Determination of Silicate and Inorganic Anions in High Purity Water using Sequential Detection and AutoPrep

INTRODUCTION

Companies that require ultra high purity water for the manufacture of their products (e.g. semiconductor companies) monitor silicate as it is one of the first ions to break through deionization cartridges used for water purification. Application Note 170 showed how an ion chromatography system equipped with an IonPac® AS17 column set can determine sub-µg/L concentrations of silicate by visible absorbance after a post-column reaction. The same companies that determine low concentrations of silicate also determine low µg/L and sub-µg/L concentrations of inorganic anions and short chain organic acids (e.g. acetate). This Application Update (AU) shows how low concentrations of inorganic anions, organic acids, and silicate can be determined in one injection. Like AN170, this AU uses AutoPrep and an RFIC system to achieve sensitive and reproducible determinations with a minimum amount of time and labor. Analytes are separated on an IonPac AS19 column set, inorganic anions and organic acids are detected by suppressed conductivity, the eluent leaving the suppressor is reacted with a post-column reagent, and the silicate is determined by visible absorbance. This method saves time by combining two assays into a single assay.

EQUIPMENT

Dionex ICS-3000 consisting of:

DP Dual Pump

DC Detector/Chromatography module with dual temperature zone equipped with,

6-port valve (Injection valve)

AM Automation Manager equipped with:

10-port valve (High Pressure valve)

3-way valve (Low Pressure valve)

EG Eluent Generator module

VWD Variable Wavelength Detector

PC10 Postcolumn Delivery Package (P/N 050601)

Chromeleon® 6.8 Chromatography Data System

2 PC-100 Pump Controllers (Trovion, P/N 590100)*

*The PC-100 Pump Controller is a 2-channel peristaltic pump. If desired, a different peristaltic pump can be used for this application.

REAGENTS AND STANDARDS

Deionized water (DI), Type I reagent grade, 18 MΩ-cm
    resistivity or better

Sodium Metasilicate Pentahydrate ($Na_2SiO_3 \cdot 5H_2O$, Ajax)

Sodium Molybdate Dihydrate($Na_2MoO_4 \cdot 2H_2O$, Fluka)

Sodium Lauryl Sulfate ($CH_3(CH_2)_{11}OSO_3Na$, Fluka)

Sodium Fluoride (NaF, Fluka)

Sodium Chloride (NaCl, Fluka)

Sodium Nitrite ($NaNO_2$, Fluka)

Sodium Bromide (NaBr, Fluka)

Sodium Nitrate ($NaNO_3$, Fluka)

Sodium Sulfate (Na_2SO_4, Fluka)

di-Sodium Hydrogen Orthophosphate (Na_2HPO_4, Fluka)

Nitric acid (HNO_3, Fluka)

35% Hydrogen Peroxide (H_2O_2, UNILAB)

PREPARATION OF SOLUTIONS AND REAGENTS

Eluent solution

The eluent generator (EG) produces the eluent
using the EluGen EGC II KOH cartridge and deionized
water supplied by the pump. The eluent concentration is
controlled by Chromeleon software. Backpressure tubing
must be added to achieve 2300–2500 psi backpressure
that will allow the EG degasser to function properly. See
the ICS-3000 Ion Chromatography System Operator's
Manual, Document No. 065031-03, for instructions on
adding backpressure.

Post-column Reagent (PCR)

***20 mM Sodium Molybdate/0.2 N Nitric acid/6 mM
Sodium Lauryl Sulfate***

Dissolve 2.42 g of sodium molybdate
($Na_2MoO_4 \cdot 2H_2O$) in 100 mL deionized water. Slowly add
9.7 g concentrated nitric acid and mix thoroughly. Add
0.86 g sodium lauryl sulfate ($CH_3(CH_2)_{11}OSO_3Na$) 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: Stock standard Solutions (1000 mg/L)

Dissolve the appropriate weight of salt (Table 1) in
100 mL deionized water.

Table 1. Masses of Compounds Used to Prepare 100 mL of 1000 mg/L Standards

Ion	Compound	Weight (g)
Fluoride	Sodium fluoride (NaF)	0.221
Silicate	Sodium metasilicate pentahydrate ($Na_2SiO_3 \cdot 5H_2O$)	0.353
Chloride	Sodium chloride (NaCl)	0.165
Nitrite	Sodium nitrite ($NaNO_2$)	0.150
Bromide	Sodium bromide (NaBr)	0.129
Nitrate	Sodium nitrate ($NaNO_3$)	0.137
Sulfate	Sodium sulfate (Na_2SO_4)	0.148
Phosphate	di-Sodium hydrogen orthophosphate (Na_2HPO_4)	0.149

Secondary Standard

The stock standard is used to prepare the standards
for the calibration standards, the MDL standard and the
spike recovery test.

