Determination of silicate in high-purity water using ion chromatography and online sample preparation

Authors
Weerapong Worawirunwong[1] and Jeffrey Rohrer[2]
[1]Thermo Fisher Scientific, Bangkok, Thailand
[2]Thermo Fisher Scientific, Sunnyvale, CA, USA

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Goal
To develop an online sample preparation and IC method that accurately determines silicate in UHPW.

Introduction

The water used in the manufacture of semiconductors and other modern electronic components must be extremely pure. This water is often referred to as ultrahigh-purity water (UHPW). The production of UHPW includes deionization to remove corrosive strong acid anions, e.g., chloride and sulfate. Deionization cartridges exhaust their capacity over time and require replacement. When these deionization cartridges begin to fail, one of the first ions to break through the cartridge and contaminate the water is silicate. Silicate can break through while the water still yields an acceptable resistivity reading of 18 MΩ·cm. Therefore, silicate is a good early indicator of cartridge depletion. Monitoring silicate and then changing deionization cartridges when silicate first appears can help prevent manufacturing failure of expensive electronic components due to the presence of the more corrosive chloride and sulfate from cartridge exhaustion.

While silicate can be separated at high pH, it has very little dissociation from its acid form at neutral pH, and therefore cannot be detected sensitively using suppressed conductivity. However, silicate will react with molybdate to form a complex that can be detected with high sensitivity at 410 nm, as shown in Thermo Scientific Application Update 113.[1]

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To ensure the early recognition of cartridge depletion, silicate must be detected at concentrations lower than 1 µg/L. These low detections limits can be achieved by preconcentrating 20 mL of UHPW on an a Thermo Scientific™ Dionex™ IonPac™ AG4A-SC column, then separating the concentrated sample on a Dionex IonPac AS17 column set. To achieve the best reproducibility and highest sensitivity, a Reagent-Free™ ion chromatography (RFIC™) system is used to prepare the eluent for the Dionex IonPac AS17, and a Thermo Scientific™ Dionex™ AutoPrep™ system is used to prepare the low-level standards for calibration and automatically generate the calibration curve. The combination of an RFIC system and a Dionex AutoPrep system minimizes the time and labor needed for a sensitive and reproducible determination of silicate in UHPW.

Experimental
Equipment
- Thermo Scientific™ Dionex™ ICS-3000 system* consisting of:

  – DP Dual Pump

  – DC Detector/Chromatography Compartment with dual temperature zone equipped with 6-port valve (injection valve)

  – AM Automation Manager equipped with 10-port valve (high-pressure valve) and 3-way valve (low-pressure valve)

  – EG Eluent Generator

  – VWD Variable Wavelength Detector

  – AS-HV High-Volume Autosampler

  – Reagent Delivery Module (RDM)

*Equivalent or improved results can be achieved using the Thermo Scientific™ Dionex™ ICS-5000⁺ HPIC™ system.

- Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS) software, version 6.8

Reagents and standards
- Deionized water (DI), Type I reagent grade, 18 MΩ·cm resistivity

*Many labs that evaluate silicate in a high-purity water source will have a silicate-free water source. This grade of water is needed for a good blank analysis. A water polishing device (CIRA from Trovion, Inc.) was used in this experiment to produce water for the Dionex AutoPrep application used to prepare the blank and the standards.

- Silicate-free deionized water*

- Sodium metasilicate pentahydrate ($Na_2SiO_3 \cdot 5H_2O$)

- Sodium molybdate dihydrate ($Na_2MoO_4 \cdot 2H_2O$)

- Sodium lauryl sulfate ($CH_3(CH_2)11OSO_3Na$)

- Nitric acid (HNO_3)

All compounds should be ACS reagent grade or better from reliable sources.

