

**Determination of Total Silica at PPB  
Levels in Ultrapure Water  
by Three Different Analytical Techniques**

**by**

**Theresa Chu and Marjorie K. Balazs**

*Presented at the Semiconductor Pure Water and Chemicals Conference (SPWCC)  
March 1993*

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# DETERMINATION OF TOTAL SILICA AT PPB LEVELS IN ULTRAPURE WATER BY THREE DIFFERENT ANALYTICAL TECHNIQUES

Theresa Chu and  
Marjorie K. Balazs  
Balazs Analytical Laboratory  
Sunnyvale CA 94089

## ABSTRACT

The presence of colloidal silica in ultrapure water can cause a silica residue to remain on wafer surfaces which later adversely affects the integrity of a semiconductor device. A general accepted approach to measuring colloidal silica is to take the difference between the values of a total silica and a dissolved silica measurement. In this study, three different techniques (colorimetry, ICP-AES and ICP-MS) were developed and evaluated for measuring total silica at ppb levels. Spike recovery data were presented to validate each method of analysis. A survey of typical silica (total and dissolved) concentrations in various DI water systems is also presented.

## INTRODUCTION

In the production of RO/DI water for semiconductor manufacturing, silica is a critical parameter that must be controlled and monitored on a routine basis (1-4). Silica exists in both the soluble and nonsoluble forms (5,6). Soluble silica is also known as reactive silica; it reacts with a molybdate solution to form a colored complex without requiring pretreatment. The nonsoluble form of silica is generally referred to as colloidal and particulate silica. In a typical RO/DI water system, both the colloidal and particulate silica are removed from the source water by the RO membrane. Since

colloidal silica is nonionic, the anion exchange resins do not effectively removed this species in addition to dissolved silica. (3) Indeed, it is believed that colloidal silica may be formed at the anion exchange resins when the anion exchanger is exhausted or near exhaustion (9).

A recent survey by the authors of this paper indicates that the final filter water of most Semiconductor DI water systems contained dissolved and total silica at very low concentrations, with typical values ranging 1.0 to 3.0 ppb. For some advance DI water systems, total silica concentration was found below 1.0 ppb. Since the concentration of silica in ultrapure water is so low, traditional methods of analysis for total and colloidal silica cannot be successfully used. Tradition methods for the analysis of total silica are the ASTM 859 gravimetric method (7), colorimetric method with alkaline digestion (5) and by graphite furnace atomic absorption (8). These methods have detection limits in the low ppm and high ppb ranges.

In this paper, a study was conducted to develop and evaluate three different methods (colorimetry with cold acid digestion, ICP-AES and ICP-MS) for the determination of total silica at low and sub ppb levels. A brief description of each technique as well as the recovery data and detection limit of each method is presented.

## **DESCRIPTION OF THE ANALYTICAL TECHNIQUES**

### **A) Colorimetry with Acid Digestion**

In this method, an ultrapure water sample is evaporated to dryness at sub-boiling points in a cleanroom environment. The remaining residue contains both the soluble and nonsoluble forms of silica. Nonsoluble silica is converted

to the soluble form by the addition of excess hydrofluoric acid at ambient temperature to the residue. Excess hydrofluoric acid is removed by a reagent and the total dissolved silica is then reacted with a molybdate solution to form a colored complex whose absorbance is measured with a spectrophotometer. The intensity of the color is directly proportional to the concentration of silica.

B) ICP-AES (Inductively Coupled Plasma-Atomic Emission Spectroscopy)

An ultrapure water sample is concentrated ten times by evaporation at sub boiling points in a cleanroom environment. For ICP-AES analysis the concentrated ultrapure water sample is first converted into fine aerosol droplets via a nebulizer-spray chamber system. The aerosol droplets are then introduced into a high temperature (6000K) argon plasma source. In the argon plasma, the fine droplets are vaporized and particles such as silica (soluble and nonsoluble) are atomized, ionized and excited. Electronically excited silicon atoms and ions emit photons during their transitions to the ground states. These photons, at a selected wavelength for silicon are measured by a detector such as a photomultiplier tube as a signal. Signal intensity is directly proportional to the concentration of Si in the water sample. The ICP-AES instrument is calibrated with standards prepared from NIST standards.

