

The determination of trace anions in concentrated phosphoric acid

Authors

Edward Kaiser and Jeffrey Rohrer
Thermo Fisher Scientific,
Sunnyvale, CA, USA

Keywords

Ion chromatography, IC, IonPac
ICE-AS6; IonPac AS11-HC; ion-
exclusion pre-separation, ICE

Introduction

The determination of trace anions in phosphoric acid is hampered by a large excess of phosphate ion. Chloride determination at 0.1 mg/L (ppm) in 85% (w/w) phosphoric acid represents a concentration ratio of 1:10⁶ (chloride to phosphate). Diluting the concentrated sample overcomes the problem of a large concentration of the interfering matrix ion, but lacks the required sensitivity for the contaminant ions of interest. An improved method for determining trace anions in concentrated phosphoric acid has been developed to overcome this problem.^{1,2} Trace inorganic anions are separated from the high concentration of phosphate by an ion-exclusion separation prior to an ion-exchange separation.

This Technical Note describes the theory, set up, and analytical procedure for the determination of chloride, nitrate, and sulfate at sub-mg/L (ppm) levels in 85% (w/w) phosphoric acid.

Summary of the method

A Thermo Scientific™ Dionex™ IonPac™ ICE-AS6 ion-exclusion column is used to separate the analyte ions from an excess of phosphate matrix ions. A selected fraction from the ion-exclusion separation is “cut” and sent to a 4 mm Thermo Scientific™ Dionex™ IonPac™ AS11-HC anion-exchange concentrator column. The concentrated ions are then eluted onto a 2 mm Dionex IonPac AS11-HC column set, where the anions of interest are separated and detected by suppressed conductivity.

Experimental

Equipment

- Thermo Scientific™ Dionex™ DX-500 Ion Chromatography system* consisting of:
 - GP50 Gradient Pump, microbore configuration
 - CD20 Conductivity Detector with a temperature controlled conductivity cell (DS3)
 - LC20 Enclosure with 2 Rheodyne® valves, PEEK™, rear loading
- * Equivalent or improved results can be achieved using the Thermo Scientific™ Dionex™ ICS-5000+ HPIC™ system.
- Thermo Scientific™ Dionex™ Dionex RP-1 single piston pump
- Pressurizable Reservoir Chamber
- (Three) 4 L Plastic bottle assemblies, 2 for external water and 1 for rinse solution (P/N 039164)
- 1 O-ring, Teflon® encapsulated, for rinse solution bottle (P/N 043523)
- 2 O-rings Teflon encapsulated, for Reservoir Chamber (P/N 037541 for 1 O-ring)
- 1 Air pressure gauge, 0–171 kPa (0–25 psi) (for external water)
- 305 cm (120 in.) of green PEEK tubing, diameter of 0.75 mm (0.030 in.), to connect columns and make a 200 µL sample loop
- Teflon bottles as sample containers (VWR, P/N 16071-041 or Thermo Scientific™ Nalgene™, P/N 1600-0004 for 125 mL narrow mouth bottles)
- Thermo Scientific™ Dionex™ PeakNet™ Chromatography Workstation

Columns

- Dionex IonPac AG11-HC guard column, 2 mm (P/N 052963)
- Dionex IonPac AS11-HC analytical column, 2 mm (P/N 052961)
- Dionex IonPac AG11-HC concentrator column, 4 mm (P/N 052962)
- Dionex IonPac AG10 as trap column, 4 mm (P/N 043119)
- Dionex IonPac ICE-AS6 analytical column, 9 × 250 mm (P/N 079798)

- Thermo Scientific™ Dionex™ Anion Self-Regenerating Suppressor™ (ASRS™), 2 mm (Replaced by Thermo Scientific™ Dionex™ AERS™ 500 (2 mm), P/N 082541)

Reagents and standards

- Deionized water (DI H₂O), Type I reagent grade, 17.8MΩ·cm resistance or better
- Sodium hydroxide, 50% (w/w) aqueous solution (Fisher Scientific)
- Thermo Scientific™ Dionex™ Chloride standard 1,000 mg/L, 100 mL (P/N 37159)
- Thermo Scientific™ Dionex™ Sulfate standard 1,000 mg/L, 100 mL (P/N 37160)
- Nitrate standard 1,000 mg/L, 100 mL (Ultra Scientific, VWR, P/N ULICC-004)

Conditions

Ion Exclusion

Column: Dionex IonPac ICE-AS6

Trap Column: Dionex IonPac AG10, 4 mm

Eluent: Deionized water

Flow Rate: 0.50 mL/min

Ion Chromatography

Analytical

Column: Dionex IonPac AS11-HC, 2 mm

Guard Column: Dionex IonPac AG11-HC, 2 mm

Concentrator

Column: Dionex IonPac AG11-HC, 4 mm

Eluent: 20 mM sodium hydroxide,
step to 200 mM sodium hydroxide

Flow Rate: 0.38 mL/min

Sample Volume: 200 µL

Detection: Suppressed conductivity, Dionex ASRS,
AutoSuppression™ external water mode

Suppressor

Current Setting: 300 mA

Expected System

Backpressure: 16.5 MPa (2400 psi)
(with concentrator column in line)

Expected

Background

Conductivity: 2–3 µS

Preparation of solutions and reagents

Eluent Solutions

20 mM Sodium hydroxide (IC eluent)

Dilute 1.60 g of 50% (w/w) sodium hydroxide with degassed, deionized water (having a specific resistance of 17.8 MΩ·cm or greater) to a final weight of 1,000 g in the eluent bottle. Avoid the introduction of carbon dioxide from air.

200 mM Sodium hydroxide (IC eluent and Dionex IonPac AG10 trap column regeneration)

Dilute 16.00 g of 50% (w/w) sodium hydroxide with degassed, deionized water (having a specific resistance of 17.8 MΩ·cm or greater) to a final weight of 1,000 g in the eluent bottle. Avoid the introduction of carbon dioxide from air.

