DETERMINATION OF SILICON IN HYDRAZINE*

Mark B. McClure
Dion Mast
Ben Greene
Honeywell Technology Solutions, Inc.
NASA Johnson Space Center White Sands Test Facility
Las Cruces, New Mexico

Miguel J. Maes
NASA Johnson Space Center White Sands Test Facility
Las Cruces, New Mexico

ABSTRACT

Inductively coupled plasma-mass spectrometry (ICP-MS) is a highly sensitive technique sometimes used for the trace determination of silicon at a mass-to-charge (m/z) ratio of 28, the most abundant natural isotope of silicon. Unfortunately, ICP-MS is unable to differentiate between other sources of m/z 28 and false positive results for silicon will result when other sources of m/z 28 are present. Nitrogen was a major source of m/z 28 and contributes to the m/z 28 signal when hydrazine sample or nitric acid preservative is introduced into the plasma. Accordingly, this work was performed to develop a sample preparation step coupled with an ICP-MS analysis that minimized non-silicon sources of m/z 28. In the preparatory step of this method, the hydrazine sample was first decomposed predominately to nitrogen gas and water with copper-catalyzed hydrogen peroxide. In the analysis step, ICP-MS was used without nitric acid preservative in samples or standards. Glass, a potential source of silicon contamination, was also avoided where possible. The method was sensitive, accurate, and reliable for the determination of silicon in monopropellant grade hydrazine (MPH) in AF-E-332 elastomer leaching tests. Results for silicon in MPH were comparable to those reported in the literature for other studies.

INTRODUCTION

Silicon species, which may be components of elastomeric fuel bladders used for hydrazine service, may leach into the fluid and potentially cause adverse effects on propulsion systems, many of which have been documented in the literature.[1] In particular, a nonvolatile residue (NVR) may deposit on transfer lines, catalyst beds, injectors, and other hot spots of systems. As a result of these problems, studies are performed to quantify silicon that is leached into hydrazine. However, the analytical determination of total silicon in hydrazine has proven to be difficult for a number of reasons.

The recent literature reports a number of analytical methods that have been used for the determination of silicon in hydrazine from elastomer leaching studies.[2] These methods include graphite furnace atomic absorption spectrometry (GFAAS), inductively coupled plasma-optical emission spectrometry (ICP-OES), and inductively coupled plasma-mass spectrometry (ICP-MS). Classical techniques, such as colorimetric methods and flame atomic absorption (FAA), may lack the required sensitivity for trace silicon determinations. Additionally, methods in which silicon speciation (organic and inorganic speciation) may affect the results for total silicon were not desirable for a total silicon study. For example, AF-E-332 contains both organic and inorganic silicon species.[3] Plasma methods are typically species-independent for elements in the absence of isotopic interferences (different elements with identical mass numbers), because, in theory, all species are converted to ionized atoms under plasma conditions. In the case of silicon, soluble inorganic silicates and organic silicon species, such as silanes or siloxanes, are expected to form silicon ion (Si^+) under plasma conditions and be detected at m/z 28,

---

[*] Approved for public release, distribution is unlimited.

which is the most abundant mass number for the naturally occurring silicon isotopes. The relative abundance of natural silicon isotopes is given in Table I.[4]

ICP-MS was the only instrument capable of trace elemental determinations available at NASA Johnson Space Center White Sands Test Facility (WSTF) to perform this work. Because ICP-MS detects and quantifies elements based on m/z number, the most abundant mass number is typically employed in the absence of interference by other isotopes or charged species. The most abundant mass number for silicon is mass 28 and was the most logical mass number to analyze in order to achieve the highest sensitivity for the method; however, in the course of method development it was necessary to assess the analysis at masses 29 and 30. All experiments were performed to develop a method as reliable as possible to apply to the determination of silicon in AF-E-332 leaching studies with monopropellant grade hydrazine (MPH).

The experimental conditions and data obtained for the method development are presented. The application of the method is additionally demonstrated by the presentation of data from silicon leaching studies performed with AF-E-332 and MPH.

AF-E-332 is an elastomeric ethylene propylene-based terpolymer containing methyl silane treated fumed silicon dioxide. Because of its use in hydrazine fuel systems, leaching of silicon into hydrazine is of great interest to tank-life longevity and propulsion system performance studies.[2]

OBJECTIVE

The objective of this paper is to describe an ICP-MS method for the trace determination of silicon in hydrazine.

