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TECHNICAL NOTE 45

Determination of trace anions in hydrofluoric acid, ammonium fluoride, and a buffered oxide etchant

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Introduction

Concentrated hydrofluoric acid (HF) is used in the semiconductor and electronics industries, both alone and as one component of a buffered oxide etchant (BOE), to remove oxide layers during device production. This HF must be of high purity, especially with respect to anionic impurities that can damage the semiconductor (e.g., chloride and sulfate). In 1997, Semiconductor Equipment and Materials International (SEMI) specified that HF must have chloride and sulfate concentrations < 200 µg/L and nitrate and phosphate concentrations < 100 µg/L.[1] Simply diluting the HF to a concentration that will not overload the anion-exchange column does not allow enough sensitivity to determine the contaminating anions.

To address this challenge, Watanabe and Ishzaki used an ion-exclusion (ICE) column to separate the strong acid anions from the fluoride, diverted the strong acid anions to an anion-concentrator column, eluted the anions from the concentrator column, and then determined them by ion chromatography (IC) with suppressed conductivity detection.[2] The diversion of part of one separation to a concentrator is sometimes called a heart-cutting technique. This basic method later was used by Wu and Chen and also applied to phosphoric acid.[3] A few years later, Kaiser, Rohrer, and Watanabe improved the method by using recently introduced concentrator and anion-exchange columns that were better suited for the application, and exploring the factors that impact method accuracy, reproducibility, and ruggedness.[4] They applied their method to phosphoric acid, HF, and glycolic acid. The methods for each acid were detailed in Thermo Scientific Technical Notes 44, 45, and 46, respectively.[5–7]

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Since the development of this method for determining strong acid anions in weak acids, there have been a number of improvements in IC. Dionex introduced eluent generation to produce high-purity potassium hydroxide eluents, high-capacity anion-exchange columns and concentrators to use with hydroxide eluents, new suppressors that lower detection limits, new IC hardware (Thermo Scientific™ Dionex™ ICS-3000 Ion Chromatography system) that facilitates heart-cutting methods, and software improvements that help produce a calibration curve in the samples to be analyzed. Since the publication by Kaiser et al., there have been some reports of using one or more of these improvements.

In 2002, Wang et al. reported using the method of Kaiser et al. but noted that sulfate was difficult to determine because of a high sulfate blank from the Thermo Scientific™ Dionex™ IonPac™ ICE-AS6 column, and that the reproducibility for phosphate determinations was not good.[8] The following year, Wilhelm Blödern of Honeywell reported the application of the same method using the Dionex IonPac AC10 concentrator and the Dionex IonPac AS10 separator column.[9] He also reported applying the method to a mixture of 25% HF and 20% ammonium fluoride. More recently, Vermeiren modified the method to use an eluent generator to produce ultrapure KOH, a Dionex IonPac AC10 concentrator, and a Dionex IonPac AS18 separator; he also replaced the Dionex IonPac ICE-AS6 column with the Dionex IonPac ICE-AS1 column.[10] Using an ultrapure hydroxide eluent improves method sensitivity. The Dionex IonPac AS18 high-capacity column is designed for use with hydroxide eluents; therefore, it is well suited for this application. The Dionex IonPac ICE-AS1 column has a much lower sulfate blank than the typical Dionex IonPac ICE-AS6 column.

This work, an update to the original TN 45, reports an improved method for determining low concentrations of strong acid anions in HF. The method design also allows determination of low concentrations of strong acid anions in an HF/ammonium fluoride mixture (BOE), and ammonium fluoride. The Dionex IonPac ICE-AS6 column was replaced by the Dionex IonPac ICE-AS1 column because internal analysis showed that the Dionex IonPac ICE-AS1 column had consistently low levels of sulfate, whereas there was a wide variation in sulfate concentrations from the Dionex IonPac ICE-AS6 column. A Dionex ICS-3000 system with Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS) software was used to execute the method using the second pump of the dual-pump module to perform ICE separation, and the standard addition feature of the software to produce the calibration curve. The strong acid anions were captured on a 4 mm Thermo Scientific™ Dionex™ IonPac AG11-HC guard column that served as the concen-trator, and then separated on a 2 mm Dionex IonPac AS11-HC column set. After each injection, the Dionex ICE-AS1 column was washed with formic acid. This wash had at least two purposes. First, it removed corrosive HF from the column, sample loop, and other tubing. Second, it produced the acidic environment necessary for determining strong acid anions in ammonium fluoride, which is not acidic. The authors also empirically determined that the wash improved reproducibility for determinations of strong acid anions in HF/ammonium fluoride mixtures. The greater sensitivity delivered by using a hydroxide eluent, eluent generation, and newer generation suppressors allowed determinations to be made with 12% HF rather than 24.5% HF, and a 500 µL injection rather than 750 µL. Only one-third of the amount of HF was injected, compared to what was required for the original version of TN 45.

