

Determination of trace anions in concentrated hydrofluoric acid

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Introduction

The determination of trace anions in concentrated hydrofluoric acid has been a difficult analytical challenge. In the past, labor-intensive manual preconcentration methods were required prior to analytical measurements. Typical preconcentration procedures involved evaporation of a specific large volume of sample for 6 to 10 hours on a hot plate before transfer to a volumetric flask and analysis. Also, a class-100 clean room environment has normally been required during sample pretreatment.

An improved method for determining trace anions in concentrated hydrofluoric acid has been developed. Trace anions are separated from the high concentration of fluoride by matrix elimination using a Thermo Scientific™ Dionex™ IonPac™ AC10 concentrator column prior to analytical separation. The retained anions of interest are eluted from the Dionex IonPac AC10 concentrator and separated on the moderate capacity Thermo Scientific™ Dionex™ IonPac™ AS10 column. The detection limits (MDL) using this method are 25 to 50 ppb for most trace anions in 5% hydrofluoric acid.

Experimental

Equipment*

- A Thermo Scientific Dionex chromatographic system comprising:
 - Gradient Pump
 - Liquid Chromatography Module, equipped with Model 9010 Rheodyne Injector
 - Conductivity Detector, equipped with 340 kPa (50-psi) back-pressure device
 - Sample Loading Pump

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

The system configuration is shown in Figure 1.

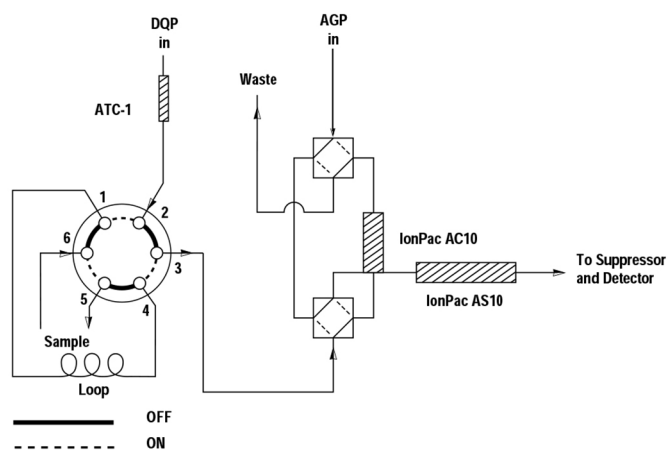


Figure 1. IC system configuration.

Reagents and standards

- Sodium hydroxide, 30% Suprapur®
- Sulfuric acid, concentrated
- Methanol, HPLC grade

Note: This application note uses Dionex IonPac microbore (2 mm) columns, but the analysis can also be performed using standard 4 mm diameter columns. For more information about microbore analyses, please contact your Thermo Scientific sales representative.

Conditions

Columns:	Dionex IonPac AS10 (2 mm) analytical Dionex IonPac AG10 (2 mm) guard Dionex IonPac AC10 (2 mm) concentrator Thermo Scientific™ Dionex™ IonPac™ ATC-1 trap (2 mm), 2 required			
Eluent 1:	Deionized water			
Eluent 2:	400 mM Sodium hydroxide			
Rinsing Reagent:	70% v/v Methanol			
Eluent Flow Rate:	0.25 mL/min			
Rinsing Flow Rate:	1.0 mL/min			
Injection Volume:	10 mL			
Detection:	Suppressed conductivity			
Regenerant:	50 mM Sulfuric acid (needed for AMMS only)			
Suppressor:	Thermo Scientific™ Dionex™ AMMS (2 mm) or Thermo Scientific™ Dionex™ Anion Self-Regenerating Suppressor (ASRS) (2 mm)			
Regenerant Flow Rate:	10 mL/min			
Gradient Program:				
Time	E1	E2	V5	V6
0.0	75	25	0	0
2.5	75	25	1	0
12.0*	75	25	0	1

*Begin sampling

Preparation of solutions and reagents

400 mM sodium hydroxide

High purity sodium hydroxide, 30% Suprapur sodium hydroxide containing less than 1 mg/L (ppm) of chloride and 5 mg/L (ppm) of sulfate (VWR Scientific), or equivalent is required. *Anion contaminants (commonly chloride and sulfate) will have a significant effect on the accuracy, precision, and detection limits of this technique.*

Degas 960 mL of 18-MΩ water in a clean 1 L eluent bottle by vacuum degassing while sonicating (15 min). Add 53.4 g (40.2 mL) of 30% Suprapur sodium hydroxide into the solution and mix well.

