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Determination of trace anions in concentrated acids by means of a moderate-capacity anion-exchange column

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ABSTRACT

The development of a moderate-capacity anion-exchange resin has resulted in new ion chromatography (IC) methods for the determination of trace anions in concentrated acids. Suppressed microbore IC offers a higher suppression capability, which allows higher-capacity analytical columns to be used. As a result, higher-capacity columns permit higher concentrations of acids to be injected into the column without overloading, thus improving trace anion detection limits. In addition, using a selective matrix elimination method, high concentrations (% levels) of weak acids (*e.g.* hydrofluoric acid and acetic acids) may be eliminated prior to analysis by IC.

INTRODUCTION

The determination of trace inorganic constituents in concentrated reagent is important in a variety of chemical and semiconductor processes. Historically, the levels of impurities have been dictated by available analytical methodologies. In the semiconductor industry, the requirements for lower impurities levels are exceeding the limits of current analytical methods. Such a case is the determination of trace anions in concentrated acids. In many cases, new specifications are being set with impurities at the low and sub-μg/l levels in concentrated acids.

The determination of trace anions in concentrated acids has been a difficult analytical challenge. Labor-intensive manual preconcentration methods have been required prior to analytical measurements. Typical preconcentration procedures involve evaporation of a specific volume of sample for 6 to 10 h on a hot plate before transfer to a volumetric flask and analysis. Most of the wet chemistry methods of analysis used are semiquantitative and insensitive. For example, turbidity assays have been used to determine chloride and sulfate contaminations in semiconductor-grade hydrofluoric acid [1]. Colorimetric methods have been used for the determinations of nitrate and phosphate in the same acid. Also, a class 100 clean room environment is normally required during sample pretreatment.

Since the invention of ion chromatography (IC) in 1975 [2], IC has not been applied to sample matrices of extreme ionic strength due to low column capacity and the low ionic strength of the eluents used in most analytical separation. Several-fold dilution of the concentrated acids is usually required in order to determine the trace anion contaminants, usually compromising the detection limits. A separation of trace component form the sample matrix on a moderate to a high capacity anion exchanger is the method of choice; however, a strong eluent is required which will overload the suppression capacity of the suppressor.

Suppressed microbore IC offers analysts a solution for trace anion determination in concentrated acids. Greater suppression capacity can be achieved at the low flow rates of the system [3–5]. 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.

This paper will describe the determination of trace anions in concentrated acids using a moderate

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capacity anion exchnage column. Using a selective matrix elimination method, the high concentration of weak acids (% levels) such as hydrofluoric acid and acetic acid can be eliminated prior to analytical determination by IC.

EXPERIMENTAL

Chromatographic system

All chromatography was performed on a Dionex DX-300 system with only minor modifications. The system consisted of a microbore advanced gradient pump (AGP), a liquid chromatography module (LCM-3), a single piston pump (DQP), and a conductivity detector (CDM-II).

Three types of columns were used in the system. An IonPac AS10 (250 × 2 mm) was used for analyte separation. An IonPac AC10 (50 mm × 2 mm) was used for sample pretreatment and matrix elimination prior to sample analysis. Two ATC-1 columns were employed for eluent purification. The ATC-1 (trap column) columns were cleaned by pumping 0.5 *M* sodium hydroxide in water–methanol (50:50) at 5.0 ml/min for 15 min followed by rinsing with 200 ml deionized water. One of the two ATC-1 columns was placed between the DQP outlet check valve and the LCM-3. This column was used to purify methanol–water (70:30) eluent. The other ATC-1 column was placed between the water eluent bottle and the AGP. The DQP pump flow-rate was set at 1.0 ml/min.

The DX-300 system was modified as shown in Fig. 1. An additional inert double stack four-way slider valve (5000 p.s.i.) was placed between a rotary injection valve and the analytical column. The rotary valve and four-way slider valve were controlled by control 5 and 6 on the AGP. The DQP was used to pump methanol–water (70:30) eluent to the rotary injection valve and pass through the IonPac AC10 concentrator located on the four-way slider valve. The NaOH eluent was delivered by the AGP to the concentrator column and to the analytical column. An anion micromembrane suppressor (AMMS, 2 mm format) was employed for eluent suppression. The sulfuric acid regenerant was delivered to the AMMS by a Dionex AutoRegen system.