C) ICP-MS (Inductively Coupled Plasma-Mass Spectroscopy)

Similar to ICP-AES, a concentrated ultrapure sample is drawn into an argon plasma (>6000K temperature) via a nebulizer-spray chamber system. In the argon plasma, the elements in the resultant aerosol droplets are vaporized, atomized and ionized. The ions generated are extracted into a mass spectrometer where the ions are identified and measured based on their mass-

to-charge ratios. The concentrations of the elements such as Si in this case is quantified by external calibration using NIST standard.

## EXPERIMENTAL

The instruments used for this study were a P-E Sciex Elan 500 ICP-MS and a P-E Model 6000 ICP-AES. For colorimetric study, the instrument used was a HACH DR 3000 spectrophotometer. Four silica sources were used in this study and they are:

- 1) NIST standard 10,000 ppm Si solution.
- 2) Fischer Scientific  $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$  powder, 99% pure.
- 3) RICCA chemical 10,000 ppm  $\text{SiO}_2$ .
- 4) Johnson Matthey 40 % colloidal silicon oxide in water.

The first three standards are soluble silica standards and the fourth standard is a silica colloidal dispersion. The silica powder from Fischer Scientific was weighed and dissolved in ultrapure water to make a 1,000 ppm solution standard.

To validate each technique, ultrapure water samples were spiked with various concentrations of each type of standards, preconcentrated by evaporation in a clean environment and then measured for total silica. For each type of standard, four spike concentrations were prepared; 10, 50, 100 and 500 ppb. The concentration unit of the solutions prepared from sources (1) and (2) is expressed as Si, whereas the concentration unit of sources (3) and (4) is expressed as  $\text{SiO}_2$  for the reason of ease of sample preparation. The ICP-MS and ICP-AES were calibrated with blanks and standard solutions prepared from the NIST stock standard. The HACH spectrophotometer was calibrated with blank and standard solutions prepared from the RICCA stock standard. The ultrapure water used to prepare all the solutions was

analyzed as the blank and served as the "zero" point of the calibration curve. This blank was not preconcentrated. All chemical reagents used in this analysis are added to the blank as well. It was shown in this study that the RICCA standard was accurate with respect to the NIST standard.

## **RESULTS AND DISCUSSION**

### **Detection Limit**

In the determination of silica by ICP-MS and ICP-AES, the ultrapure water samples and spikes were concentrated ten times before analysis. The instrument detection limits obtained were calculated based on three times the standard deviation of the background noise of the blank. Since the samples were concentrated, the instrument detection limit is divided by the concentration factor. With ten times concentration of the sample, the detection limits obtained for both the ICP-MS and ICP-AES are 1 ppb and 3 ppb as Si or about 2 and 6 ppb as SiO<sub>2</sub> respectively.

Samples for colorimetry were concentrated 20 times before analysis. A large concentration is required because of the large dilution of the samples caused by the addition of the necessary chemical reagents. The detection limit of colorimetry method is estimated in the same manner as the spectroscopic techniques and is found to be 0.25 ppb as Si or 0.5 ppb as SiO<sub>2</sub>.

### **Spike Samples and Recovery Data**

The recovery data for spiked ultrapure water samples analyzed by ICP-MS and ICP-AES are presented in Tables 1a, 1b, 2a and 2b. The results indicate that the percent recoveries obtained for the soluble and colloidal silica sources in the spiking

range of 10 to 500 ppb are generally good (85 to 115%). However, the low range sample (10 ppb spike) appears to have more errors for both the soluble and colloidal sources. The reason for this observation is most likely because the low concentration is closer to the detection limit of these techniques and is subjected to more background noise fluctuations. For more accurate results, the sample can be preconcentrated more, up to 20 times to minimize this problem.

In addition, a larger variation in the recovery data was observed for the samples spiked with colloidal silica. This probably was caused by some slight settling of the colloidal silica during sample preparation or nebulization. This problem was not observed in the colorimetric technique as shown in Table 3.

The percent recoveries for ultrapure water samples spiked with soluble and colloidal silica by colorimetry with and without an acid digestion step are shown in Tables 3a, 3b, 4a and 4b. Very good recoveries and precision of results are obtained by the acid digestion/colorimetry method for soluble and colloidal silica (Tables 3a and 3b). No significant loss of silica was observed during sample preparation with the use of HF. It can be seen from Table 4b, that without acid digestion, colloidal silica is not measured by colorimetry.

After repeated use, it was found that the colorimetry method with HF digestion is precise and reproducible. In addition, because of its excellent detection limit, it is a more useful method compared to ICP-MS and ICP-AES for the measurement of total silica in ultrapure water samples.