Conditions

Concentrator:	Dionex IonPac AG4A-SC, 4 × 50 mm (P/N 043175)
Columns:	Dionex IonPac AG17 guard, 4 × 50 mm (P/N 055684) Dionex IonPac AS17 analytical, 4 × 250 mm (P/N 055682)
Eluent Source:	Thermo Scientific Dionex EGC II KOH Eluent Generator cartridge with the Thermo Scientific Dionex CR-ATC Continuously Regenerated Anion Trap column

Eluent Concentration:

Time (min)	Concentration (mM)	Curve
−20.0	50	5
−7.1	50	5
−7.0	1	5
0.0	1	5
2.0	10	6
4.0	20	4
10.0	20	5

Large Loop Volume:	20 mL
Temperature:	30 °C
Detection:	Visible absorbance at 410 nm
Noise:	≤100 mAU
Postcolumn Conditions:	20 mM Sodium molybdate 0.2 N Nitric acid 6 mM Sodium lauryl sulfate Reaction Coil: 1500 µL (P/N 042630) Flow Rate: 0.5 mL/min

Preparation of solutions and reagents
Eluent solution
The eluent generator (EG) produces the eluent using the Dionex EGC II KOH cartridge and deionized water supplied by the pump. The eluent concentration is controlled by Chromeleon CDS software. Because the Dionex IonPac AG17/AS17 column set does not produce 2000 psi of backpressure, backpressure tubing must be added to achieve 2300–2500 psi backpressure that will allow the EG degasser to function properly. See the Dionex ICS-3000 Operator's Manual[2] for instructions on adding backpressure.

Postcolumn reagent (PCR)
20 mM sodium molybdate / 0.2 N nitric acid / 6 mM sodium lauryl sulfate
Dissolve 2.42 g of $Na_2MoO_4 \bullet 5H_2O$ in 100 mL of deionized water. Slowly add 9.7 g of concentrated nitric acid and mix thoroughly. Add 0.86 g sodium lauryl sulfate and mix. Dilute to a final volume of 500 mL with deionized water. The PCR is stable for several days. Prepare fresh at least weekly.

Standard solutions
Stock standard
Prepare all silicate standards using silicate-free water.* This standard should be prepared from the highest purity sodium metasilicate pentahydrate available. To prepare the 1,000 mg/L silicate standard, add 0.353 g of sodium metasilicate pentahydrate to a 100 mL volumetric flask and bring to volume. This standard is stable for at least one month when stored at 4 °C.

Secondary standards
The stock standard is used to prepare the standards for the volume calibration, the calibration standards, and the method detection limit (MDL) standard.

1. Volume calibration requires the preparation of two different standards (see the Dionex AutoPrep Application, Volume Calibration section, which follows), the concentrate standard, and the dilution standard. To prepare the 2 mg/L concentrate standard, add 200 µL of the 1000 mg/L stock silicate standard to a 100 mL volumetric flask and bring to volume with silicate-free water. Prepare the dilution standard by further diluting the 2 mg/L silicate standard 1,000-fold (e.g., 100 µL to 100 mL).

2. Dionex AutoPrep calibration requires the analyst to prepare only a single standard. To prepare a 200 µg/L silicate standard, add 200 µL of the 1,000 mg/L stock silicate standard to a 1 L volumetric flask and bring to volume with silicate-free water. The Dionex AutoPrep system then prepares the standards in Table 1 and uses them for the calibration.

3. Prepare the MDL standard by diluting the 200 µg/L calibration standard 1000-fold.

Dionex AutoPrep application
Volume calibration
Volume Calibration is the method used to calibrate the volumes of the large and small loops at a 1,000:1 ratio in volume. The small loop volume can be roughly calculated from the i.d. and length of the PEEK tubing. However, the tubing i.d. can vary from batch to batch, resulting in an inaccurate injection volume calculation. In addition, the 10-port valve dead volume can further contribute to inaccuracy of the calibration. For example, if a small loop with a calculated volume of 20 µL is prepared and installed in an injection valve, the volume delivered to the IC system from this loop might be anything from 15 to 25 µL.