APPROACH

Two of the most problematic aspects of trace silicon determination were first minimized: (1) background contamination due to glassware and (2) mass spectral interference due to background m/z 28. Use of glass was avoided where practicable. Tests with various nitrogen containing species and helium and nitrogen sparged solutions were performed to evaluate the formation of $^{14}N_2$ and subsequently gave a false positive interference at m/z 28. Calibration curves for m/z 29 and 30 were also evaluated at the same time as m/z 28. Hydrazine decomposition experiments were performed to develop a procedure to minimize the amount of nitrogen contributed from hydrazine in the silicon analytical solutions. Hydrazine decomposition was evaluated with copper (II) oxide, silver membrane, iridium wire, hydrogen peroxide, and hydrogen peroxide containing copper (II) nitrate hemipentahydrate. The hydrazine decomposition method was then selected based on the optimum results of these experiments. The analytical method, including sample preparation and ICP-MS conditions, was evaluated by the analysis of MPH samples spiked with silicon and MPH samples. The method was applied to the determination of silicon in AF-E-332 leaching tests with MPH.

Table I. Relative Isotopic Abundance of Silicon

Mass number	Abundance (%)
28	92.23
29	4.67
30	3.1

EXPERIMENTAL

REAGENTS AND APPARATUS

MPH meeting the requirements of MIL-PRF-26536E[5] was obtained from the Defense Energy Support Center (Texas). Silicon ICP-MS standards were obtained from Inorganic Ventures (New Jersey). Ammonium chloride, hydrazine hydrochloride, hydrogen peroxide (30 percent) was Fluka Trace Select grade, copper(II) nitrate hemipentahydrate, sodium nitrate, and urea was obtained from Aldrich.®* AF-E-332 was obtained from Pressure Systems, Inc. (California). Reagent water obtained at WSTF was first treated by reverse-osmosis water then deionized. Ultrex II ultrapure nitric acid (70 percent) was obtained from J.T. Baker (New Jersey). Copper (II) oxide and silver membrane were obtained from common laboratory stock. Iridium wire was obtained from Alfa Aesar (Massachusetts). All analyses were performed using an Agilent Model 4500 ICP-MS, some using a scandium internal standard and some without it as noted below.

ICP-MS conditions were set as recommended by Agilent for normal plasma mode with an external silicon calibration curve.

HYDRAZINE SAMPLE PREPARATION

Acidification of Hydrazine with Nitric Acid

MPH samples for initial characterization studies in nitric acid were prepared by the addition of a sufficient volume of hydrazine to 11 percent (v/v) nitric acid to produce a final solution that was 5 percent (v/v) hydrazine. This volume of acid was greater than a 1-molar excess of that required to produce monoprotonated hydrazine.

Evaluation of 1 Percent Nitrogen Containing Solutions and Gas Sparged Solutions

Experiments with solutions containing 1 percent nitrogen as various species were performed to evaluate the nitrogen contribution to the m/z 28 signal. Solutions of ammonium chloride, hydrazine hydrochloride, nitric acid, sodium nitrate, and analyzed by ICP-MS at m/z 28. Additionally several deionized water blanks were run after sparging them with helium and nitrogen gas. The calibration curves for m/z 29 and 30 were evaluated at this time as well.

AF-E-332 Leaching with MPH

MPH samples obtained from leaching studies were prepared as follows: prior to leaching tests, AF-E-332 was pre-cleaned for hydrazine service by agitating it for 10 min in a 1-percent solution of Simple Green®† in reagent water; rinsed with reagent water; and then dried under nitrogen for 12 h prior to testing. Samples of AF-E-332 were cut to 1 x 1 x 0.2 cm dimensions to produce a surface area of 50.4 cm^2 and were immersed in 10 mL MPH in high-density polyethylene (HDPE) containers to achieve an AF-E-332 surface area to MPH volume (S/V) of 5.0 cm^{-1}. Blanks were prepared by adding 10 mL MPH to high density polyethylene (HDPE) containers. The MPH was removed from the HDPE containers containing AF-E-332 at 1 h, 6 h, 12 h, 24 h, 48 h, 7 d, 14 d, 30 d, 45 d, and 60 d. The MPH was removed from the blank HDPE containers at 0 h, 12 h, 24 h, 48 h, 7 d, 14 d, 30 d, 45 d, and 60 d. The MPH removed from the HDPE containers at the indicated times.

