

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 an IonPac® AC10 concentrator column prior to analytical separation. The retained anions of interest are eluted from the IonPac AC10 concentrator and separated on the moderate capacity IonPac AS10 column. The detection limits (MDL) using this method are 25 to 50 ppb for most trace anions in 5% hydrofluoric acid.

EQUIPMENT

A 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

The system configuration is shown in Figure 1.

REAGENTS AND STANDARDS

Sodium hydroxide, 30% Suprapur®

Sulfuric acid, concentrated

Methanol, HPLC grade

CONDITIONS

| | |
|-----------------------|---|
| Columns: | IonPac AS10 (2-mm) analytical IonPac AG10 (2-mm) guard IonPac AC10 (2-mm) concentrator 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 µL |
| Detection: | Suppressed conductivity |
| Regenerant: | 50 mN Sulfuric acid (needed for AMMS only) |
| Suppressor: | AMMS (2-mm) or 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

Note: This application note uses 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 Dionex sales representative.

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-M Ω 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

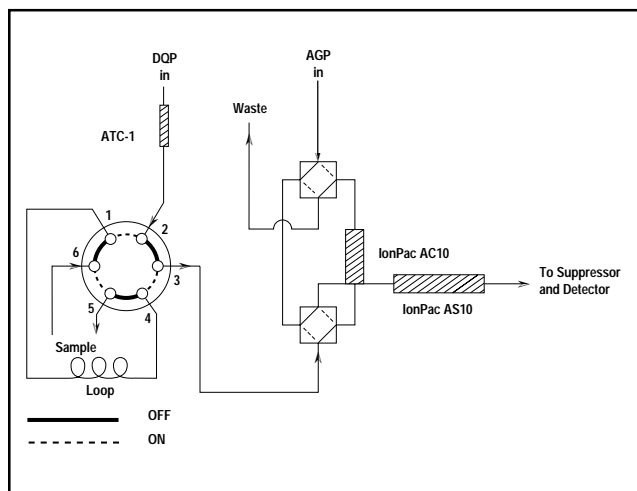


Figure 1 IC system configuration

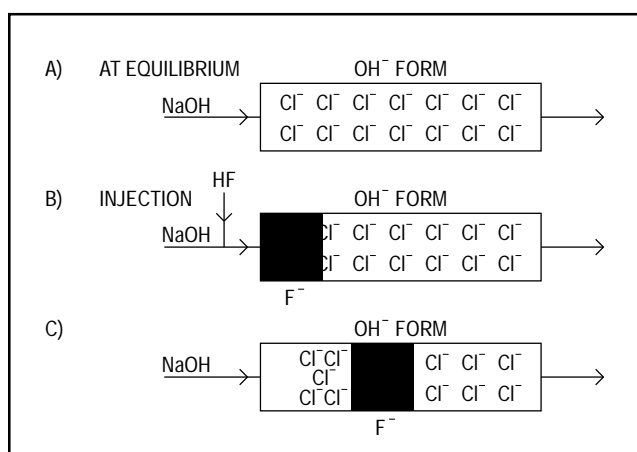


Figure 2 Analytical blank caused by high ionic strength sample

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

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 |

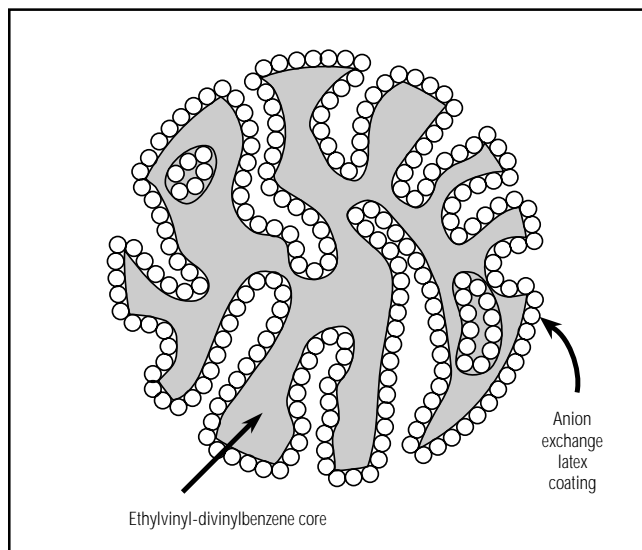


Figure 3 Diagram of the IonPac AC10 MicroBead microporous resin

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 $\mu\text{g/L}$ (ppb) concentrations.