Table 1. Standard concentrations for method calibration and calibration results.

Analyte	Concentration (ng/L)				Results		
	Level 1	Level 2	Level 3	Level 4	R-square (%)	Offset	Slope
Silicate	200	400	800	1600	99.9427	–0.022	0.0321

Because the volume of injected silicate is directly proportional to the IC system response, a plot of known silicate concentration against volume can be used to determine the exact volume of the small loop. This is accomplished using two different standards with a concentration ratio of 1:1,000, such as 2 µg/L and 2,000 µg/L (2 mg/L) silicate. The 2 µg/L silicate is loaded into the large loop with loading volumes of 5, 10, 15, and 20 mL, and each is analyzed separately by the IC system. The silicate responses are plotted against the corresponding loading volume. Next, the 2,000 µg/L silicate is loaded onto the small loop and analyzed by IC.

When the measured response of silicate from the small loop is compared to the concentration plot from the large loop, the volume of the small loop will be one-thousandth of the corresponding volume of the large loop. For example, the result of the small loop measurement is equivalent to a 20.598 mL injection on the large loop. The small loop volume is 20.598 mL divided by 1,000, equal to 0.020598 mL or 20.598 µL. Once the small loop volume is known and calibrated, the accurate volume of preconcentration from the large loop can be established. For example, Figure 1 shows representative chromatograms of 5, 10, 15, and 20 mL injections of 2 µg/L silicate.

Column: Dionex IonPac AG17/AS17, 4 mm
Eluent: KOH gradient

Time (min)	Concn (mM)
−12.0	50
−7.1	50
−7.0	1
0.0	1
2.0	10
4.0	20
10.0	20

Eluent Source: Dionex EGC II KOH
Flow Rate: 1.0 mL/min
Inj. Volume: Loop calibration, 5, 10, 15, and 20 mL
Temperature: 30 °C
Detection: Visible absorbance, 410 nm
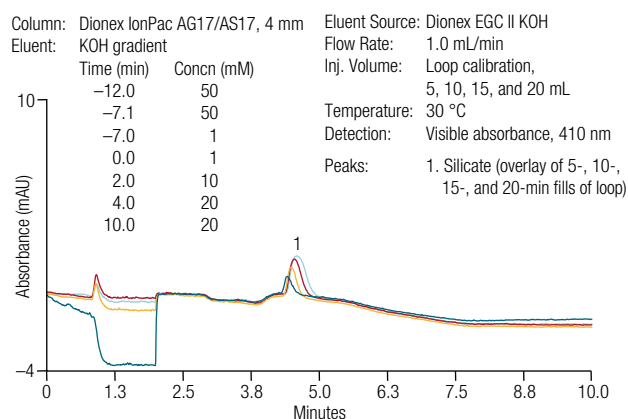Peaks: 1. Silicate (overlay of 5-, 10-, 15-, and 20-min fills of loop)

Figure 1. An overlay of the chromatograms from the four-point calibration (5, 10, 15, and 20 mL loading of the 2 µg/L silicate standard to the concentrator) for Dionex AutoPrep loop calibration.

The linearity results are shown in Table 1. Table 2 shows data from the three small loop injections of the 2000 µg/L silicate. The average value of 20.598 mL is now used for the loading volume. Because the loading flow rate is 1 mL/min, the loading time is 20.598 min.

Table 2. Data from three injections of the concentrate standard (2 mg/L silicate) using the small loop.

Sample #	Silicate Amount (mL)
1	20.6389
2	20.5666
3	20.5872
Average	20.598
RSD	0.18%

Note: The result of loop calibration is that 20.598 min will be used as the loading time for this experiment.

Configuration

Figure 2 shows the configuration of the Dionex AutoPrep system application for this Application Note. The DC needs to be equipped with one ten-port valve (AM-HP valve), one six-port valve (injection valve), and one low-pressure valve (AM-LP valve).

