DIONEX

Application Update 113

Determination of Dissolved Silica and Common Anions Using Dual Detection

INTRODUCTION

One of the most abundant elements on earth, silicon is found in a variety of forms, many of which are polymeric, and all being weakly acidic. Silicon and its compounds are used in the manufacture of glass, ceramics, building materials, transistors, semiconductors, preservatives, dessicants, and detergents, as well as stationary phases for chromatography columns.

Dissolved silica can be measured in solution as silicate using ion chromatography. As the anion of a weak acid, silicate is generally poorly retained by anion exchange columns. Because it has almost no dissociation at pH 7, the ion cannot be determined by suppressed conductivity detection. As a weak acid, it is adequately retained by anion exchange, eluting later than fluoride. Silicate can be derivatized post-column with sodium molybdate reagent to form a complex that can be detected with high sensitivity by visible absorbance at 410 nm. This acidic reagent will also react with phosphate to form a complex that is detectable at the same wavelength.

In this application, silicate and seven common anions, (fluoride, chloride, nitrite, nitrate, bromide, phosphate, and sulfate) are separated using the IonPac® AS22, a column designed for fast, high-resolution separations using carbonate/bicarbonate eluent. After separation and detection by suppressed conductivity, the output from the suppressor is derivatized with molybdate reagent to detect silicate using visible absorbance. This reaction also provides a second detection of phosphate. If desired, the suppressor can be removed and the method used solely for silicate and phosphate determinations.

Dual detection applications are easily achieved with the ICS-3000 system. In this instance, the sytem is configured with both conductivity and absorbance detectors. The second pump of the DP Dual Pump module is used to add the molybdate reagent after the conductivity detector. This application is ideal for determining silicate at mg/L concentration in a variety of samples, including laundry detergent.

INSTRUMENTATION

Dionex ICS-3000 ion chromatograph consisting of:

DP Dual Gradient Pump
DC Detector Chromatography Module
AS Autosampler
PDA-100 Photodiode Array Detector
Chromeleon® 6.8 Chromatography Workstation

For this application, a dual isocratic pump can also be used in place of the dual gradient pump, the AS40 autosampler can be used in place of the AS, and the VWD absorbance detector can be used in place of the photodiode array detector.

REAGENTS AND STANDARDS

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

Sodium fluoride (NaF)

Sodium chloride (NaCl)

Sodium nitrite ($NaNO_2$)

Potassium bromide (KBr)

Sodium nitrate ($NaNO_3$)

Sodium sulfate (Na_2SO_4)

Potassium dihydrogen phosphate (KH_2PO_4)

Sodium metasilicate pentahydrate ($Na_2SiO_3.5H_2O$)

Sodium molybdate dihydrate ($Na_2MoO_4 2H_2O$)

Nitric acid (HNO_3)

Sodium lauryl sulfate ($CH_3(CH_2)_{11}OSO_3Na$)

Sodium carbonate 0.5 M (Na_2CO_3), (Dionex P/N 37162)

Sodium bicarbonate 0.5 M ($NaHCO_3$), (Dionex P/N 37163)

All compounds were ACS reagent grade or better from reliable sources.

Conditions

Columns:	IonPac AS22 Analytical, 4 × 250 mm (P/N 064141) IonPac AG22 Guard, 4 × 50 mm (P/N 064139)
Eluent:	4.5 mM Na_2CO_3/1.4 mM $NaHCO_3$
Flow Rate:	1mL/min
Column Temperature:	30 °C
Injection Volume:	100 µL (full loop)
Detection #1:	Suppressed conductivity; ASRS® ULTRA II, external water mode
Suppressor current:	36 mA
Detection #2:	Visible absorbance; 410 nm
Post-column reagent conditions:	
	20 mM sodium molybdate
	0.2 N nitric acid
	6 mM sodium lauryl sulfate
Reaction coil:	1500 µL (P/N 42630)
Flow rate:	0.5 mL/min (DP Pump 2)

Preparation of Solutions and Reagents

Eluent: 4.5 mM Na_2CO_3/1.4 mM $NaHCO_3$

Add 9.0 mL of 0.5 M Na_2CO_3 and 2.8 mL of 0.5 M $NaHCO_3$ to a 1 L volumetric flask and bring to volume with DI water.