CONDITIONS

Column: IonPac AS19 analytical,
    2 × 250 mm (P/N 062886)

Guard: IonPac AG19 guard,
    2 × 50 mm (P/N 062888)

Concentrator: IonPac AG4A-SC guard,
    4 × 50 mm (P/N 043175)

Trap Column: IonPac ATC-HC trap column,
    9 × 75 mm (P/N 059604)

Eluent Source: EGC II KOH Cartridge
    (P/N 058900) with CR-ATC
    (P/N 060477), Gradient mode

Gradient: See Table 2

Flow Rate: 0.3 mL/min

Small Loop Volume: 10 µL

Large Loop Volume: 10 mL (P/N 066345)

Column Temperature: 35 °C

Pressure: ~2300 psi

SRS Current: 50 mA

Suppressor: Suppressed Conductivity
    ASRS-300, 2-mm (P/N 064555),
    External water mode
    CRD-200, 2-mm (P/N 062986),
    External Chemical Mode
    (200 mM NaOH)

Detection:	Conductivity (for anions, except silicate)
	Visible absorbance at 410 nm (for silicate)
Post Column Reagent (PCR):	20 mM Sodium Molybdate
	0.2 N Nitric acid
	6 mM Sodium Lauryl Sulfate
Reaction Coil:	375 µL (P/N 043700)
PCR Flow Rate:	0.15 mL/min

AutoPrep Application Schematic

Figure 1 shows a schematic of the configuration of this application. To understand this application, it is necessary to explain the commands that control the 10-port valve (AM_HP1), 6-port valve (Injection Valve), 3-way valve (AM_LP1), and one of the PC-100 Pump Controllers. Table 2 lists the states or positions of the three valves during the execution of this application.

Table 2. Gradient and Valve Switching for AutoPrep						
Time (min)	KOH Concentration (mM)	Curve	AM_LP1	AM_HP1	Injection Valve	External Pump
−15.00	50	5	*1	A	Inject	
−12.00	50	5		A	Load	
−10.10	50	5		A	Load	
−10.00	15	5		B	Load	
				*2		*2
0.00	15	5		A	Inject	
			*3			*4
12.00	15	5		A	Inject	
30.00	50	7		A	Inject	
34.90	50	5		A	Inject	
35.00	0.5	5		A	Inject	

Notes

*1. AM_LP1 between −15.00 and −10.00 min

    Open   for Standard run
    Closed   for Sample run

*2. AM_HP1 and External Pump between −10.00 and 0.00 min

Between -10.00 min and 0.00 min for a standard run, add pairs of commands for the AM_HP1 to go between states A and B depending on how many small loop volumes of the concentrated standard need to be loaded onto the concentrator. For example, for the Level 3 calibration standard (Table 4), there would need to be 4 pairs of commands. The External Pump needs to be On at the start of the pairs of commands for the AM_HP1 valve and turned Off after the last pair of AM_HP1 commands.

*3. AM_LP1 after 0.00 min

After time 0.00 min the AutoPrep can prepare the next injection depending on whether the next injection is a sample or standard. If the next sample is a standard, the AM_LP1 valve needs to be "Open" in the program and if the next injection is a sample, the AM_LP1 valve needs to be "Closed" in the program.

