Hydrofluoric acid-assisted dissolution of biological samples for silicon determination by ICP-MS: examining silicon volatility under HF digestions

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NEMC 2022, August 1-5, 2022 Crystal City VA

Silicon – benefits

- Silicon is a ubiquitous element representing a major fraction of Earths' crust.
- Silicic acid is water-soluble - ortho (mono), meta, di, and tri-silicates, found in natural waters.
- Orthosilicic acid (H_4SiO_4) is only bioavailable form to living organisms owing to its small molecular size and lack of charge.

Silicon and silicic acids - ortho, meta, di- and tri-silicates.

- Silicon is an essential element, required for normal cell growth in diatoms and corals.
- In plants, it enhances nutrient uptake from soils, and reduces biotic and abiotic stresses.
- In humans, silicon enhances bone calcification, connective tissue health, immune system health, and reduces risk for atherosclerosis and metal accumulation in Alzheimer's disease.
- Dietary uptake of water-insoluble silicates, such as silicon dioxide and diatomaceous earth are reported to lower blood cholesterol in rats and humans, respectively.

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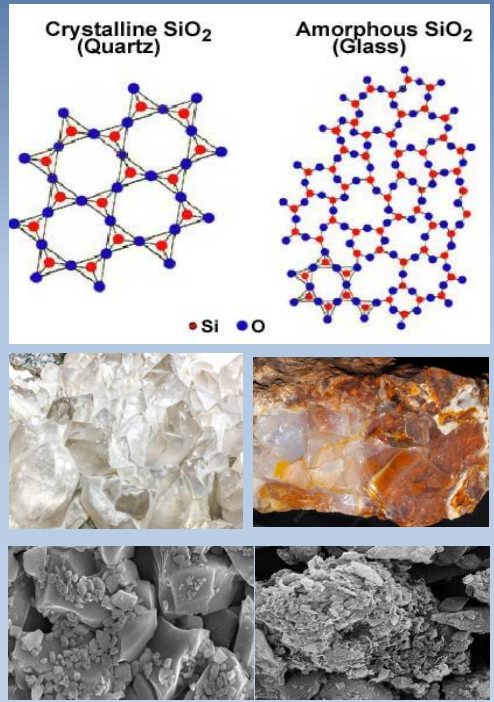
Silicon – toxicity

Adverse effects from silicon are due to inhalation exposure to insoluble silicates, such as asbestos and coal dust.

- **Crystalline silica** more hazardous.
- Inhalation of crystalline silica dust leads to increased risk for

  silicosis, tuberculosis, chronic bronchitis, chronic obstructive pulmonary disease (COPD), lung cancer, chronic kidney disease and various autoimmune diseases, including rheumatoid arthritis and systemic sclerosis (scleroderma).

- **Amorphous silica** is considered less hazardous, and effects are more reversable.
- Amorphous silica (17% by composition) in ash and particulate matter ($PM_{2.5}$) from burning of dead foliage was suspected to be leading cause of elevated kidney dysfunction among sugarcane workers in Guatemala.



Crystalline versus amorphous silica. Crystal structures, physical appearances and SEM images.

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Literature on silicon determination

Journal of Analytical Atomic Spectrometry, October 1997, Vol. 12 (1123–1130)

Determination of Silicon in Biological Tissue by Electrothermal Atomic Absorption Spectrometry Using Slurry Sampling of Original and Pre-ashed Samples

M. HORNUNG AND V. KRIVAN*

Sektion Analytik und Höchstreinigung, Universität Ulm, D-89069 Ulm, Germany

$Pd(NO_3)_2$-$Mg(NO_3)_2$ chemical modifiers

ANALYTICAL CHEMISTRY, VOL. 52, NO. 1, JANUARY 1980 • 121

Determination of Silicon and Aluminum in Biological Matrices by Inductively Coupled Plasma Emission Spectrometry

F. E. Lichte[1] and S. Hopper

Environmental Trace Substances Research Center, University of Missouri, Columbia, Missouri 65201