50 mN sulfuric acid (regenerant required for AMMS)

Place 3 L of deionized water in a clean 4 L polyethylene container. Add 10.3 g (5.6 mL) of sulfuric acid (conc.) to the solution. Dilute to 4 L with deionized water. This regenerant is not required if an Anion Self-Regenerating Suppressor (ASRS) is used.

70% v/v methanol

Place 700 mL of HPLC-grade methanol in a clean 1 L eluent bottle. Add 300 mL of 18-M Ω water and mix well. Degas before using.

Sample preparation

Samples of up to 5% hydrofluoric acid (1:10 v/v) can be injected directly. Higher concentrations should be diluted to 5% with high purity water.

Discussion of results

The determination of trace anions in concentrated acids and bases by ion chromatography has long been an analytical challenge. Ion chromatography has not been applied to sample matrices of extreme ionic strength due to low column capacity and the low ionic strength eluents used in most analytical separations. A several-fold dilution of the concentrated acids is usually required to determine the trace anion contaminants, which typically compromises the detection limits.

Suppressed microbore ion chromatography (IC) offers analysts a solution for trace anion determination in concentrated weak acids. Greater suppression capacity can be achieved at the low flow rates of the microbore system. Improved background suppression allows higher capacity analytical columns to be used. As a result, higher capacity columns permit higher concentration of acids to be injected onto the column without overloading, thus improving trace anion detection limits.

The matrix effect remains a serious problem in the determination of trace anions in concentrated reagents. The term *matrix effect* is defined as the interference imposed by the matrix on the analytical separation and detection. In this case, the matrix disrupts the equilibrium concentrations of trace anion contaminants in the ion exchange column causing the elution of those contaminants (system blank) along with the analyte anions. Consequently, the major contaminants commonly

found in the eluent are a limiting factor in analyzing trace anions. The “system blank” caused by a high ionic strength sample is illustrated in Figure 2. At equilibrium (A), where the analytical column is in the hydroxide form, the chloride present in sodium hydroxide eluent is also equilibrated in the column. The concentration of chloride in the stationary phase is determined by the distribution coefficient of the anion exchanger for chloride and the level of chloride impurity in the eluent used. Upon injection of concentrated hydrofluoric acid (B), the high concentration (percent level) of fluoride behaves similar to an eluent, eluting “blank” chloride from the stationary phase along with the “analyte” chloride (C). Table 1 presents the results of determining trace anions in various concentrations of hydrofluoric acid. Note that the system blank induced by the hydrofluoric acid at various concentrations is not consistent and is sometimes more than twice the analyte concentration. Ultrapure eluents are required to accurately determine anions at mg/L (ppb) concentrations.

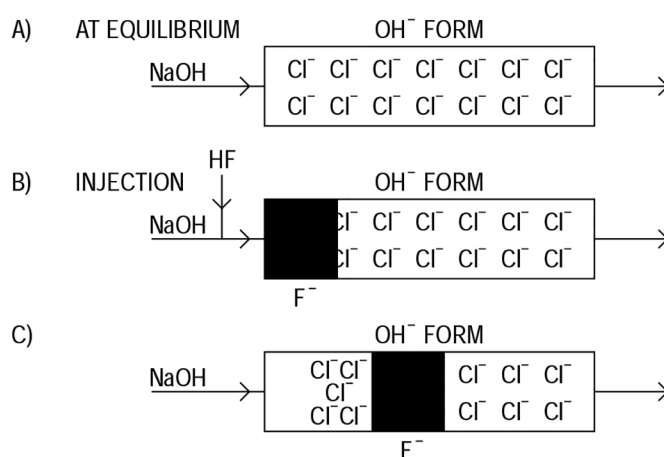


Figure 2. Analytical blank caused by high ionic strength sample.

Table 1. Spike recovery of chloride in hydrofluoric acid using direct injection (no matrix elimination).

% HF	Expected (mg/L)	Found	% Recovery (mg/L)
0.25	0.039	0.039	100
0.50	0.078	0.190	250
1.00	0.156	0.590	380
2.00	0.312	0.880	280
3.13	0.487	1.440	290
4.17	0.649	2.000	310

Sample pretreatment techniques prior to analytical measurements have long been used to eliminate the matrix effect. Unfortunately, most anion exchange resins are not effective due to poor selection for anions of the same charge. Another approach is the separation of matrix components from analytes based upon hydrophobicity differences. Weak acids such as hydrofluoric acid, formic acid, propionic acid, and acetic acid have pKa s between 3.5 and 4.8. Below this range they remain protonated and uncharged. Using methanol/water as a wash at low pH, most of the weak acid matrix component can be removed prior to analytical measurement.

