin may serve as carriers for the ferric hydroxide: spongin sponges and jute have been used successfully.[75]

3. Volatilization

The same reaction used in gravimetric silica analyses to determine silica by loss in weight can be used to purify silica by distillation from the other elements,[76] $SiO_2 + 4HF \rightarrow SiF_4\uparrow + 2H_2O$. The distillation is not rapid in the presence of large amounts of Al, Zr, B, nor from gelatinous SiO_2 but is usually effective with all substances which may be decomposed or dissolved by H_2SO_4 or $HClO_4$. Normally the solution temperature is held at 135°C, but from sulfuric or phosphoric acids, distillation temperature may go up to 165°C. Carryover of acid is one limitation on the purification; volatility of some fluorides is another; presence of complexing ions (Al^{+3}, borate, Ca^{+2}) is yet a third problem. Precipitation of solids, especially chlorides, late in the distillation tends to cause bumping.[77] Use of N_2 as a carrier gas speeds the distillation and reduces bumping.[78]

An adaptation of this technique was used by Mullins and Leddicotte[79] in the determination of trace silicon in metals. Volatilization of SiF_4 can achieve complete separation of silicon from specimens containing Fe, Sr, Co, Se, Cr, Ba, Zr, Nb, Zn, Sb, As, Ru, Cs, Mn, Sc, Ta, and W. Pure SiO_2 precipitate was obtained by dehydration of the distillate in concentrated H_2SO_4.

Holt[80] separated micrograms of silica from uranium, plutonium, steels, or phosphoric acid by distilling SiF_4 into a solution of boric and molybdic acids. He then determined the yield colorimetrically. Ehrlich and Keil[81] made a similar distillation from Al_2O_3 and Hozdic[82] from minerals.

4. Solvent Extraction

Amongst the water soluble silicon compounds, only the heteropoly acids are known to separate by solvent extraction. At acidities less than 1M, phosphomolybdate or arsenomolybdate may be extracted into a number of solvents, such as isoamylacetate or into isoamylacetate + 17% alcohol, leaving silicomolybdate in the aqueous phase. The esters are the most selective solvents.

At acidities above 2-3M, silicomolybdic acid extracts easily into diethyl ether[83] or ethyl acetate.[47,48] Silicotungstic acid also extracts under these concentrations.[49] Under less acid conditions isobutanol will extract both phospho- and silicomolybdic acid, but several extractions are necessary for complete removal from the aqueous phase. Wadelin and Mellon have reviewed some of the literature on solvent extraction of the heteropoly acids, but generally overlook the importance of acidity.[46]

Bock and Herrmann[84] have shown that less than 0.1% Si^{+4} is extracted from a 20M HF aqueous solution with ethyl ether while Nb^{+5}, Ta^{+5}, and Re^{+7} are more than 50% extracted; 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} are partially extracted. Silicon (as well as Sn^{+4}, Ti^{+4}, Mn^{+2}, Zr^{+4}, and Hf^{+4}) does not extract into diisopropylketone from a mineral acid-hydrofluoric aqueous solution (6M HCl - 0.4m HF).[85]

5. Chromatography

Silicates have been separated from borates and molybdates in an atmosphere saturated with 5% HCl in 2-butanone[86] by use of 5% conc. HCl in acetone as a solvent. The silicate ions did not move, whereas the molybdate and borate ions were eluted in that order. Isopropanol-water-acetic acid solvents have been used to separate oligosilicic acids.[87] Chromatography is often used in separation of organosilicon compounds.

6. Ion Exchange

Silicic acid is removed by mixed-bed ion-exchange water purifiers. Strongly basic resin in hydroxide form is the effective agent, reducing the silica concentration to less than 1μM when the resin is fresh. Silica is one of the earliest substances to break through, however; columns used for removal of silica must be discarded much earlier than is necessary for removal of other, more abundant impurities in tap water. Weakly basic anion exchangers are not effective in silica removal. In acid solutions the formation of silicate ions is reduced and the uptake is not as effective.[88]

Silica is even more efficiently removed by strong anion exchangers (in chloride form) if $Si(OH)_4$ is first converted to silicofluoride by addition of HF to a concentration of 7.5 mM (assuming no other fluoride complexes form).

C. Dissolution of Samples Containing Silicon

When acids are used to solubilize siliceous materials, precipitation of silica usually results.[89]. Possible losses of silicon as SiF_4 can occur, depending upon the types of materials being put into solution. Silicon, silicon alloys, and silicides are usually solubilized by an acid mixture of either HNO_3-HF or $HClO_4$-HF. In such an acid attack, the solution should be dilute in HF and held at room temperature (or lower) in order to prevent the escape of fluosilicic acid by distillation.

Sodium peroxide fusion is another common means of solubilizing either silicon, ferrosilicon, or molybdenum disilicide. Presence of Na_2O_2 insures conversion of Si to silicate.[90]

Decomposition of volatile and organic silicon compounds is frequently achieved by hydrolysis; some other compounds must be decomposed in a nickel bomb containing excess potassium metal and Na_2O_2. Possible effects of fluorine and boron must be anticipated when these elements are present. Rochow[91] has developed a procedure for combustion of silicones in a stream of O_2. Shell[61] has reviewed these procedures briefly.

Hillebrand[52] has an excellent review of procedures for dissolving silicate minerals and rocks. For those insoluble in acid, the Na_2CO_3 fusion is generally preferred. Other common fluxes are: mixtures of sodium and potassium carbonate; B_2O_3, $Na_2B_4O_7$, or a mixture of borate with Na_2CO_3; Na_2O_2; NaOH; or $CaCO_3$. Flame fusions with the carbonates are slightly reducing, so an electric muffle furnace is preferred when iron, lead, zinc, or other easily reduced metals are present. If borate is used, it will precipitate with SiO_2 and distill with SiF_4, hence must subsequently be separated.

Wherever possible, the alkaline fusion with Na_2CO_3 or Na_2O_2 should be used in the radiochemistry of silicon. The addition of silicon carrier, before dissolution will assist in achieving isotopic exchange of radioactive and stable atoms during the processing of the material. Using isotopically enriched stable silicon, it may even be possible, in some cases, to add carrier before irradiation.

D. Analytical Methods for Silicon Compounds

In the development of any radiochemical procedure, a number of analytical methods must be employed to monitor progress. Nearly all analyses of silicon are either gravimetric or colorimetric, applying chemical principles outlined in this monograph. Shell[51] gives a review of these methods and no further discussion is offered here.

Silicon may also be determined by atomic absorption spectroscopy, emission spectroscopy, or by neutron activation analysis. Silicon determination by atomic absorption is carried out with a neon-filled, high-brightness silicon lamp[92] using the 2516 Å wave length and an N_2O-acetylene flame. The detection limit is 0.1 ppm. This method has some advantages over the Hill method[70] for the analysis of silicon with a large amount of iron. A sample of steel is dissolved in H_2SO_4, boiled with persulfate, cooled, filtered and run with the atomic absorption spectrometer.[93]

In neutron activation analysis, the thermal neutron reaction Si^{30} (n,γ) Si^{31} or the reaction $Si^{30}(d,p)Si^{31}$ have long been used. The chemical procedures employed will be described in the following section.