HYDRAZINE DECOMPOSITION

Hydrazine decomposition experiments were performed to optimize a procedure to minimize the amount of nitrogen contributed from hydrazine in the silicon analytical solutions. Initial experiments were performed for screening purposes to evaluate the physical characteristics of hydrazine decomposition using hydrogen peroxide and hydrogen peroxide containing copper species.

---

[*] Aldrich® is a registered trademark of Sigma-Aldrich Biotechnology, Highland, Illinois.

[†] Simple Green® is a registered trademark of Sunshine Makers, Incorporated, Huntington Harbor, California.

HYDRAZINE DECOMPOSITION SCREENING

Ten Percent Aqueous Hydrazine and Copper Oxide. Approximately 2 mL of 10 percent hydrazine was added to a beaker containing 0.25 g CuO.

Hydrazine and Copper Oxide. Approximately 5 mg of CuO, a brown material, was added to a beaker containing 2 mL neat hydrazine.

Ten Percent Aqueous Hydrazine and Silver Membrane. Approximately 2 mL of 10 percent hydrazine was added to a beaker containing approximately 1 cm^2 silver membrane.

Hydrazine and Silver Membrane. Approximately 0.25 mL of 10 percent aqueous hydrazine was added to a beaker containing approximately 1 cm^2 silver membrane.

Hydrazine and Iridium Wire. Iridium wire was immersed in 2 mL hydrazine.

Ten Percent Aqueous Hydrazine and Hydrogen Peroxide. Ten percent aqueous hydrazine was added drop wise to 30 percent hydrogen peroxide in an open beaker.

Hydrazine and Hydrogen Peroxide. Hydrazine was added dropwise to 30 percent hydrogen peroxide in an open beaker.

Hydrazine, Hydrogen Peroxide, and Copper (II). Hydrazine was added dropwise to 30 percent hydrogen peroxide with approximately 5 mg of copper (II) nitrate hemipentahydrate in it.

HYDRAZINE DECOMPOSITION PROCEDURE

Five grams of hydrazine was reacted with 55 g of 30 percent hydrogen peroxide containing 100 µL of 1 percent by weight copper(II) nitrate hemipentahydrate solution in a HDPE container. The hydrazine was added drop wise, to the hydrogen peroxide three drops at a time followed by swirling and cooling the container on ice to dissipate heat. This process was repeated until hydrazine addition was complete. The resulting solution was then adjusted to 50 mL volume to create a net 1/10 dilution of the original hydrazine sample. The samples were then analyzed for silicon by ICP-MS.

Silicon Spike Recovery from MPH

Three 5 mL samples of blank MPH were spiked with the silicon standard solution prior to being decomposed by the process in the preceding paragraph.

RESULTS

Nitric acid acidification of hydrazine minimized hydrazine vapor hazards for safety purposes and to avoid potential contamination of instrument softgoods. The initial analysis of MPH samples showed high silicon results for both the samples and the blanks (Table II), suggesting that hydrazine and/or nitric acid-N was a source of m/z 28. These data suggest the plasma decomposition of nitric acid forms $^{14}N_2$, which is subsequently ionized and detected at m/z 28 (the analytical m/z for silicon). The formation of $^{14}N_2^+$ (N_2^+) in the argon plasma is feasible because the ionization potential of N_2 is 15.576 eV, which is lower than the ionization potential of Ar (15.759 eV)[6]. The detection of $^{14}N_2^+$ would result in a positive interference for silicon at m/z 28 and therefore necessitate the elimination of nitric acid from samples analyzed for silicon at m/z 28. For m/z 29 the background signal was about an order of magnitude lower than m/z 28, but the lower natural abundance of mass 29 resulted in the low 20 ppb silicon standard only being twice the background signal, whereas m/z 28 was ten times the background. The background signal for m/z 30 was so high a calibration was indiscernible at the concentrations being used.