*4. External Pump after 0.00 min

After time 0.00 min for the AutoPrep program to prepare the next sample, the External Pump needs to be On using the "Closed" command.
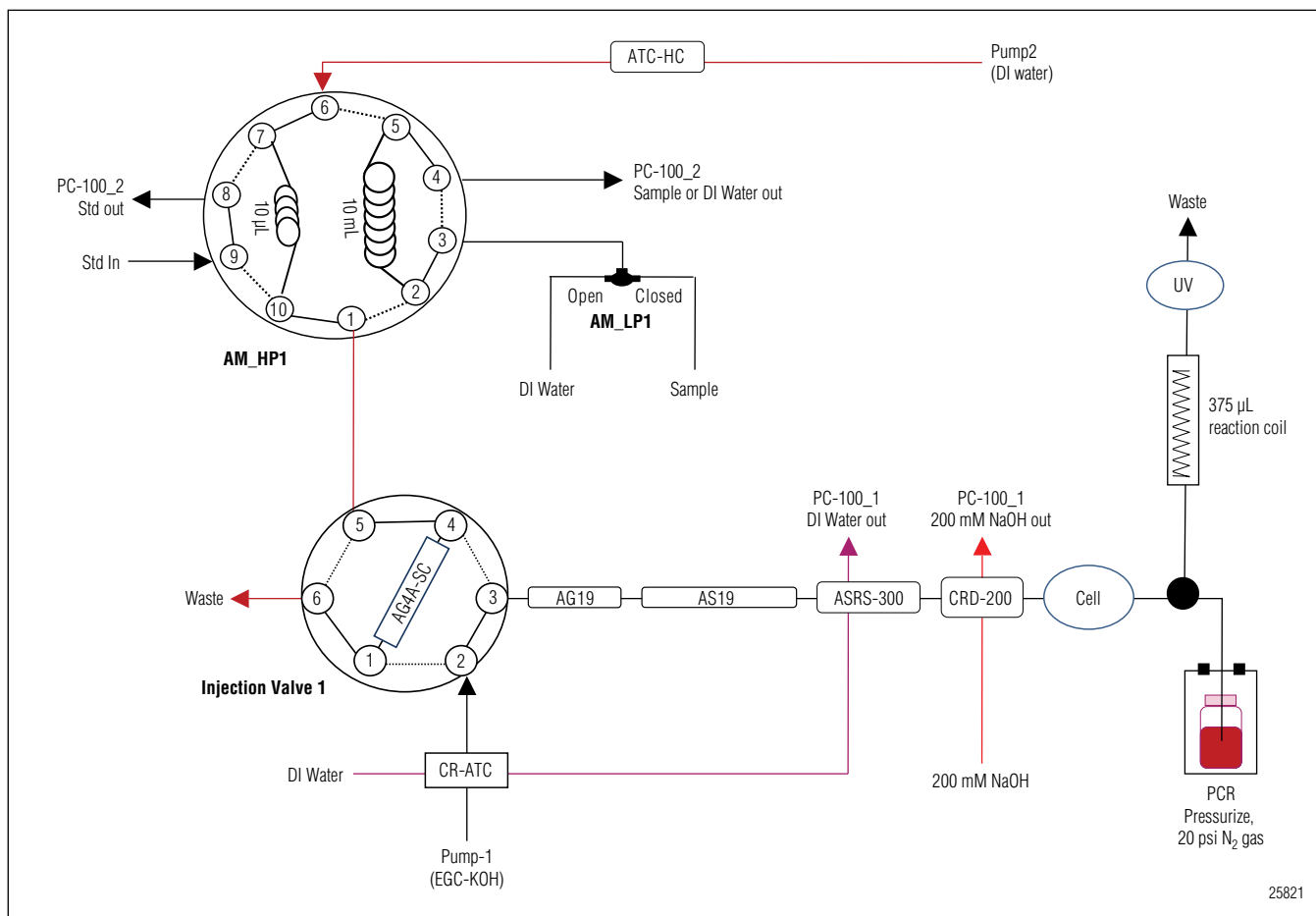
Figure 1. Schematic of the System Configuration for this Application

Commands

The following explains the commands to control the accessories listed above.

1. AM_HP1

The command AM_HP1.State is a command to control the 10-port valve. This valve has two states, or positions, A and B. When the valve state is A, the 10-port valve is in 10-1 position, and when the valve state is B, the 10-port valve is in 1-2 position.

Example commands:

AM_HP1.State A	= 10-1 position
AM_HP1.State B	= 1-2 position

2. Injection Valve

The injection valve has two states or positions, Load and Inject. The Load position allows the liquid from the 10-port valve to flow to the concentrator installed in the 6-port valve. In the Inject position, liquid can not flow from the 10-port valve to the concentrator.

Example commands:

InjectValve_1.StateInjectPosition	= 1-2 position
InjectValve_1.State LoadPosition	= 6-1 position

3. AM_LP1

The command AM_LP1 is a command to control the 3-way valve. This valve has two states, or positions, Open and Closed. The Open command puts DI-Water inline to run the standard program and the Closed command puts the sample in line to run the sample program.