System operation

The chromatographic conditions are listed in Table I. At 0.0 min, valves 5 and 6 were OFF. The sample was loaded into the sample loop while the DQP was pumping methanol–water (70:30) to the

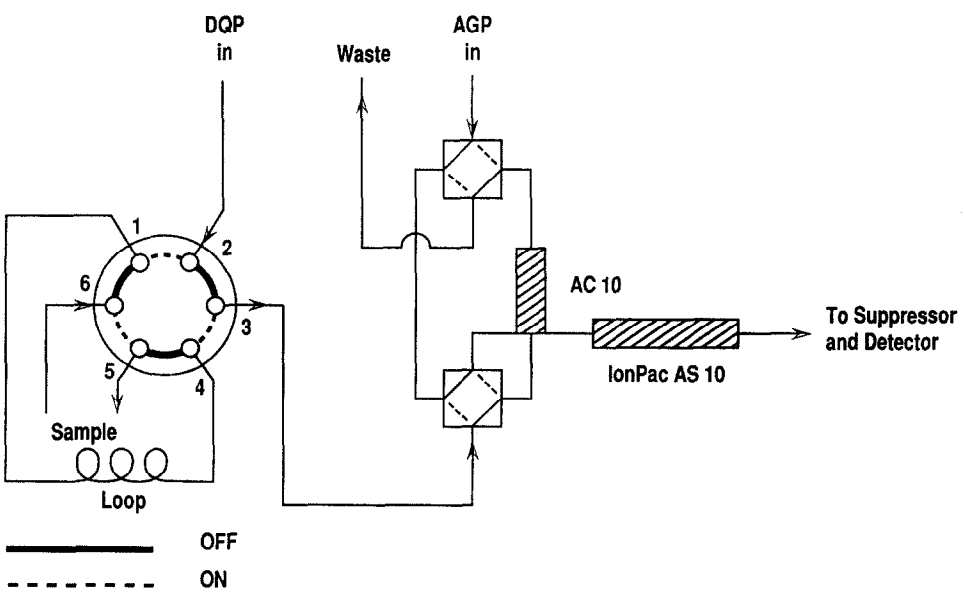

Fig. 1. Microbore suppressed IC system configuration.

TABLE I

CHROMATOGRAPHIC CONDITIONS

Columns	IonPac AS10 (2 mm) IonPac AG10 (2 mm) IonPac AC10 (2 mm)			
Trap Column	ATC-1 (2 required)			
Eluent	E1 deionized water E2 400 m*M* NaOH			
AGP Program				
Time (min)	E1	E2	5INJ	6AUX
0.0	75	25	0	0
2.5	75	25	1	0
12.0 (Begin sampling)	75	25	0	1
Rinsing reagent	methanol–water (70:30)			
Flow-rate	0.25 ml/min			
Injection volume	10 μl			
Detection	Suppressed conductivity			
Regenerant	25 m*M* sulfuric acid			
Regenerant flow-rate	10 ml/min			
Suppressor	AMMS (2mm)			

IonPac AC 10 column. During this time, the AGP was pumping 100 m*M* NaOH to the IonPac AS10 column. At 2.5 min, valve 5 was switched ON and valve 6 kept OFF. Concurrently, the methanol–water eluent delivered by the DQP flushed the sample loop and passed through the IonPAC AC10 column. At this point, most weak acids (*e.g.* acetic acid, hydrofluoric acid) would be eluted off the concentrator to waste while strongly retained species such as chloride, nitrate and sulfate would be concentrated by the concentrator. At 12.0 min, valve 5 was switched OFF and valve 6 switched ON. The IonPAC AC10 was switched in line with the IonPac AS10 at which point the retained anions were eluted to the analytical column. The analysis time was approximately 25 min.

Reagents

The high-purity sodium hydroxide, 30% Suprapur NaOH (VWR Scientific), was used for the entire study. First, 960 ml of 18-MΩ water was degassed in a clean 1-l eluent bottle by vacuum degassing while sonicating (15 min). Then, 53.4 g (40.2 ml) of 30% Suprapur NaOH was added to the solution and mixed well. HPLC-grade methanol (Baker) was used to prepare methanol–water (70:30) eluent.

RESULTS AND DISCUSSION

A moderate-capacity anion exchanger, IonPac AS10, allows for the separation of trace anions in high-ionic-strength matrices. The IonPac AS10 is a macroporous pellicular resin which consists of a highly cross-linked inert solid core penetrated by channels through which solutions can flow. This core is coated with a thin layer of anion-exchange particles. The anion-exchange particles (65 nm diameter) are small enough to coat the inside of the macroporous resin (200 nm pore size). This results in good mass transfer, while providing higher capacity and higher efficiency of the AS10 resin compared to the conventional surface-aminated type macroporous anion exchanger [4].

