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Ion chromatographic analysis of anions in ammonium hydroxide, hydrofluoric acid, and slurries, used in semiconductor processing

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Abstract

In this study, ion chromatography (IC) with suppressed conductivity detection was used for the determination of trace anions in 29% (w/w) ammonium hydroxide, 49% (w/w) hydrofluoric acid and slurries. For these samples, various sample pretreatment methods were applied to eliminate matrix interferences. For concentrated ammonium hydroxide, an on-line electrochemical neutralizer (SP10 AutoNeutralization module) was used to neutralize the base prior to the IC analysis. For concentrated hydrofluoric acid, a heart cutting technique with an ion-exclusion column was used to separate the anions of interest prior to an IC separation. A method was also developed to analyze chloride in silica slurries by IC. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Ion chromatography has become a valuable technique in analytical laboratories in the semiconductor industry. It is widely used for analyzing ultra-trace levels (ng/l) of inorganic anions and cations in ultrapure water (UPW). As the size of semiconductor devices continues to decrease, there is a growing demand for more stringent control of anionic contaminants in semiconductor processing chemicals [1]. In the past, analysis of anions in semiconductor processing chemicals such as hydrofluoric acid and ammonium hydroxide, was carried out with wet chemical methods based on measuring the turbidity or absorbance of the samples [1,2]. These wet chemical methods were laborious, time-consuming and each anion had to be determined separately. In

addition, the sensitivity of these wet chemical methods was poor at mg/l levels.

Application of ion chromatography (IC) for the analysis of anions in semiconductor processing chemicals also suffers from a sensitivity problem. This is because the samples need to be diluted with large volume of deionized water in order to reduce the matrix interference on the chromatographic separation [3]. In order to improve detection limits, two IC methods using on-line sample pretreatment to eliminate the matrix interferences have recently been developed [4–10]. One of the methods employed an on-line membrane-based suppressor to neutralize concentrated ammonium hydroxide prior to anion determinations [4–6]. Other concentrated bases such as sodium hydroxide, potassium hydroxide and tetramethylammonium hydroxide (TMAOH) have also been successfully analyzed by the same method.

The other application [7–9] was developed for the determination of anions in concentrated hydrofluoric acid. The method utilized an ion-exclusion column to

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pre-separate anions such as chloride, nitrate, sulfate and phosphate from the hydrofluoric acid matrix. The front fraction eluted from the ion-exclusion column containing the anions of interest was “cut” and separated by ion-exchange chromatography, thus eliminating the fluoride interference on the chromatographic separation. Similar procedures have also been reported for the determination of anions in phosphoric [8,12] and glycolic [8,13] acids.

In this work, the performances of these IC methods were evaluated with respect to 29% (w/w) ammonium hydroxide and 49% (w/w) hydrofluoric acid. An alternative sample pretreatment procedure using sub-boiling evaporation was developed to overcome the difficulty of analyzing sulfate and phosphate in hydrofluoric acid with the on-line pretreatment method.

In addition, a method for the analysis of chloride in slurries by IC is also presented. These slurries are colloidal solutions that contain high content of silica or other metal oxide particles of less than 0.1 μm . When using wet chemical methods for the analysis of anions, the presence of the colloidal particles interferes with the turbidity and absorbance measurements. Chloride analysis in slurries by ion-selective electrode generally gives detection limit at the mg/l levels and is not sensitive enough for some trace applications.

2. Experimental

2.1. General precautions

For trace anion analysis, special care was taken to minimize contamination from the laboratory environment and the sample containers used. All analyses were performed inside a Class 1000 cleanroom. The cleanroom air was monitored routinely for airborne ionic and particulate contamination. High-density polypropylene bottles, flasks and disposable syringes used for blanks, samples and standards preparation were thoroughly leached and rinsed with deionized water before use.