T. W. Osborn*

The Procter & Gamble Company, Miami Valley Laboratories, P.O. Box 39175, Cincinnati, Ohio 45247

Na_2CO_3-NaOH fusion

Fresenius J Anal Chem (2001) 370 : 246–250

SPECIAL ISSUE PAPER

S. Hauptkorn · J. Pavel · H. Seltner

Determination of silicon in biological samples by ICP-OES after non-oxidative decomposition under alkaline conditions

Microwave-assisted autoclave digestion with TMAH

Nuclear Instruments and Methods in Physics Research A 353 (1994) 601–605

Determination of silicon in biological and botanical reference materials by epithermal INAA and Compton suppression

S. Landsberger [a,*], S. Peshev [a], D.A. Becker [b]

[a] *Department of Nuclear Engineering, University of Illinois at Urbana-Champaign, 214 Nuclear Engineering Laboratory, 103 S. Goodwin Avenue, Urbana, Illinois 61801, USA*

[b] *National Institute of Standards and Technology, Nuclear Methods Group, IARD / CSTL, Gaithersburg, Maryland 20899, USA*

1834 *Anal. Chem.* 1989, *61*, 1834–1836

Determination of Silicon in National Institute of Standards and Technology Biological Standard Reference Materials by Instrumental Epithermal Neutron Activation and X-ray Fluorescence Spectrometry

Ernest S. Gladney*

Health and Environmental Chemistry, Group HSE-9, MS K-484, Los Alamos National Laboratory, Los Alamos, New Mexico 87545

Peter E. Neifert and Nathan W. Bower

Chemistry Department, Colorado College, Colorado Springs, Colorado 80903

1118 *J. Agric. Food Chem.* 1991, *39*, 1118–1119

Autoclave-Induced Digestion for the Colorimetric Determination of Silicon in Rice Straw†

C. L. Elliott and George H. Snyder*

Everglades Research and Educational Center, University of Florida (IFAS), Box 8003, Belle Glade, Florida 33430

Alkaline digestion followed with ammonium molybdate reaction for blue silicomolybdous acid complex.

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Challenges in silicon determinations

Sample introduction and matrix issues

- Hydrofluoric acid (HF) is required for dissolution of silicon/silicates,
- HF is detrimental to glass and quartz sample introduction components,
- Digestions with HF produce silicon species that are volatile under heating,
- Reagents (e.g., boric acid) used for complexing excess HF increases salt content in solutions.

Spectral interferences in ICP-MS

- Major isotopes of Si are ^{28}Si (92.23%) and ^{29}Si (4.68%) and ^{30}Si (3.09%)
- Isobaric overlaps on ^{28}Si: AlH, BO, N_2, CO, $^{56}Fe^{++}$
- Isobaric overlaps on ^{29}Si: SiH, BO, N_2, CO, $^{58}Ni^{++}$
- Isobaric overlaps on ^{30}Si: SiH, NO, CO, $^{60}Ni^{++}$

Lack of suitable QA/QC materials

- Silicon is a refractory element and determination is rather difficult using atomic spectrometric techniques.
- Accuracy testing was difficult in silicon analysis of biological samples due lack of appropriate QA/QC materials.

Misconceptions/Lack of knowledge

- Volatility issues are not well-understood – how volatile are silicon species not known?
- *Some believe/assume that silicon species are stable in solution unless solutions are heated to total dryness!*