Standard solutions

Stock standard solution (1,000 mg/L)

Use Thermo Scientific Dionex or commercially available 1,000 mg/L ion standard solution.

Working standard solution (1 mg/L)

To prepare a mixed working standard solution, combine 1.00 mL of each anion stock solution with deionized water and dilute to a final volume of 1,000 mL.

Calibration

Prepare calibration standards at a minimum of three concentration levels by diluting the working standard. Select a range similar to the expected concentrations in the samples. The method of standard addition (adding one or more increments of a standard solution to sample aliquots of the same size) can be used to minimize the effect of the concentrated acid matrix on the measured conductivity of the analytes of interest.³

To minimize dilution of the concentrated acid sample, it is recommended that small aqueous aliquots be used for the method of standard addition. Each of these additions will have a consistent volume while the concentration for the anions of interest varies. A convenient sample size for spiked standards in 85% phosphoric acid is 20 mL (34 g) with a 0.020 mL aqueous spike. This represents a dilution of 0.1% (0.020 mL spike/20 mL sample = 0.1% dilution).

To minimize introducing contamination through sample handling, the concentrated acid can be dispensed directly into the sample container, by weight, on a top-loading balance. Table 1 illustrates how aqueous standards are diluted and prepared. The following formula can be used to calculate concentrations in mg/L for dilutions:

$$\begin{aligned} (\text{Conc. of stock solution, mg/L}) * (\text{Vol. of stock solution, mL}) = \\ (\text{Conc. of dilute standard, mg/L}) * (\text{Vol. of dilute standard, mL}) \end{aligned}$$

Dionex Ionpac AG10 trap column regeneration

The Dionex IonPac AG10 column must first be regenerated. Monitoring the blank will indicate when regeneration is necessary. Typically, monthly regeneration is necessary, but it will depend on the quality of the deionized water and usage rate of the instrument. Increased contamination in the water blank indicates that the Dionex IonPac AG10 needs to be regenerated. The procedure is as follows:

1. Pump 200 mM sodium hydroxide through the Dionex IonPac AG10 column at 1.0 mL/min for 50 minutes.
2. Follow with a rinse of deionized water at the same flow rate for 20 minutes.

Table 1. Method of standard additions for concentrated phosphoric acid.

	Concentration of stock standard (mg/L)	Amount of stock to make a 10 mL final volume of working standard in deionized water (mL)	Concentration of working standard (mg/L)	Concentration of 20 mL 85% phosphoric acid when 20 µL of working standard is added (mg/L)
Chloride	1,000	0.500	50	0.050
Sulfate	10,000	2.00	2,000	2.0
Nitrate	1,000	1.00	100	0.10

Discussion of method

This method addresses the challenge of determining trace concentrations of contaminant ions such as nitrate, chloride, and sulfate in a matrix composed of a high concentration of phosphate ion. This is accomplished in two steps: an ion-exclusion (ICE) pre-separation followed by injection of a portion of the ICE separation to an ion chromatographic (IC) separation.

The ion-exclusion mechanism separates ionized species from nonionized or weakly ionized species. This occurs because of a negatively charged hydration shell on the stationary phase surface called the Donnan membrane.⁴ Figure 1 illustrates the application of the ICE mechanism to the separation of 85% concentrated phosphoric acid that was injected onto a Dionex IonPac ICE-AS6 ion-exclusion column. This chromatogram is a measurement of the unsuppressed conductivity response for the ICE separation. The strong acid ions, such as nitrate, chloride, and sulfate, are excluded and elute as a small peak at 12 minutes. The weakly ionized phosphate matrix ions are retained and elute as a large peak. This separation is not applicable to dilute phosphoric acid samples because dilute phosphoric acid is partially ionized.

A series of schematics (Figures 2–5) illustrates the operation of the chromatography hardware. The concentrated phosphoric acid sample is loaded via a pressurized reservoir into the 200 μL sample loop

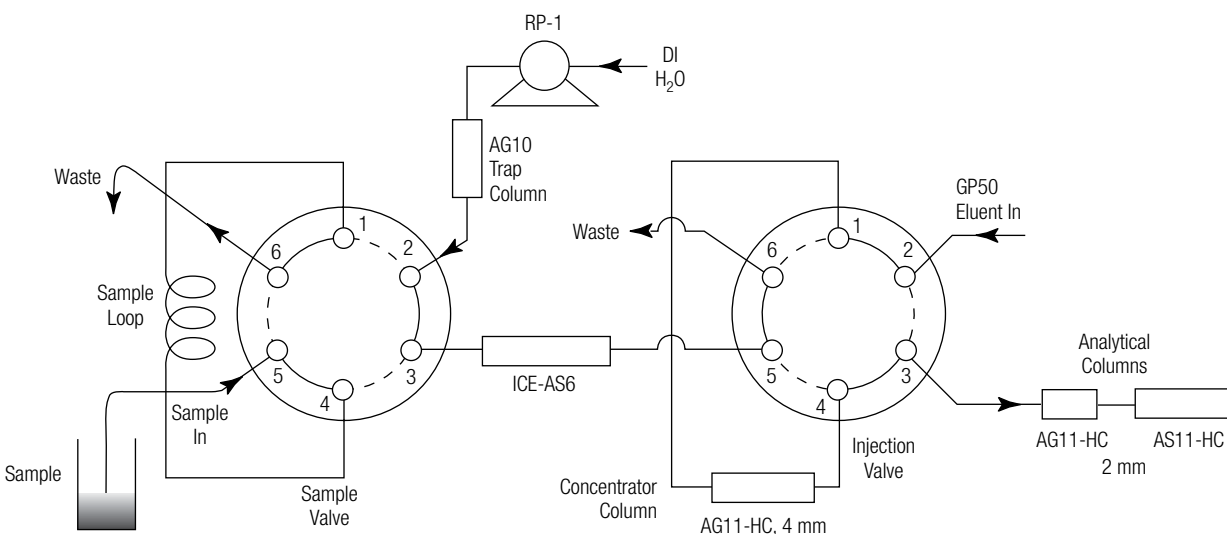


Figure 2. Loading the sample loop.