Another activation procedure involves the reaction of 14 Mev neutrons to produce $Si^{28}(n,p)Al^{28}$. The latter reaction has the advantage of a 30-fold more abundant target isotope, and the use of Al^{28} gamma emission eliminates the necessity of chemical separations; however, there is a possibility of interference from $Al^{27}(n,\gamma)Al^{28}$ (thermal neutrons) or from $P^{31}(n,\alpha)Al^{28}$, and $Fe^{56}(n,p)Mn^{56}$, 1.80 Mev (by fast neutrons). The latter can be distinguished by half life. Using the fast neutron technique, analyses can be performed in less than 10 minutes with a precision of ±3% and an accuracy of ±5%; sensitivity of about 0.1 ppm is greater than can be obtained with the thermal neutron reaction.[94]

IV. SAFETY PRACTICES

Seldom will there be any need to create dangerous amounts of silicon radioactivity. Dangerous amounts of Si^{32} are almost impossible to make, and it is unnecessary and undesirable to create high levels of silicon-31 in neutron activation analysis. However, high levels of activity from other materials may be created in irradiations. No worker unfamiliar with radiological safety practices should handle the material from a neutron source or from an accelerator. 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[95] and in the International Atomic Energy Agency's publication on the "Safe Handling of Radioisotopes".[96] Similar sources of information are also usually available from any laboratory engaged in work with radioactive materials. It is important that such information sources be consulted in order to establish an operational procedure for safe handling of radioactive material.

Most non-radioactive silicon compounds can be handled safely. Toxicology of silicon compounds may be checked in Pieters and Creyghton[97] and in Sax.[98] Quartz or siliceous dust inhaled over a considerable length of time may cause silicosis — a sometimes fatal disease of the lungs. All silicate dusts should be avoided. Volatile compounds which hydrolyze to SiO_2 — e.g. silane, ethyl silicate — must not be inhaled. Inhalation or

ingestion of the fluosilicates must be avoided. Short exposure to small quantities may be serious. Hydrofluosilicic acid (fluosilicic) is similarly to be avoided.

V. RADIOCHEMICAL PRACTICES AND COUNTING TECHNIQUES

A. Silicon-31

Silicon-31 (2.62 h) was, for a long time, the only radioisotope of practical importance. It can be produced by thermal neutron activation of Si^{30} and it decays with the emission of 1.48 Mev beta and less intense (0.007%) 1.26 Mev gamma in coincidence with a 0.2 Mev beta. The gamma radiations are seldom measured, although gamma spectrometry might be utilized in the presence of very high activities. More commonly, the silicon is separated and counted by standard beta measurement techniques. The short half-life limits the value of this isotope as a tracer.

All separation procedures have employed silicon carrier, although the solvent extraction and chromatography methods would probably work carrier-free.

Procedure I

Source: Rudstam, G., Stevenson, P. C., and Folger, R. C., Nuclear Reactions of Iron with 340 Mev Protons, Phys. Rev. 87, 358-65 (1952).

This procedure employed precipitation of SiO_2 to separate Si^{31} from an iron target following bombardment by 340 Mev protons in the 184" synchrocyclotron. The time required was short and decontamination excellent.

Procedure:

1. Dissolve the target in 12 N HCl (or 3N HNO_3) and add $(NH_4)_2SiF_6$ carrier to the dissolving solution.

2. After solution is complete, bring down SiO_2 by addition of H_3BO_3 solution to complex the fluoride, followed by digestion with hot, concentrated H_2SO_4.

3. Wash the precipitate using a minimum of water, then dissolve in KOH.

4. Add a few milligrams of Ti^{+4} (a). Filter.

5. Add holdback carriers (Fe, Co, Cr, V, Y), then digest with HCl to precipitate SiO_2. Filter and wash.

6. Repeat the cycle.

7. Transfer the SiO_2 to a tared planchet and determine chemical yield, then count beta activity in a Geiger system.

Procedure 2

Source: Mullins, W. T., and Leddicotte, G. W., Silicon (Isotopic Carrier Precipitation) Method, Neutron Activation Analyses Method #5 11770, ORNL Master Analytical Manual.

The precipitation of SiO_2 has been used to separate Si^{31} from a number of substances (titanium,[99] zirconium) and related metals following neutron activation. The method achieves complete decontamination in 4 hours with 55-60% chemical yield.

Procedure - irradiation:

1. Wrap a test sample of at least 0.1 g metal in aluminum foil.

2. Separately wrap about 0.1 g of $(NH_4)_2SiF_6$ as a comparator sample.

3. Irradiate the known amounts of test and comparator in a thermal neutron flux of 1×10^{13} n/sec/cm^2 for 2.5 hours (b).

Procedure - the test sample treatment:

1. Transfer the irradiated sample to a plastic container and add a known amount of silicon carrier (as 1.0 ml Na_2SiO_3 solution, approximately 0.6 M).

2. Dissolve the sample in 5 ml H_2O, 0.2 ml 19 M NaOH (c), followed by 0.5 ml conc. H_2SO_4 and 0.2 ml conc. HF. Do not use glass with HF present.

(a) $Ti(OH)_4$ precipitation is intended to scavenge contaminant radionuclides from solution. Care should be taken that it does not also scavenge silica.

(b) With this flux the sensitivity of the method allows detection of 0.2μg of Si. Better sensitivity is achieved with higher fluxes.

(c) NaOH is added to complex the SiF_4 and prevent loss by volatilization.

3. Add 0.1 ml conc. HF every 15-20 minutes until solution is complete. About 0.5 ml conc. HF will dissolve 0.1 g titanium metal. Solution time is usually $1\frac{1}{2}$-2 hours (d).

4. When solution is complete, complex the fluoride ion with 10 meq. excess saturated $Al(NO_3)_3$. Transfer to centrifuge tube (glass will serve).

5. Cautiously add 15 ml conc. H_2SO_4, with stirring. Precipitate SiO_2 by bringing solution to a boil for 30 seconds over flame.

6. Cool and centrifuge. Wash SiO_2 twice with water.

7. Dissolve SiO_2 with 0.5 ml fresh saturated NaOH. Dilute to 10 ml with water and add 5 mg Fe holdback (e). Stir well and centrifuge.

8. Transfer supernate to another centrifuge tube and discard the $Fe(OH)_3$ precipitate.

9. Cautiously add 15 ml conc. H_2SO_4, with stirring. Precipitate SiO_2 by bringing solution to a boil for 1 minute over flame.

10. Cool and centrifuge. Wash the precipitate twice with 6 M HCl and filter on Whatman #40 paper.

11. Ignite in an electric muffle furnace at 1000°C for 30 minutes.

12. Mount the precipitate on a tared planchet and weigh to determine yield.

Procedure - comparator treatment:

1. After irradiation, quantitatively transfer comparator sample to a 50 ml volumetric flask and dissolve in 25 ml water. Add 5 ml of saturated $Al(NO_3)_3$ to complex F^- and dilute to 50 ml with water. Mix well.

2. Transfer 1.0 ml aliquot into a second 50 ml volumetric flask and dilute to volume with water. Mix well.

3. Transfer 1.0 ml of this solution into a 50 ml centrifuge tube and into it pipette exactly 1.0 ml silicon carrier solution. Mix well.