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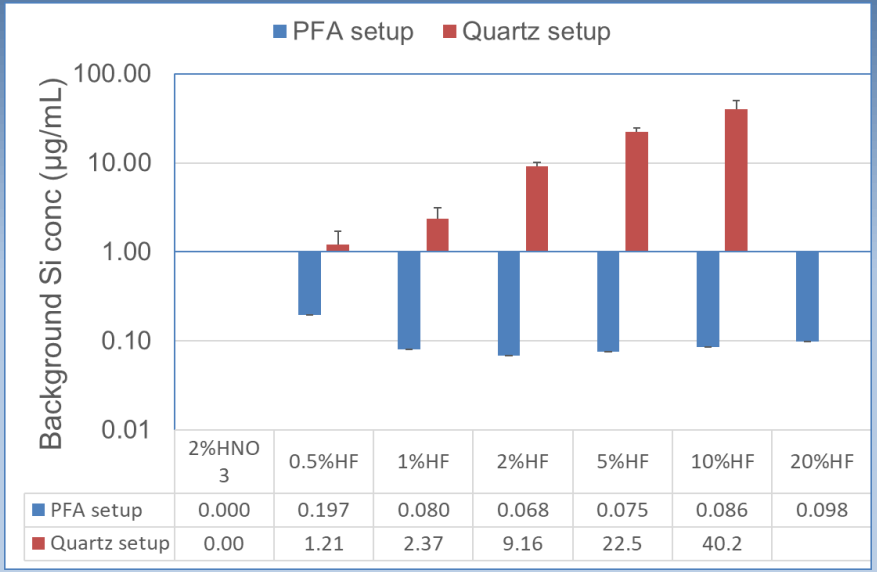
HF-induced silicon background



	2%HNO3	0.5%HF	1%HF	2%HF	5%HF	10%HF	20%HF
PFA setup	0.000	0.197	0.080	0.068	0.075	0.086	0.098
Quartz setup	0.00	1.21	2.37	9.16	22.5	40.2	

Effect of Hydrofluoric acid on silicon background signals using Teflon PFA (HF-resistant) and quartz-based sample introduction systems.

PFA setup: Teflon PFA spray chamber, Teflon nebulizer, quartz torch with sapphire injector.

Quartz setup: Teflon PFA spray chamber, Teflon nebulizer, quartz torch with quartz injector.

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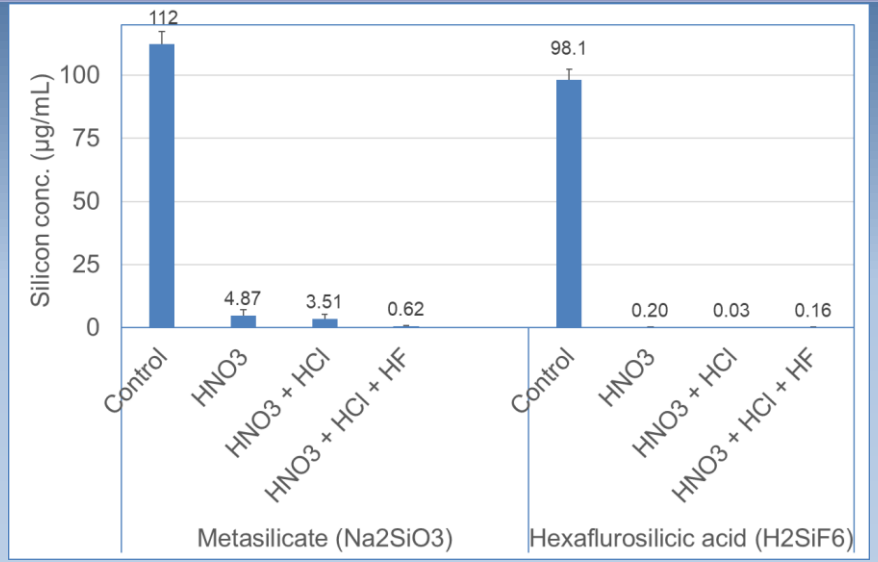
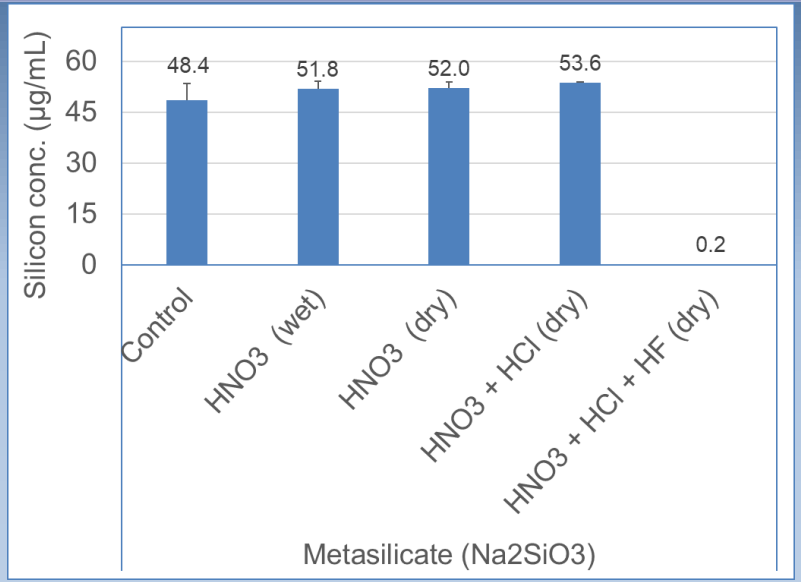
Silicon volatility under HF-digestions