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 pK_a 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 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 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 ATC-1 trap column between the eluent glass bottle (E1) and the AGP. The two 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 IonPac AC10 concentrator column. The IonPac AC10 contains a solvent-compatible, highly cross-linked substrate, layered with MicroBead™ latex resin (see Fig. 3). The sample is injected onto the IonPac AC10, 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 IonPac AC10 to the IonPac AS10 analytical column, where they are re-solved. Although the matrix component may not be completely eliminated using the IonPac AC10, 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 Fig. 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.

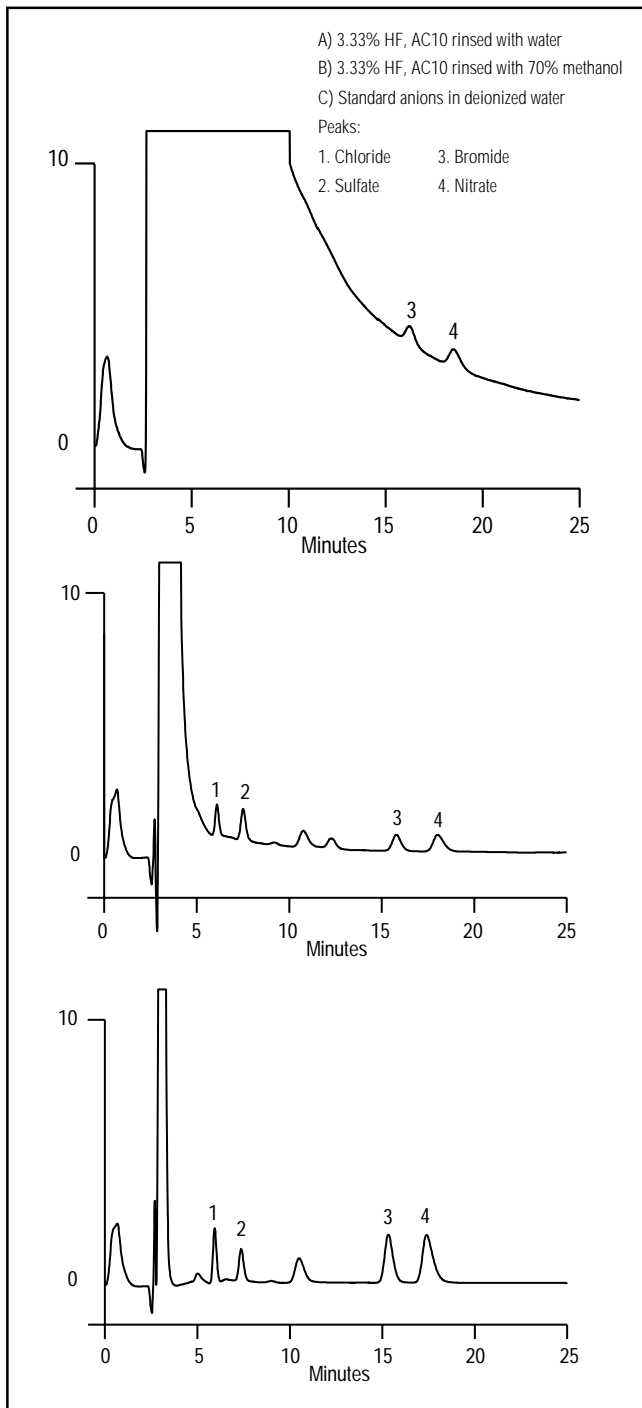


Figure 4 Determination of trace anions in 3.33% hydrofluoric acid by IC

| 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 |

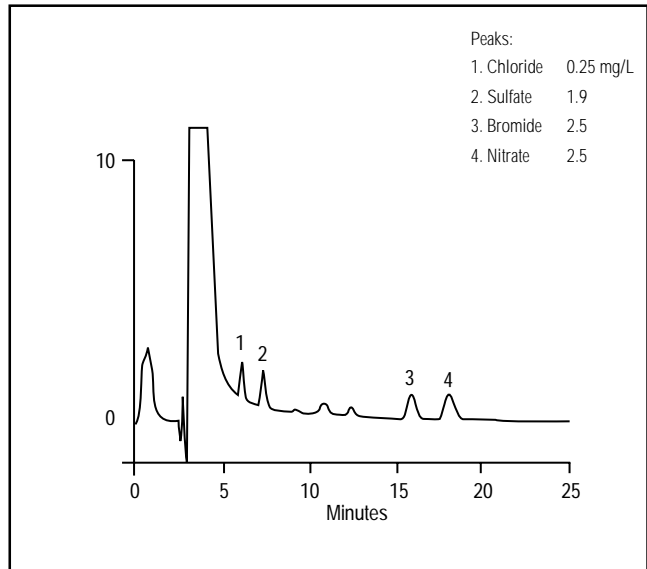


Figure 5 Determination of trace anions in 5% hydrofluoric acid by IC

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