4. Dilute the mix with 5 ml water and add 15 ml concentrated H_2SO_4.

5. Continue from Step 9 in test sample procedure.

(d) Zirconium metal may be similarly dissolved; most other metals are dissolved by acid solution or alkali carbonate fusion. Omit HF if possible.

(e) This step will result in the loss of some SiO_2 by $Fe(OH)_3$ scavenge.

Procedure - measurement of activity:

1. Count the 1.47 Mev beta in a geiger counter. Repeat the measurement about every half hour to establish purity through the decay rate.

2. Extrapolate the Si^{31} component of the activities back to time when irradiation ended.

3. Adjust observed activities for respective chemical yield based on known SiO_2 carrier added, compared to weight of SiO_2 in counter.

4. Adjusted activity ratio is equal to the weight ratio of silicon in the two samples.

Procedure 3

Source: Mullins, W. T. and Leddicotte, G. W., "Silicon (Isotopic Carrier-Distillation-Precipitation) Method", Neutron Activation Analysis Method #5 117701, ORNL Master Analytical Manual.

Silicon may be distilled from Zr, Nb, Be, Al, W, and ammonium paratungstate as the fluoride following production of Si^{31} by neutron activation. Separation requires 2.5 hours with a chemical yield of 55-60% and decomination $>10^6$.

Procedure - irradiation:

1. Wrap a test sample of at least 0.1 g metal in aluminum foil.

2. Separately wrap about 0.1 g of $(NH_4)_2SiF_6$ as a comparator sample.

3. Irradiate the known amounts of test and comparator in a thermal neutron flux of 1×10^{13} n/sec/cm^2 for 2.5 hours (f).

Procedure - the test sample treatment:

1. Transfer the irradiated sample to a distillation flask (g) and add a known amount of silicon carrier (as 1.0 ml Na_2SiO_3 solution, approximately 0.6M).

2. Dissolve the sample in 5 ml conc. HNO_3 and 2 ml conc. HF.

(f) With this flux the sensitivity of the method allows detection of 0.2μg of Si. Better sensitivity is achieved with higher fluxes.

(g) The distillation flask is a 250 ml high density polyethylene or polypropylene wide mouth bottle, capable of withstanding temperatures up to 120°C.

3. Connect the distillation flask as shown in Figure 5. Tubing should be 6 mm polyethylene about 50 cm long. The distillate trap is a 50 ml plastic tube containing 10 ml H_2O.

4. Bubble air or N_2 through the solution in the distillation flask. Lower the flask into a bath of boiling water and allow 5 minutes for dissolution of the sample.

5. From the H_2SO_4 dispenser add 20 ml of conc. H_2SO_4. Then remove the flask from the bath (caution: don't let the condenser tube come out of the trap fluid) and swirl to mix H_2SO_4 into the solution.

6. Lower the flask back into the bath and allow 10 minutes for distillation of SiF_4 into the trap.

7. When distillation is complete, remove the trap and transfer contents to a 150 ml beaker. Add 30 ml of saturated $Al(NO_3)_3$ to complex the fluoride. Mix well.

8. Add 30 ml conc. H_2SO_4. Mix well.

9. Bring the solution to a boil on a hot plate to precipitate SiO_2.

10. Transfer contents quantitatively to two 50 ml centrifuge tubes. Centrifuge and discard the supernate. Wash twice with water.

11. Dissolve SiO_2 with 0.5 ml fresh saturated NaOH. Dilute to 10 ml with water and add 5 mg Fe holdback (h). Stir well and centrifuge.

12. Transfer supernate to another centrifuge tube and discard the $Fe(OH)_3$ precipitate.

13. Cautiously add 15 ml conc. H_2SO_4, with stirring. Precipitate SiO_2 by bringing solution to a boil for 1 minute over flame.

14. Cool and centrifuge. Wash the precipitate twice with 6 M HCl and filter on Whatman #40 paper.

15. Ignite in an electric muffle furnace at 1000°C for 30 minutes.

16. Mount the precipitate on a tared planchet and weigh to determine yield.

Procedure - comparator sample treatment:

1. After irradiation, quantitatively transfer comparator sample to a 50 ml volumetric flask and dissolve in 25 ml water. Add 5 ml of

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(h) This step will result in the loss of some SiO_2 by $Fe(OH)_3$ scavenge.

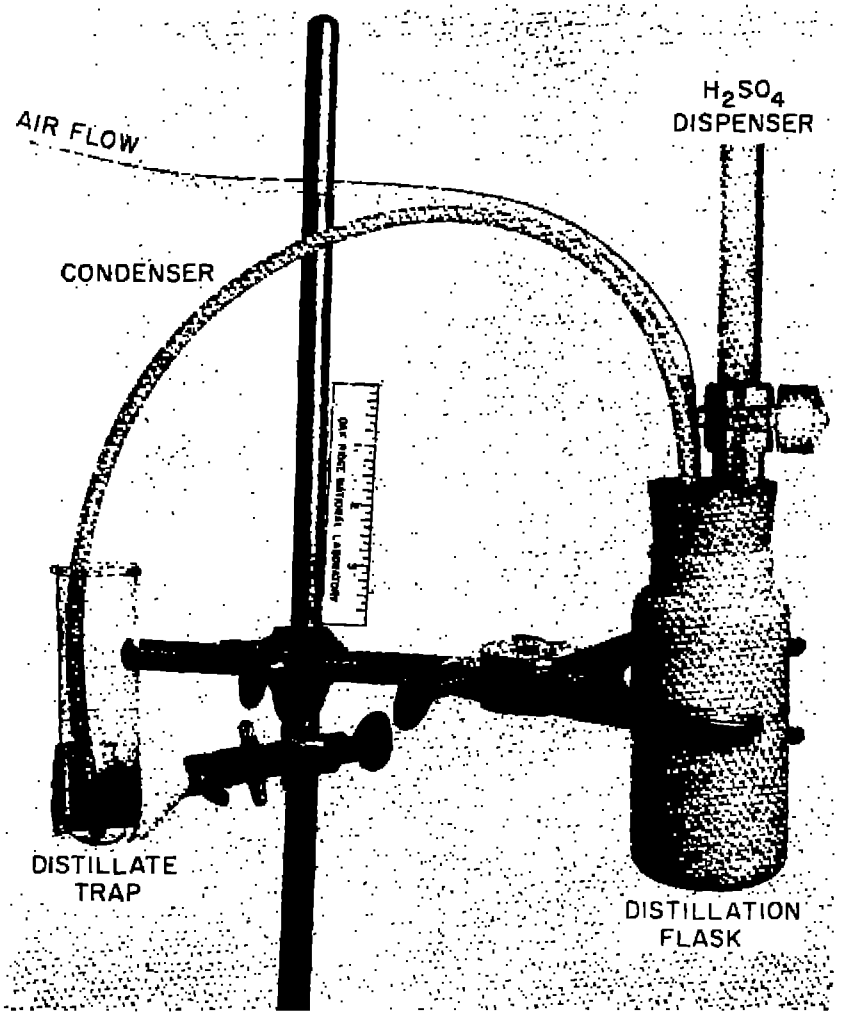

Figure 5. Apparatus for Distillation of Silicon Tetrafluoride

saturated $Al(NO_3)_3$ to complex F^- and dilute to 50 ml with water. Mix well.