2.2. Reagents

All single anion 1000 mg/l calibration standard

solutions were purchased from the National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA) and second source anion standards were prepared from high-purity chemicals (Fluka, Milwaukee, WI, USA) dissolved in deionized water. The ion concentration values were calibrated with the NIST anion standards. On a daily basis, quality control check standards prepared from the second source standards were analyzed to check the accuracy and stability of the anion concentration values. Suprapur grade 30% (w/w) sodium hydroxide from EM Science (Gibbstown, NJ, USA) and reagent-grade sodium carbonate (Fluka) were used to prepare the 20 mM and 100 mM sodium hydroxide eluent solutions and the isocratic eluent solution of 1.5 mM of sodium hydroxide and 8.0 mM sodium carbonate. The deionized water (DIW) used for the preparation of blanks, standards, samples and eluents was produced in-house from a reverse osmosis/deionized water (RO/DI) system. Before use, the DIW was further purified with a point-of-use Millipore purification unit to achieve anion levels of $<0.05 \mu\text{g/l}$. Semiconductor-grade 29% (w/w) ammonium hydroxide and 49% (w/w) hydrofluoric acids were obtained from Arch Chemicals (Queens Creek, AZ, USA), Ashland (Columbus, OH, USA) and HTP (Oakland, CA, USA). Slurries samples were provided by Intel (Santa Clara, CA, USA) and Kobe Precision (Hayward, CA, USA).

2.3. Sample preparation

All handling and preparation of chemical samples were performed in an exhausted cleanhood in a cleanroom. Extreme care was taken in the handling of concentrated chemicals to prevent contact with skin and inhalation. No sample preparation was required for 29% (w/w) ammonium hydroxide since the chemical was directly injected into the IC. For hydrofluoric acid analysis, the 49% (w/w) hydrofluoric acid was diluted 1:1 with DIW by carefully adding the hydrofluoric acid into an equal amount of DIW in a clean polypropylene container to obtain the 24.5% (w/w) hydrofluoric acid sample. For sulfate and phosphate analysis in 49% (w/w) hydrofluoric acid, 10 g of the sample was gently heated in a 30-ml PTFE beaker (Fisher, Pittsburgh, PA, USA) on a hotplate under sub-boiling point ($<80^\circ\text{C}$) con-

dition in an exhausted cleanhood. The sample was evaporated to ~0.1 ml, to which 5 ml of DIW was then added. The sample was further heated to evaporate off the hydrofluoric acid until only ~0.05 ml remained. The sample was then diluted with DIW to 5 ml for analysis.

For trace anion analysis in slurries, the samples were first centrifuged at ~15 000 rpm for 10–15 min, and the supernatants were collected and diluted if necessary. For basic slurry of pH ~10–11, ~3 ml of supernatant was passed through a Dionex OnGuard-H ion-exchange sample pretreatment cartridge before ion chromatographic analysis.

2.4. Chromatographic systems

Anion analyses of 29% (w/w) ammonium hydroxide and basic slurries were carried out on a Dionex (Sunnyvale, CA, USA) DX-300 ion chromatographic system that consisted of a quaternary gradient pump (AGP), a chromatographic module and a pulsed electrochemical detector (PED) operating in the conductivity mode. Dionex chromatography data system software AI-450 was used to control instrument operation and data processing.

For all analyses performed on the DX-300, an IonPac AS11 (250×4 mm) and an IonPac AG11 (50×4 mm) guard column were used as separation columns. A 4-mm anion self-regenerating suppressor (ASRS), ASRS-Ultra, from Dionex was used in recycle mode to reduce the conductivity of the eluent. The valves in the system were configured into either of the following two modes: the concentrating mode used in combination with the SP10 AutoNeut-

Table 2
Eluent gradient program for direct injection method

Time (min)	E1%	E2%	E3%
0.0	0	0	100
0.1	0	0	100
2.0	3	0	97
5.0	25	0	75
15.0	16	35	49

E1: 20 mM NaOH.
E2: 100 mM NaOH.
E3: deionized water.
Flow rate: 2.0 ml/min.

ralization module for the analysis of 29% (w/w) ammonium hydroxide; or the direct injection mode with a 375- μ l sample loop made from polyether ether ketone (PEEK). A Dionex TAC-LP1 anion-exchange concentrator column (50×4 mm) was used in concentrating mode. All injections were performed manually with 10-ml polypropylene syringes. The direct injection mode was used for the analysis of sulfate and phosphate in the evaporated 49% (w/w) hydrofluoric acid samples and for the analysis of chloride in slurries. The sodium hydroxide gradient elution programs used with the SP10 and the direct injection methods are given in Tables 1 and 2, respectively. The eluent flow rate was 2.0 ml/min for both programs.