To prepare the small loop (20 µL), use 10.18 cm of 0.02 inch i.d. PEEK tubing. Prepare the large loop (20 mL) using a length of 0.0625 inch i.d. tubing that is greater than 1,042.62 cm. The length of the large loop needs to be longer than the 1,042.62 required for 20 mL to ensure that during the loading step eluent does not flow to the concentrator. Note, although we have provided exact tubing lengths, these lengths assume a uniform tubing diameter that is not observed in practice. Because the loop will be calibrated, the tubing lengths need only be close approximations of those provided.

To create the silicate-free water for this application, the CIRA water polishing device from Trovion was used. This device was either used to prepare water from a pressured bottle of deionized water (Figure 2A) or online with the second pump of the DP taking the water that exited the regenerant line of the Dionex CR-ATC and directed it to the CIRA, which delivered the polished water to the large loop when required (Figure 2B). If a lab/facility has silicate-free water, it can simply be put into a 4 L bottle (P/N 039164) which is pressurized, and the loop filled with silicate-free water when the valve is open (Figure 2C).
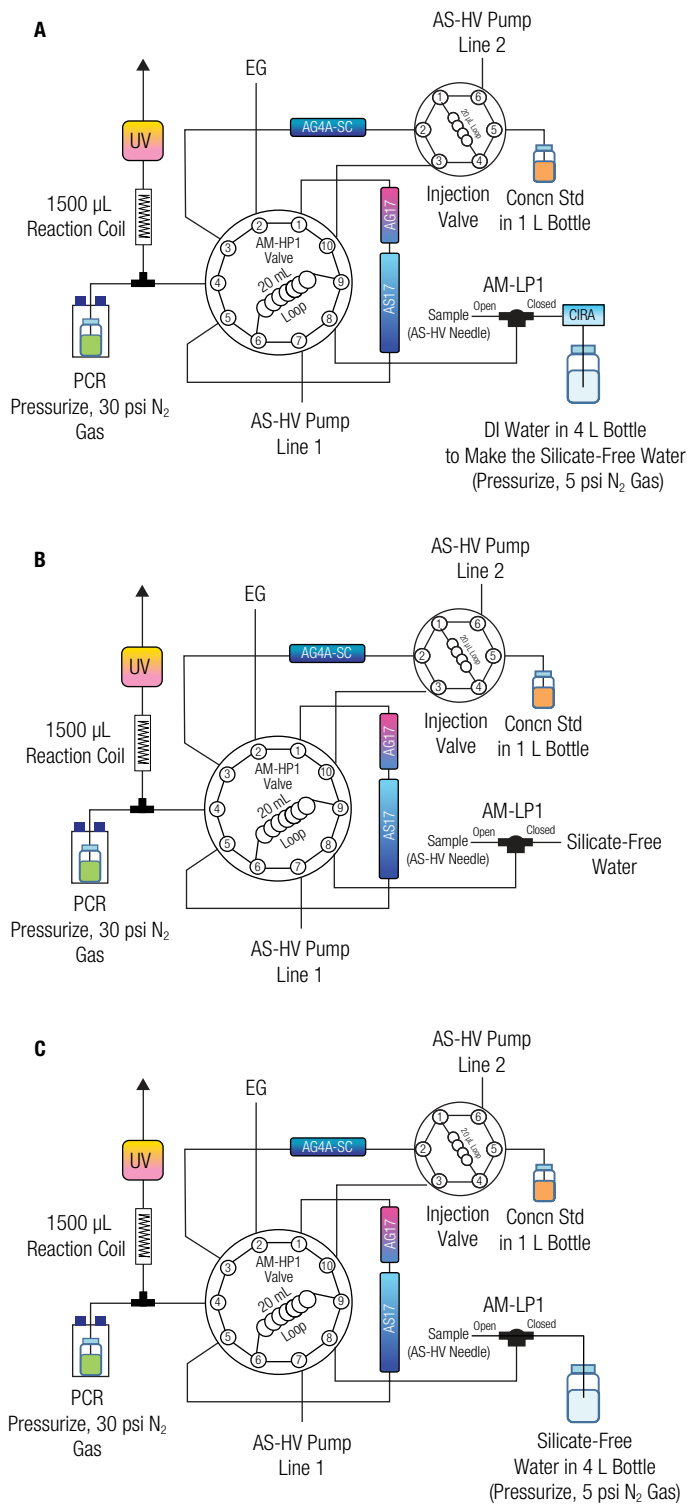
Figure 2. Three configurations of this Dionex AutoPrep application.
A) The silicate-free water is prepared by pressurizing deionized water in a 4 L bottle to supply the CIRA. B) The silicate-free water is prepared by the CIRA from the exiting regenerant of the Dionex CR-ATC using the second pump of the DP. C) Silicate-free water in a 4 L bottle is pressurized. In all three configurations the concentrate standard is in a 1 L bottle.