Column: Dionex IonPac ICE-AS6
 Trap Column: Dionex IonPac AG10, 4 mm
 Eluent: Deionized water
 Flow Rate: 0.50 mL/min
 Sample Volume: 200 μL
 Detection: Conductivity
 Peaks: 1. Nitrate/Chloride/Sulfate
 2. Phosphate

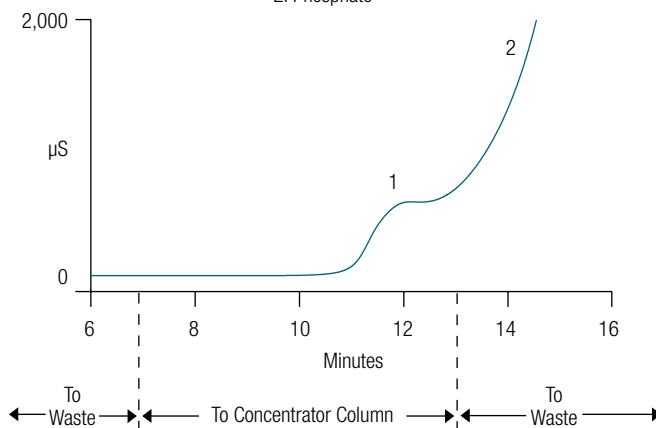


Figure 1. Ion exclusion separation of trace anions in 85% phosphoric acid. chlorate, bromate, oxalate, phosphate, nitrite, and nitrate.

sample out of the sample container into the sample loop at a flow rate of 0.1 mL/min (6 mL/hr). This technique ensures that a representative sample of the concentrated phosphoric acid sample is loaded into the sample loop. It is important to pass at least 4 loop volumes through the sample loop to ensure reproducible sampling.⁵ While the 40 minute IC separation is taking place, approximately 4 mL of sample will have been pushed through the sample loop with the pressurized reservoir.

The concentrated phosphoric acid sample is then delivered with the high-purity water carrier stream to the Dionex IonPac ICE-AS6. A Dionex IonPac AG10 is placed after the Dionex RP-1 pump to act as an anion trap column for the deionized water. Any contaminants present in this water will impact the quality of the blank. The first portion of the ICE separation from 0.0 to 7.0 minutes is sent to waste (Figure 3). Then, the

concentrator column is placed in-line with the ICE column and the portion from 7.0 to 13.0 minutes is captured on the concentrator column (Figure 4). After 13.0 minutes the 4-mm Dionex IonPac AG11-HC concentrator column is placed in-line with the 2 mm Dionex IonPac AS11-HC analytical column set and the concentrated ions are separated (Figure 5). This time window should ensure the concentration of all the nitrate, chloride, and sulfate with minimal concentration of phosphate.

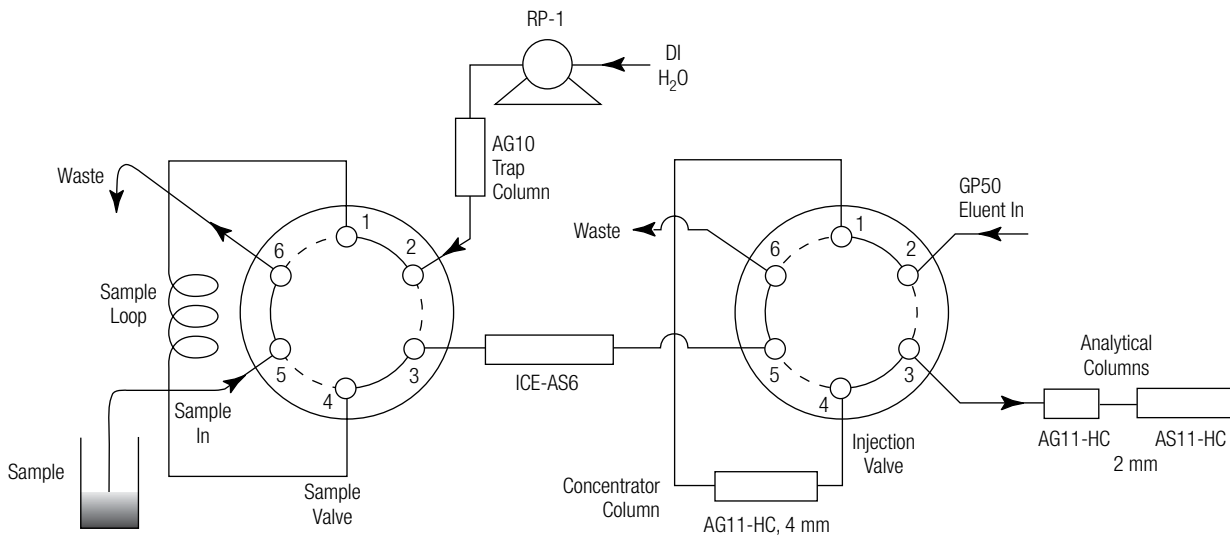


Figure 3. First portion of the ICE separation (time 0.0–7.0 min).