Experimental

Equipment

- Dionex ICS-3000 system* including:
  - Thermo Scientific™ Dionex™ DP Dual Pump
  - Thermo Scientific™ Dionex™ DC Detector/ Chromatography module with dual-temperature zone equipped with an injection valve
  - Thermo Scientific™ Dionex™ AM Automation Manager with 10-port valve
  - Thermo Scientific™ Dionex™ EG Eluent Generator module
  - Thermo Scientific™ Dionex™ AS Autosampler
  - Thermo Scientific™ Dionex™ DXP Pump

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

- Thermo Scientific™ Chromeleon™ software Version 6.80 SP6

Reagents and standards

- Deionized water (DI), Type I reagent-grade, 18 MΩ·cm resistivity or better
- 50% Hydrofluoric acid (HF, Ajax)
- 98 to 100% Formic acid (CH_3COOH, Merck)
- Ammonium hydrogen difluoride ($NH_4F{\cdot}HF$, Ajax) (referred to as ammonium fluoride)
- Sodium fluoride (NaF, Honeywell Fluka™)
- Sodium chloride (NaCl, Honeywell Fluka)
- Sodium nitrate ($NaNO_3$, Honeywell Fluka)
- Sodium sulfate (Na_2SO_4, Honeywell Fluka)
- Disodium hydrogen orthophosphate (Na_2HPO_4, Honeywell Fluka)
- 400 g/L Sodium hydroxide solution (NaOH, Kanto)

Preparation of reagents and standards

Eluent solution

The eluent generator produces the eluent using the Dionex EluGen EGC II KOH cartridge and DI water supplied by the pump, with the eluent concentration controlled by the Chromeleon software. Backpressure tubing must be added to achieve 2,000 to 2,500 psi backpressure that will allow the Dionex EG degasser to function properly. See the Dionex ICS-3000 Ion Chromatography System Operator's Manual (P/N 065031-03) for instructions on adding backpressure.

25% Formic acid

Add approximately 250 mL DI water to a 500 mL volumetric flask and carefully transfer 125 mL formic acid to the same volumetric flask. Bring to volume with DI water and mix well.

200 mM Sodium hydroxide

Dilute 20 g of 40% (w/w) sodium hydroxide with degassed DI water to a final weight of 1,000 g in an eluent bottle. Avoid the introduction of carbon dioxide from the air into the aliquot of 40% sodium hydroxide and DI water being used to make the eluent.

Standard and sample solutions

To do the analysis using the method of standard additions, the calibration standard solutions must be prepared in the sample solution, and the concentration of sample in each solution must be the same. To meet these criteria, mix 2× the desired concentration of the working standard solutions and the sample solution in a 1:1 ratio.

100 mg/L Stock standard solutions

Prepare 1,000 mg/L stock standard solutions of fluoride, chloride, nitrate, sulfate, and phosphate by dissolving 0.221, 0.165, 0.137, 0.148, and 0.149 g of NaF, NaCl, $NaNO_3$, Na_2SO_4, and Na_2HPO_4, respectively, in separate 100 mL volumetric flasks with DI water. Prepare 100 mg/L stock standard solutions by diluting 10 mL of 1,000 mg/L stock standard solutions to 100 mL.

Calibration standard stock solutions

Prepare standards of 2× the desired final concentration in the sample by diluting 100 mg/L anion stock standard solutions using the volumes listed in Table 1.

Table 1. Concentrations of calibration standard stock solutions and volumes of 100 mg/L stock standard solutions used for standard additions.

Sample	Anion	Concentration (µg/L)			Volume of 100 mg/L Standard Solution (µL) in Total Volume 100 mL		
		1	2	3	1	2	3
Hydrofluoric acid	Chloride	20	40	80	20	40	80
	Nitrate	20	40	80	20	40	80
	Sulfate	20	40	80	20	40	80
	Phosphate	20	40	80	20	40	80
Ammonium fluoride and simulated BOE	Chloride	20	40	80	20	40	80
	Nitrate	200	400	800	200	400	800
	Sulfate	400	800	1,600	400	800	1,600
	Phosphate	20	40	80	20	40	80

Sample stock solutions

These solutions are prepared at 2× the desired concentration for analysis.

24% Hydrofluoric acid

Accurately weigh 26 g DI water into a 100 mL polypropylene bottle. Slowly add 24 mL (27.84 g) of 50% HF into the same bottle.

Simulated BOE sample solution

Dissolve 40 g ammonium fluoride in 60 mL DI water. To 30 mL of this solution, carefully add 5 mL of 50% HF and mix. Dilute 20 mL of this solution to 100 mL with DI water and mix.

Ammonium fluoride sample solution

Dilute 25 mL ammonium fluoride solution prepared for BOE preparation with 75 mL DI water and mix.

Calibration standard and sample solutions

The calibration standard solutions were prepared by mixing the calibration standard stock solutions with sample stock solutions 1:1. The sample solutions with known amounts of added standards are referred to as Spiked 1, Spiked 2, and Spiked 3.The added standard concentrations of each spiked sample are shown in Table 2. Stock sample solutions are mixed 1:1 with DI water and referred to as Unspiked.