Prep: 100 µg/mL Si heated to incipient dryness in Teflon vials at 120 °C . Residue heated again **gently in 2 mL 10% HNO_3** and diluted to 10 mL.
Control: No heat - 100 µg/mL Si in 2% HNO_3.
HNO_3: 1 mL HNO_3.
HNO_3 + HCl: 1 mL HNO_3 and 0.5 mL HCl.
HNO_3 + HCl + HF: 1 mL HNO_3, 0.5 mL HCl and 0.5 mL HF.



Prep: 50 µg/mL Si heated to dryness in Teflon vials at 120 °C . Residue heated again in **closed-vessels in 4 mL 10% HNO_3 and 0.5 mL HF** for 30 min and diluted to 10 mL.
Control: No heat - 50 µg/mL Si in 4% HNO_3 + 5% HF.
HNO_3: 1 mL HNO_3.
HNO_3 + HCl: 1 mL HNO_3 and 0.5 mL HCl.
HNO_3 + HCl + HF: 1 mL HNO_3, 0.5 mL HCl and 0.5 mL HF.

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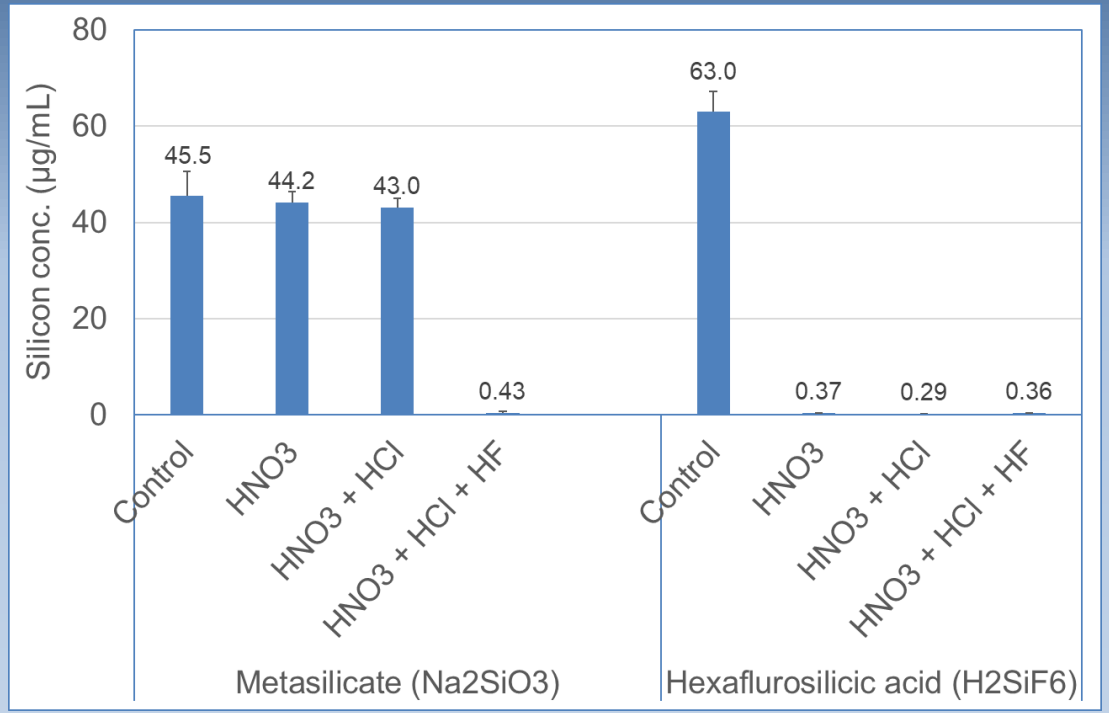
Preliminary information-subject to revision. Not for citation or distribution.