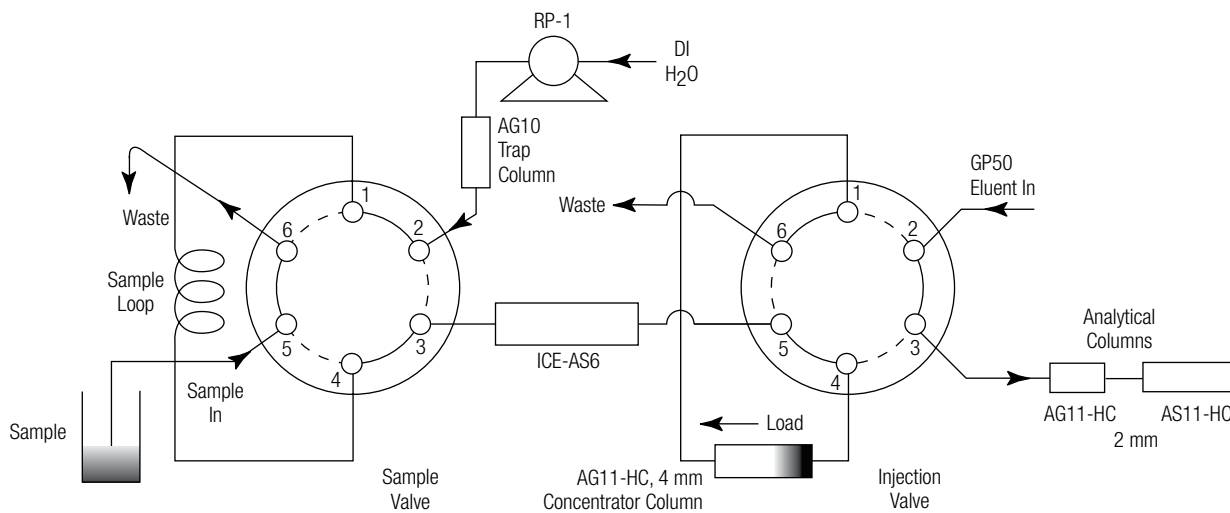


Figure 4. Concentrating the “cut” portion from the ICE separation (time 7.0–13.0 min).

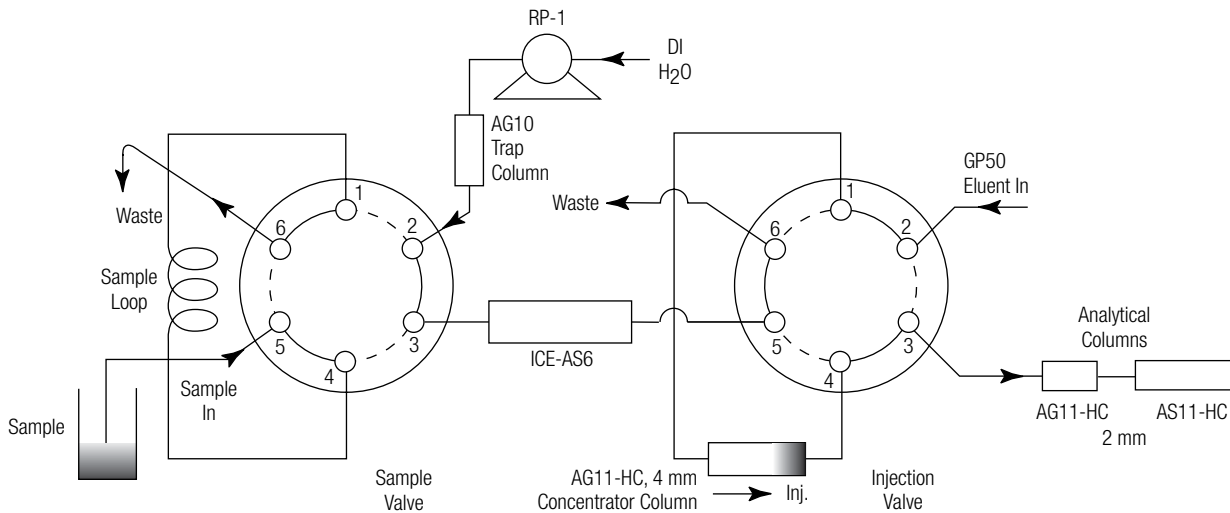


Figure 5. Separating the retained ions.

The IC separation utilizes the Dionex IonPac AS11-HC column with an isocratic eluent of 20 mM sodium hydroxide. The high capacity of the Dionex IonPac AS11-HC column allows injection of these relatively concentrated samples without overloading. Figure 6 shows a separation of the common anions with the 4 mm Dionex IonPac AS11-HC column under standard conditions. The attractive feature of this separation is that phosphate elutes last.

A 2-mm microbore column was chosen because it has a 4-fold increase in mass sensitivity over the standard bore column. This facilitates faster loop loading because

Column:	Dionex IonPac AS11-HC, 4 mm	Peaks:	1. Fluoride	2 mg/L (ppm)
Eluent:	30 mM Sodium hydroxide		2. Chloride	5
Temperature:	30 °C		3. Nitrite	10
Flow Rate:	1.5 ml/min		4. Sulfate	10
Inj. Volume:	10 µL		5. Bromide	20
Detection:	Suppressed conductivity, AutoSuppression mode		6. Nitrate	20
			7. Phosphate	30

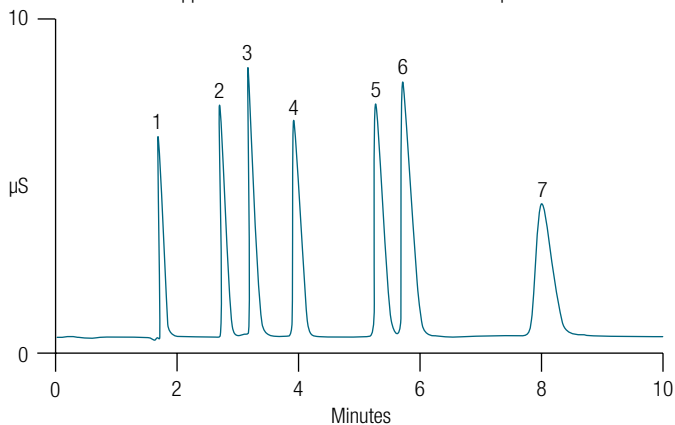


Figure 6. Isocratic separation of the common anions.

smaller sample amounts are required. The microbore format also offers low eluent consumption as well as less waste generation. A Dionex IonPac AG11-HC ion exchange column was used as the concentrator column in the 50 × 4 mm format instead of 50 × 2 mm because the 4 mm column had four times more capacity than the 2 mm column and lower back pressure at the microbore flow rate. No significant degradation in separation efficiency was observed when coupling a 4 mm concentrator column with a 2 mm analytical column set.