IonPac trap column regeneration

The Thermo Scientific™ Dionex™ IonPac™ ATC-HC Anion Trap Column-High Capacity first must be conditioned; the same procedure is used to regenerate the column. Monitoring the blank will indicate when regeneration is necessary. Regeneration typically is necessary on a monthly basis, but frequency will depend upon the quality contamination in the water blank indicates that the Dionex IonPac ATC-HC column needs to be regenerated. The procedure is as follows:

1. Pump 200 mM sodium hydroxide through the Dionex IonPac ATC-HC column at 1.0 mL/min for 50 min.

2. Follow with a rinse of DI water at the same flow rate for 20 min.

Table 2. Concentrations of added standards in the spiked sample solutions (µg/L)

Sample	Anion	Spiked 1	Spiked 2	Spiked 3
Hydrofluoric acid	Chloride	10	20	40
	Nitrate	10	20	40
	Sulfate	10	20	40
	Phosphate	10	20	40
Ammonium fluoride and simulated BOE	Chloride	10	20	40
	Nitrate	100	200	400
	Sulfate	200	400	800
	Phosphate	10	20	40

Conditions	
Ion Exclusion	
Column:	Dionex IonPac ICE-AS1, 9 × 250 mm (P/N 043197)
Eluent:	Deionized water
Trap Column:	Dionex ATC-HC, 9 × 75 mm (P/N 059604)
Flow Rate:	See Table 4
Ion Chromatography	
Analytical Column:	Dionex IonPac AS11-HC, 2 × 250 mm (P/N 052961)
Guard Column:	Dionex IonPac AG11-HC, 2 × 50 mm (P/N 052963)
Concentrator Column:	Dionex IonPac AG11-HC, 4 × 50 mm (P/N 053962)
Eluent Source:	Dionex EGC II KOH cartridge (This has been replaced by the Dionex EGC III KOH cartridge, P/N 074532) with Thermo Scientific™ Dionex™ CR-ATC trap column (P/N 060477)
Gradient:	See Table 4
Flow Rate:	0.38 mL/min
Sample Volume:	500 µL
Column Temperature:	30°C
Pressure:	~2100 psi
SRS Current:	30 mA
Detection:	Suppressed conductivity, Thermo Scientific™ Dionex™ Anion Self-Regenerating Suppressor™ ASRS™ 300 (P/N 64555), 2 mm, external water mode

System preparation

To configure the system, refer to Figure 1 and Table 3, which summarize the types and lengths of tubing required for system configuration. The chromatographic hardware is divided into two parts: the ion-exclusion pretreatment portion with a Dionex IonPac ICE-AS1 column, and the IC analysis portion with a 2 mm Dionex IonPac AS11-HC column set.

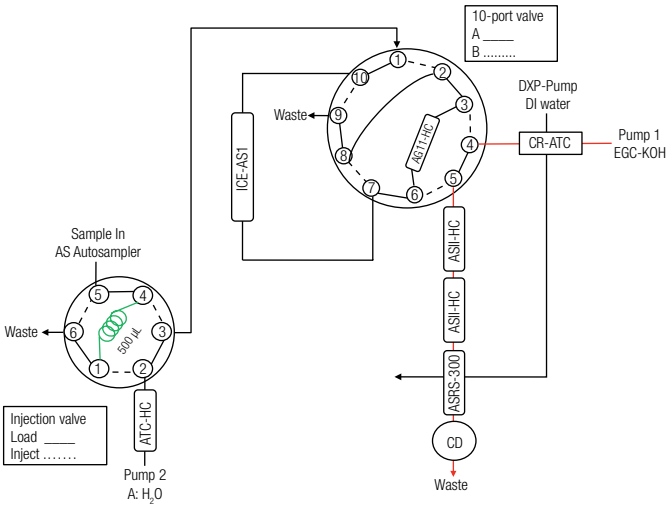

Figure 1. System configuration.

To successfully perform this analysis, it is important to use the same type and length of tubing that is listed in Table 3. Changes in tubing length and types will result in a different (and likely incorrect) "cut" from the Dionex IonPac ICE-AS1 column being delivered to the Dionex IonPac AS11-HC concentrator column. Tubing colors correspond to the internal diameters listed in Table 3.

Ion exclusion pretreatment

1. Prepare the Dionex IonPac ATC-HC trap column according to directions in the IonPac Trap Column Regeneration section. Caution: Before the Dionex IonPac ATC-HC trap column is installed in the system, ensure that sodium hydroxide used for storage or cleaning the Dionex IonPac ATC-HC trap column is completely rinsed away because the Dionex IonPac ICE-AS1 column is not compatible with hydroxide eluent.

2. Cut a 110 cm portion of the green polyetheretherketone (PEEK™) tubing to make a 500 µL sample loop and install this loop between Ports 1 and 4 of the injection valve.