Since high purity grade methanol (trace anion grade) is not commonly available, further purification is required. First, clean the two Dionex IonPac ATC-1 trap columns by pumping 0.5 M sodium hydroxide/50% methanol at 5.0 mL/min for 15 min, followed by rinsing with 200 mL of deionized water. Then, place one of the two Dionex IonPac ATC-1 trap columns between the DQP outlet check valve and valve 6 (BF-2 double stack pneumatic valve in the LCM-3 or LC-20). Place the other Dionex IonPac ATC-1 trap column between the eluent glass bottle (E1) and the AGP. The two Dionex IonPac ATC-1 trap columns will help to reduce trace anion contaminants in the reagents used in this method.

The matrix reduction of weakly retained anions is performed by the Dionex IonPac AC10 concentrator column. The Dionex IonPac AC10 concentrator column contains a solvent-compatible, highly crosslinked substrate, layered with Thermo Scientific™ Dionex™ MicroBead™ latex resin (see Figure 3). The sample is injected onto the Dionex IonPac AC10 concentrator column, which has previously been equilibrated with 70% methanol/water. The weak acid matrix component is eluted with methanol, while chloride, sulfate, bromide,

and nitrate are retained in the column (phosphate in its acid form is not quantitatively retained under this condition). The retained anions are then eluted from the Dionex IonPac AC10 concentrator column to the Dionex IonPac AS10 analytical column, where they are resolved. Although the matrix component may not be completely eliminated using the Dionex IonPac AC10 concentrator column, it is reduced sufficiently to minimize the matrix effect. Figure 4 shows the comparison of a direct injection versus the column pretreatment technique for a 3.33% hydrofluoric acid matrix. This technique can measure hydrofluoric acid concentrations up to 5% (see Figure 5). The matrix effect is determined by analyzing various concentrations of hydrofluoric acid. The results in Table 2 show that the experimental anion concentrations agree well with the expected values after incorporating the pretreatment technique.

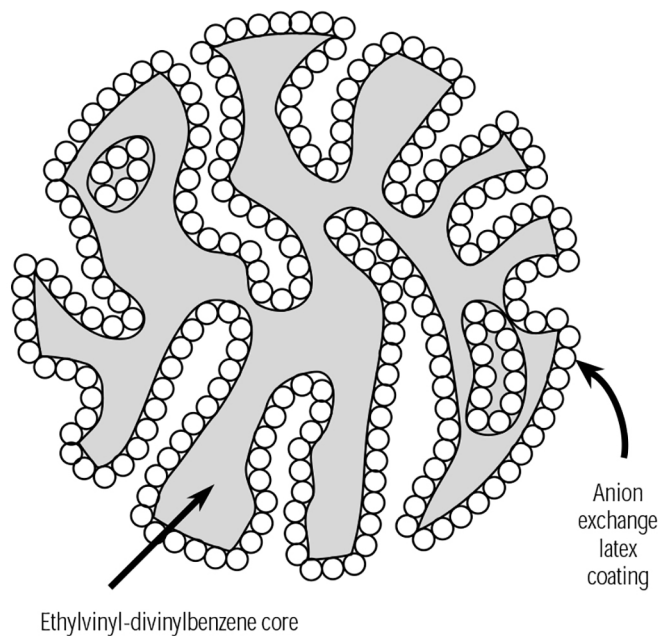


Figure 3. Diagram of the Dionex IonPac AC10 MicroBead microporous resin.