For this method the Dionex IonPac AS11-HC column standard conditions were modified. The eluent strength was reduced from 30 mM to 20 mM sodium hydroxide to optimize the separation of the trace anions from the excess of phosphate matrix ions. The method was run at ambient temperature.

During the IC separation, the pressurized vessel is filling the sample loop for the next analysis. The deionized water rinses the Dionex IonPac ICE-AS6 column and associated tubing to ensure there is no contamination from the previous sample.

After the phosphate has eluted from the column, the eluent concentration is stepped from 20 to 200 mM sodium hydroxide for 5 minutes. This ensures that the column is rinsed of residual phosphate. The method returns the system to equilibrate at 20 mM sodium hydroxide for the next injection. If this cleanup step is not used, phosphate will continue to build up on the analytical column and cause a gradual decrease in retention time for phosphate and the other analytes.

System preparation and test

Refer to the system configuration schematics in Figures 2–5 and Table 2, which summarize the types and lengths of tubing required for system configuration. The chromatography hardware is divided into two parts: the ion-exclusion pretreatment portion with the Dionex IonPac ICE-AS6 column and the IC analysis portion with the Dionex IonPac AS11-HC column.

IC system

1. Prepare the Dionex ASRS suppressor by following the Quickstart instructions (Dionex Document 031368-01) included with the Instructions and Troubleshooting Guide for the ASRS.
2. Install the 2 mm Dionex IonPac AG11-HC and AS11-HC column set by using the red 0.125 mm (0.005 in.) tubing. To minimize dead volume, use the smallest possible lengths of tubing and ensure that the ends of the tubing are smooth and level.
3. Construct a 5 μ L sample loop by cutting a 9.9 cm (3.9 in.) portion of the black 0.25 mm (0.010 in.) PEEK tubing.
4. Install this loop in place of the 4 mm Dionex IonPac AG11-HC concentrator column between ports 1 and 4 of the injection valve in the IC analysis system.
5. Install the Dionex ASRS suppressor and configure it in the external water mode as described in the SRS manual.

6. Establish eluent flow through the 2 mm Dionex IonPac AG11-HC and AS11-HC analytical column set. The expected background conductivity is 2–3 μ S. (Note: For trace analysis, it will take at least 5 hours for the system to achieve a stable background conductivity.)
7. Verify proper operation of the IC portion of the system by injecting a low-level ppm standard to replicate the column test chromatogram.
8. Remove the 5 μ L sample loop and install the 4 mm Dionex IonPac AG11-HC concentrator column. Make sure that the arrow indicating flow on the column is pointed from port 1 to port 4 and that the tubing length connecting the outlet of this column and port 4 is as short as possible.
9. Configure the IC valve so that the 4 mm Dionex IonPac AG11-HC concentrator column is in-line with the 2 mm Dionex IonPac AG11-HC and AS11-HC analytical column set. Check for leaks. The expected system backpressure for these three columns at 0.38 mL/min is ~2,400 psi (16.5 MPa).

Ion-exclusion sample pretreatment system

This section describes the preparation of the pretreatment portion of the system. It is important that the same type and length of tubing as described in Table 2 be used to successfully perform this analysis. Changes in tubing length will result in a different “cut” from the Dionex IonPac ICE-AS6 column being delivered to the Dionex IonPac AS11-HC concentrator column.

Table 2. Details of tubing configuration for trace anions in phosphoric acid.

Connection Points	Tubing Description	Length (cm)	Remarks
ICE exit to Port 5	Green 0.75 mm (0.030 in.)	30	
ICE input to Port 3	Green 0.75 mm (0.030 in.)	70	
Port 1 to Port 4	Green 0.75 mm (0.030 in.)	44	200- μ L sample loop
4-mm AG11-HC to Port 4	Red 0.125 mm (0.005 in.)	3	Should be as short as possible
4-mm AG11-HC to Port 1	Black 0.25 mm (0.010 in.)	25	
Port 3 to analytical column	Red 3 0.125 mm (0.005 in.)	3	Should be as short as possible

1. Cut a 44 cm (17 in.) portion of the 0.75 mm (0.030 in.) PEEK green tubing to make a 200 μ L sample loop and install this loop between port 1 and 4 of the sample valve.
2. Prepare the Dionex IonPac AG10 trap column according to the directions in the section titled "Dionex IonPac AG10 Trap Column Regeneration." (Caution: Before the Dionex IonPac AG10 is installed in the system, it is important that the sodium hydroxide solution used for storage or cleaning be completely rinsed away. The Dionex IonPac ICE-AS6 column is not compatible with sodium hydroxide eluents.)
3. The entire pathway from the Dionex RP-1 pump to port 5 of the IC valve is plumbed with the 0.75 mm (0.030 in.) PEEK green tubing. Install the Dionex IonPac AG10 column at the exit port of the Dionex RP-1 pump.
4. Install the Dionex IonPac ICE-AS6 column using a 70 cm piece of green tubing between the exit of the Dionex IonPac ICE-AS6 column and port 5 of the injection valve. Use a 30 cm portion of green PEEK tubing between port 3 of the sample valve and the input of the Dionex IonPac ICE-AS6 column.
5. Check to see that there is about 34.5 kPa (5 psi) of head pressure on the incoming deionized water that feeds the Dionex RP-1 pump.
6. Connect the exit port of the reagent reservoir to port 5 of the sample valve with the 0.75 mm (0.030 in.) green tubing.
7. Configure a waste line from port 6 of the sample valve with the green tubing.
8. Connect the reagent reservoir to helium pressure of about 34.5 KPa (5 psi).
9. Begin with a container filled with deionized water as a sample to rinse the sample lines of any trace contamination.
10. Set a flow rate of 0.50 ± 0.02 mL/min for the Dionex RP-1 pump by adjusting the dial on the pump. This should be measured with the 4 mm Dionex IonPac AG11-HC concentrator column out of line. Measure the flow rate by collecting the waste coming out of port 6 of the IC valve. It is critical for the success of this method that the flow rate be consistent.
11. Pump deionized water at 0.50 mL/min through the Dionex IonPac ICE-AS6 column to waste without the 4 mm Dionex IonPac AG11-HC column in line for 1 hour. This will remove the 0.4 mM heptafluorobutyric acid storage solution. Sulfate is usually found in the blank. Typical initial blank sulfate values will be ~ 200 μ g/L.
12. The Dionex IonPac ICE-AS6 column can be further conditioned by rinsing it with 100 mM phosphoric acid for 2 hours at 0.50 mL/min followed by a 1-hour rinse with 17.8 M Ω ·cm deionized water. This will reduce the sulfate blank to 150 μ g/L or less. Continue to monitor the blank, especially when starting up the system after it has been idle for more than two days.