3. Cut a 37 cm portion of the black PEEK tubing and connect this tubing between Port 3 of the injection valve and Port 1 of the 10-port valve.

4. Install the Dionex IonPac ICE-AS1 column by connecting a 4 cm piece of the black PEEK tubing between Port 10 of the 10-port valve and the Dionex IonPac ICE-AS1 column inlet. Use a 32 cm piece of black PEEK tubing between the Dionex IonPac ICE-AS1 column outlet and Port 7 of the 10-port valve.

5. Cut a 5 cm portion of black PEEK tubing and install between Ports 2 and 8 of the 10-port valve.

6. Connect the Dionex AS Autosampler injection-port tubing to Port 5 of the injection valve. The injection-port volume must be calibrated before use.

7. Cut appropriate lengths of green PEEK tubing for waste lines and connect those pieces of tubing to Port 6 of the injection valve and Port 9 of the 10-port valve.

Table 3. Details of tubing configuration.

Connection Points	Tubing Description	Length (cm)	Remark
Port 1=>Port 4 (Injection valve)	Green 0.75 mm (0.033 in)	110	500 µL sample loop
Port 3 (injection valve)=> Port 1 (10-port valve)	Black 0.25 mm (0.010 in)	37	
Port 10=>ICE inlet (10-port valve)	Black 0.25 mm (0.010 in)	4	
ICE outlet=>Port 7 (10-port valve)	Black 0.25 mm (0.010 in)	33	
Port 6=>AG11-HC outlet (10-port valve)	Black 0.25 mm (0.010 in)	5	
AG11-HC inlet=>Port 3 (10-port valve)	Black 0.25 mm (0.010 in)	5	
Port 2=>Port 8 (10-port valve)	Black 0.25 mm (0.010 in)	4	
Port 5=>Analysis (10-port valve)	Red 0.125 mm (0.005 in)	28	Should be as short as possible

IC analysis

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 guard and Dionex IonPac AS11-HC column set at Port 5 of the 10-port valve using red tubing. To minimize dead volume, use the shortest possible lengths of tubing and ensure that the ends of tubing are cut flush.

3. Install the Dionex IonPac AG11-HC 4 mm concentrator using two 5 cm pieces of black PEEK tubing. Connect one end of tubing to each end of the Dionex IonPac AG11-HC 4 mm column and connect the free ends to Ports 3 and 6 of the 10-port valve in the correct eluent flow direction (inlet connected to Port 6 and the outlet connected to Port 3).

4. Put the 10-port valve in position B so that the 4 mm Dionex IonPac AG11-HC column is in-line with the 2 mm Dionex IonPac AG11-HC and AS11-HC column set. Check for leaks. The expected system backpressure for these three columns at 0.38 mL/min is ~ 2,000 psi.

Determining the fraction time

To find the fraction (cut) time, the tubing connections were changed so that the conductivity cell was between the Dionex IonPac ICE-AS1 column and the Dionex IonPac AG11-HC concentrator. The DI water flow rate delivered by pump 2 was set to 0.5 mL/min and the 10-port valve was in position A. The mixture of 20 mg/L chloride and 100 mg/L fluoride was injected onto the Dionex IonPac ICE-AS1 column. The separation of chloride and fluoride on the Dionex IonPac ICE-AS1 column is shown in Figure 2. Based on this experiment, the first 11 min of the ICE separation were established as the collection period for sample analysis. After establishing the fraction time, the conductivity cell was plumbed in the system as shown in Figure 1.

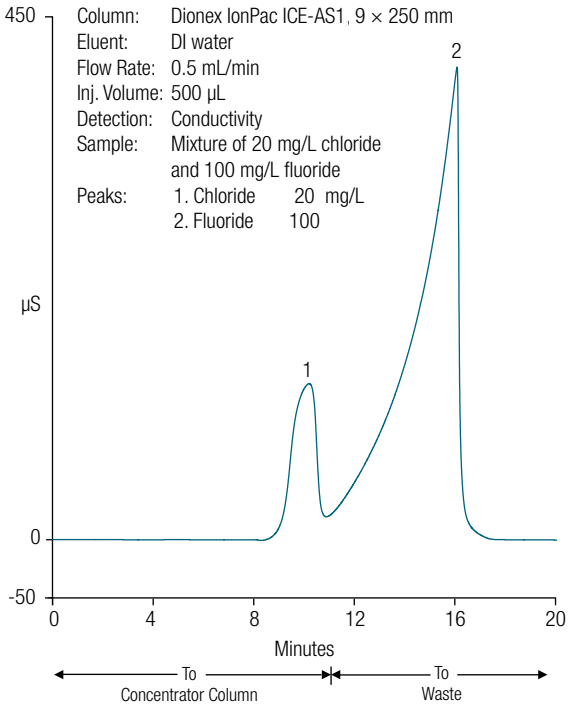

Figure 2. Ion exclusion chromatography of 20 mg/L chloride and 100 mg/L fluoride.