Table II. Nitric Acid MPH Solution Silicon Data

Time	MPH Blank µg/L	MPH AF-E-332 exposed µg/L
0 h	1700	NA*
1 h	NA	4000
6 h	NA	2600
12 h	2500	2300
24 h	2500	2200
48 h	2000	5000
7 d	3400	7900
14 d	1700	3500
*NA = Not Analyzed		

These results show that the presence of hydrazine and/or nitric acid is deleterious to the determination of silicon at m/z 28 due to its contribution to the background signal, giving false positive results. Consequently, the method does not employ nitric acid as either a sample preservative of external silicon standards prior in the analysis of samples for silicon by ICP-MS at m/z 28.

Analysis of the 1 percent Nitrogen Solutions and Blanks

The results of the 1 percent nitrogen solutions are shown in Table III. It was found that all the nitrogen species gave rise to an increase in m/z 28 counts. The urea was found to be especially bad, but it may be reasonably expected to generate CO ions that are also of m/z 28 in addition to the nitrogen-sourced ions. The DI blank, helium and nitrogen sparged DI water were all similar in counts. Table IV shows the background counts per second (CPS) for m/z 7 to 82 of a typical DI water blank. Only m/z 23, 30 and 39 are worse than m/z 28. Elements with m/z 85 to 238 typically have a blank CPS of < 100, none were over 1000.

N_2 derived from ^{14}N has m/z of 28. A reasonable explanation of the data is that $^{14}N_2$ forms in the plasma as result of the decomposition of various nitrogen containing species. As described above, the formation of $^{14}N_2^+$ in the argon plasma is feasible because the ionization potential of N_2 is 15.576 eV, which is lower than the ionization potential of Ar (15.759 eV).[6] The detection of $^{14}N_2^+$ would result in a positive interference for silicon and therefore necessitate the elimination of hydrazine from samples analyzed for silicon at m/z 28. Consequently, the method employed a hydrazine decomposition step prior to the analysis of samples for silicon by ICP-MS.

Arguably atmospheric nitrogen is a very likely source of contribution to m/z 28, but the results shown in Table III would indicate that dissolved nitrogen in the sample solutions is not a significant source of interference.

Non-nitrogen neutral molecules that are sources of m/z 28 that can be ionized in an argon plasma ion are identified in Table V.

Table III. 1 Percent Nitrogen Solutions

Sample ID	m/z 28 Counts Per Second
DI Blank	2.82×10^4
DI sparged He 15 min	2.75 x 104
DI sparged N_2 15 min	2.63 x 104
$NaNO_3$	9.26 x 104
HNO_3	1.53 x 105
N_2H_5Cl	1.58 x 105
NH_4Cl	2.86 x 105
Urea	> 2 x 106

Table IV. Blank Data

Element	m/z	CPS
Li	7	105
Be	9	61
B	11	5410
Na	23	430000
Mg	24	439
Al	27	1400
Si	28	138000
Si	29	11500
Si	30	503000
K	39	1300000
Ca	43	702
Sc	45	1170
Ti	47	87
V	51	528
Cr	53	243
Mn	55	2400
Fe	57	19300
Co	59	518
Ni	60	20300
Cu	63	26000
Zn	66	2350
Ga	69	65
Ge	72	437
As	75	4400
Se	82	1570

Table V. Non-nitrogen Neutral Molecules Ionized in an Argon Plasma Ion

Non-nitrogen Species	Chemical Formula	Ionization Potential (eV)[a]
Carbon Monoxide	CO	14.013 ± 0.004
Ethylene	C_2H_4	10.5

[a] Weast, R.C., editor. *CRC Handbook of Chemistry and Physics*. CRC Press, Inc., Boca Raton, Florida 1983.

CO can be formed from hydrazine solutions because of the presence of carbon and oxygen sources, including atmospheric carbon dioxide, carbazic acid, aniline, dissolved oxygen, and water. Ethylene can be formed from hydrazine solutions because of the presence of carbon and hydrogen sources, including atmospheric carbon dioxide, carbazic acid, aniline, and water. Oxygen from air surrounding the plasma/detector interface might also be a contributor. In order to eliminate sources of atmospheric contamination by CO_2 and oxygen, all solutions would need to be thoroughly purged, such as with argon, maintained under an argon blanket. Additionally, the ICP-MS instrument would be require operation under an argon blanket or purge. The very high count rate for the 1 percent urea solution may be explained by the presence of CO ions.