## **A SURVEY OF SILICA CONCENTRATIONS IN VARIOUS RO/DI WATER SYSTEMS**

The dissolved and total silica concentrations presented in Table 5 are

representative values obtained from about ten RO/DI water systems. It can be seen that for most DI water systems, silica (dissolved and total) were found at very low concentrations ( 0.2 to 3.0 ppb) and the total silica concentration was significantly different from the dissolved silica concentration (Group II). This indicates the presence of non-reactive or colloidal silica in most final filter water. The last column of Table 5 shows the concentration of "colloidal" silica which was calculated from the difference of the total and dissolved silica. In this table, final filter water with a difference of less than 1 ppb was considered to have no significant colloidal silica (Group I). This limit was arbitrary set, it was based on the imprecision of subtracting two concentration values.

Table 6 shows the concentrations of dissolved and total silica concentrations of the different sites of three RO/DI water systems. The source water of the first two systems contained very little non-soluble (colloidal and particulate) silica. However, the third system contained a high concentration of silica with a substantial amount of non-soluble silica. Interestingly, for these systems, the presence of non-soluble silica in the source water was reflected in the final filter water. Systems which contained small amounts of non-soluble silica produces ultrapure water with relatively low colloidal silica concentration. Furthermore, it is clear from the results, that the third DI/RO water system is not designed to handle source water with such high silica concentration. The system not only had unacceptably high colloidal silica concentration, it also has very high dissolved silica concentration.



## CONCLUSION

In this study it was shown that most RO/DI water systems in the semiconductor industry contain very low levels of silica (total and dissolved) in the final filter water. The total silica concentration found is normally in the range of 0.5 to 3.0 ppb. Dissolved silica measured is generally lower than the total silica indicating the presence of colloidal silica in most DI water system.

Of the three techniques studied, it is found that the colorimetric method with acid digestion is most suitable for measuring total silica in ultrapure water, especially for concentrations less than 10 ppb. For concentrations greater than 10 ppb, ICP-MS and ICP-AES can be used if the ultrapure water samples are first concentrated at least 10 to 20 times before analysis. For water samples containing a significant amount of organics, ICP-MS may not be used because of possible background interference from  $\text{CO}^+$  species with the determination of silicon at mass 28. With both spectroscopic techniques, the background signal intensities are relatively high therefore, blank subtraction is not reproducible causing higher errors in the samples with silica concentrations close to the detection limits.

In terms of equipment cost, an ICP-MS is approximately \$250,000 and the ICP-AES is about \$130,000. On the other hand, the colorimetric method is much less expensive but the procedure is more tedious, and involved the addition of up to 5 chemical reagents. The ICP-AES and ICP-MS is a less complicated procedure in terms sample preparation and chemical reagents and a water sample can be analyzed in about 10 minutes after the instrument has been set up. However, both instruments require skilled operators and a high maintenance cost.

## ACKNOWLEDGEMENT

The authors wish to thank Dr. Samantha Tan for reviewing this paper and providing technical advise on the spectroscopic techniques. We also wish to thank the laboratory staff for assisting the lab work associated with this study.

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**Table 1a. Determination of Total Silica in Water Samples Spiked with Soluble Silica by ICP-MS.**

[Spike] ppb Si or SiO <sub>2</sub>	Silica Source 2		Silica Source 3	
	[Measured] ppb Si	% Recovery	[Measured] ppb SiO <sub>2</sub>	% Recovery
10	10.6	106	14	140
50	49	98	49.5	99
100	97	97	97	97
500	500	100	481	96

**Table 1b. Determination of Total Silica in Water Samples Spiked with Colloidal Silica by ICP-MS.**

[Spike] ppb SiO <sub>2</sub>	Silica Source 4	
	[Measured] ppb SiO <sub>2</sub>	% Recovery
10.3	9.2	89
51.3	41	80
102.6	80	78
513	378	74

**Table 2a. Determination of Total Silica in Water Samples Spiked with Soluble Silica by ICP-AES.**

[Spike] ppb Si or SiO <sub>2</sub>	Silica Source 2		Silica Source 3	
	[Measured] ppb Si	% Recovery	[Measured] ppb SiO <sub>2</sub>	% Recovery
10	11.5	115	13.4	134
50	55	110	51.4	103
100	110	110	92.7	93
500	497	99	492	98

**Table 2b. Determination of Total Silica in Water Samples Spiked with Colloidal Silica by ICP-AES.**

[Spike] ppb SiO <sub>2</sub>	Silica Source 4	
	[Measured] ppb SiO <sub>2</sub>	% Recovery
10.3	15.3	149
51.3	36	70
102.6	103	100
513	428	83

Table 3a. Determination of Total Silica in Water Samples Spiked with Soluble Silica by Colorimetry and Digestion Method.