System operation

Initial experiments established that ICE column cleaning was required after sample injection in order to extend the basic method of the original TN 45 to BOE containing ammonium fluoride, and ammonium fluoride. To accomplish this, two programs were used for each sample injection (Table 4), and two sample lines were written in the sequence for each sample. The sample preparation program (ICE separation) was executed by the first sample line. The subsequent anion analysis and ICE column cleaning were executed by the second sample line.

Sample preparation program

For this program, the 10-port valve was in position A. The sample was loaded into the sample loop by the Dionex AS Autosampler and flushed to the Dionex IonPac ICE-AS1 column with DI water delivered by pump 2. The strong acid anions excluded by the Dionex IonPac ICE-AS1 column were collected on the Dionex IonPac AG11-HC concentrator. The sample fraction collection was stopped by switching off the flow of pump 2 at 11 min.

Table 4. Sample preparation, analysis, and ICE column cleaning program description.

Program	Time (min)	Flow Rate Pump 2	Injection Valve Position	10-Port Valve Position	Eluent Concentration (mM)	Remark
Sample Preparation	Init	0.5	Load	A	8	Dionex AS Autosampler starts loading sample to sample loop.
	0	0.5	Inject	A	8	Start fraction collection by flushing sample to concentrator.
	11	Off	Inject	A	8	End fraction collection by switching off pump 2.
Analysis and ICE Column Cleaning	Init	Off	Load	B	8	Dionex AS Autosampler starts loading 25% formic acid to the sample loop for ICE column cleaning.
	0	0.8	Inject	B	8	Start ICE column cleaning and sample analysis. The ICE column is cleaned by flushing 25% formic acid from the sample loop to the column.
	7	0.8	Inject	B	8	
	15	0.8	Inject	B	8	
	30	0.8	Inject	B	30	
	35	0.5	Inject	B	30	
	40	0.5	Inject	B	8	

Analysis and ICE column cleaning program
For this program, the 10-port valve was switched to position B. The excluded anions collected on the Dionex IonPac AG11-HC concentrator were eluted and separated on a Dionex IonPac AS11-HC column set. Formic acid (25%) was loaded to the sample loop by the Dionex AS Autosampler and flushed to the Dionex IonPac ICE-AS1 column by DI water delivered by pump 2.

Discussion of the method

This method addresses the challenge of determining trace concentrations of contaminant ions such as chloride, nitrate, sulfate, and phosphate in a matrix composed of a high concentration of fluoride ions. This is accomplished in two steps: ion exclusion chromatography (ICE) to separate the strong acid anions from the large excess of fluoride, followed by an IC analysis of the strong acid anions automatically collected from the ICE separation.

The ion-exclusion mechanism separates ionized species from nonionized or weakly ionized species. This occurs because of repulsion of the strong acid anions by the negatively charged hydration shell on the stationary phase surface called the Donnan membrane. Figure 2 illustrates the application of this ICE mechanism to the separation of 20 mg/L chloride from 100 mg/L fluoride.

To determine the amount of strong acid anions (e.g., chloride and sulfate) in HF, the method of standard additions was used to account for the sample matrix effect. Before analysis, three different concentrations of standards were added to the same volume of sample and the samples were labeled Spiked 1, Spiked 2, and Spiked 3. This yielded three samples with the anion concentrations equal to the amount in the unspiked sample plus the known amount. After analysis of the unspiked and three spiked samples, the peak areas for all samples were plotted against the concentration of the added standard (zero for the unspiked sample). The Y-axis of this plot yielded the anion concentration of the unspiked sample. All described processes were executed by Chromeleon software. For more information about sequence and QNT file setup for the method of standard additions, go to the Chromeleon software help function and view standard addition.

Results and discussion

Figure 3 shows the chromatography of 12% HF. The concentrations of chloride, sulfate, and other anions are much higher than observed for 24.5% HF used in the original version of TN 45. For example, Figure 3 in this update shows ~ 17 µg/L chloride in 12% HF, whereas the 24.5% HF sample in the original TN 45 had ~ 8 µg/L chloride. When the original work was performed, a customer provided a sample of high-purity HF used for semiconductor applications, which was not available for this update. Therefore, to judge the required sensitivity for the intended application, the method detection limit (MDL) for each anion was estimated using the standard deviation of found anions in seven replicate sample injections and the Student's *t* value for the 99.5% confidence level. Table 5 displays the estimated MDLs in 12% HF. These values are not as low as determined in the original TN 45, but they easily meet the recommended SEMI specifications for 49% HF. For example, the previous work reported an MDL of 0.64 µg/L chloride for 24.5% HF, while this update reports 1.23 µg/L for 12% HF. Both measures are well under the SEMI specification of 100 µg/L (1.28 and 5.02 µg/L, respectively). Recall that the current method injects only one-third the amount of HF used for the original method. If more sensitivity is needed, the method can be optimized for more concentrated HF and/or a larger injection volume. The percentage HF and injection volume used were chosen to increase method ruggedness.