HYDRAZINE DECOMPOSITION

Ten Percent Hydrazine and Copper Oxide

The CuO was a brown material that initially was agglomerated at the bottom of the beaker. No immediate reaction was observed. Slight bubbles in the fluid at the surface of the CuO appeared after about 30 min. After 2 h, the CuO appeared to have formed a slurry in the solution. The fluid appeared unchanged except for very slight bubbles. A reaction between copper (II) oxide and hydrazine is:

$$N_2H_4 + 2CuO \rightarrow 2Cu + N_2 + 2H_2O^{7}$$

Because supported CuO materials have been demonstrated successful in the decomposition of hydrazine, the lack of reaction observed under the conditions of this experiment may be due to inadequate CuO surface area.

Hydrazine and CuO

The CuO added to neat hydrazine accumulated at the bottom of the beaker. There was no initial reaction. After about 2 min slight effervescence was observed, which continued over about one hour after which the test was terminated. There were no signs of gross decomposition of the fluid. The material formed a slurry similarly to what was observed with the 10 percent aqueous hydrazine. A possible explanation for these observations is described for 10 percent hydrazine and copper oxide above.

Ten Percent Aqueous Hydrazine and Silver Membrane

The Ag membrane was a white/gray material that stayed at the bottom of the beaker. Slight initial bubble formation was observed. After about 5 min bubbles were not observed. After 2 h the very minor bubbles were observed on the membrane and the fluid appeared unchanged. Although hydrazine is known to decompose on a silver surface,[1] the silver decomposition method was not suitable for preparing hydrazine samples for silicon analysis because the apparent hydrazine decomposition rate was too slow for practical lab use.

Hydrazine and Silver Membrane

Similar results were observed with the neat hydrazine as with the 10 percent aqueous hydrazine except there were slightly more bubbles. After 2 h the fluid appeared slightly yellow. This method was not suitable for preparing hydrazine samples for silicon analysis because the apparent hydrazine decomposition rate was too slow for practical lab use. Additionally, if hydrazine were fully decomposed by silver the products would be expected to be gaseous and possibly result in loss of volatile silica species. It would be necessary to add water to prevent the solution from decomposition to dryness and that would be expected to even further slow the decomposition reaction.

Hydrazine and Iridium Wire

No initial reaction was observed. A few bubbles formed and adhered to the surface of the wire, which continued for 1 h after which the test was terminated. There were no signs of gross fluid decomposition or material change. Although hydrazine is known to decompose on an iridium surface,[1] the iridium decomposition method was not suitable for preparing hydrazine samples for silicon analysis because the apparent hydrazine decomposition rate was too slow for practical lab use.

Hydrazine and Hydrogen Peroxide

No immediate reaction was observed. After 3 min, an exothermic reaction accelerated violently. This method was not suitable for preparing hydrazine samples for silicon analysis because the initial hydrazine decomposition rate was slow and once the reaction was visually apparent, it was too violent to control in a practical manner.

Hydrazine, Hydrogen Peroxide, and Copper (II)

An immediate exothermic reaction was observed potentially causing fluid to escape from the beaker. This method was suitable for preparing hydrazine samples for silicon analysis because the apparent hydrazine decomposition rate was rapid and ultimately controllable by cooling, limiting the Cu (II) available and by slow addition of the hydrazine.

HYDRAZINE DECOMPOSITION PROCEDURE

The moderate addition of 3-drop aliquots of hydrazine in an incremental manner to the hydrogen peroxide/copper (II) nitrate hemipentahydrate solution was exothermic but was controllable by intermittent swirling and cooling. There was no visible loss of fluid from the reaction vessel using this method. Samples were processed at a rate of approximately 2/h. This method was relatively easy and safe to perform without loss of sample and in a repetitive manner.

The reaction for the copper (II) catalyzed reaction of hydrazine and hydrogen peroxide is:

$$N_2H_4 + 2H_2O_2 \xrightarrow{Cu(II)} N_2 + 4H_2O^1$$

For a complete reaction, the hydrazine-N source contribution to m/z 28 is eliminated by the formation of gaseous nitrogen that is evolved from the solution.