System operation

After all aspects of the instrumentation have been prepared, the system is ready for analysis.

1. Load the PeakNet method shown in Table 3.
2. Fill the 200 μ L sample loop with deionized water. Use helium gas pressure to push the deionized water sample using the reagent reservoir (Figure 2).
3. Analyze a blank by loading deionized water as the sample. It may take several runs until the system has been rinsed of contamination.
4. After an acceptable blank has been established, the system is ready for analysis.
5. Exercise caution when handling concentrated phosphoric acid. Consult the applicable Material Safety Data Sheet (MSDS) for specific details about protective equipment, reactivity, storage, disposal, and health effects.
6. Concentrated phosphoric acid, 85% (w/w), can be loaded directly into the 200 μ L loop by the reagent delivery module. At this concentration the phosphoric acid is viscous and moves slowly to fill the sample loop. Ensure that the loop has had enough sample pass through by collecting the liquid that exits port 6 of the sample pretreatment valve. A good practice is to load at least 4 loop volumes. The method is set up so that the reagent reservoir pushes sample into the sample loop during the IC separation. With a pressure of 34.5 KPa (5 psi), 4 mL of concentrated phosphoric acid will have been passed through the sample loop in 40 minutes.
7. Ensure that the Dionex RP-1 pump is consistently delivering 0.50 ± 0.02 mL/min. Figure 7 illustrates what happens when the flow rate is faster or slower. At the slower flow rate, not enough of the sample is cut from the ICE separation, resulting in incomplete recovery of the anions of interest. At the faster flow rate, too much of the ICE separation is cut, resulting in the phosphate peak almost obscuring the analytes of interest.
8. Other factors will also affect the quality and consistency of the ICE pre-separation. Changing the cut time window specified in the method (7.0 to 13.0 minutes) will impact the amount of analyte and matrix ions that are delivered to the concentrator column. Varying the sample volume will also affect the character of the ICE separation. For example, doubling the sample volume from 200 to 400 μ L increases the sensitivity for trace determinations. Method development will be needed to ascertain the impact of any changes from the specified method.

Table 3. PeakNet method for the analysis of concentrated phosphoric acid.

Total Time (min)	ICE Time (min)	IC Time (min)	Injection Valve	Column Valve	%A 200 mM NaOH	%B 20 mM NaOH	Figure	Comment
Init			Inject	A	0	100	2	Load the sample loop
0.00			Inject	A	0	100	2	
8.00	0.00		Inject	B	0	100	3	Begin ICE separation
15.00	7.00		Load	B	0	100	4	Send cut portion from ICE separation to Dionex IonPac AG11-HC column, 4 mm
21.00	13.00	0.00	Inject	B	0	100	5	Begin IC separation. Concentrator column in-line.
45.49		24.49	Inject	A	0	100	5	
45.50		24.50	Inject	A	100	0	5	Step to 200 mM sodium hydroxide for cleaning
50.50		29.50	Inject	A	100	0	5	End 200 mM sodium hydroxide
50.51		29.51	Inject	A	0	100	5	Equilibrate at 20 mM sodium hydroxide
61.00		40.00	Inject	A	0	100	5	

A = Inject

B = Load

9. Quantifying the levels of anions in phosphoric acid is best accomplished by the method of standard additions. This involves adding one or more increments of a standard solution to sample aliquots of the same size (see the Calibration section).

Results and discussion

A representative blank is shown in Figure 8. It was found that after concentrated phosphoric acid had been in the sample loop pathway, several runs of deionized water were required to completely rinse away the high concentration of phosphate matrix ions. A blank was established after seven replicate runs yielded reproducible results. These levels, quantified based on a calibration curve for these ions in deionized water, are below the expected concentrations for high-purity grade concentrated phosphoric acid. The anion values, of this deionized water blank, were subtracted from the levels found in the concentrated phosphoric acid samples. A small amount of phosphate was detected in the blank, as carryover from previous injections. This will not significantly impact sample analysis.

A chromatogram for the analysis of 85% (w/w) phosphoric acid is shown in Figure 9. The large phosphate matrix (peak 5) is well separated from the anions of interest. Chloride determination was hampered by a dip before the peak. A feature in the PeakNet chromatography software called “void treatment” was utilized to reliably quantitate this peak. A detail of the chloride peak is shown in Figure 10. The peak that starts at 29 minutes is a result of the step to the higher eluent concentration. Any residual phosphate left in the column is eluted with this high eluent concentration.

To verify proper quantification of analytes in the phosphoric acid matrix, increasing concentrations of chloride, nitrate, and sulfate were added into 85% phosphoric acid. Spikes of 30, 100, and 300 µg/L of chloride; 100, 300, and 1,000 µg/L of nitrate; and 300, 1,000, and 3000 µg/L of sulfate yielded coefficients of determination (r^2) values greater than 0.99.