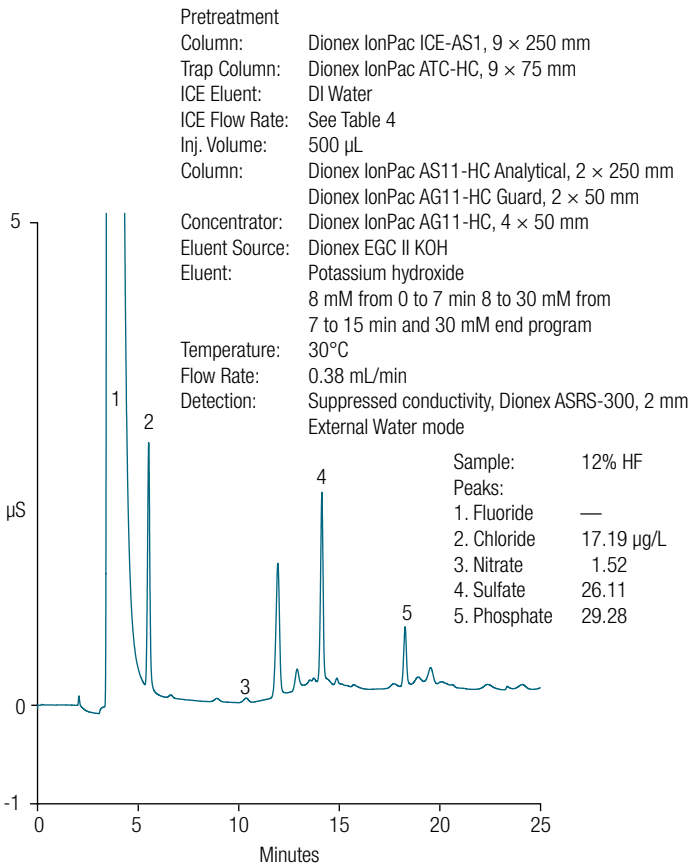

Figure 3. Determination of anions in unspiked 12% HF.

Before estimating MDLs, the method was calibrated using standard additions with the added standard concentrations reported in Table 2. Figure 4 shows the chromatography of this experiment for 12% HF, and Table 6 reports the calibration results for all three samples. Calibration is linear for all samples, suggesting that the fraction of the ICE column sent to the concentrator column is not overloading the concentrator column and causing analyte loss. The good peak shapes in chromatograms for the unspiked 8.33% ammonium fluoride (Figure 5) and the unspiked simulated BOE sample (Figure 6) also suggest that overloading is not occurring. As an accuracy check, the authors prepared fresh samples, spiked them with 10 µg/L each of chloride, nitrate, sulfate, and phosphate, and then measured the recoveries.

Table 5. Anion MDLs for each high fluoride sample.

Anion	MDL (µg/L)		
	Hydrofluoric Acid (12%)	Ammonium Fluoride (8.33%)	Simulated BOE (10x Dilution)
Chloride	1.23	0.81	0.71
Nitrate	1.01	2.25	3.17
Sulfate	2.49	5.48	1.81
Phosphate	9.86	4.83	1.14

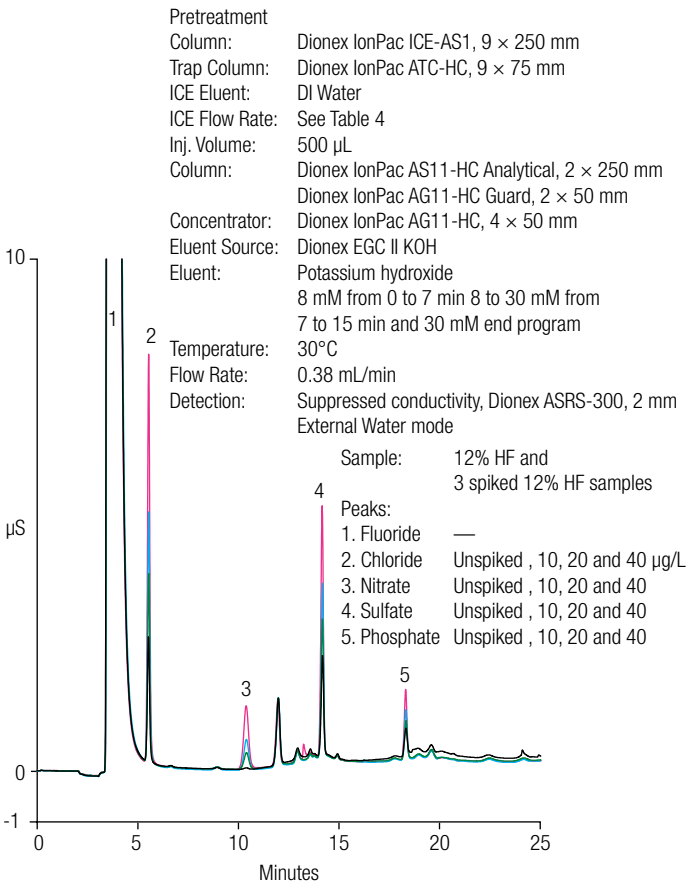

Figure 4. Overlay of chromatograms of HF and three samples of HF spiked with different concentrations of anions.