Suppressed microbore IC allows greater suppression of high eluent concentration than the standard IC format due to the lower flow-rate of the system. In the standard 4 mm format, the suppressor can be used to suppress at least 100 m*M* NaOH eluent at a flow-rate of 1.0 ml/min and regenerant flow of 10 ml/min. While the microbore IC operates at 0.25 ml/min and the suppressor regenerant flow-rate remains unchanged, the resulting combination allows the use of strong eluent concentrations of at least 300 m*M* NaOH [3]. Improved background suppression allows higher capacity analytical columns to be used. Consequently, higher concentrations of acids (% levels) can be injected onto the column without overloading, thus improving trace anion detection limits.

System blank caused by high-ionic-strength matrices

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 between the eluent and 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 used are a limiting factor in analyzing trace anions.

The system blank was observed when samples of HF at various concentrations were analyzed by direct injection. The NaOH gradient used started at

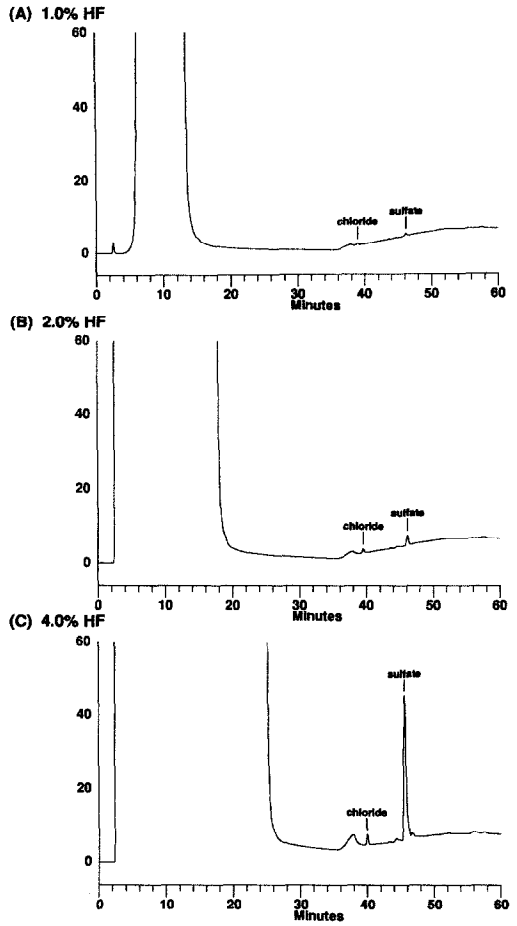

Fig. 2. Analysis of various HF concentrations. (A) 1% HF, (B) 2% HF, (C) 4% HF. Injection volume: 10 μl; column: IonPac AS10 (250 mm × 0.2 mm); suppressor: Microbore AMMS; eluent: time 0.0 —10 m*M* NaOH, time 30 min —10 m*M* NaOH, time 45 min —200 m*M* NaOH; eluent flow: 0.25 ml/min; regenerant: 25 m*M* sulfuric acid; regenerant flow: 10 ml/min; detector: conductivity (CDM-II).

10 m*M* for 30 min where the majority of fluoride was eluted off the column. Then, the analytes of interest were separated when the NaOH concentration increased to 200 m*M* in 15 min. The equilibration time used before the next analysis was 15 min, making the total analysis time of 75 min per sample. Fig. 2 shows the chromatograms of various HF concentrations using NaOH gradient. The results showed that increasing HF concentration from 0.125% to 0.25% HF (2×), chloride concentration increased from 0.11 mg/l to 0.21 mg/l (2×). However, increasing HF concentrations from 1% (0.58 *M*) to 2% (1.16 *M*) and to 4% (2.32 *M*), chloride concentrations found did not increase proportionally to HF concentrations. Similar behavior was found in the case of sulfate. Fig. 2 also shows that sulfate concentration increases more than 100 times, from 0.58 mg/l (A) to 61 mg/l, (C), when HF concentration increases from 1% to 4%. From this experiment, it was concluded that chloride and sulfate contaminants in NaOH contribute to the system blank when analyzing high ionic strength samples.