Example commands:

AM_LP1.State	Open	= DI-Water Line open
AM_LP1.State	Closed	= Sample Line open

4. PC-100

This is a Trovion Peristaltic Pump that has two channels allowing it to sample from two different sources. Two PC-100s are needed for this application. The first PC-100 is used for the external chemical mode of the CRD-200 and the external water mode of the CR-ATC and ASRS-300. The second PC-100 is used for loading either the standard or sample for the analysis. The first PC-100 is always On during analysis and no commands are used to control it. The second PC-100 can be turned either on or off using the power output of the DC Relay.

Example commands

`DC_ACRelay_1.Open`   = PC-100 Pump Controller is Off

`DC_ACRelay_1.Closed`   = PC-100 Pump Controller is On

RESULTS AND DISCUSSION

Application Note 170 (AN170) uses an IonPac AS17 column set to determine silicate. In this AU, we have changed the separation column set to an IonPac AS19 column set and reduced the column diameter from 4 to 2 mm. While the column change adds 20 min per injection, the peak shape of silicate is improved, and the reduction in column diameter reduces the amount of eluent used and waste generated. The reduction in flow rate also allows for a reduction in the flow rate of the post-column reagent used to detect silicate, saving post-column reagent and reducing waste. Though the separation time increases from 10 to 35 min, the increase in method time is only 20 min because sample loading time was reduced by 5 min. Sample loading time was reduced as a result of reducing the sample size from 20 to 10 mL, which was possible with the reduction in column diameter.

Like AN170, this AU using AutoPrep to calibrate the method and to automatically load the large sample volume from a pressurized reservoir. For more details on the AutoPrep application please see AN170. In order to accurately determine low concentrations of silicate, it is important that the water used for the AutoPrep application be low in silicate. Figure 2 shows the results of measuring the anions in 10 mL of the water used for chromatography and the AutoPrep application. Panel A displays the suppressed conductivity detection and shows small peaks for nitrite and nitrate and three larger unknown peaks. The earliest eluting unknown peaks are most likely acetate and

Columns:	IonPac AS19 analytical, 2 × 250 mm, IonPac AG19 guard, 2 × 50 mm	Detection A:	Suppressed conductivity, ASRS-300, external water mode,CRD-200, external chemical mode (200 mM NaOH)
Eluent Source:	EGC II KOH		
Eluent:	Potassium hydroxide: 15 mM from 0 to 12 min and 15 to 50 mM from 12 to 35 min	Detection B: Post Column Reagent (PCR):	Visible absorbance at 410 nm 20 mM Sodium Molybdate 0.2 N Nitric acid
Temperature:	35 °C		6 mM Sodium Lauryl Sulfate
Flow Rate:	0.3 mL/min	Reaction Coil:	375 µL
Small Loop Volume:	10 µL	PCR Flow Rate:	0.15 mL/min
Large Loop Volume:	10 mL	Sample:	DI water

Peaks : 1. Unknown – ng/L
2. Unknown –
3. Nitrite –
4. Unknown –
5. Nitrate –

Figure 2. Chromatograms of DI water, (A) conductivity and (B) absorbance.

formate. The first of the unknown peaks is not baseline resolved from fluoride and the third is not baseline resolved from nitrate (Figure 4A), but both fluoride and nitrate can be easily integrated and neither is expected at a significant concentration in high purity water. Figure 2B shows no detectable silicate, and therefore the water is silicate-free for this application.
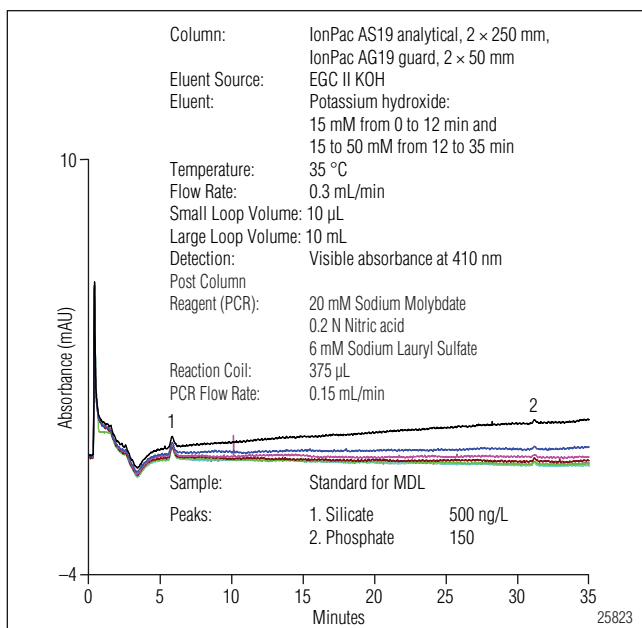
Column: IonPac AS19 analytical, 2 × 250 mm,
IonPac AG19 guard, 2 × 50 mm
Eluent Source: EGC II KOH
Eluent: Potassium hydroxide:
15 mM from 0 to 12 min and
15 to 50 mM from 12 to 35 min
Temperature: 35 °C
Flow Rate: 0.3 mL/min
Small Loop Volume: 10 μL
Large Loop Volume: 10 mL
Detection: Visible absorbance at 410 nm
Post Column
Reagent (PCR): 20 mM Sodium Molybdate
0.2 N Nitric acid
6 mM Sodium Lauryl Sulfate
Reaction Coil: 375 μL
PCR Flow Rate: 0.15 mL/min