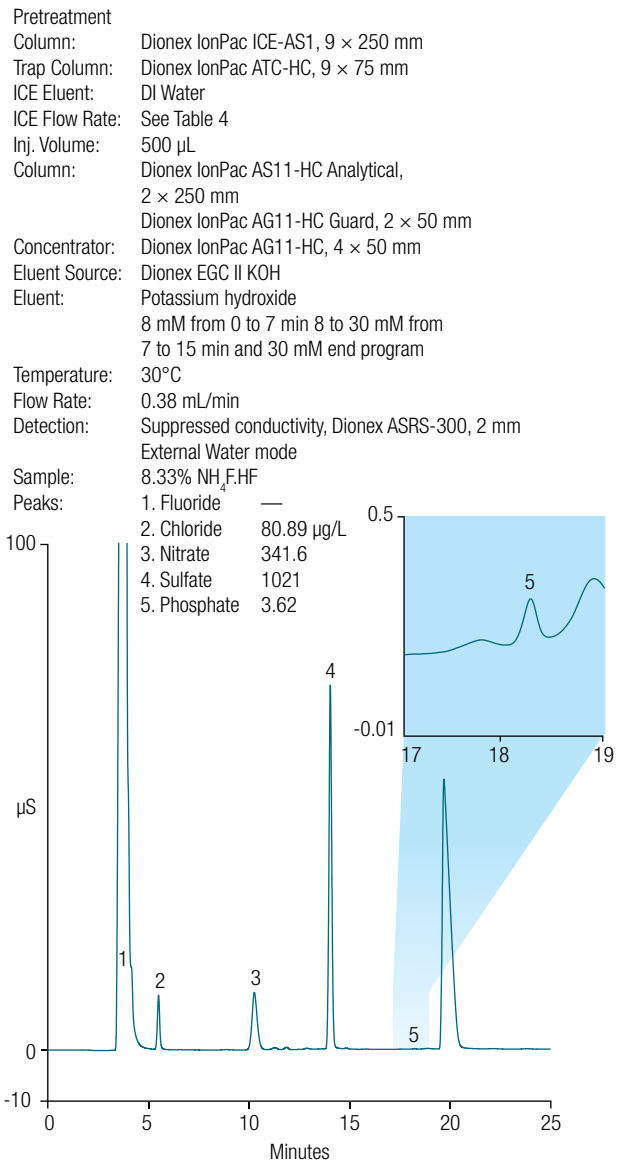

Figure 5. Determination of anions in ammonium fluoride.

Table 6. Calibration results reported by Chromeleon software.

Analyte	Number of Points	% R-Squared		
		Hydrofluoric Acid (12%)	Ammonium Fluoride (8.33%)	Simulated BOE (10× Dilution)
Chloride	4	99.52	99.94	100.00
Nitrate	4	99.89	100.00	99.99
Sulfate	4	99.98	99.97	100.00
Phosphate	4	99.90	99.94	99.85

Pretreatment
Column: Dionex IonPac ICE-AS1, 9 × 250 mm
Trap Column: Dionex IonPac ATC-HC, 9 × 75 mm
ICE Eluent: DI Water
ICE Flow Rate: See Table 4
Inj. Volume: 500 µL
Column: Dionex IonPac AS11-HC Analytical, 2 × 250 mm
Dionex IonPac AG11-HC Guard, 2 × 50 mm
Concentrator: Dionex IonPac AG11-HC, 4 × 50 mm
Eluent Source: Dionex EGC II KOH
Eluent: Potassium hydroxide
8 mM from 0 to 7 min 8 to 30 mM from
7 to 15 min and 30 mM end program
Temperature: 30°C
Flow Rate: 0.38 mL/min
Detection: Suppressed conductivity, Dionex ASRS-300, 2 mm
External Water mode
Sample: 10× dilution BOE