TABLE II

SPIKE/RECOVERY OF CHLORIDE IN HF USING DIRECT INJECTION METHOD

HF (%)	Cl^- in HF[a] (mg/l)	Spiked (mg/l)	Found (mg/l)	Corrected (mg/l)	Recovery (%)
0.25	0.041[b]	0.039	0.080	0.039	100
0.50	0.082[c]	0.078	0.272	0.190	250
1.0	0.164[c]	0.156	0.754	0.590	380
2.0	0.328[c]	0.312	1.208	0.880	280
3.13	0.513[c]	0.487	1.953	1.440	290
4.17	0.684[c]	0.649	2.683	2.0	310

[a] Chloride in original sample.
[b] Determined experimentally.
[c] Estimated from concentration of chloride in 0.25% HF.

The "system blank" caused by high-ionic-strength sample can be explained as follows. At equilibrium where the analytical column is in the hydroxide form, the chloride present in he NaOH 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 relative to hydroxide and the level of chloride impurity in the eluent used. Upon direct injection of concentrated HF, the high concentration of F^- behaves like an eluent, eluting "blank" chloride from the stationary phase along with the "analyte" chloride. Table II illustrates the determination of trace chloride in various HF concentrations. All analytical results presented in Table II are based upon aqueous calibration standards. The 0.25% HF sample was first analyzed and found to contain 0.041 mg/l chloride. Then, the sample was spiked with 0.039 mg/l chloride, the result

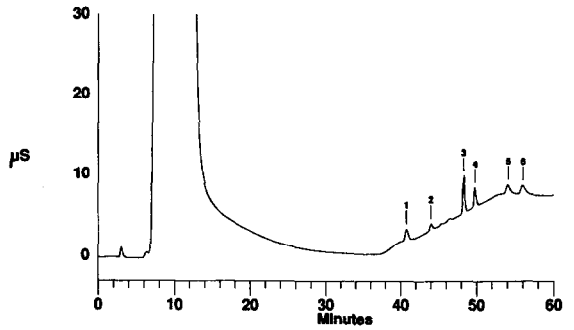

Fig. 3. Analysis of spiked acetic acid by direct injection. Sample concentration: 0.5 *M* acetic acid; 1 = chloride (2 mg/l); 2 = nitrite (2 mg/l); 3 = sulfate (4 mg/l); 4 = phosphate (10 mg/l); 5 = bromide (2 mg/l); 6 = nitrate (4 mg/l). Chromatographic conditions as for Fig. 2.

showed a good recovery reflecting the fact that the 0.25% HF did not cause the system blank and the concentration of chloride in 0.25% is accurate. At more than 0.5% HF, the recoveries of chloride were more than 250%. All the experimental values were corrected in proportion with the chloride concentration found in 0.25% HF. For example, 0.082 mg/l chloride was used to subtract the experimental value of 0.272 mg/l giving 0.19 mg/l recovery in 0.5% HF. Therefore, the direct injection method using the analytical-grade NaOH (as specified in experimental section) is only quantitative for HF concentrations less than or equal to 0.25% since the system blank induced by the HF at various concentrations is not consistent and is sometimes more than twice the analyte concentration and the system blank increases when sample concentration is increased.

Figs. 3 and 4 show the direct injection of 0.5 *M* acetic acid and hydrochloric acid. By using a gradient separation on the IonPac AS10 column, the analytes were cleanly separated from the anion matrix. However, the results of the analysis were not quantitative due to the system blank caused by the acid matrices.

The detection limits by direct injection method are between 0.04 to 0.08 mg/l for chloride, sulfate, phosphate, bromide and nitrate. Since the analyte loading is limited by the system blank, several-fold

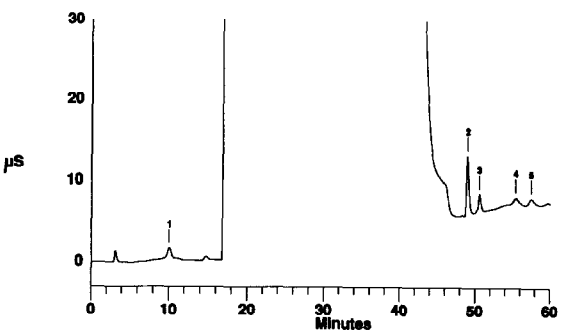

Fig. 4. Analysis of spiked hydrochloric acid by direct injection. Sample concentration: 0.5 *M* hydrochloric acid; 1 = fluoride (1.5 mg/l); 2 = sulfate (5 mg/l); 3 = phosphate (5 mg/l); 4 = bromide (1.5 mg/l); 5 = nitrate (3.0 mg/l). Chromatographic conditions as for Fig. 2.