Ion Exclusion Column:	Dionex IonPac ICE-AS6	Eluent:	20 mM Sodium hydroxide step to 200 mM Sodium hydroxide
Trap Column:	Dionex IonPac AG10, 4 mm	Flow Rate:	0.38 mL/min
Eluent:	Deionized water	Sample Volume:	200 µL
Flow Rate:	A: 0.55 mL/min B: 0.50 mL/min C: 0.45 mL/min	Detection:	Suppressed conductivity, Dionex ASRS-ULTRA, AutoSuppression external water mode
Ion Chromatography		Peaks:	1. Unidentified 2. Unidentified 3. Phosphate
Analytical Column:	Dionex IonPac AS11-HC, 2 mm		
Guard Column:	Dionex IonPac AG11-HC, 2 mm		
Concentrator Column:	Dionex IonPac AG11-HC, 4 mm		

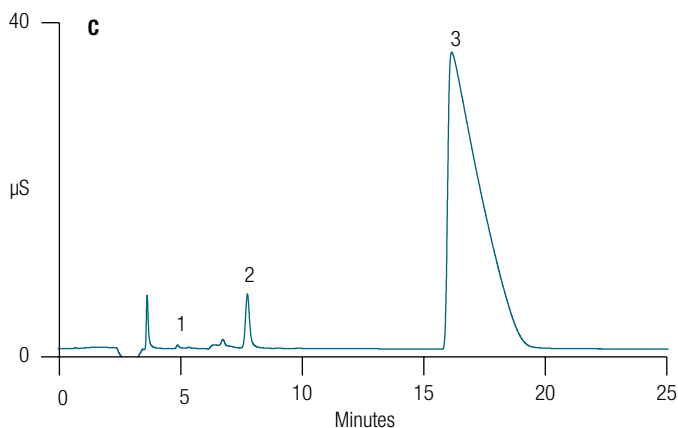
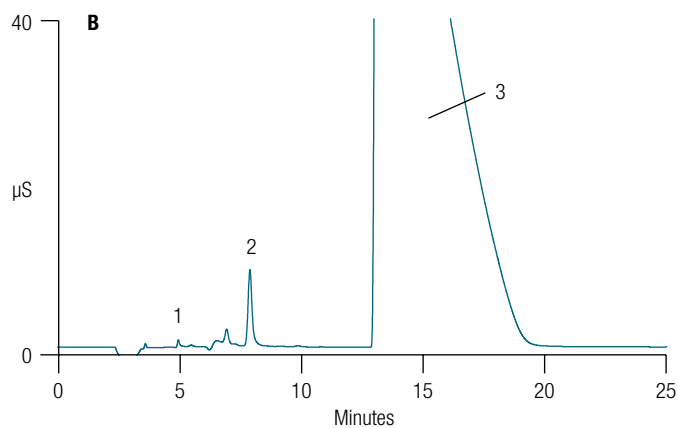
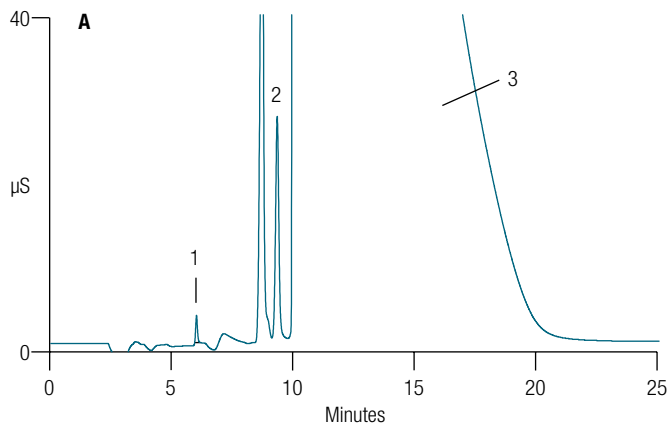


Figure 7. Effect of ICE eluent flow rate on IC separation.

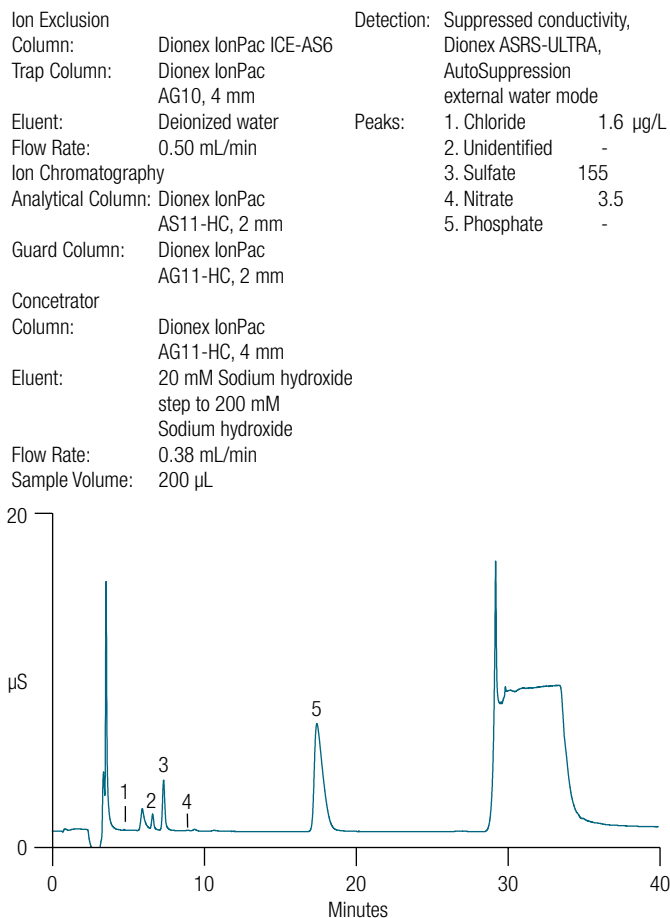


Figure 8. Representative blank.

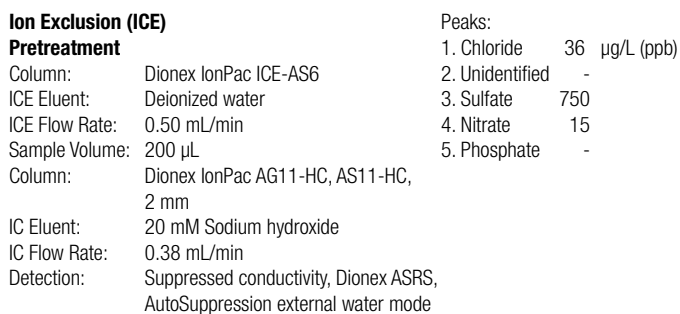


Figure 9. Determination of trace anions in high purity 85% phosphoric acid.