Postcolumn Reagent

20 mM Sodium Molybdate/0.2 N Nitric Acid/6 mM Sodium Lauryl Sulfate

Dissolve of 2.42 g of $Na_2MoO_4 2.H_2O$ in 100 mL of deionized water in a 500 mL volumetric flask. Slowly add 9.7 g of concentrated nitric acid and mix thoroughly. Next, add 0.86 g dissolved sodium lauryl sulfate. Bring to volume with DI water. The PCR reagent is stable for several days. Prepare fresh weekly.

STANDARD SOLUTIONS

Stock Standards

Prepare 1000 mg/L standards for each of the anions in DI water. Table 1 provides the amounts needed to prepare 100 mL of each standard. Concentrated standards are stable for at least one month when stored at 4 °C.

Table 1. Masses of Compounds Used to Prepare 100 mL of Stock Anion Standards

Anion	Compound	Amount (g)
Fluoride	Sodium fluoride	0.221
Chloride	Sodium chloride	0.165
Nitrite	Sodium nitrite	0.150
Bromide	Potassium bromide	0.149
Nitrate	Sodium nitrate	0.137
Sulfate	Sodium sulfate	0.148
Phosphate	Potassium dihydrogen phosphate	0.143
Silicate	Sodium metasilicate pentahydrate	0.354

Secondary Standards

The stock standards are used to prepare the calibration standards listed in Table 2. For example, the level 4 standard is prepared by adding the following volumes of the 1000 mg/L stock standards to a 100 mL volumetric flask: fluoride, 80 µL; chloride, 160 µL; nitrite, 160 µL; bromide, 320 µL; nitrate, 320 µL; sulfate, 160 µL; phosphate, 320 µL; silicate, 800 µL, and bringing to volume with DI water. The MDL standard was prepared by making a 20-fold dilution of the level 1 calibration standard.

Table 2. Standard Concentrations for Method Calibration

Analyte	Concentration (mg/L)			
	Level 1	Level 2	Level 3	Level 4
Fluoride	0.1	0.2	0.4	0.8
Chloride	0.2	0.4	0.8	1.6
Nitrite	0.2	0.4	0.8	1.6
Bromide	0.4	0.8	1.6	3.2
Nitrate	0.4	0.8	1.6	3.2
Sulfate	0.2	0.4	0.8	1.6
Phosphate	0.4	0.8	1.6	3.2
Silicate	1.0	2.0	4.0	8.0

METHOD

Configure the ICS-3000 system as described above, installing the column and suppressor as recommended in their respective manuals. Inject 100 µL of the DI water used to prepare the standards; this is a blank analysis for both conductivity and absorbance detectors. If the chromatograms are free of peaks (Figures 1 and 2), and the baseline noise is acceptable (for conductivity: ≤ 2nS and VIS: ≤ 100 µAU), inject one of the mixed anion standards. Figures 3 and 4 show Level 2 calibration standards with detection by suppressed conductivity and visible absorbance, respectively. All seven anions are well resolved; if acetate is present, the column will resolve it from fluoride. Figure 4 shows 2 mg/L silicate detected after reaction with acidified sodium molybdate. Silicate is not detected by suppressed conductivity in Figure 3. Figure 4 also shows the 0.8 mg/L phosphate detected after reaction with molybdate.

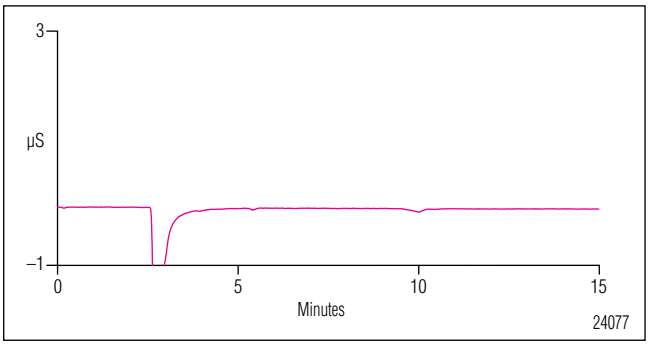

Figure 1. Blank (100 µL water) using suppressed conductivity detection.