2. Transfer 1.0 ml aliquot into a second 50 ml volumetric flask and dilute to volume with water. Mix well.

3. Transfer 1.0 ml of this solution into a 50 ml centrifuge tube and into it pipette exactly 1.0 ml silicon carrier solution. Mix well.

4. Dilute the mix with 5 ml water and add 15 ml concentrated H_2SO_4.

5. Cautiously add 15 ml conc. H_2SO_4, with stirring. Precipitate SiO_2 by bringing solution to a boil for 1 minute over flame.

6. Cool and centrifuge. Wash the precipitate twice with 6 M HCl and filter on Whatman #40 paper.

7. Ignite in an electric muffle furnace at 1000°C for 30 minutes.

8. Mount the precipitate on a tared planchet and weigh to determine yield.

Procedure - measurement of activity:

1. Count the 1.47 Mev beta in a geiger counter. Repeat the measurement about every half-hour to establish purity through the decay rate.

2. Extrapolate the Si^{31} component of the activities back to time when irradiation ended.

3. Adjust observed activities for respective chemical yield based on known SiO_2 carrier added compared to weight of SiO_2 in counter.

4. Adjusted activity ratio is equal to the weight ratio of silicon in the two samples.

B. Silicon-32

This isotope has seldom been used because of the difficulty in obtaining significant amounts. The production by cosmic rays in the atmosphere yields a detectable amount and the number of measurements in natural waters, ice, and air is growing. Much radiochemistry of silicon-32 concerns the collection of very dilute silicon activity from large samples. The redeeming feature of the very dilute Si^{32} is its decay to P^{32} (1.7 Mev beta emitter, 14 day). This allows measurement -- by milking the phosphorus daughter -- of silicon-32 in very low specific activity samples. Activities as low as 0.003 dpm/ton of sea water have been measured, and determination of a few dpm per kilogram of silicon is quite feasible. Naturally, very

low background counting techniques are employed[100] and excellent radiochemical purity is required.

Using the low background counting systems now commercially available, Si^{32} can become a useful tracer for a variety of chemical, geochemical, and industrial applications. The isotope deserves much greater attention.

Because Si^{32} radiochemistry involves the extraction and purification of P^{32}, much of the information on these techniques is to be found in the monograph on Radiochemistry of Phosphorus.[101] Only an outline of the common P^{32} milking and purification procedure is included here. For a more complete treatment the reader should consult the phosphorus monograph.

In geochemical applications -- currently the major utilization of the isotope -- the primary problem is concentration of Si^{32}. Although some rather unorthodox "radiochemistry" is involved, these concentration procedures are an important part of the total method for measurement of Si^{32} in natural systems, and they are, therefore, included in this section.

A number of other silicon-32 procedures have been employed, usually on a "one time" basis. Some of these are not well worked out, but they are included here under the heading, "Special Methods", as examples of what may be done.

Special Method 1

Source: Lindner, M., New Nuclides Produced in Chlorine Spallation, Phys. Rev. 91, 642 (1953).

To determine the presence of silicon-32 in a sodium chloride target following 340 Mev proton bombardment, remove P^{32}, precipitate SiO_2 carrier, and count Si^{32} and P^{32} growth. No decontamination from Si^{31} except by time, other decontamination factors and chemical yield unknown.

Procedure:

1. Wrap 5 g NaCl in aluminum foil and bombard in high energy (340Mev) high flux proton beam. (Si^{32} formation cross section ~5 mb.)

2. Allow the short lived activities to decay out.

3. Dissolve the sodium chloride in water. Add Fe^{+3} and precipitate with NaOH (j).

(j) These ferric hydroxide scavenges will seriously diminish the final yield due to silica scavenging by the $Fi(OH)_3$. This procedure is not recommended.

4. Filter the solution, discarding the precipitate.

5. To solution, add 1 mg Si as $(NH_4)_2SiF_6$, followed by conc. H_2SO_4. Heat to fumes of SO_3.

6. Cool and dilute to 10N H_2SO_4. Filter off the gelatinous precipitate.

7. Dissolve the SiO_2 in NaOH and make several $Fe(OH)_3$ scavenges, discarding the precipitate (j).

8. Add HCl to bring the solution to 6N acid.

9. Add 1 mg phosphorus as H_3PO_4. Follow with Zr^{+4} to precipitate zirconium phosphate; filter and discard precipitate.

10. Heat the filtrate with concentrated H_2SO_4 until fumes of SO_3 are evolved.

11. Filter the SiO_2 precipitate, wash and mount for beta counting in a Geiger system.

12. A few hours bombardment will produce Si^{31} activity about 10^8 greater than Si^{32}, but the shorter half life removes it in several days. Si^{32} decay is masked by P^{32} within several days after phosphorus removal.

Special Method 2

Source: Roy, L. P., and Yaffe, L., Search for Successive Neutron Capture Reactions on Mg^{28}, Si^{30}, and Cr^{54}, Can. J. Chem. 35, 176-79 (1957).

To discover silicon-32 in neutron irradiated quartz, the silica was precipitated repeatedly, then set aside for P^{32} buildup. Phosphorus was precipitated with zirconium, and converted to $MgNH_4PO_4$. The yield and time required are not given, but a decontamination factor of 10^8 is claimed.

Procedure:

1 1. Seal samples of spectroscopically pure silica (enriched in Si^{30}) in a quartz ampoule.

2. Irradiate in a high neutron flux for a few weeks (k).

3. Dissolve the silica in boiling 6N NaOH.

4. Treat solution with 6N HNO_3 and evaporate to dryness to precipitate SiO_2.

(k) This irradiation produced less than 5 cpm.

5. Take up in HNO_3 (dilute) and centrifuge.

6. Evaporate supernate to recover additional SiO_2.

7. Repeat the Steps 3 - 6 many times, then add a known amount of phosphorus carrier and let sample stand 4 - 6 weeks.

8. Dissolve the silica and precipitate zirconium phosphate.

9. Dissolve zirconium phosphate in HF and scavenge the solution repeatedly with lanthanum fluoride and arsenic sulfide precipitations.

10. Precipitate phosphorus as ammonium phosphomolybdate, then convert to zirconium phosphate.

11. Repeat 9 - 10 many times.

12. Convert zirconium phosphate to Mg NH_4PO_4.

13. Count P^{32} with geiger counter.

Special Method 3

Source: Geithoff, D., Uber die Herstellung von Si^{32} durch einen (t,p) - Prozess. Radiochimica Acta 1, 3-6 (1962).

Si^{32}, prepared by (t,p) reaction on lithium silicide, can be separated from the target by SiF_4 distillation and SiO_2 precipitation. Chemical recovery is about 50%, but decontamination is very good.

Procedure:

1. Place lithium silicide, Li_2Si, in a neutron flux of 2×10^{13} $n/cm^2/sec$ for 24 days. The neutrons produce tritons when interacting with lithium. The tritons react with the natural Si^{30} to produce Si^{32}.