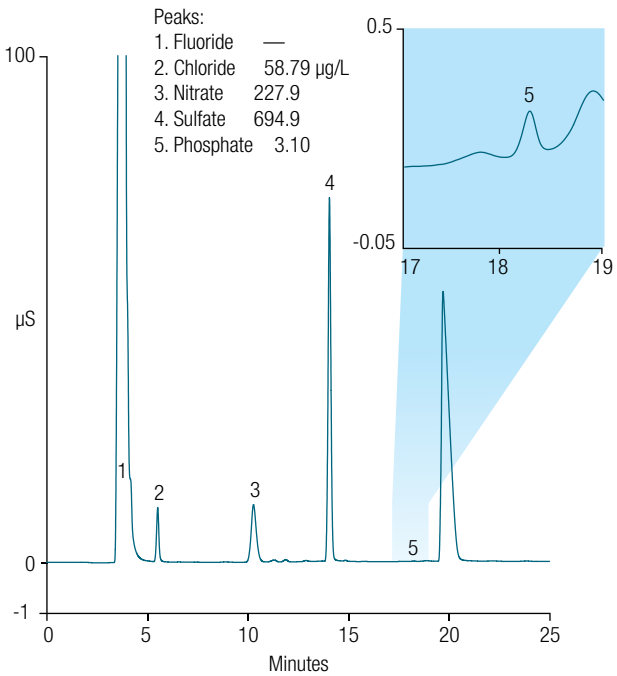

Figure 6. Chromatogram of an unspiked BOE sample (10× dilution).

All four anions showed recoveries greater than 90% in all three samples (Table 7). Phosphate recovery is a good measure of method success. Phosphoric acid is the weakest acid within the group that includes hydrochloric, nitric, and sulfuric acids. Therefore, phosphoric acid will be the first anion affected if the properties of the ICE column change, thereby altering the fraction concentrated from the ICE column so that not all phosphate is captured. It is also possible that a change in the ICE column and fraction concentrated can deliver too much fluoride to the concentrator column, thereby overloading it. Because phosphate is trivalent, its retention and recovery will be impacted before that of the other anions.

To assess method reproducibility, retention time precision was calculated using an experiment that evaluated all three samples. For each of the three sample types, there were 17 injections that included samples spiked with known quantities of anions. Table 8 shows that retention time was reproducible for these 51 injections; no trend toward longer or shorter time was observed.

Table 7. Recovery results.

Sample		Anion			
		Chloride	Nitrate	Sulfate	Phosphate
Hydrofluoric Acid (12%)	Spiked Concentration (µg/L)	10	10	10	10
	Concentration in Sample (µg/L)	17.19	1.52	26.11	29.28
	Concentration in Spiked Sample (µg/L)	26.30	10.51	35.92	40.22
	Recovery (%)	**96.73**	**91.20**	**99.46**	**102.4**
Ammonium Fluoride (8.33%)	Spiked Concentration (µg/L)	10	100	200	10
	Concentration in Sample (µg/L)	80.89	341.6	1021	3.62
	Concentration in Spiked Sample (µg/L)	92.58	438.4	1224	12.97
	Recovery (%)	**101.9**	**99.28**	**100.2**	**95.20**
Simulated BOE (10x Dilution)	Spiked Concentration (µg/L)	10	100	200	10
	Concentration in Sample (µg/L)	58.79	227.9	694.9	3.10
	Concentration in Spiked Sample (µg/L)	68.86	324.6	893.2	11.88
	Recovery (%)	**100.1**	**99.01**	**99.81**	**90.63**

Table 8. Retention time reproducibility for 51 sample injections.

Retention Time	Anion			
	Chloride	Nitrate	Sulfate	Phosphate
Average Retention Time (min)	5.51	10.30	14.09	18.27
RSD (%)	0.42	0.62	0.27	0.07

Precautions

Exercise extreme caution when handling concentrated HF, which can corrode glass containers. Therefore, plastic containers must be used for handling HF. High-density polypropylene, high-density polyethylene, or Teflon® containers are recommended and Teflon is preferred. To minimize contaminating ions, containers should be soaked with 17.8 MΩ·cm DI water (or better) for at least 24 h before use. All sample preparations with HF should be done in a fume hood. Work behind a shield and wear a face shield, goggles, and gloves designed for handling HF. Calcium gluconate gel should be available in case of HF contact with exposed skin. Consult your safety officer before working with HF.

The Dionex IonPac ICE-AS1 column is not compatible with hydroxide eluent, so sodium hydroxide must be flushed out of the Dionex IonPac ATC-HC trap column after regeneration or initial startup of the trap column. The backpressure of the ICE-AS1 column should not exceed 1,000 psi, as noted in the Dionex IonPac ICE-AS1 Product Manual. Therefore, set the maximum pressure limit to 1,000 psi to avoid column damage.

The success of this application depends on a consistent flow rate of DI water delivered by the pump to the Dionex IonPac ICE-AS1 column in order to produce the correct fraction on the Dionex IonPac AG11-HC concentrator. Periodically recalibrate the pump flow rate to ensure delivery of the appropriate fraction.

Long-term exposure to concentrated HF will damage the Dionex IonPac ICE-AS1 column and PEEK tubing. Rinsing the Dionex IonPac ICE-AS1 column and sample loop with 25% formic acid and using only 12% HF should improve column and tubing lifetime, compared to earlier methods; however, the Dionex IonPac ICE-AS1 column may require replacement after approximately 500 injections. Using more concentrated HF solutions will shorten column lifetime. For best results, replace the sample loop and all tubing that comes in contact with HF at least once a year.

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