Because the second pump of the DP was used to generate the silicate-free water, the postcolumn reagent for silicate detection was added using an RDM. If the lab has a source of silicate-free water, it can use the second pump of the DP to deliver the postcolumn reagent as demonstrated in Thermo Scientific Application Update 113.

Dionex AutoPrep program

The Dionex AutoPrep program is separated into two different batch sequences; one sequence for the volume calibration method and the other for the standard calibration method.

1. Volume calibration method

Table 3 shows the time sequences of the volume calibration programs. The Chromeleon CDS software programs of the volume calibration method use nearly all the same commands, with the difference being the state of the AM-HP1 valve (10-port valve). The AM-LP1 is open for loading the dilution standard into the large loop. The volume of the dilution standard concentrated on the concentrator is controlled by the AM-HP1. The AM-HP1 valve is switched to position B to program the dilution standard loading time of 5, 10, 15, and 20 min. The 1× program is used to concentrate the volume of the small loop on the concentrator.

2. Standard calibration program

Table 4 shows the time sequences of the standard calibration programs. The Dionex AutoPrep system automatically prepares a calibration curve by concentrating multiple fills of the small loop. The injection valve is switched from load to inject multiple times during the same chromatography program to load multiple complete fills of the small loop with concentrate standard onto the concentrator. The concentration of the standard used to fill the small loop is 1,000× that to be measured in the large loop. Therefore one fill of the small loop with a 200 µg/L standard will represent a 200 ng/L sample in the large loop. To prepare a calibration curve of 200, 400, 800 and 1,600 ng/L, the small loop will be filled 1×, 2×, 4×, and 8× with concentrate standard, respectively, and these samples will be loaded onto the concentrator.

Table 3. Program for the volume calibration method.

| | | | **Program Name** | 5 min | 10 min | 15 min | 20 min | 1×* |
Time (min)	KOH Concn (mM)	Curve	AM-LP1			AM-HP1		
−20.500							A	A
−20.000					A	A		
−15.000	50							
−10.000				A				
−7.100		5					B	B
−7.000			Open		B	B		
−5.000	1			B				
0.000								
2.000	10	6		A	A	A	A	A
4.000	20	4						
10.000		5						

Note 1: The Dionex AutoPrep loop calibration command:

AM-LP1

Open = Port connected to the AS-HV autosampler needle

Closed = Port connected to silicate-free water

* AM-LP1 is closed during the 1× program

AM-HP1

A = Valve at 10-1 position, eluent is equilibrating the concentrator, guard column, and analytical column in preparation for the analysis.

The AM-LP1 line loads the dilution standard to the large loop.

B = Valve at 1-2 position, the dilution standard (in the large loop) is loaded on the concentrator by the eluent pump.

Note 2: The 1× program also needs the LoadPosition and InjectPosition commands between the program times −20.000 to −1.000 to load the small loop with the concentrate standard that is then sent to the concentrator.