Anion analysis of ammonium hydroxide with the SP10 AutoNeutralization module was achieved following the published procedure [4]. In the procedure, 29% (w/w) ammonium hydroxide was directly injected into a 100- μ l PEEK sample loop in the SP10 module and then flushed with DIW into the anion

Table 1
Eluent gradient program for analyzing anions in 29% (w/w) ammonium hydroxide

Time (min)	E1%	E2%	E3%	Comment
0.0	2	0	98	SP10 neutralization
8.0	2	0	98	Flush sample onto concentrator
10.0	2	0	98	
13.0	40	0	60	
16.0	80	20	0	
20.0	60	40	0	

E1: 20 mM NaOH.
E2: 100 mM NaOH.
E3: DIW.
Flow rate: 2.0 ml/min.

self-regenerating neutralizer (ASRN) for two cycles of neutralization. The neutralized effluent was then flushed onto the TAC-LP1 concentrator in the DX-300 IC for pre-concentration. A sodium hydroxide eluent (Table 2) was used to backflush the concentrated anions onto the analytical columns for separation and conductivity detection.

Anion analysis of the 24.5% (w/w) hydrofluoric acid diluted from the 49% (w/w) sample was carried out on a Dionex DX-500 ion chromatographic system consisting of a chromatography module, GP50 gradient pump and a CD20 conductivity detector. The set-up and operation of the IC system is similar to published analytical procedure [7,8]. The 24.5% (w/w) hydrofluoric acid sample was manually injected into a 750- μ l PEEK sample loop through a 10-ml polypropylene syringe. A Dionex RP-1 pump delivered the DIW to flush the sample from the sample loop into an IonPac ICE-AS6 (250 \times 9 mm) ion-exclusion column. The ICE-AS6 column was used for on-line separation of the anions of interest from the fluoride matrix. In this step, a front fraction of the effluent from the ICE-AS6 column containing the analyte anions was cut and concentrated onto an IonPac AG9-HC (50 \times 4 mm) anion-exchange concentrator column. The concentrated analyte anions were then eluted onto an IonPac AS9-HC anion-exchange column (250 \times 2 mm) for separation. An IonPac AG9-HC anion-exchange column (50 \times 2 mm) was used as guard column. An isocratic eluent of 8.0 mM sodium carbonate and 1.5 mM sodium hydroxide was used. A 2-mm ASRS-Ultra suppressor was used in the external water mode. Dionex chromatographic data system PeakNet 6 software was used to control instrument operation and data collection.

3. Results and discussion:

3.1. Anion analysis in 30% (w/w) ammonium hydroxide

As observed in previous work [4], the sulfonated membranes and screens in the ASRN unit release sulfate ions at low- μ g/l levels. As a result, the ASRN unit was cleaned by pumping through 0.5 M sodium hydroxide at 2 ml/min for at least 2–3 h

followed by rinsing with DIW for 1 h before use. A system blank containing 6 μ g/l of chloride and 52 μ g/l of sulfate was reported [4].

In this study, it was found that the initial cleaning of the ASRN unit was indeed important to reduce the sulfate background in the system blank. After cleaning, the system blank showed \sim 1 μ g/l of chloride and 5 μ g/l of sulfate (Fig. 1A). However, it was found that although the sulfate background in the system blank stabilized with the injection of DIW, the conditioned ASRN released more sulfate ions during first few injections of 29% (w/w) ammonium hydroxide. Repeat injections of ammonium hydroxide eventually brought the sulfate background to a consistent level of 5–8 μ g/l. Therefore, it is important to make multiple injections of the concentrated base samples until a consistent level of sulfate background is obtained before actual sample analysis begins. It was also observed that if the system was left idle for more than a few hours, the first injection of ammonium hydroxide also yielded higher sulfate concentration than subsequent injections. We found that in order to obtain accurate anion concentrations, it was important that the sulfate background was carefully controlled and evaluated.

A calibration curve for each anion was calculated from regression analysis of peak area against the corresponding anion concentration from five level standards (one replicate) ranging from 10 to 200 μ g/l (Table 3). All calibration curves of anions showed good linearity with correlation coefficients $r^2 > 0.996$.