Sample: Standard for MDL
Peaks: 1. Silicate 500 ng/L
2. Phosphate 150

Figure 3. Chromatograms of five consecutive standard injections used for the MDL determinations.

A 500 ng/L silicate standard was analyzed to determine if this application had the required sensitivity. Figure 3 shows five injections of the 500 ng/L silicate standard that also contained seven other anions at low concentrations for determination of MDLs using both detection methods (Table 3). Please note the improved peak shape for the 500 ng/L silicate compared to the 200 ng/L sample in AN170 Figure 3. While the concentration of the standard in this AU is 2.5 times that in AN170, the amount of silicate is similar. In AN170, we loaded 20 mL of a 200 ng/L standard onto an AS17 column set, or 0.4 ng. In this AU, 10 mL of a 500 ng/L standard, or 0.5 ng of silicate was loaded onto the AS19 column set. This method meets the required sensitivity. The MDLs for the other anions determined by suppressed conductivity were all well below 1 μg/L (Table 3). Note the small peak for 150 ng/L phosphate in Figure 3. The post column reagent used to detect silicate will also detect phosphate, but with less sensitivity than conductivity detection. We did not calibrate the visible detection method for phosphate because the lowest concentration (100 ng/L) for conductivity calibration was too low for the visible detection method.

Having established the method blank and ascertained method sensitivity, we calibrated the system using AutoPrep. The anion concentrations used for calibration are listed in Table 3, while Figure 4 and Table 5 show the chromatography and calibration results, respectively. There was good linear peak area response with concentration increase over the concentration range chosen for all eight anions.

A check standard was analyzed periodically to assess the accuracy of the calibration curve and check the recovery of phosphate which can be lost due to microbial contamination. Figure 5 shows the chromatography of five injections of the check standard (concentrations in Table 6) using the sample program (10 mL loop). The method exhibited good accuracy and recovery (Table 6).

Table 3. Data from Seven Injections of the Standard for MDL Determinations							
Height (nS)							
Injection # / Amount	Fluoride 10 ng/L	Silicate 500 ng/L	Chloride 15 ng/L	Nitrite 20 ng/L	Bromide 30 ng/L	Nitrate 30 ng/L	Sulfate 60 ng/L	Phosphate 150 ng/L
1	54.13	359.2	46.88	64.83	19.74	84.80	17.31	52.17
2	61.43	356.5	48.57	72.01	20.58	85.50	19.09	50.44
3	53.69	357.5	45.60	69.48	19.60	85.44	18.07	50.27
4	59.36	373.3	45.76	69.40	20.50	87.14	17.66	52.05
5	58.03	377.0	46.40	74.57	20.01	86.83	16.87	50.97
6	60.09	413.0	48.11	76.34	20.03	86.75	15.35	50.71
7	60.55	375.8	48.96	84.86	20.71	86.50	16.84	49.85
Average	**58.18**	**373.2**	**47.18**	**73.07**	**20.17**	**86.14**	**17.31**	**50.92**
RSD	**5.34**	**5.28**	**2.89**	**8.79**	**2.15**	**1.03**	**6.72**	**1.74**
MDL (ng/L)	**1.68**	**82.9**	**1.36**	**5.52**	**2.02**	**0.97**	**12.66**	**8.17**