Table 4. Program for standard calibration.

| | | | **Program Name** | **Standard Program (1×, 2×, 4×, and 8×)** | | **Sample** | |
Time (min)	KOH Concn (mM)	Curve	AM-HP1	AM-LP1	Injection Valve	M-LP1	Injection Valve
−21.000			A				
−20.598							
−15.000	50						
−10.000			B				
−7.100		5			See Note 2		
−7.000				Closed		Open	No command for the sample program
−5.000	1						
0.000							
2.000	10	6	A				
4.000	20	4					
10.000		5					

Note 1: n× (n = 1, 2, 3,…) as program name, where "n" is the number of the injection valve switches from load to inject position.

Note 2: Add the LoadPosition and InjectPosition commands the number of times indicated by the program name to load the concentrate standard to the concentrator. For example, if it is the 4× program, there needs to be four pairs of Load/Inject commands.

Note 3: For the connections and explanation of functions of AM-LP1 and AM-HP1, please see Table 3 and Figure 2.

Results and discussion

To evaluate whether the method delivered the required sensitivity, the MDL was determined by making a 200 ng/L silicate sample with silicate-free water and loading the large loop using the sample program of the Dionex AutoPrep system (Table 4). Figure 3 shows the chromatogram of 200 ng/L silicate and Table 5 shows the reproducibility of seven injections of the MDL standard. The calculated MDL from the peak height is 32.34 ng/L. This method easily meets the required sensitivity of <1 µg/L silicate.

Column: Dionex IonPac AG17/AS17, 4 mm
Eluent: KOH gradient

Time (min)	Concn (mM)
−12.0	50
−7.1	50
−7.0	1
0.0	1
2.0	10
4.0	20
10.0	20

Eluent Source: Dionex EGC II KOH
Flow Rate: 1.0 mL/min
Inj. Volume: 20 mL
Temperature: 30 °C
Detection: Visible absorbance, 410 nm
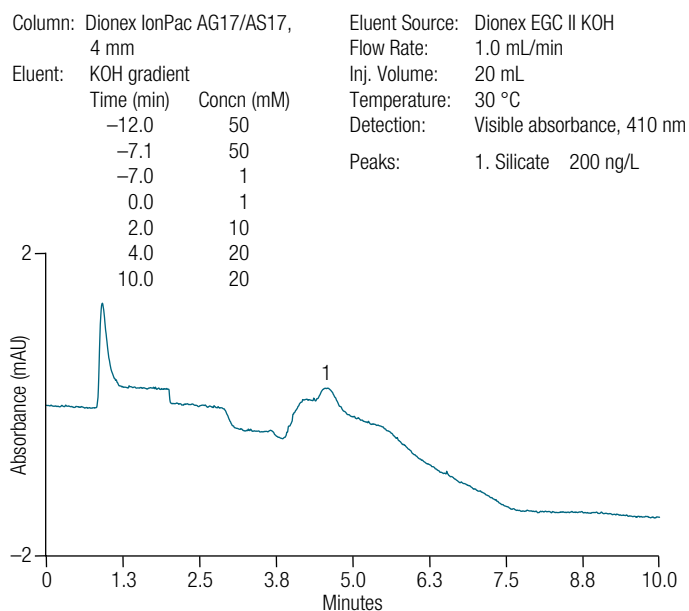
Peaks: 1. Silicate 200 ng/L

Figure 3. Chromatogram of one of the 200 ng/L silicate injections used for the MDL determination.

Table 5. Data from seven injections for the silicate MDL determination.