Silicon volatility - verified



Prep: 50 µg/mL Si heated at 120 °C to dryness in Teflon vials. Residue heated again in **closed-vessels** in **0.5 mL HNO_3 and 0.5 mL HF** for 1 h and diluted to 10 mL.
Control: No heating - 50 µg/mL Si in 5% HNO_3 + 5% HF.
HNO_3: 50 µg/mL Si in 2 mL HNO_3.
HNO_3 + HCl: 50 µg/mL Si in 2 mL HNO_3 and 0.5 mL HCl.
HNO_3 + HCl + HF: 50 µg/mL Si in 2 mL HNO_3, 0.5 mL HCl and 0.5 mL HF.

Volatility of silicon in metasilicate and hexaflurosilic acid forms.

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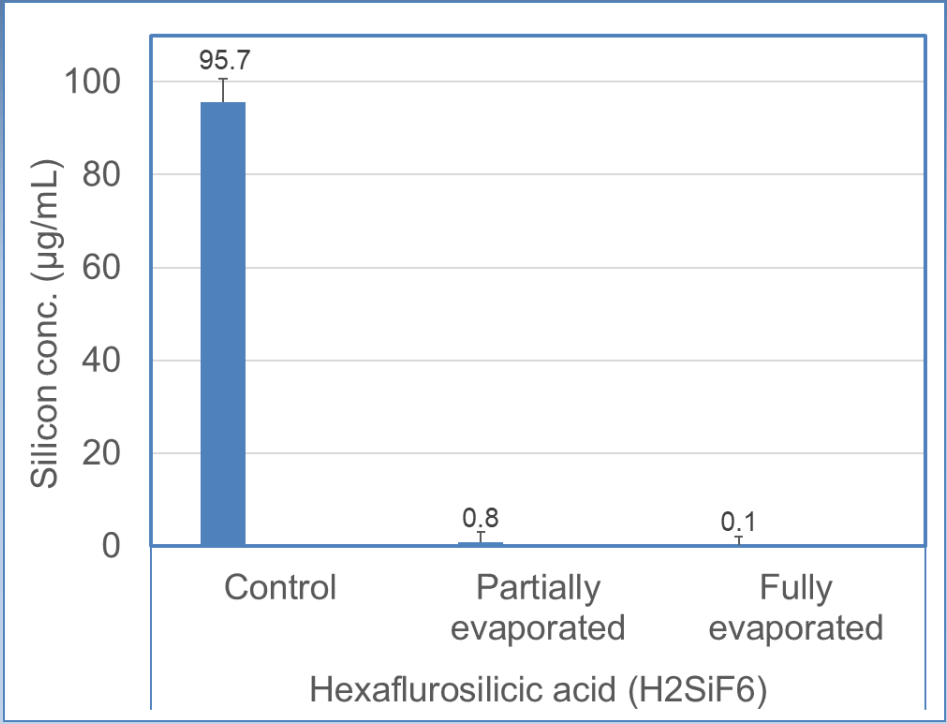
How volatile are silicon species?