2. Wait about 7 months for undesirable activities to decay out (especially Si^{31}). Substantial contaminant activities will remain, however.

3. Transfer the lithium silicide to a stainless steel reaction vessel (Figure 6) and add CaF_2 and conc. H_2SO_4.

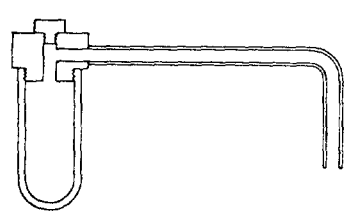

Figure 6. Stainless Steel Reaction Vessel

4. Heat strongly for about 60 minutes to distill over SiF_4.

5. Collect the SiF_4 in a water filled container. Add NH_4OH + NH_4Cl solution to precipitate SiO_2.

6. Filter the precipitate and repeat the distillation, carefully avoiding carry-over or back-transfer.

7. Again precipitate with the buffered alkaline solution, filter the SiO_2, wash and ignite.

8. To observe Si^{32} activity directly, mount the SiO_2 for counting in a proportional counter. The weak Si^{32} beta activity will encounter substantial self-absorption in this sample.

9. The P^{32} growth can be observed in the SiO_2 directly by covering the sample with a 40 mg/cm^2 Al absorber.

10. P^{32} can be separated, with phosphorus precipitated as $MgNH_4PO_4$, and counted in this form.

Special Method 4

Source: Honda, M. and Arnold, J. R., Radioactive species produced by cosmic rays in the Aroos meteorite, Geochim. et. Cosmochim. Acta 22, 219 (1961).

The cosmic ray productions of Si^{32} in an iron meteorite may be determined by separation of various major elements, and precipitation of SiO_2. Decontamination was excellent; recovery was 40%.

Procedure:

1. Wash the meteorite (250 g) with acetone, 0.1 M HNO_3 and water.

2. Place it in 5 l flask and add acid: first 3 M HNO_3; then 9 M HNO_3. Solution takes about three hours and 16 moles of acid.

3. Filter through a glass filter. Final volume 2.5 l, residue 3 g.

4. Add 40 mg Si carrier as Na_2SiO_3 solution (0.2 mg/ml) by pouring slowly into the cold solution with continuous stirring.

5. Reduce volume to 1 liter by evaporation in a Vycor dish.

6. Saturate the cold solution with gaseous HCl and repeat evaporation.

7. Add 800 ml conc. HCl to 700 ml solution.

8. Solvent extract iron in four steps using a total of 1.8 liter isopropyl ether.

9. Eliminate ether from solution by heating over a hot plate.

10. Pass the solution through a 700 ml column of Dowex 1 (anion exchanger) which has been previously washed with 9 M HCl.

11. Wash the column with 550 ml of 9 M HCl.

12. If a colorless gelatinous precipitate is found in the eluant, filter off and combine with SiO_2 from Step 23

13. Evaporate filtrate and washings to 300 ml -- reducing HCl content.

14. Dilute to 800 ml and neutralize with excess NH_4OH.

15. Digest and filter off the grey hydroxide precipitate.

16. Add 100 mg of Fe^{+++} to the filtrate and filter off the hydroxide precipitate.

17. Combine the precipitates and dissolve in 100 ml of 1 M HCl + 0.2% H_2O_2.

18. The reddish brown solution contains most of the silica, iron, phosphate, Ni, Mn, V, and others.

19. Pass the solution through 50 ml of Dowex 50 (cation exchanger) in the acid form. Follow with 75 ml 1 M HCl.

20. Silica and vanadium (red) will be in this first fraction. Add 4 mg Fe^{+++} and heat with excess Na_2O_2. Then filter. The filtrate will be yellow from a small fraction of chromate, and also will contain vanadium and most of the silica.

21. Acidify and reduce the solution with Na_2SO_3. Form vanadium cupferrate[52] and extract into $CHCl_3$.

22. Extract the perchromate from the oxidized aqueous layer of the cupferrate extraction, using ethyl acetate.[102]

23. After the perchromate extraction, evaporate the aqueous solution and treat with conc. HCl. Filter off SiO_2.

24. Combine the SiO_2 with the precipitate from Step 12. Fuse with Na_2CO_3 and reprecipitate from acid solution.

25. Again fuse with Na_2CO_3. Take up in acetic acid. When CO_2 evolution is complete, pass through 10 ml cation exchange column (acid form).

26. Add a few ml H_2SO_4 and 5 mg H_3PO_4 holdback carrier. Evaporate to precipitate SiO_2.

27. Filter, ignite, weigh, and mount for counting.

28. Measure P^{32} activity as it grows into the sample.

Special Method 5

Source: Brodzinski, R. L., Finkel, J. R., Conway D. C., β-spectrum of ^{32}Si, J. Inorg. Nucl. Chem. 26, 677-81 (1964).

To determine the decay energy of Si^{32} produced by proton spallation from NaCl, the silicon was converted to $Si(C_2H_5)_4$ by Grignard reagent and counted in a liquid scintillation spectrometer (1). Chemical yield and decontamination factors were not reported.

Procedure:

1. Pass HCl into a saturated solution of NaCl to precipitate the salt.

2. Mount 0.3 g of the NaCl precipitate between aluminum foils with 1 cm^2 target area and irradiate with 420 Mev protons.

3. Several months later, dissolve the sample in 0.5 ml of 6N NaOH. Add 16 mg SiO_2 (as Na_2SiO_3) to the dissolving solution (m).

4. Add 0.1 g P_4, S_8, PO_3^{-3}, SO_3^{-2}, and extract the elements with CS_2.

5. Oxidize the holdback carriers to PO_4^{-3} and SO_4^{-2} with $Na_2S_2O_8$ in H_2SO_4, then precipitate SiO_2 with conc. H_2SO_4.

6. Dissolve the SiO_2 in NaOH and repeat Steps 4 - 5 several times.

7. Dissolve SiO_2 in 30% HF (in platinum). Add stoichiometric amount of KF to precipitate K_2SiF_6.

8. Evaporate to dryness on hot plate.

9. Grind sample with carrier Na_2SiF_6.

10. Convert the silicofluoride by Grignard reaction to $Si(C_2H_5)_4$ using C_2H_5MgBr as the Grignard reagent.

11. When reaction is complete, add the mixture to 75% H_2SO_4 solution and extract with benzene to separate $Si(C_2H_5)_4$ from the ether solvent.

12. Strip off most of the benzene by fractional distillation to 110°C.

13. The residual liquid containing $Si(C_2H_5)_4$ (bp 153°C) is distilled from the solid by vacuum distillation (n).

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(1) Ronzani and Tamers[104] used $SiCl_4$ for liquid scintillation counting of Cl^{36} which would seem to be a better procedure.

(m) At this point the expected impurities were only P^{32}, P^{33}, S^{35}.

(n) After several days the solution became cloudy and a dark precipitate formed. Redistillation seemed to solve the problem.

14. After two years, purify the $Si(C_2H_5)_4$ by gas liquid chromatography. Verify the sample peak by infrared spectrum[103] on similarly treated inactive silicon.

15. Count the sample by liquid scintillation spectrometry. About 10.6 ml of silicon tetraethyl is diluted by toluene containing 0.4% POP and 0.005% POPOP.