[Spike] ppb Si	Silica Source 2	
	[Measured] ppb Si	% Recovery
10	11.3	113
50	56	112
100	114	114
500	545	109

Table 3b. Determination of Total Silica in Water Samples Spiked with Colloidal Silica by Colorimetry and Digestion Method.

[Spike] ppb SiO <sub>2</sub>	Silica Source 4	
	[Measured] ppb SiO <sub>2</sub>	% Recovery
10.3	9.6	93
51.3	50.4	98
102.6	102.6	100
513	460	90

**Table 4a. Determination of Dissolved Silica in Water Samples Spiked with Soluble Silica by Colorimetry without an Acid Digestion Step.**

[Spike] ppb Si or Si	Silica Source 1		Silica Source 2	
	[Measured] ppb Si	% Recovery	[Measured] ppb Si	% Recovery
10	10.6	106	11.7	117
50	50.1	100	57	114
100	103	103	114	114
500	492	98	541	108

**Table 4b. Determination of Dissolved Silica in Water Samples Spiked with Colloidal Silica by Colorimetry without an Acid Digestion Step.**

[Spike] ppb SiO <sub>2</sub>	Silica Source 4	
	[Measured] ppb SiO <sub>2</sub>	% Recovery
10.3	<0.5	0
51.3	<0.5	0
102.6	1.2	1.2
513	2.7	0.5

Table 5. A survey of Dissolved and Total Silica in Various DI Systems at the Final Filter.

	Dissolved Silica ppb SiO <sub>2</sub>	Total Silica ppb SiO <sub>2</sub>	"Colloidal" Silica ppb SiO <sub>2</sub>
GROUP I	0.2	0.7	0.5
	0.7	0.9	0.2
	0.5	1.2	0.7
	0.6	1.7	0.9
	9.0	9.8	0.8
GROUP II	0.2	3.3	3.1
	0.2	1.4	1.2
	0.4	2.7	2.3
	0.4	2.2	1.8
	0.2	1.4	1.2
	0.2	1.2	1.0
	0.8	2.7	1.9
	3.0	19	16
	10	20	10
	23	68	45

Table 6. Total and Dissolved Silica Measured at Different Sites of a DI System.

Sites	Systems with Low "Colloidal" Silica				System with high "Colloidal" Silica	
	Total SiO <sub>2</sub> ppb	Dissolved SiO <sub>2</sub> ppb	Total SiO <sub>2</sub> ppb	Dissolved SiO <sub>2</sub> ppb	Total SiO <sub>2</sub> ppb	Dissolved SiO <sub>2</sub> ppb
City Water	12,800	12,400	12,300	12,200	49,500	18,800
Post RO	107	98	122	109	6,150	2,010
Post Primary Resin	2.7	0.2	1.3	0.6	-	3.0
Post Polishing Resin	3.4	0.3	2.0	0.5	-	23
Post FF	2.7	0.3	1.2	0.5	68	23



## AUTHOR BIOGRAPHIES

THERESA CHU, Laboratory Manager, Water and Chemical Divisions, joined Balazs in 1983. Her specialized competence is in the area of QC monitoring of RO/DI water and system problem resolution; analytical chemical instrumentation used to measure inorganic and organic materials; bacteriological evaluations by culturing, epi fluorescence or SEM; and Microcontamination identification. She has five published papers and is a member of the American Chemical Society and the Bay Area Ion Chromatography User's Group. She received her B.S. Degree in Chemistry in 1979.

MARJORIE K. BALAZS, is the founder and president of Balazs Analytical Laboratory in Sunnyvale, California and Austin, Texas. She has worked in the semiconductor industry since 1968. Prior to her work in the semiconductor industry, she spent ten years at Stanford Research Institute and taught for six years at the University of San Francisco. She received her M.A. Degree in chemical education at Stanford University. She is a member of ECS, ASTM, ACS, ATFA, SEMI and SEMATECH. In 1986, she received an award from President Reagan as one of the 80 outstanding women entrepreneurs in the United States.

This paper was presented at SPWCC, March 2-4, 1993, in Santa Clara, California.