Prep: 100 µg/mL Si in 2 mL HNO_3, 0.25 mL HCl and 0.1 mL HF heated partially or to incipient dryness at 120 ^oC in Teflon vials .
Control: No heating
Partially evaporated (0.6-0.7 mL solution recovered): Recovered solution diluted to 5 mL with 2 mL 10%HNO_3 and 0.1 mL HF (4% HNO_3 + 0.2% HF).
Fully evaporated: Residue heated again gently in 2 mL 10%HNO_3 and 0.1 mL HF and diluted to 5 mL.

Volatility of silicon under partial and total evaporation.

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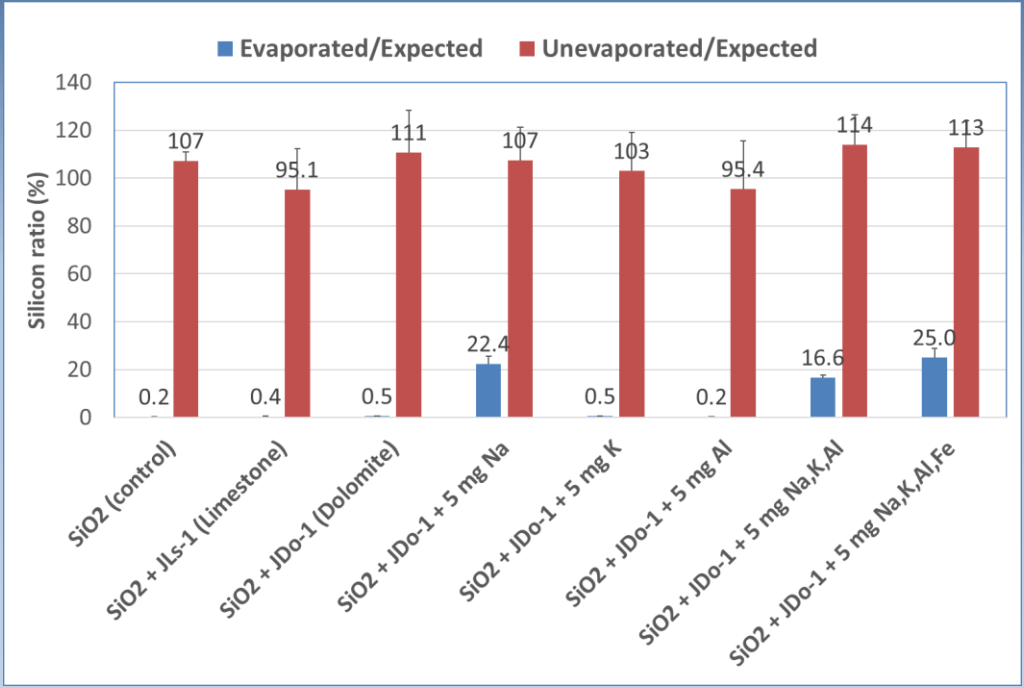
Could silicon species be stabilized in solution?



Effect of sample matrix on stability of silicon species.

SiO_2 – 46.7% Si
JLs-1 (Limestone): 55% CaO and 0.6% MgO
JDo-1 (Dolomite): 33.9% CaO and 18.6% MgO

Prep: About 20 mg SiO_2 (99.95%) are spiked with either ~20 mg Limestone, ~20 mg Dolomite or ~20 mg Dolomite plus major elements (Na, K, Al, Fe). Contents digested in 2 mL HNO_3, 0.5 mL HCl and 1 mL HF heated for 3h at 130 ^oC in Teflon vials (closed-vessel). Digests cooled to room temperature and diluted to 10 mL.
Evaporation: 5 mL of digests taken and evaporated to incipient dryness at 120 ^oC. Residue heated in 1 mL HNO_3 and 0.5 mL HF for 30 min, then diluted to 5 mL.