Special Method 6

Source: Jantsch, K. Reaktionen von Tritonen mit ^{30}Si. Kernenergie 9,, 127-132 (1966).

In a study of Si^{32} production, it was required to separate silicon from targets of Li_4Si_2 alloy, Li_2SiO_3, phosphorus, or sulfur.

Procedure:

1. Irradiate targets for about 100 hours, monitoring flux with Au^{198} and Co^{60}.

2. Remove targets and wait three months for contaminant activities to die out.

3. For phosphorus and sulfur targets:
   a. dissolve in concentrated HNO_3.
   b. normally the slight impurities initially present in the target will contain enough silicon to obviate carrier addition.
   c. coprecipitate SiO_2 with gelatine from H_3PO_4/HNO_3; or completely evaporate H_2SO_4/HNO_3 and recover SiO_2 from residue.

4. For Li_4Si_2 alloy targets:
   a. dissolve in 5N NaOH
   b. evaporate with HCl to precipitate SiO_2.

5. For Li_2SiO_3:
   a. decompose in Na_3CO_3/K_2CO_3
   b. evaporate with HCl to get SiO_2.

6. The SiO_2 from 3, 4, or 5 can be repeatedly dissolved and reprecipitated to enhance the purity.

7. Final purification is achieved by mixing the SiO_2 with CaF_2/H_2SO_4 in plastic and distilling SiF_4 at 100°C.

8. Pass the SiF_4 into NaOH and recover the Si as SiO_2 with $(NH_4)_2CO_3$.

9. The final SiO_2 is extremely pure. Measurement of Si^{32} is by P^{32} daughter in the standard way.

COLLECTION METHOD 1

Source: Lal, D., Goldberg, E. G. and Koide, M., Cosmic Ray Produced Silicon-32 in Nature, Science 131, 332 (1960).

The simplest and perhaps most ingenious technique for concentrating SiO_2 from sea water is to collect and analyze the siliceous skeleton of sponges growing at the sea floor in the water of interest.

Procedure:

1. Clean sponges of organic matter and foreign material not incorporated in the opaline structure by digestion in HNO_3.
2. Wash repeatedly with water and acetone.
3. Grind the sample and dissolve in 50% NaOH, with heating. Add H_2O_2 to complete decomposition or organic matter.
4. Treat any insoluble residue with H_2SO_4 and heat to near dryness. Take up in HNO_3 and add this to the acid solution formed during SiO_2 + NaCl precipitation (see Standard Milking, Purification and Counting section).

COLLECTION METHOD 2

Source: Schink, D. R., Measurement of Dissolved Silicon-32 in Sea Water, Thesis, Univ. of Calif., San Diego (1962).

Dissolved silica can be extracted from sea water using a Honda column to perform the ferric hydroxide scavenge. Water may be processed at 200 liters/min with 50-80% recovery, but a considerable amount of special equipment is needed.

Equipment:

1. A deionizer tank 75 cm in diameter and 150 cm high, rubber or plastic lined with polyvinyl chloride slotted pipe collector system at the bottom and a spreader system at the top. Figure 7 shows the extractor equipment schematically. The resin bed is supported by a graded bedding of acid resistant silica free material; acid leached, Alundum tumbling abrasive was used. The tank is filled with 300 liters of Dowex 50-X4 (50-100 mesh) in acid form. The associated piping and valves are polyvinyl chloride (mostly 1½").

2. A pump capable of moving 200 liters/min at pressures up to 5 kg/cm^2 (70 psi) is required. An electric motor of about 7 HP is required to drive the pump. Most ships can furnish D.C. more readily than A.C. for driving such a motor.

3. A flowmeter is useful to monitor the total through-flow.

4. Also needed are suction hose (5 cm diameter) for sample pickup and discharge hose (3.7 cm) for disposing of the water overboard.

5. A stainless steel or plastic pump capable of handling 40 liters/min is needed for column elution and subsequent sample handling. Garden hose and plastic fittings are also necessary.

6. Polyethylene drums (200 l) are required for holding (closed head drums) and processing (open head drums) the eluant solutions.

7. A canoe paddle serves as a stirring rod for the 200 liter drums.

Procedure:

1. Soak a sample of the ion exchange resin in dilute (1%) HCl for 8 hours and test for release of silica. If serious release occurs, soak the resin in dilute HF before making up the column.

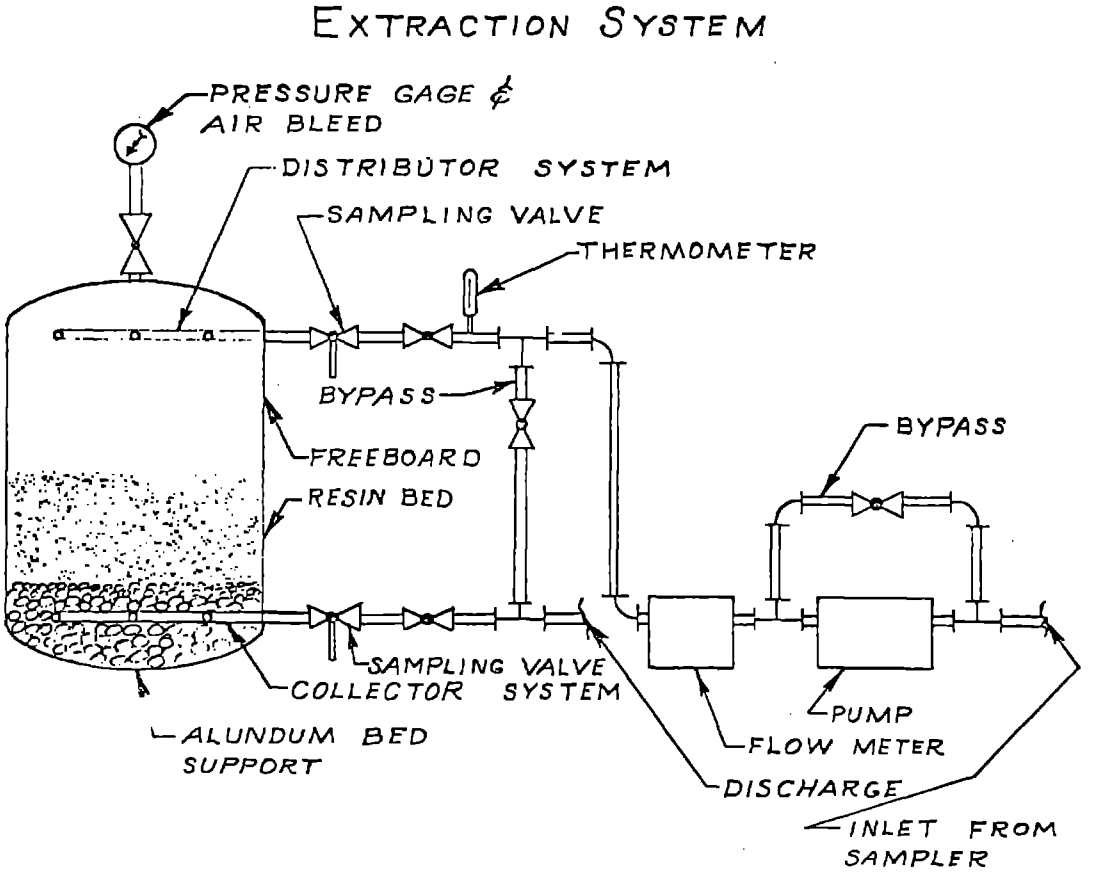
EXTRACTION SYSTEM
PRESSURE GAGE & AIR BLEED
DISTRIBUTOR SYSTEM
SAMPLING VALVE
THERMOMETER
BYPASS
FREEBOARD
RESIN BED
BYPASS
SAMPLING VALVE
COLLECTOR SYSTEM
ALUNDUM BED SUPPORT
PUMP
FLOW METER
DISCHARGE
INLET FROM SAMPLER

FIGURE 7

2. Fill deionizer tank with 200 liters of resin. Rinse resin with distilled water, then pump in 400 liters of 2.5 M ferric chloride solution at the rate of 10 liters per minute, discard the effluent.