Columns: IonPac AS19 analytical, 2 × 250 mm,
IonPac AG19 guard, 2 × 50 mm
Eluent Source: EGC II KOH
Eluent: Potassium hydroxide:
15 mM from 0 to 12 min and
15 to 50 mM from 12 to 35 min
Temperature: 35 °C
Flow Rate: 0.3 mL/min
Small Loop Volume: 10 µL
Large Loop Volume: 10 mL
Detection A: Suppressed conductivity,
ASRS-300, external water mode ,
CRD-200, external chemical mode
(200 mM NaOH)
Detection B: Visible absorbance at 410 nm
Sample: Four mixed standards for calibration
Post Column
Reagent (PCR): 20 mM Sodium Molybdate
0.2 N Nitric acid
6 mM Sodium Lauryl Sulfate
Reaction Coil: 375 µL (P/N 043700)
PCR Flow Rate: 0.15 mL/min

Peaks A:
1. Fluoride 10, 20, 40 and 80 ng/L
2. Unknown –
3. Unknown –
4. Chloride 10, 20, 40 and 80
5. Nitrite 20, 40, 80 and 160
6. Bromide 15, 30, 60 and 120
7. Unknown –
8. Nitrate 10, 20, 40 and 80
9. Sulfate 60, 120, 240 and 480
10. Phosphate 100, 200, 400 and 800

Peaks B:
1. Silicate 500, 1000, 2000 and 800
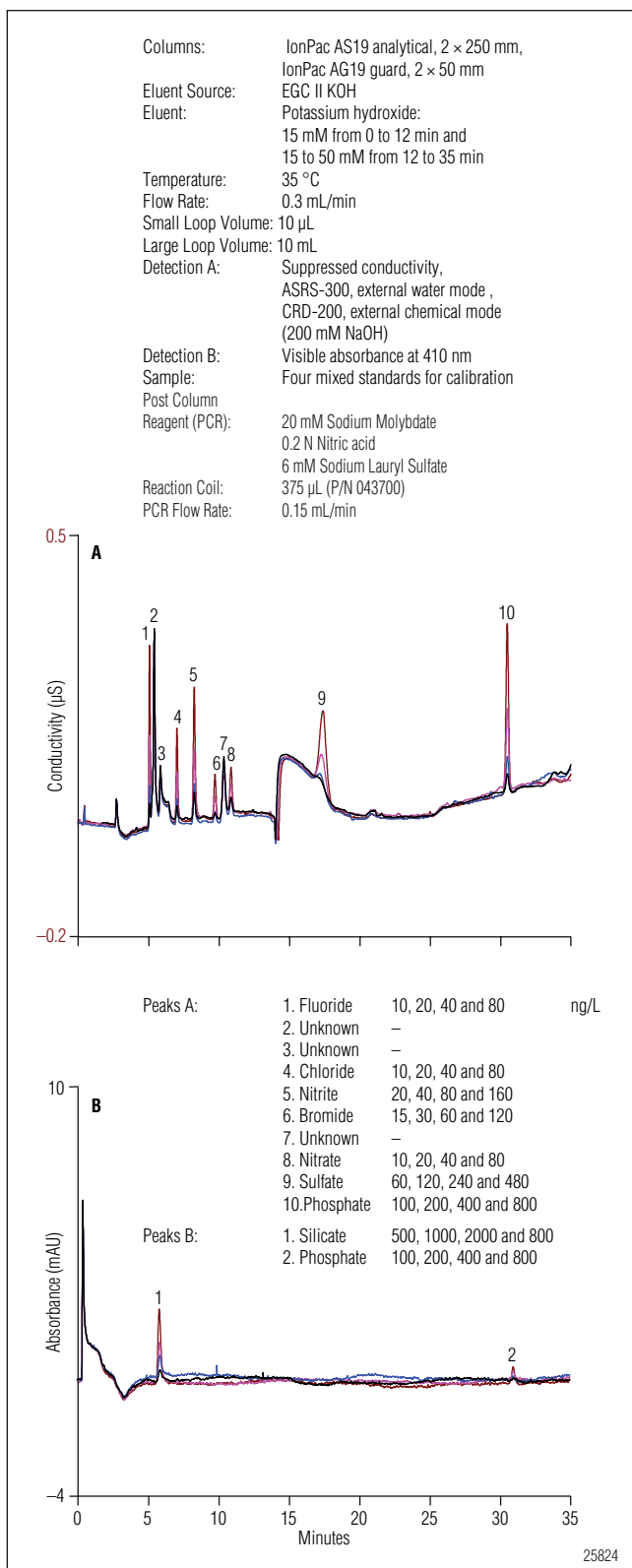2. Phosphate 100, 200, 400 and 800