The method detection limits (MDLs) for the anions of interest by IC were determined following the Semiconductor Equipment and Materials International (SEMI) guideline using triplicate analyses of two standards in DIW at 20 and 40 μ g/l [11]. The results obtained were fitted to a linear model ($y = mx + b$) with the ordinary least squares (OLS) methods using the regression function in Microsoft Excel. A three-sigma equivalent of the intercept at the risk level of 0.13% (confidence level = 99.87%) was defined as the MDL. The calculated MDL values for the six anions are shown in Table 4. It can be seen that MDL values obtained were at the low- μ g/l levels. Therefore, the capability of this technique exceeded the requirement for the determination of the anion concentrations of even the best

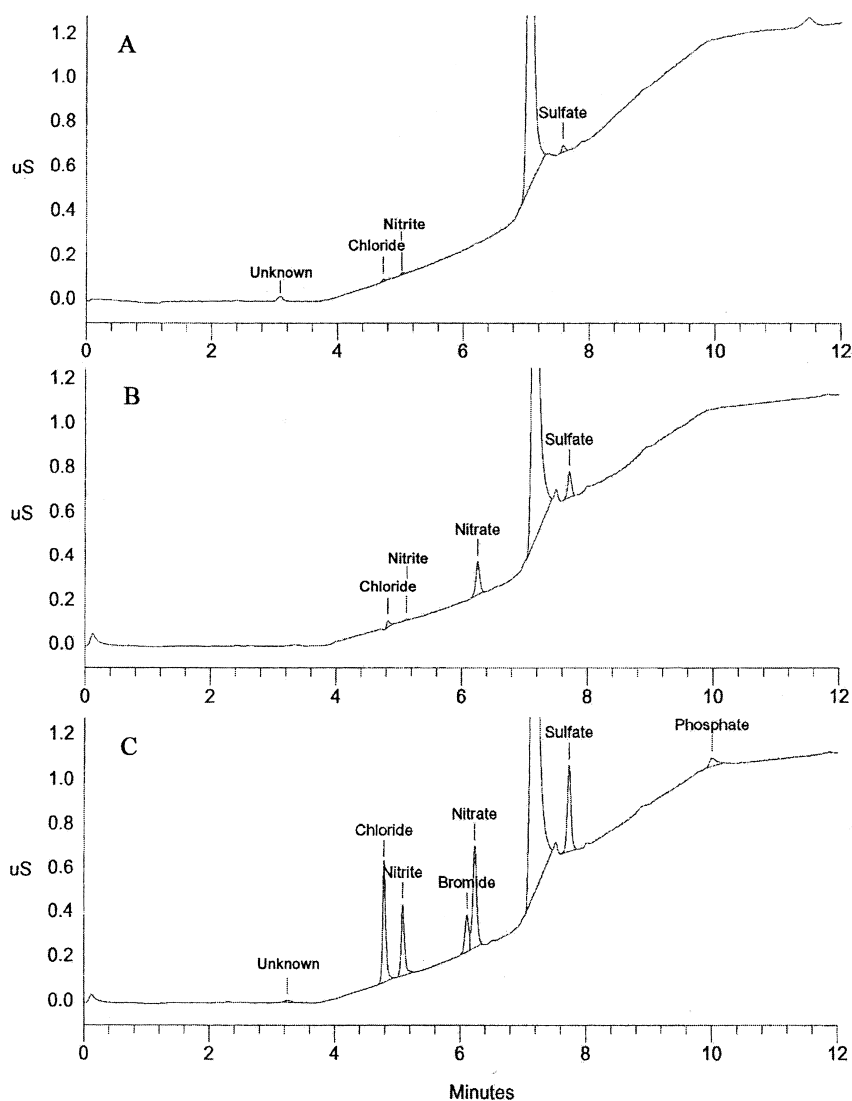


Fig. 1. Trace anion analysis in 29% (w/w) ammonium hydroxide. (A) DIW blank; chloride: 1.0 $\mu\text{g/l}$, nitrite: 1.5 $\mu\text{g/l}$, and sulfate: 5.1 $\mu\text{g/l}$. (B) A 29% (w/w) ammonium hydroxide sample; chloride: 2.0 $\mu\text{g/l}$, nitrite: 1.2 $\mu\text{g/l}$, nitrate: 49 $\mu\text{g/l}$, and sulfate: 21 $\mu\text{g/l}$. (C) Spike of 50 $\mu\text{g/l}$ anions in the 29% (w/w) ammonium hydroxide; chloride: 57 $\mu\text{g/l}$, nitrite: 58 $\mu\text{g/l}$, bromide: 54 $\mu\text{g/l}$, nitrate: 104 $\mu\text{g/l}$, sulfate: 70 $\mu\text{g/l}$, and phosphate: 48 $\mu\text{g/l}$. Sample: 100 μl . Pretreatment: SP10 AutoNeutralization module. Concentrator column: TAC-LP1. Analytical column: IonPac AS11 (250 \times 4 mm). Guard column: IonPac AG11 (50 \times 4 mm). Detection: conductivity. Suppression: ASRS-Ultra with recycle water mode. Gradient conditions: see Table 1.