Injection #	Retention Time (min)	Area (mAU·min)	Height (mAU)
1	4.587	0.0694	0.24
2	4.54	0.0767	0.25
3	4.587	0.0803	0.26
4	4.567	0.0776	0.25
5	4.587	0.0714	0.24
6	4.547	0.0691	0.22
7	4.58	0.0697	0.24
Average:	4.571	0.073	0.241
RSD (%):	0.44	6.29	5.15

To confirm that the silicate-free water is indeed silicate-free and can be used to prepare the standards (thus confirming that the MDL standard only had silicate from the sodium metasilicate pentahydrate and not the water used to prepare it), the large loop was filled with the silicate-free water and a blank analysis run (sample program in Table 4). Figure 4 shows the chromatogram of the silicate-free water, confirming that it is indeed silicate-free.

Column: Dionex IonPac AG17/AS17, 4 mm
Eluent: KOH gradient

Time (min)	Concn (mM)
−12.0	50
−7.1	50
−7.0	1
0.0	1
2.0	10
4.0	20
10.0	20

Eluent Source: Dionex EGC II KOH
Flow Rate: 1.0 mL/min
Inj. Volume: 20 mL
Temperature: 30 °C
Detection: Visible absorbance, 410 nm

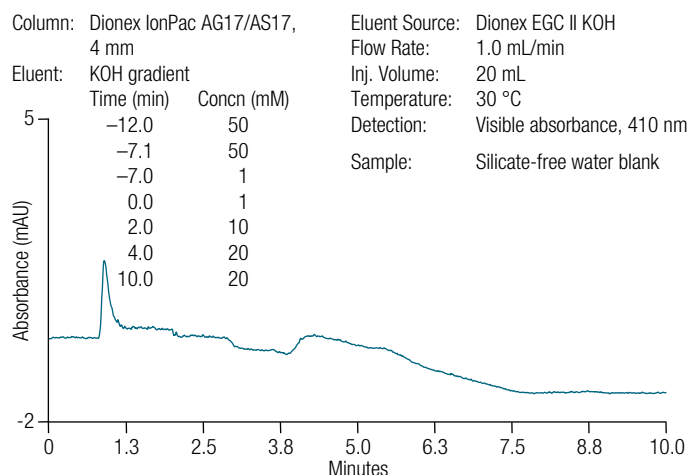Sample: Silicate-free water blank

Figure 4. Chromatogram of the silicate-free water blank.

The Dionex AutoPrep system was used to calibrate this method (Table 4, standard program). The four standards used by the system for method calibration were 200, 400, 800, and 1,600 ng/L. Figure 5 shows an overlay of these four standards. The efficiencies of these silicate peaks are higher than the silicate peak in the MDL standard due to sending a smaller volume to the concentrator. Chromeleon CDS software reported that calibration had an R-square of 99.96% with a slope of 4×10^{-4} mAU*min/(ng/L) and a y-intercept of 1.8×10^{-3} mAU·min. To check the accuracy of the standard calibration, a 800 ng/L standard was prepared and injected using the sample program in Table 4. Five injections of this standard had an RSD of 1.13% and an average concentration of 739.96 ng/L, a 92.50% recovery.
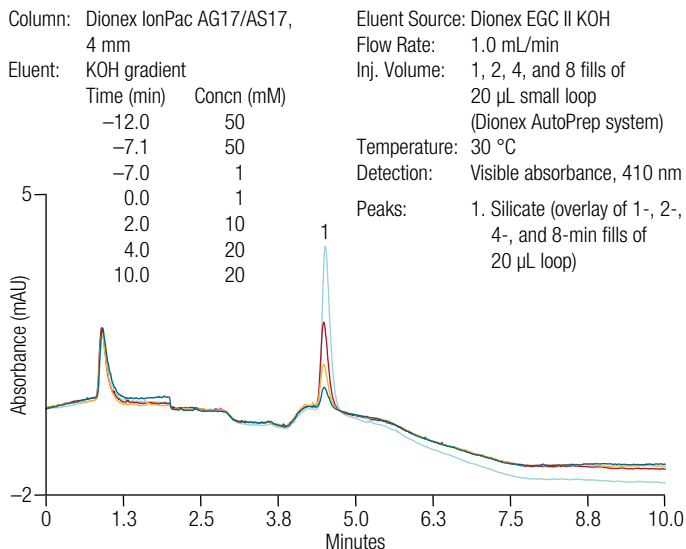
Column:	Dionex IonPac AG17/AS17, 4 mm	Eluent Source:	Dionex EGC II KOH
		Flow Rate:	1.0 mL/min
Eluent:	KOH gradient	Inj. Volume:	1, 2, 4, and 8 fills of 20 µL small loop (Dionex AutoPrep system)