*Figure 4. Chromatograms of the Four Mixed Standards used
for Calibration. See Table 4 for standard concentrations.
(A) Conductivity and (B) absorbance.*

Table 4. Concentrations of the Four Standard Mixtures used for Calibration				
	Concentration (ng/L)			
Peak Name	**Level 1 (1×)**	**Level 2 (2×)**	**Level 3 (4×)**	**Level 4 (8×)**
Fluoride	10	20	40	80
Silicate	500	1000	2000	4000
Chloride	10	20	40	80
Nitrite	20	40	80	160
Bromide	15	30	60	120
Nitrate	10	20	40	80
Sulfate	60	120	240	480
Phosphate	100	200	400	800

Table 5. Calibration Report from Chromeleon				
Peak Name	**# of Points**	**Coeff.Det.**	**Offset**	**Slope**
Fluoride	4	99.9204	−0.0008	0.0005
Silicate	4	99.8890	−0.0183	0.0002
Chloride	4	99.9155	0.0000	0.0003
Nitrite	4	99.9627	0.0035	0.0002
Bromide	4	99.9636	0.0004	0.0001
Nitrate	4	99.9897	0.0028	0.0002
Sulfate	4	99.9512	−0.0044	0.0002
Phosphate	4	99.8922	−0.0018	0.0001

SUMMARY

This AU shows that sub µg/L concentrations of inorganic anions and small organic acids can be determined in the same injection as sub µg/L concentrations of silicate by using an ICS-3000 ion chromatography system with suppressed conductivity detection followed by a postcolumn reaction and visible absorbance detection to determine silicate. This application saves time by requiring only one injection for two separate determinations, by using a RFIC system to prepare the eluents, and by using the AutoPrep application to calibrate the method and automate sample delivery in a closed system that minimizes sample contamination.
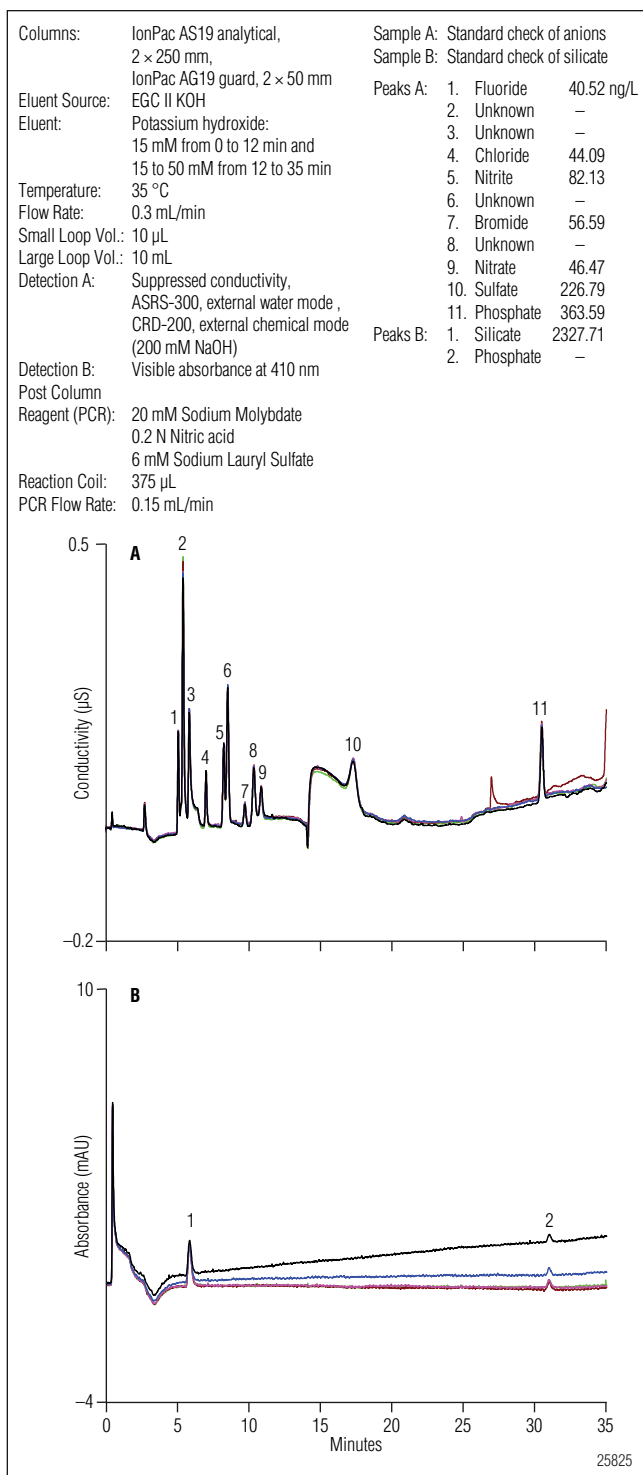
Columns:	IonPac AS19 analytical, 2 × 250 mm,		Sample A:	Standard check of anions
	IonPac AG19 guard, 2 × 50 mm		Sample B:	Standard check of silicate