3. When iron solution has drained to the top of the resin bed, add 200 liters of distilled water at 10 liters/min.

4. When water has fallen to bed level pass 450 liters of distilled water through the column as rapidly as possible.

5. When water level has dropped to bed level add 200 liters of 2.5 M NH_4OH at 10 l/min. Drain to bed level.

6. Rinse column with 200 liters of 0.7 NaCl solution and drain to bed level, then pump 200 liters of salt solution in through the bottom of the column to stir the bed. Drain rapidly to 2-5 cm above bed level.

7. Seal tank entrances.

8. Start the large pump moving water through bypass line to overboard discharge. Flush with 800 liters of water.

9. Open tank inlet and outlet and close the column bypass. Vent air through tank head until column is full. Regulate pressure and/or flow rate by pump bypass valve.

10. Repeatedly collect 50 ml portions inflowing and outflowing water during sample processing to determine column efficiency.

11. When sample processing is complete, drain water to bed level, rinse column with 200 liters distilled water and discard rinse, begin elution immediately.

12. Pass in 200 liters of 1% HCl (.12 M). Collect effluent from the tank and return to top of column by elution pump.

13. Circulate dilute acid at approximately 40 l/min adding conc. HCl to hold pH about 1.5 at the top of the tank. When pH of effluent is the same as pH at the tank top, silica desorption will begin. Also some iron will go into solution.

14. Continue acid circulation for several hours, collecting samples for silica analysis (Methods: Hill, etc.[70]). Eluant solution can carry only about 30 grams SiO_2; if more is on the column, additional eluant will be required. When no further silica is entering solution, drain the eluant, analyze final volume and compare with amount on the column based on IN and OUT samples during processing. After elution, rinse column with 200 l of 1% HCl and add rinse to the eluant.

15. The eluant is most conveniently held in closed-head drums (which originally carried reagents) until returned to laboratory for further treatment.

16. Regenerate column for next sample by repeating steps 5 - 7. Occasionally more iron solution must also be added to replace the small amount washed off during elution.

17. Transfer the eluant to open head drums. Add Fe^{+3} if necessary to bring Fe:Si ratio up to 10. (Iron addition may be avoided by making the solution 0.06 M in Ca^{++} and raising the pH to 10, thus precipitating CaH_2SiO_4.) Bubble in NH_3 until pH>8 (preferably 9). Stir and allow to settle overnight.

18. Decant supernate (by pump) and pump sludge onto a large filter cloth spread out over a receptacle or drain. Allow to drain overnight. Discard filtrate.

19. Collect ferric hydroxide in 20-40 liter plastic vessel and dissolve in conc. HCl.

20. Filter the solution. Discard the residue unless there is substantial gelatinous material.

21. Adjust HCl content of the solution by bubbling in gaseous HCl. Extract most of the iron by shaking with isopropyl ether. The ether may be washed free of iron by distilled water, then reused. (Normally, isopropyl ether extraction requires at least 6M HCl concentration, but the high chloride content of included salts reduces the acid level required. Optimum acidity is best established by trial extractions.)

22. After extraction, evaporate aqueous HCl solution to dryness. This is the most tedious step.

23. Take up the residue from evaporation in dilute HCl.

24. Filter the gelatinous SiO_2 through Whatman #54 paper and wash with 10% HCl.

25. Redissolve the precipitate in a minimum volume of conc. NaOH. Filter the solution.

26. Precipitate SiO_2 by bubbling in HCl while the solution is cooled in an ice bath.

27. Repeat steps 24-25. Store the solution for phosphorus milking.

COLLECTION METHOD 3

Source: Lal, D., Arnold, J. R. and Somayajulu, B. L. K., A Method for the Extraction of Trace Elements from Sea Water, Geochimica et Cosmochimica Acta 28, 1111-1117 (1964).

Extraction of silica from the upper layers of the sea can be achieved by towing $Fe(OH)_3$ loaded materials through the water. Attempts are underway to adapt this procedure to deep water.

Procedure:

1. Soak several kilograms of natural sponge (spongin) for about 12 hours in a solution of 10% HF plus 20% HCl to remove natural constituent silica.
2. Rinse. Then dip sponges in saturated ferric chloride solution.
3. Remove from ferric chloride solution, shake, and immerse in ammonium hydroxide.
4. Wash off excess ferric hydroxide. Load sponges into container which will allow free flow through of water while towing.
5. Tow for about 6 hours through water greater than 2μM in $Si(OH)_4$ (p).
6. Shake the sponges in distilled water if suspended matter is trapped on them.
7. Dip sponges in 1:1 HCl to dissolve $Fe(OH)_3$.
8. Discard sponge. Dehydrate the HCl solution to precipitate SiO_2.
9. Extract and purify silicon by standard methods.

(p) I have had only negative results with this method in the very low silica surface waters of the Atlantic. Lal, et al. report 0.66% SiO_2 per weight of sponge.

COLLECTION METHOD 4

Source: Kharkar, D. P., Nijampurkar, V. N. and Lal, D., The Global Fallout of Si-32 Produced by Cosmic Rays, Geochim. et. Cosmochim. Acta. 30, 621-31 (1966).

Silicon-32 can be extracted from rain and other fresh waters by ferric hydroxide scavenge.

1. With conc. HCl and distilled water, clean a wading pool or plastic lined tank capable of holding 3-5 thousand liters. To reduce dust input and evaporation loss, cover the tank with a plastic sheet tapered conically toward the center with a central opening of 20 cm.

2. Collect rain or other fresh water in the tank. Measure the volume, and compare with rain gauge to ascertain evaporation loss.

3. Extract an aliquot to determine stable silicon content.

4. Add carrier (Na_2SiO_3 solution) to raise SiO_2 content to 10 ppm (167μM). Mix well and check resultant concentration with another aliquot.

5. Add 125 g of iron (as $FeCl_3$) for each 1000 liters of water.

6. Add NH_4OH slowly with stirring to bring pH to 7. Wait one hour, then raise pH to 9.5. Stir vigorously.

7. Settle overnight.

8. Decant the clear layer by siphoning.

9. Filter the precipitate through a fine mesh filter cloth suitable for oil filtration.

10. Dry the precipitate and dehydrate repeatedly with HCl. Dissolve the iron in hot HCl (1:3) and filter off.

11. Dissolve crude SiO_2 in NaOH and reprecipitate with HCl. Repeat twice.

12. Dry SiO_2 at 800°C for 2 hours and determine recovery. Overall yield varies between 60-95% with the higher values more common.