SPIKE RECOVERY

Three samples of MPH were spiked with a silicon solution to yield a net 1000 ppb value of silicon above the baseline concentration. They were then hydrolyzed by the process described in the paragraph above. The resulting analysis yielded 730, 780 and 750 ppb for and average spike recovery of 75 percent.

REPORTING LIMITS

The instrument-reporting limit was 20 ppb, yielding a method-reporting limit of 200 ppb. In the case of silicon, the results reported are the sample concentration minus the hydrogen peroxide blank concentration (21 to 35 ppb), and then multiplied by the dilution factor (10). It is important to note that a glass spray chamber was used because it was all that was available at the time. An inert spray chamber is preferable for the analysis of trace silicon.

LEACHING TEST RESULTS FOR SILICON

Results for silicon in AF-E-332 leaching tests with MPH are shown in Table VI.

Table VI. Leaching Test Results for Silicon

Time	AF-E-332 in MPH	MPH Blank
	(µg/L)	
0 h	NA[a]	210
1 h	180	NA
6 h	280	NA
12 h	240	200
24 h	300	210
48 h	500	220
7 d	1150	220
14 d	2000	240
30 d	1600	0
45 d	1800	20
60 d	1400	220

[a] NA indicates not applicable.

DISCUSSION

The initial work analytical work utilizing nitric acid neutralized hydrazine solutions was unusable due to the interference of nitrogen containing species at m/z 28. Samples and blanks were all analyzed to be approximately 2400 ppb due to the interfering species. The isotopic abundance of silicon is primarily mass 28 making measurements at m/z 29 and 30 less desirable. The background CPS at m/z 30 is worse than M/Z 28. So effort was focused on removing the interfering nitrogen species to allow the use of m/z 28 on the ICP-MS. The Cu(II)- catalyzed hydrogen peroxide decomposition of hydrazine was used to remove the interfering nitrogen containing species, allowing analyses to be performed using m/z 28. The hydrogen peroxide used needs to be analyzed for silicon content to subtract from the samples.

CONCLUSIONS

A method for the determination of silicon in hydrazine by ICP-MS is reported. The method eliminates interfering non-silicon sources of m/z 28, which is the most abundant natural silicon isotope. Non-silicon sources of m/z 28 that were eliminated were nitric acid and hydrazine, from which nitrogen was the source of the m/z 28. Hydrazine is decomposed by hydrogen peroxide under controlled conditions to eliminate its m/z 28 spectral interference. The reporting limit for silicon in hydrazine is about 200 ppb depending on background hydrogen peroxide levels. The method was applied to the determination of silicon, as well as zinc and calcium, in AF-E-332 leaching studies in MPH. The method allows samples to be prepared and analyzed the same day. The hydrazine decomposition step lowered the hydrazine content below 10 ppb, which avoids potential safety and instrument contamination concerns associated with hydrazine in samples.

REFERENCES

1. Schmidt, E.W. *Hydrazine and Its Derivatives.* New York, NY: John Wiley & Sons, Inc., 2001.

2. Christofferson, S. and Wucherer, E.J. *AF-E-332 Elastomer Material Effects on Small Hydrazine Rocket Engines. AIAA-98-3360.* American Institute of Aeronautics and Astronautics. 1998.

3. MIL-R-83412A (USAF). *Military Specification of Rubber, Ethylene-Propylene, Hydrazine Resistant*. Military Standard, United States Department of Defense, Washington, DC, June 30, 1977.

4. Hewlett Packard. “Relative Isotopic Abundance Table.” Part No. G1820-90008 (undated document).

5. DESC. MIL-PRF-26536E. *Performance Specification Propellant, Hydrazine,* Military Standard, Defense Energy Support Center, Kelly Air Force Base, Texas, 1997, Amended January 2000.

6. Weast, R.C., editor. *CRC Handbook of Chemistry and Physics*. CRC Press, Inc., Boca Raton, Florida 1983.

7 Minier, L. M. Davis, D. D., Greene, B., Baker, D. L., Morgan, L. M., Gerron, R. A., and Benz, F. J. WSTF-TR-587-001, *Laboratory-Scale Evaluation of Prototype Supported Copper (II) Oxide Materials for the Control of Hydrazine Spills*, July 5, 1991.