Eluent Source:	EGC II KOH	Peaks A:	1. Fluoride	40.52 ng/L
Eluent:	Potassium hydroxide:		2. Unknown	–
	15 mM from 0 to 12 min and		3. Unknown	–
	15 to 50 mM from 12 to 35 min		4. Chloride	44.09
Temperature:	35 °C		5. Nitrite	82.13
Flow Rate:	0.3 mL/min		6. Unknown	–
Small Loop Vol.:	10 µL		7. Bromide	56.59
Large Loop Vol.:	10 mL		8. Unknown	–
Detection A:	Suppressed conductivity,		9. Nitrate	46.47
	ASRS-300, external water mode ,		10. Sulfate	226.79
	CRD-200, external chemical mode		11. Phosphate	363.59
	(200 mM NaOH)	Peaks B:	1. Silicate	2327.71
Detection B:	Visible absorbance at 410 nm		2. Phosphate	–
Post Column				
Reagent (PCR):	20 mM Sodium Molybdate			
	0.2 N Nitric acid			
	6 mM Sodium Lauryl Sulfate			
Reaction Coil:	375 µL			
PCR Flow Rate:	0.15 mL/min			

Figure 5. Chromatograms of the Check Standard Injections.

PRECAUTIONS

1. 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.

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

3. When the system needs to be shut down, use the PC10 Pneumatic Controller to turn off or remove the pressure from Pressurizable Chamber containing the PCR. Before the eluent pump is shut down, make sure that the PCR is not flowing. If the PCR enters the CRD-200 and ASRS-300 it can cause a noisy baseline.

4. If the system has microbiological contamination there can be a loss of sensitivity for phosphate. When phosphate loss occurs, clean the sample loop and sample bottle. Clean the sample loop by pumping the 3% H_2O_2 through the sample loop for approximately 30 min followed by DI water for 30 min. To clean the sample bottle, fill the sample bottle with 3% H_2O_2, until full and wait for approximately 30 min before washing the sample bottle with DI water.

REFERENCES

1. Dionex Corporation. Determination of Silicate in High Purity Water Using Ion Chromatography and AutoPrep, Application Note 170: LPN 1992. Sunnyvale, CA, 2007.

2. Dionex Corporation. *ICS-3000 Ion Chromatography System Operator's Manual,* Document No. 065031-03.

Table 6. Results of the Analysis of the Five Check Standard Injections								
	Amount							
Injection #	**Fluoride 40 (ng/L)**	**Silicate 2000 (ng/L)**	**Chloride 40 (ng/L)**	**Nitrite 80 (ng/L)**	**Bromide 60 (ng/L)**	**Nitrate 40 (ng/L)**	**Sulfate 240 (ng/L)**	**Phosphate 400 (ng/L)**
1	40.04	2065	44.19	80.74	58.84	51.12	214.84	365.65
2	40.74	2271	45.21	82.02	55.38	44.55	225.41	359.54
3	40.26	2454	43.80	82.16	53.99	45.42	232.75	364.20
4	40.98	2512	42.75	81.67	58.28	47.84	233.01	366.91
5	40.56	2337	44.48	84.07	56.44	43.44	227.94	361.65
Average	**40.52**	**2328**	**44.09**	**82.13**	**56.59**	**46.47**	**226.79**	**363.59**
RSD	**0.93**	**7.52**	**2.06**	**1.48**	**3.55**	**6.58**	**3.27**	**0.82**
%Recovery	**101.3**	**116.4**	**110.2**	**102.7**	**94.31**	**116.2**	**94.50**	**90.90**

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