semiconductor grade 29% (w/w) ammonium hydroxide that has SEMI maximum impurity limits of 30 $\mu\text{g/l}$ for chloride, nitrate, sulfate and phosphate [1].

The accuracy of the anion concentration determined by this method was evaluated by spiking 50

$\mu\text{g/l}$ of each anion of interest into eight different lots of 29% (w/w) semiconductor grade ammonium hydroxide samples. Typical chromatograms of an ammonium hydroxide sample and a 50- $\mu\text{g/l}$ spiked ammonium hydroxide sample are shown in Fig. 1B and C, respectively. The average % recoveries of

Table 3
Calibration^a results for trace anions in 29% (w/w) ammonium hydroxide

Anions	r^2	Slope $\times 10^{-4}$	Intercept $\times 10^{-4}$
Chloride	0.9999	3.44 \pm 0.018	-4.67 \pm 1.86
Nitrite	0.9995	1.95 \pm 0.025	3.41 \pm 2.57
Bromide	0.9998	1.19 \pm 0.0098	-1.37 \pm 1.01
Nitrate	0.9994	1.7 \pm 0.025	-4.66 \pm 2.54
Sulfate	0.9965	2.12 \pm 0.072	6.44 \pm 7.44
Phosphate	0.9999	0.688 \pm 0.0097	-1.07 \pm 1.00

^a Calibration curves based on the ordinary least squares linear regression for mixed anion standard solutions in DIW. Concentration levels: 10, 20, 50, 100 and 200 $\mu\text{g/l}$ with one replicate at each level. Values after the \pm sign are standard deviations based on a 95% confidence interval.

anions for these eight different lots of 29% (w/w) ammonium hydroxide samples are summarized in Table 4. It can be seen that the spike recovery values obtained were in the range of 88–101% for the six anions evaluated. Typical concentrations of anions in high-purity 29% (w/w) ammonium hydroxide samples from various suppliers are given in Table 5. As shown, although the anion concentrations in the 29% (w/w) ammonium hydroxide were below the SEMI specification for chloride, nitrate and phosphate, the sulfate concentrations of ammonium hydroxide samples from suppliers B and C did not meet the specification limit of 30 $\mu\text{g/l}$.

Table 4
Method performance of anion analysis in 29% (w/w) ammonium hydroxide

Anions	MDL ($\mu\text{g/l}$) ^a	Recovery (%) ($n=8$) ^b	SEMI maximum impurity limits ($\mu\text{g/l}$) ^c
Chloride	1.4	93 \pm 6	30
Nitrite	2.0	88 \pm 5	N/A
Bromide	5.7	89 \pm 8	N/A
Nitrate	2.3	92 \pm 9	30
Sulfate	3.5	101 \pm 8	30
Phosphate	7.5	94 \pm 6	30

^a MDLs were determined with the SEMI guidelines [11], using OLS regression (confidence level=99.87%) of triplicate measurements of two levels of standards in DIW at 20 and 40 $\mu\text{g/l}$ each.

^b The tests were performed by spiking 50 $\mu\text{g/l}$ of each anion into eight different lots of 29% (w/w) ammonium hydroxide. The values after the \pm sign are standard deviations of % recovery.

^c SEMI C21-0600 Specifications and Guidelines for Ammonium Hydroxide, Tier D [1].