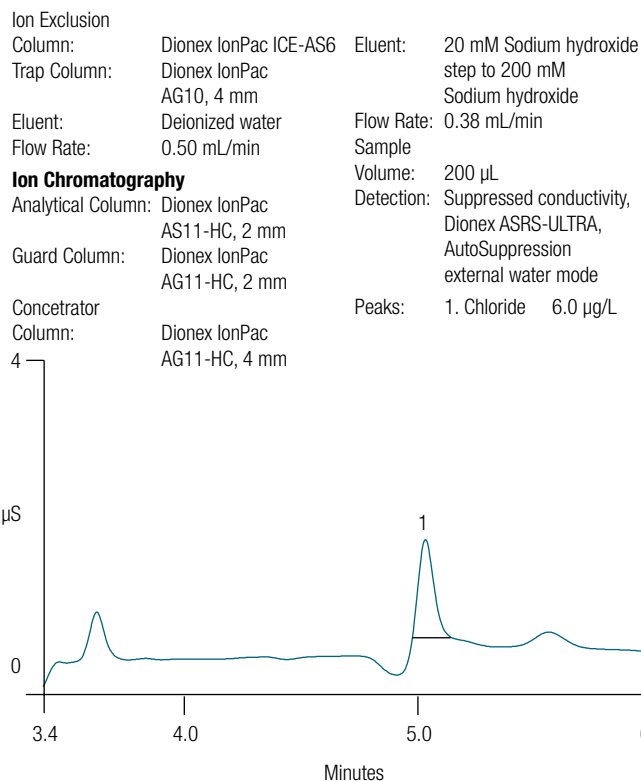


Figure 10. Detail of chloride peak.

Based on this calibration curve, a spike of 50 µg/L chloride, 2,000 µg/L sulfate, and 100 µg/L nitrate yielded recoveries between 84 and 111%. These values are within the SEMI (Semiconductor Equipment and Materials International) recommended guidelines of 75–125% recovery at 50% of the specified maximum limit of impurity. Table 4 summarizes the spike/recovery data.

To determine method precision, a sample of a highpurity grade 85% phosphoric acid was analyzed by this method. For n=7, a relative standard deviation (RSD) of less than 6% was obtained for 34 µg/L chloride and 730 µg/L sulfate. Nitrate levels were determined to have an average concentration of 16 µg/L with an RSD of 21%. At these low nitrate concentrations, partial coelutions of other analytes with nitrate cause a higher variability in the nitrate peak integration.

Table 4. Spike recovery of trace anions in 85% phosphoric acid.

Anion	Phosphoric Acid Blank ($\mu\text{g/L} \pm \text{SD}$)*	Spike ($\mu\text{g/L}$)	Found-Blank ($\mu\text{g/L} \pm \text{SD}$)	Recovery (%)
Chloride	34 \pm 2.1	50	51 \pm 2.1	102
Sulfate	730 \pm 40	2,000	2,220 \pm 44	111
Nitrate	16 \pm 3.4	100	84 \pm 4.3	84

* Corrected for system blank

For n = 7

Method detection limits (MDLs) were calculated using the standard deviation of seven replicate injections multiplied by the Student's *t*-value for the 99.5% confidence level.

MDLs for chloride, sulfate, and nitrate are in the low $\mu\text{g/L}$ (ppb) range. The MDLs for this method are substantially below the maximum limit of impurity guidelines for phosphoric acid⁶ established by SEMI for the purest grade of phosphoric acid, as shown in Table 5.

Table 5. Method detection limits and SEMI specifications for trace anions in high purity phosphoric acid.

Anion	Method Detection Limits ($\mu\text{g/L}$)	SEMI C7.11-93 Specification ($\mu\text{g/L}$)
Chloride	0.15	1,000
Sulfate	31	8,000
Nitrate	2.5	200

Method Detection Limit = (SD) \times (t_{α})_{99.5%} where (t_{α}) is for a single-sided Student's *t*-test distribution for n = 7.

Precautions

Exercise caution when handling concentrated phosphoric acid. Consult the Material Safety Data Sheet (MSDS) for more specific details about protective equipment, reactivity, and health effects. Use only the highest quality deionized water for the preparation of standards and eluents. Any ionic contamination present in the deionized water will adversely affect results. Teflon containers are recommended for holding the concentrated acid samples for delivery to the sample loop. Containers should be soaked for at least 24 hours with 17.8 M Ω -cm deionized water prior to use. It is good practice to dedicate all containers for trace analysis and keep them filled with deionized water when not in use.

Method success depends on maintaining a consistent flow rate of deionized water from the Dionex RP-1 pump. Verify that the flow rate is 0.50 \pm 0.02 mL/min. If the deionized water container feeding the Dionex RP-1 pump is not pressurized to at least 34.5 KPa (5 psi), the pump may be prone to losing prime. Do not leave concentrated phosphoric acid in the sample loop and sample inlet lines for more than 6 hours. The PEEK tubing can degrade after extended contact time with the concentrated acidic sample.

References

1. Watanabe, K. Presented at the International Ion Chromatography Symposium, Dallas, TX, October 1995; Poster 66.
2. Wu, M.; Chen, J. *Micro.* 15(10), 1997, 74.
3. Bader, M. *J. Chem Educ.* 57, 1980, 730.
4. Weiss, J. *Ion Chromatography*, 2nd ed., VCH, Weinheim, Germany, 1995, 209–210.
5. "Troubleshooting Guide for HPLC Injection Problems." Rheodyne: Cotati, CA, 1992.
6. SEMI International Standards: Semiconductor Equipment and Materials International, Mountain View, CA, Chemical/Reagents Volume, 1997.

Find out more at thermofisher.com/IC

ThermoFisher
SCIENTIFIC