Time (min)	Concn (mM)
−12.0	50
−7.1	50
−7.0	1
0.0	1
2.0	10
4.0	20
10.0	20

Temperature: 30 °C
Detection: Visible absorbance, 410 nm

Peaks: 1. Silicate (overlay of 1-, 2-, 4-, and 8-min fills of 20 µL loop)

Figure 5. Overlay of the four chromatograms used for the method calibration.

The laboratory deionized water was evaluated for silicate using the method in this application note. As the chromatogram in Figure 6 shows, the water had 571 ng/L silicate. It clearly could not be used to prepare standards for this application and was the reason an in-line water polisher was installed to prepare silicate-free water.
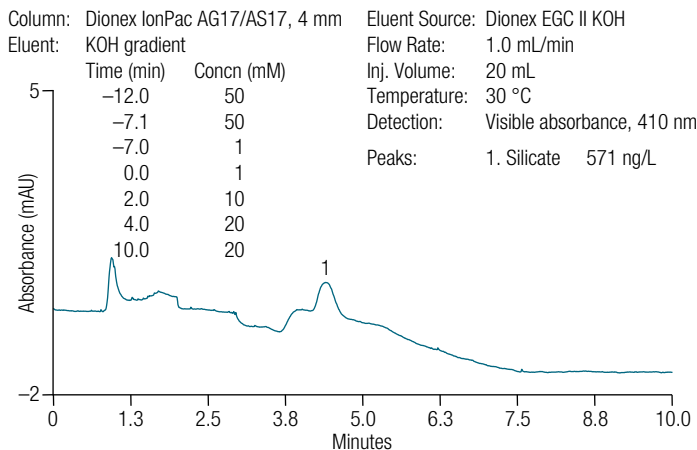
| Column: | Dionex IonPac AG17/AS17, 4 mm | Eluent Source: | Dionex EGC II KOH |
| Eluent: | KOH gradient | Flow Rate: | 1.0 mL/min |

Time (min)	Concn (mM)
−12.0	50
−7.1	50
−7.0	1
0.0	1
2.0	10
4.0	20
10.0	20

Inj. Volume: 20 mL
Temperature: 30 °C
Detection: Visible absorbance, 410 nm

Peaks: 1. Silicate   571 ng/L

Figure 6. Chromatogram of laboratory DI water. Peak 1 is silicate at a concentration of 571 ng/L.

Conclusion

This application note shows how the combination of RFIC and the Dionex AutoPrep system minimizes the time and labor needed for sensitive and reproducible determinations of silicate in UHPW.

Precautions

The sodium molybdate reagent must be prepared fresh at least weekly. This reagent can precipitate in tubing and check valves. If the system will be idle for longer than one day, flush the pump and tubing with 0.5 M NaOH for 2 h at the same flow rate used for analysis. Even when used constantly, the system should be shut down at least once a week to flush the pump and tubing as described above.

The peak width of the silicate peak may increase over time. When the peak width becomes unacceptable, replace the Dionex IonPac AG4A-SC column.

References

1. Thermo Scientific Application Update 113: Determination of Dissolved Silica and Common Anions Using Dual Detection. Sunnyvale, CA, 2009. [Online] www.dionex.com/en-us/webdocs/4180- AU113-IC-DissolvedSilica-DualDetection-13Aug2009-LPN1936-02.pdf (accessed Jan 9, 2014).

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