Table 5
Anion concentrations ($\mu\text{g/l}$) of 29% (w/w) ammonium hydroxide from three suppliers

Anions	Supplier A	Supplier B	Supplier C
Chloride	4.3	11	13
Nitrate	12	21	15
Sulfate	22	32	45
Phosphate	<7.5	<7.5	<7.5

3.2. Anion analysis in 49% hydrofluoric acid

It has been demonstrated that the application of ion exclusion for pre-separation of the anions of strong acids such as chloride, nitrate, sulfate and phosphate from a concentrated weak acid matrix such as hydrofluoric acid is a feasible procedure [7–9]. However, a major problem experienced was the unacceptably high and unstable sulfate background caused by the release of sulfate from the sulfonated resin of the ICE-AS6 column. In this study, after initial off-line conditioning of ICE-AS6 column with 5% (w/w) hydrofluoric acid (~100 ml) and repeated injection ($n>30$) of 24.5% (w/w) hydrofluoric acid samples, the sulfate background obtained was still ~35 $\mu\text{g/l}$ (Fig. 2A). Even of more of a problem was that it was found that the sulfate concentration was not stable. The sulfate concentration for the same 24.5% (w/w) hydrofluoric acid sample could vary more than 50% per day, even after correction of the DIW background for each day of analysis. Therefore, it was decided that the sulfate result obtained by this method was not accurate.

Another problem was observed for the analysis of phosphate in hydrofluoric acid by this method. The sensitivity for phosphate dropped significantly (40–60%) compared to other anions after a few weeks of operation. Attempts to re-optimize experimental condition, particularly the ion-exclusion pre-separation step, failed to improve the phosphate sensitivity. Attempts to use standard addition method also met difficulties because the sensitivity of the phosphate was found to be unstable, varying 20–40% for each day of use.

The poor and unstable phosphate recovery observed in the current study contradicts two previous reports of similar studies [8,9] in 24.5% (w/w) hydrofluoric acid. In one study [8], good recovery of