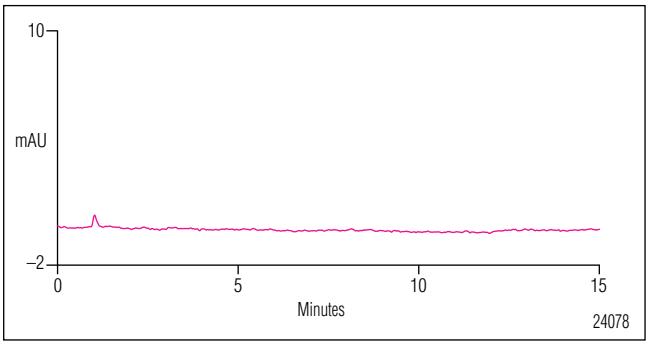

Figure 2. Blank (100 µL water) using visible absorbance detection.

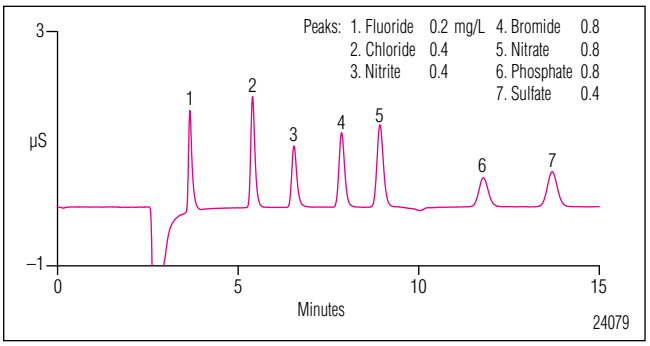

Figure 3. Seven standard anions detected by suppressed conductivity detection.

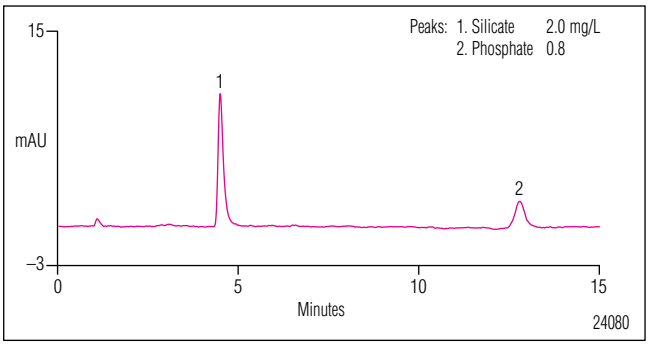

Figure 4. Silicate and phosphate detected by visible absorbance after reaction with sodium molybdate.

To determine the MDL, make seven injections of a low concentration mixed standard (See Tables 4 and 5, Figures 5 and 6). The MDL for silicate was 42 µg/L. The signal-to-noise ratio of the 50 µg/L silicate peak in Figure 6 is approximately 3. This method should allow reliable silicate quantification to approximately 0.2 mg/L, depending on the sample. When evaluating the MDL for a sample, one must account for the sample matrix by checking for interfering peaks and possible column overload, especially if the sample has a high ionic strength. Dionex Application Note 167 shows MDLs determined in a simulated sample of drinking water. Figures 5 and 6 show reproducibility of seven injections of the MDL standard using suppressed conductivity and visible absorbance detection, respectively. The MDLs calculated from those injections are shown in Table 4; and the peak area and retention time reproducibility are shown in Table 5. If lower MDLs are required, more sample can be injected, provided it does not overload the column. Alternately, larger volumes of low ionic strength samples can be preconcentrated.

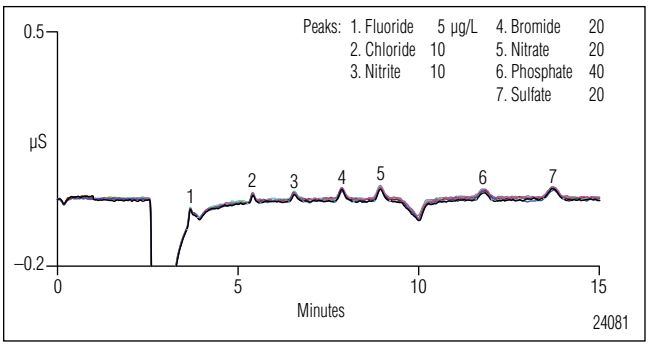

Figure 5. Overlay of seven injections of mixed anion standard for determination of the MDL of seven anions by suppressed conductivity detection.