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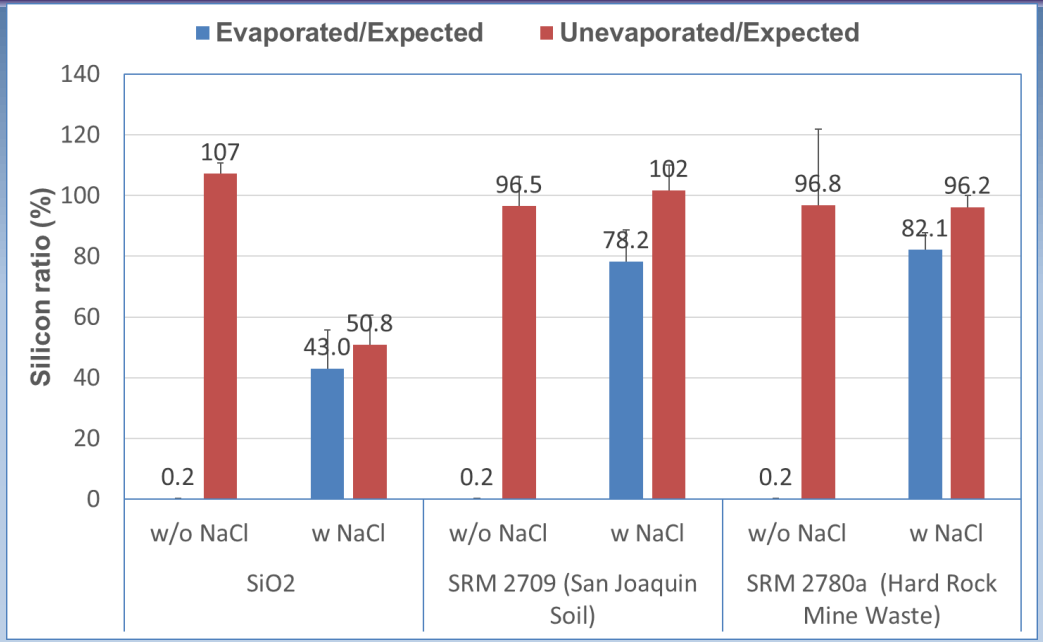
Can silicon species be stabilized in solution?



Effect of NaCl matrix on stability of silicon species in solution.

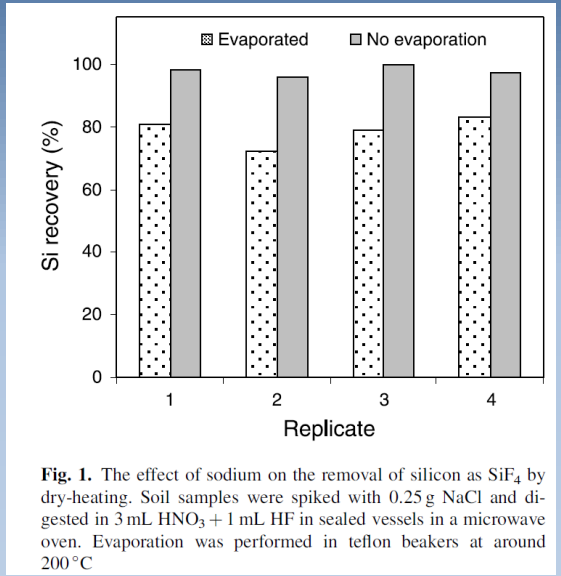


Fig. 1. The effect of sodium on the removal of silicon as SiF_4 by dry-heating. Soil samples were spiked with 0.25 g NaCl and digested in 3 mL HNO_3 + 1 mL HF in sealed vessels in a microwave oven. Evaporation was performed in teflon beakers at around 200 °C

Arslan & Tyson, Microchimica Acta 160 (2008) 219–225.

Prep: About 20 mg SiO_2 (99.95%) and 50 mg SRM 2709 and SRM 2780a digested in 4 mL HNO_3, and 1 mL for 4h at 130 °C in Teflon vials (closed-vessel). Digests cooled to room temperature and diluted to 10 mL. NaCl set are spiked with 0.1 g NaCl (99.999%).Evaporation: 2.5 mL of digest taken and evaporated to incipient dryness at 120 °C. Residue heated in 1 mL HNO_3 for 10 min, then diluted to 5 mL.