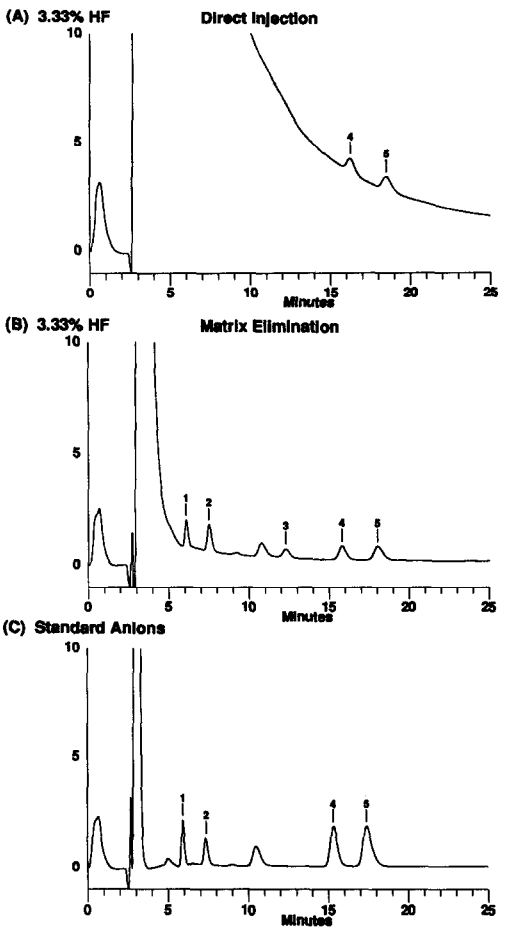

Fig. 5. Comparison of direct injection and matrix elimination methods of 3.33% HF. (A) Direct injection of 3.33% HF, (B) matrix elimination of 3.33% HF and (C) standard anions: 1 = chloride; 2 = sulfate; 3 = phosphate; 4 = bromide, 5 = nitrate.

dilution of concentrated acid is required and it compromises the detection limits of this method. For instance, the concentrated HF (50% or 28.9 *M*) Must contain at least 10 mg/l of anions of interest in order to be analyzed by direct injection method. Therefore, other means of sample preparation techniques were explored to eliminate the sample matrix and to increase analyte loading thus improving the detection limits.

Matrix elimination prior to IC analysis

Sample pretreatment techniques prior to analytical measurement have long been used to eliminate the matrix effect. Unfortunately, most of the anion-exchange resins are not selective for anions of the same charge. The matrix elimination method using anion-exchange resin prior to analytical technique was reported [6]. However, this method is limited to low matrix concentration due to the low capacity of the anion exchange pretreatment column. 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 values between 3.0 and 4.8. At low pH, they remain protonated and uncharged. In solvents these acids are even weaker. Using an organic solvent-containing solution such as methanol–water as a wash, the matrix component at low pH can be removed prior to analytical measurement.

This matrix reduction of weakly retained anions was performed by the IonPac Anion Concentrator 10 (AC10). The IonPac AC10 is a microporous styrene–divinylbenzene copolymer resin that is agglomerated with a quaternary amine-functionalized latex and has the same selectivity as the IonPac AS10. The acid sample (10 μl) was injected onto the AC 10 which had previously been equilibrated with methanol–water eluent. The weak acid matrix component was eluted with methanol while chloride, sulfate, bromide and nitrate were retained in the column (phosphate is not quantitatively retained under these conditions). As long as the acid matrix remains protonated, it does not cause the system blank in the concentrator column. The retained anions were then eluted from the AC10 to the IonPac AS10 where they were separated. Although the matrix component may not have been completely eliminated using the AC10, it was reduced to the point that it did not cause the matrix effect on the analytical column. Since the matrix concentration was greatly reduced, an isocratic separation could be applied. Using 100 m*M* NaOH eluent, the analysis time was reduced from 75 to 30 min. Fig. 5 shows the comparison of the direct injection and the matrix elimination method for a 3.33% HF matrix. The HF samples of up to 4.9% were successfully analyzed by this technique (see Fig. 6).