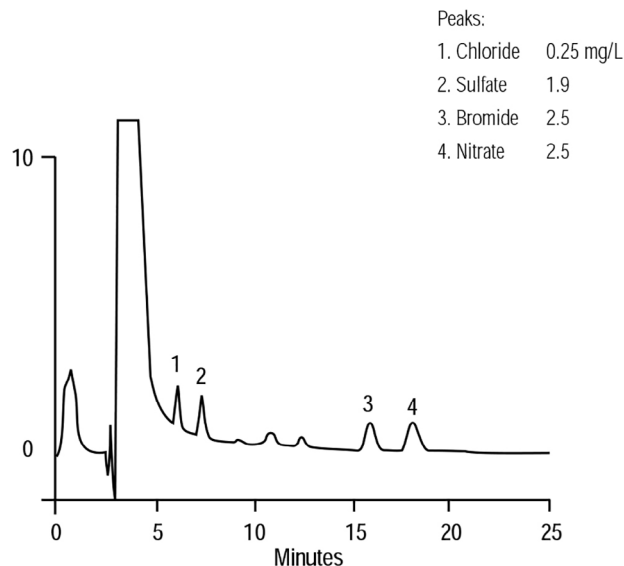
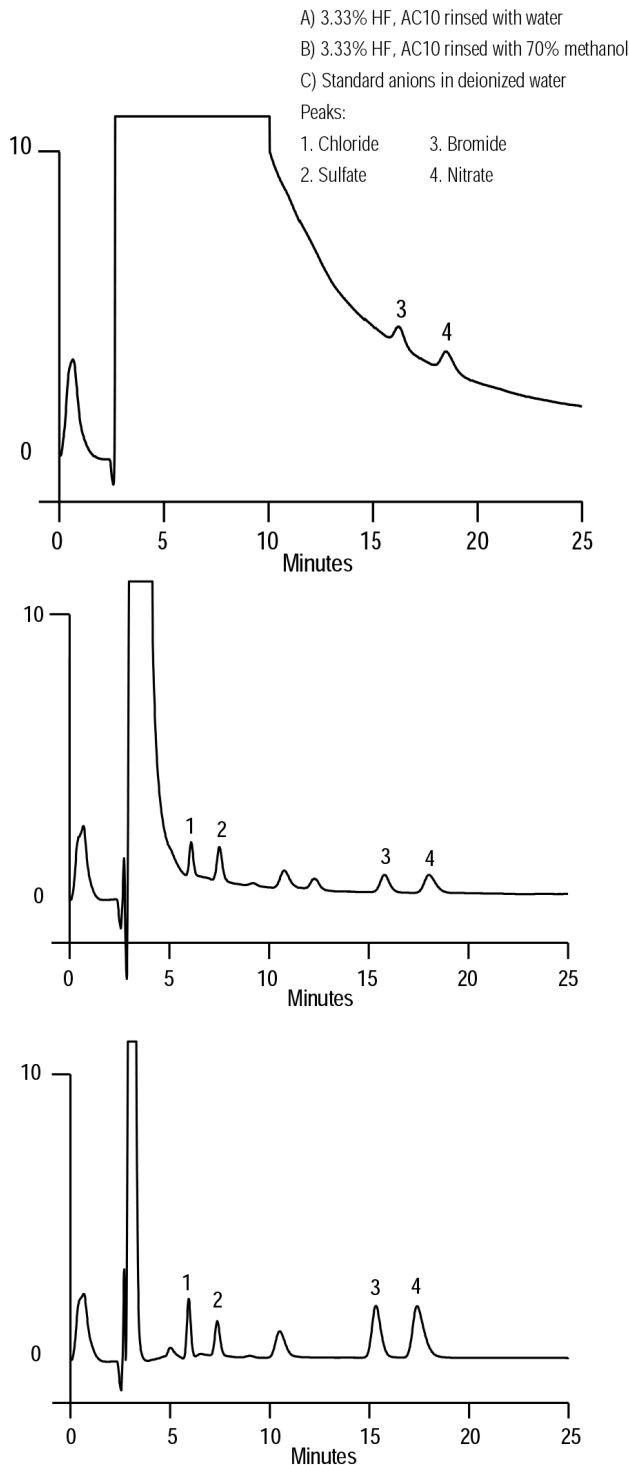


Figure 5. Determination of trace anions in 5% hydrofluoric acid by IC.

Table 2. Spike recovery of chloride, sulfate, bromide and nitrate in 3.33 to 5% hydrofluoric acid.

Anion	% HF	Spike (mg/L)	Found (mg/L)
Chloride	3.33	0.46	0.54 ± 0.01
	4.17	0.57	0.57 ± 0.03
	5.00	0.69	0.67 ± 0.02
Sulfate	3.33	0.86	0.98 ± 0.03
	4.17	1.07	1.01 ± 0.02
	5.00	1.29	1.17 ± 0.07
Bromide	3.33	1.66	1.75 ± 0.03
	4.17	2.08	1.89 ± 0.04
	5.00	2.50	2.42 ± 0.06
Nitrate	3.33	1.66	1.75 ± 0.02
	4.17	2.08	2.10 ± 0.07
	5.00	2.50	2.50 ± 0.04

Figure 4. Determination of trace anions in 3.33% hydrofluoric acid by IC.

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