STANDARD MILKING, PURIFICATION AND COUNTING TECHNIQUE

Sources: Lal, D., Goldberg, E. G. and Koide, M., Cosmic Ray Produced Silicon-32 in Nature, Science 131, 332 (1960).

Kharkar, D. P., Nijampurkar, V. N. and Lal, D., The Global Fallout of Si-32 Produced by Cosmic Rays, Geochim. et Cosmochim. Acta 30, 621-31 (1966).

Kharkar, D. P., Krishnaswami, S. and Schink, D. R., The Radiochemistry of Phosphorus, NAS-NS 3056 (1969).

This procedure is the one commonly used for determination of Si-32 in natural samples at the level of about 10 dpm/kg SiO_2. About two days is required to bring the sample to the counter. Decontamination is excellent and yields are about 75%.

Procedure - milking

1. The silica extracted from natural systems may contain P-32 at the time of collection. To clean it, add 25 mg H_3PO_4 to a NaOH solution of the silica. Precipitate SiO_2 by adding conc. HCl or HCl gas. Allow the solution and precipitate to digest for 30 minutes, then cool and filter through Whatman #54 paper on a Buchner funnel. A layer of glass wool between the funnel and the filter pad will speed filtration.

2. Dry the filtered silica under an infrared lamp, crush it in a mortar and wash with HCl.

3. Redissolve the silica in a minimum of conc. NaOH. Determine the phosphorus retained in the silica (Method: Chen, 1956[105]).

4. Add a known amount of phosphorus carrier as H_3PO_4 and set the solution aside for 1 - 3 months for P-32 buildup. Withdraw an aliquot to determine the SiO_2 present.

5. Reprecipitate SiO_2 with HCl. Hydrochloric acid will contain about 0.1 dpm P-32 per liter due to cosmic ray produced neutron reactions with the chlorine[108], hence special precautions should be taken. The HCl may be stored several meters underground for a month or two before use. Preferably, the HCl may be produced from gaseous HCl (stored underground) by bubbling the HCl first through a water (sat. HCl) bath. Fresh HCl should be prepared every few days.

6. Filter as in Step 1. Repeat Step 2. Combine the filtrate and the wash for phosphorus purification.

7. Repeat Steps 3 and 4 for subsequent remilking.

Procedure - phosphorus purification

A separation time of 48 hours is required for complete decontamination of the sample. Chemical recovery is 60-80%.

1. Evaporate solution nearly to dryness (q).

2. Remove NaCl by filtering. Wash the precipitate with conc. HCl on a sintered glass funnel.

3. Repeat 1 - 2 several times until NaCl almost entirely removed.

4. Add 50 ml (1:4) HNO_3. Heat the solution, cool and filter through Whatman #42 filter paper.

5. Neutralize the solution with filtered conc. NH_4OH. Then make slightly acid with 6N HNO_3.

6. Warm the solution to just 60°C and add one equal volume of warm molybdate reagent solution (100 g MoO_3 + 80 ml conc. NH_4OH in 400 ml water. Stir until dissolved. Filter and add filtrate slowly, with stirring, to a cold solution of 6N HNO_3. Filter just before use.)

7. Digest precipitate at 60°C for ½ hour, then allow to stand several hours.

8. Filter the precipitate through Whatman #42 and wash with 10 - 15 ml of 10% NH_4NO_3 solution.

9. Dissolve the precipitate by passing 20 ml 6N ammonium hydroxide through the filter paper. Wash with several portions of 1M NH_4OH, followed by warm dilute HCl.

10. To the final volume of less than 100 ml, add 1 drop methyl red indicator and neutralize with 6N HCl.

11. Add 5 ml 50% citric acid solution, followed by 15 ml magnesia reagent (50 g $MgCl_2 \cdot 6H_2O$ dissolved + 100 g NH_4Cl and slight excess of NH_4OH. Stand overnight. Filter if cloudy. Make slightly acid with HCl, then dilute to 1000 ml).

(q) Throughout evaporations to dryness, overheating (>150°C) should be avoided lest H_3PO_4 be lost or meta- and pyrophosphates formed[107].

12. Cool the solution in an ice bath. Then add cold conc. filtered NH_4OH dropwise with rapid stirring until a white precipitate forms. (Avoid scratching the beaker since precipitate adheres very firmly to scratches.)

13. When precipitate formation appears complete add 5 ml conc. NH_4OH and let stand in ice bath for 2 hours.

14. Filter the precipitate through Whatman #54 paper and wash with cold 1 M NH_4OH.

15. Dissolve the precipitate by passing 14 ml warm 3M HCl through the filter pad. Rinse pad with 50 ml warm 1% HCl.

16. Pass the dilute HCl solution containing phosphate through a 10 ml column of Dowex 50 (at 2-3 ml/min). Column must be pre-washed with conc. HCl, then dilute HCl.

17. Collect the effluent from the column.

18. Rinse column with distilled water until effluent is neutral. Combine rinse with effluent from Steps 16 - 17.

19. Add 2 ml magnesia mixture and 5 ml citric acid. Repeat Steps 12 - 14.

20. Ignite the $MgNH_4PO_4$ precipitate in a muffle furnace at 1100°C for one hour.

21. Weigh the $Mg_2P_2O_7$ after ignition, then mount on a copper planchet for which the background and area are known. Use a slurry of 0.01% agar-agar to bind the precipitate to the planchet. Reweigh crucible to determine amount of $Mg_2P_2O_7$ mounted.

22. Cover the planchet with a mylar film of 0.9 mg/cm^2 (or less).

Procedure - counting

1. Count the sample for 8 hour periods repeatedly over 2 - 3 months. Use a low background ($\leq$0.3 cpm) beta counter system, with frequent background determinations.

2. Plot the gross counting rate at time t (C_t) against $e^{-\lambda t}$ where $\lambda = 0.0485$ day^{-1}. If background (B) is constant and the contamination (X) is longer lived than P-32 (short-lived contamination will disappear after the first count) the data should fall on a straight line given by the relation

$$C_t = C_o e^{-\lambda t} + (B + X)$$

t is the time since phosphorus and silicon were separated.

The value (B + X) is given by the count rate after several months. The value C_o is the slope of the plot, or can be taken from the value $C_t = C_o - B - X$ as given by the extrapolated value of C_t at the intercept $e^{-\lambda t} = 1$.

3. Calibrate the counter using fine powder deposits of reagent grade KCl. Correct samples for self-absorption using Lerch's formula[108] and half-thickness values of 67 and 84 mg/cm^2 for K-40 and P-32, respectively.

4. Calculate the equivalent Si-32 activity based on the buildup time between the last phosphorus cleanout and the separation of this phosphorus from the silicon sample.

$$\frac{A_{P-32}}{A_{Si-32}} = 1 - e^{-\lambda_p t}$$

where A represents dpm in the silicon and phosphorus samples (Phosphorus corrected for chemical yield.); λ_p is the decay constant for P-32; t is the buildup time.

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