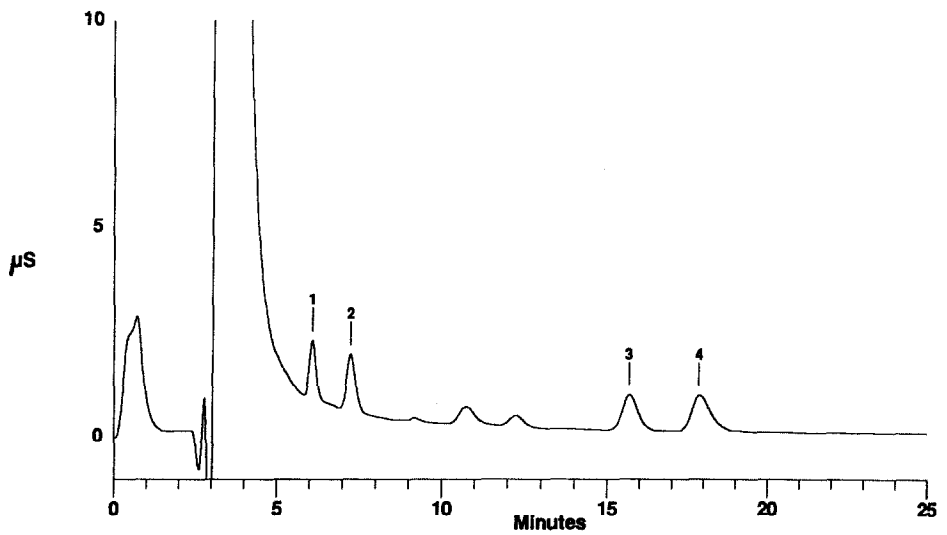

Fig. 6. Anion analysis in 4.9% HF by matrix elimination. 1 = Chloride (0.25 mg/l); 2 = sulfate (1.0 mg/l); 3 = bromide (0.25 mg/l); 4 = nitrate (2.5 mg/l).

TABLE III

SPIKE/RECOVERY OF ANIONS IN 3–5% HF USING MATRIX ELIMINATION METHOD

All values are average of 4 replicates.

Anion	HF (%)	Spike (mg/l)	Found (mg/l)
Chloride	3.33	0.46	0.53 ± 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
Nitrate	3.33	1.66	1.79 ± 0.02
	4.17	2.08	2.10 ± 0.07
	5.00	2.50	2.50 ± 0.04
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

In order to evaluate the matrix effect on the concentrator and the analytical column using matrix elimination method, an experiment similar to that used to generate the data in Table II was performed. Knowing that the IonPac AC10 column capacity is estimated at 1.0 μequiv. per column, a breakthrough study of chloride in varying HF concentrations was also studied. The HF concentrations ranging from 0.25% to 16.67% were used to determine the dynamic range of this technique. Table III summarizes the spike/recovery of anions in various HF concentrations reflecting excellent recoveries for all anions studied. Table IV shows the chloride breakthrough study revealing the dynamic range of the matrix elimination method. HF concentrations greater than 6.0% (10-μl loop) begin to elute chloride off the IonPac AC10 concentrator. All analytical results presented in Tables III and IV are based upon aqueous calibration standards. The aqueous standards were treated the same as the acid samples. The chromatographic conditions used are listed in Table I. The detection limits based upon a signal-to-noise ratio of 3 are 25 to 50 μg/l for most anions.

TABLE IV

SPIKE/RECOVERY OF CHLORIDE IN 0.25% TO 16.67% HF USING MATRIX ELIMINATION METHOD

All values are blank corrected.

HF (%)	Spike (mg/l)	Found (mg/l)	Recovery (%)
0.25[a]	0.028	0.028	100
0.50	0.056	0.060	107
1.00	0.112	0.130	116
2.00	0.224	0.270	120
3.13	0.350	0.370	105
4.17	0.466	0.510	115
6.25	0.700	0.670	95
8.33	0.933	0.750	80
10.42	1.166	0.780	66
12.50	1.400	0.820	59
16.67	1.865	0.840	26

[a] 0.25% HF contains 0.041 ± 0.007 mg/l chloride.

CONCLUSIONS

An improved method for the determination of trace anions in concentrated weak acids has been developed. Using microbore IC with chemical eluent suppression, trace anions can be determined in high-concentration weak acids such as acetic acid and hydrofluoric acid using a moderate-capacity anion-exchange column. Due to the system blank caused by the high ionic strength of the sample, the eluent impurity was found to be a limiting factor when determining trace anions in concentrated acid. An alternative method, a matrix elimination method, has also been developed. This method involves eliminating most of the weak acid using methanol–water eluent on an IonPac AC-10 concentrator column prior to analytical separation. The retained anions of interest are eluted from the AC10 concentrator and separated on the moderate capacity IonPac AS10 column. The detection limits for most anions are 25 to 50 μg/l.

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