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Digestion procedure

Two step hot-block digestion procedure for preparing plant and tissue samples:

- Weigh about 0.1-0.3 g sample and place into Teflon vials.
- Add 4 mL HNO_3 and 1 mL HCl and heat samples at 120 ^oC until foaming ceases (15-20 min).
- Optional - add 1 mL $HClO_4$, close lids and digest contents at 140 ^oC for 5 h.
- Open lids and evaporate solutions to incipient dryness at 120 ^oC.
- At dryness, add 0.5 mL HNO_3 and 0.5 mL HF, close lids and digest contents at 130 ^oC for 2 h.
- Remove digests from hot block, cool to room temperature, and dilute to 10 or 15 mL with water in 15-mL tubes.
- If necessary, dilute as appropriate. Analyze by ICP-MS.

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Analysis of plant reference materials

Reference material	Silicon concentration	(µg/g)		
	This study		Literature values	
	^{74}Ge (IntStd)	^{103}Rh (IntStd)	Reference	Technique
Tomato Leaves SRM 1573a	2966 ± 158	3111 ± 179	3120 ±106[a]	EINA
Pine Needles SRM 1575	1758 ± 283	1813 ± 308	1630 ± 37[a] 1310 ± 200[b] 1300 ± 200[b] 1410 ± 139[c]	EINA XRF EINA colorimetry
Peach Leaves SRM 1547	950 ± 198	1012 ± 216	1067 ± 20[a] 2160 ± 293[c]	EINA colorimetry
Citrus Leaves SRM 1572	2346 ± 198	2495 ± 173	1900 ± 400[b] 2100 ± 400[b]	XRF EINA
SRM 1572 Citrus Leaves*	2423 ± 548	2614 ± 552	1900 ± 400[b] 2100 ± 400[b]	XRF EINA

a. Landsberger et al., Nuclear Instruments and Methods in Physics Research A 353 (1994) 601-605.
b. Bell and Its'd Simmons, Soil Sci. Soc. Am. J. 61 (1997) 321-322.
c. Gladney et al., Anal. Cham. 61 (1989) 1834-1836.

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Preliminary information-subject to revision. Not for citation or distribution.

Analysis of tissue reference materials

Reference material	Silicon concentration	(µg/g)		
	This study		Literature values	
	^{74}Ge (IntStd)	^{103}Rh (IntStd)	Reference	Technique
Oyster Tissue (SRM 1566b)	1014 ± 23	1054 ± 22		
Bovine Liver (SRM 1577b)	13.9 ± 4.6	16.4 ± 4.9	BDL, nd[a] 5.6 ± 0.5[d] 3.9 ± 0.3[e]	EINA ETAA ICP-OES
Plankton (BCR 414)	10120 ± 543	10579 ± 573	13316 ± 1356[f]	ICP-MS
Dogfish Liver (DOLT-4)	1102 ± 217	1172 ± 219		
Dogfish Liver (DOLT-4)*	1062 ± 223	1104 ± 222		
Dogfish Muscle (DORM-3)	7602 ± 384	7929 ± 479		
Dogfish Muscle (DORM-3)*	7252 ± 359	7467 ± 296		
Lobster Hepatopancreas (TORT-1)*	259 ± 70	269 ± 65		
Dogfish Liver (DOLT-3)*	155 ± 17	165 ± 18		

d. Huang and Krivan, Spectrochimica Acta Part B 62 (2007) 297–303.
e. Hauptkorn et al., Fresenius J Anal Chem (2001) 370 :246–250
f. Arslan et al., Fresenius J Anal Chem 366 (2000) 273–282

* Digestion performed without $HClO_4$

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Preliminary information-subject to revision. Not for citation or distribution.

Conclusions

- Silicon species in HF-digests are highly sensitive to heat.
- Closed-vessel digestion is critical to avoid silicon loss from solution.
- Presence of sodium provides stability to some extent.
- NaCl matrix substantially improves silicon stability in HF digests.
- NaCl effect is noteworthy and deserves future investigations for HF-free determination of silicon.
- Volatility of silicon species could bring the advantage of gas phase introduction of silicon for more sensitive determinations.

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