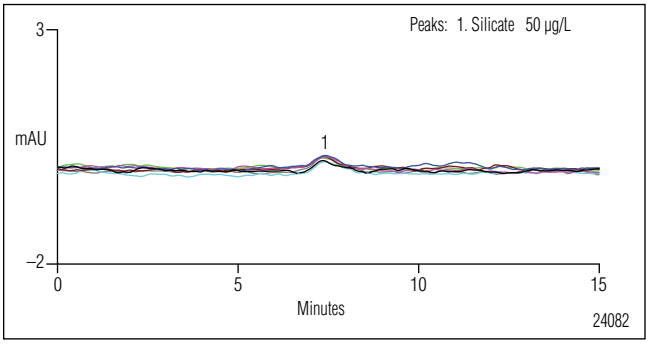

Figure 6. Overlay of seven injections of mixed anion standard containing silicate for determination of the MDL of silicate by visible absorbance detection.

Table 3. Method Calibration Results as Reported by Chromeleon*

Peak Name	%R-Square	%Coeff. Det.	Offset	Slope
Fluoride	99.969	99.9691	–0.0050	1.0503
Silicate - Vis	99.922	99.9221	–0.1102	0.9361
Chloride	99.958	99.9583	–0.0245	0.7105
Nitrite	99.990	99.9947	–0.0076	0.4531
Bromide	99.976	99.9902	–0.0137	0.3101
Nitrate	99.994	99.9762	–0.0171	0.3888
Phosphate	99.978	99.9943	–0.0075	0.1980
Phosphate - Vis	99.987	99.9783	–0.0168	0.8547

*A single injection was made for each calibration level.

Table 4. Determination of MDLs for Common Anions and Silicate*

Analyte	Concentration (µg/L)	RSD (%)	MDL (µg/L)
Fluoride	5.0	4.21	0.66
Silicate	50.0	27.02	42.42
Chloride	10.0	6.23	1.96
Nitrite	10.0	16.645	5.23
Bromide	20.0	10.68	6.71
Nitrate	20.0	8.48	5.33
Phosphate	40.0	21.32	26.78
Sulfate	20.0	10.87	6.83

*Seven injections were made using the combined anion standard with concentrations listed.

Table 5. Short Term Method Reproducibility of the MDL Mixed Anion Standard*

		RSD	
Analyte	Concentration (µg/L)	Retention Time	Peak Area
Fluoride	5.0	0.14	4.21
Silicate	50.0	0.18	27.02
Chloride	10.0	0.11	6.23
Nitrite	10.0	0.12	16.63
Bromide	20.0	0.07	10.68
Nitrate	20.0	0.06	8.48
Phosphate	40.0	0.23	21.32
Sulfate	20.0	0.13	10.87

*Seven injections were made using the the combined anion standard with concentrations listed.

RESULTS

Linear responses were obtained for all anions in their respective ranges for both detection techniques (Tables 2 and 3). A narrow calibration range is ideal in this case, where the target concentration of the anion or anions of interest is known. Dionex Application Note 154 shows an example of linearity for suppressed conductivity detection of standard anions over a wider concentration range, using a larger injection volume and a higher capacity column.

SUMMARY

This Application Update demonstrates a dual-detection method for simultaneous determination of seven common inorganic anions plus silicate on an ICS-3000 system by direct injection. Using this method, detection limits in the mg/L range can be obtained.

PRECAUTIONS

The sodium molybdate reagent must be prepared fresh weekly. This reagent can form a precipitate in tubing and check valves, therefore, if the system will be idle for longer than one day, flushing the pump and tubing with 0.5 M NaOH for two hours at the same flow rate used for analysis is recommended. When used continually, it is also advisable to shut down the system once per week to flush the pump and tubing as described above.

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