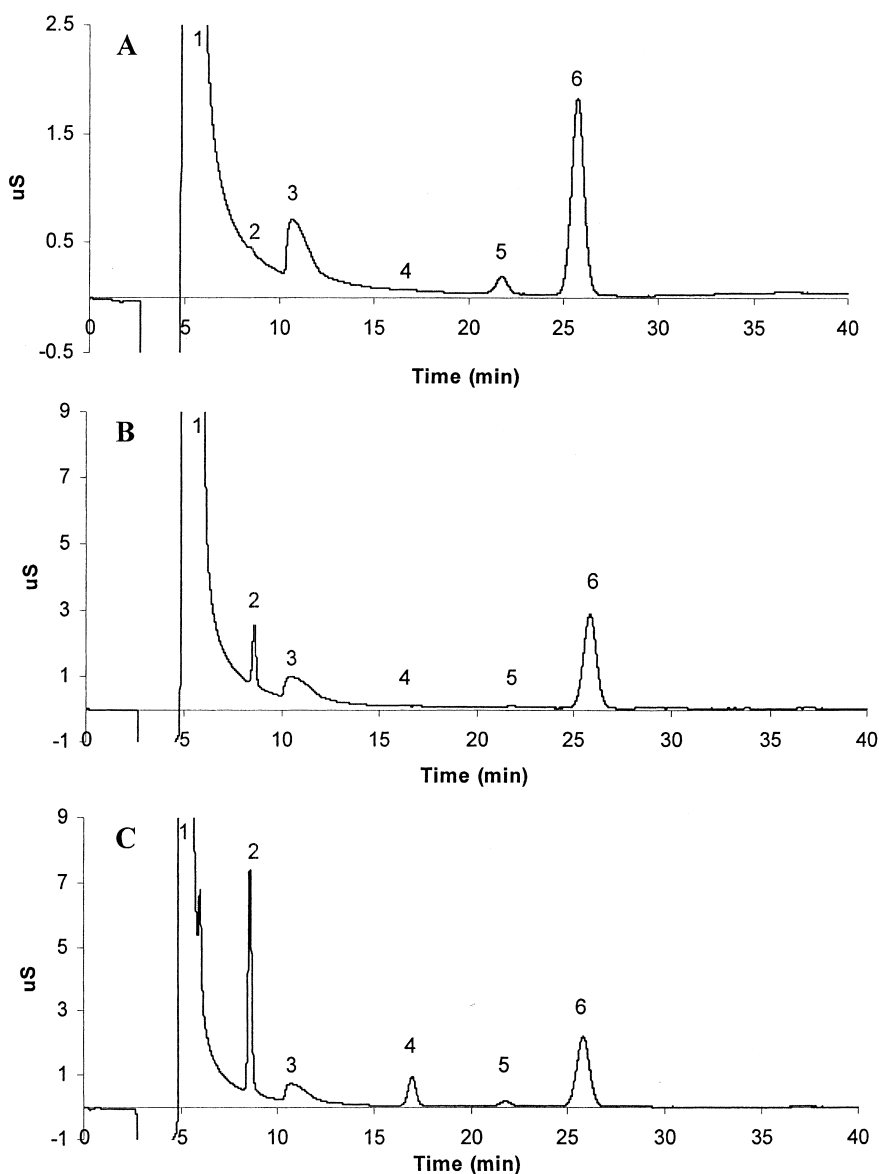


Fig. 2. Trace anions in 24.5% (w/w) hydrofluoric acid. Peaks: 1=fluoride; 2=chloride; 3=carbonate; 4=unknown; 5=nitrate; 6=sulfate. (A) A DIW blank; chloride: ~ 1.0 $\mu\text{g/l}$, and sulfate: 35 $\mu\text{g/l}$. (B) A 24.5% (w/w) hydrofluoric acid sample; chloride: 20 $\mu\text{g/l}$, and sulfate: 47 $\mu\text{g/l}$. (C) Spike of 49 $\mu\text{g/l}$ of chloride and nitrate in the 24.5% (w/w) hydrofluoric acid; chloride: 72 $\mu\text{g/l}$, nitrate: 44 $\mu\text{g/l}$, and sulfate: 40 $\mu\text{g/l}$. Sample volume: 750 μl . Pretreatment column: IonPac ICE-AS6 (250 \times 9 mm). Concentrator column: IonPac AS9-HC (50 \times 4 mm). Analytical column: IonPac AS9-HC (250 \times 2 mm). Guard column: IonPac AG9-HC (50 \times 2 mm). Detection: conductivity. Suppression: ASRS-Ultra with external water mode. Eluent: 8.0 mM sodium carbonate and 1.5 mM sodium hydroxide. Eluent flow rate: 0.25 ml/min.

87 \pm 4% ($n=5$) was obtained for phosphate with external calibration with anion standards prepared in DIW. In the other study [9], poor and unstable recoveries (<50%) were obtained for nearly all the

anions, including phosphate (11–51%), when using the external standard calibration method, but good and stable recoveries for anions were obtained after using the standard addition method for quantitation.

The phosphate recovery reported in the study was $90.2 \pm 9.6\%$ ($n=5$). The poor sensitivity of phosphate in hydrofluoric acid matrix was perhaps due to the fact that phosphoric acid is a relatively weak acid ($K_{a1} = 7.5 \cdot 10^{-3}$) compared to hydrochloric acid and nitric acid. Therefore, molecular phosphoric acid coelutes with the molecular hydrofluoric acid ($K_a = 6 \cdot 10^{-4}$) matrix during ion-exclusion pre-separation. Because of such uncertainty and difficulty, we did not use this approach to determine phosphate in concentrated hydrofluoric acid.

Since sulfate and phosphate cannot be reliably analyzed by using the ion-exclusion pre-separation, only the chloride and nitrate were analyzed by this method. Calibration curves for chloride and nitrate were calculated from analysis of five levels of standards each with one replicate in DIW ranging from 10 to 200 $\mu\text{g}/\text{l}$ (Table 6). As shown, good linear calibration curves were obtained for both anions within the concentration range. The MDL values for chloride and nitrate were determined using the same SEMI guideline [11]. The MDL results obtained are listed in Table 7. It can be seen that MDL values at the low- $\mu\text{g}/\text{l}$ levels were achieved for these two anions, exceeding the requirement for analysis of semiconductor grade 49% (w/w) hydrofluoric acid.

Similarly, for evaluating the accuracy of the results, six 24.5% (w/w) hydrofluoric acid samples were spiked with 50 $\mu\text{g}/\text{l}$ of the chloride and nitrate. Representative chromatograms of a 24.5% (w/w) hydrofluoric acid sample and a spike sample are given in Fig. 2B and C, respectively. Average spike recoveries of 50 $\mu\text{g}/\text{l}$ of the two anions in six hydrofluoric acid (24.5%, w/w) samples are summa-

Table 6
Calibration^a results for trace anions in 24.5% (w/w) hydrofluoric acid

Anions	r^2	Slope	Intercept
Chloride	0.9975	0.0203 ± 0.0059	-0.102 ± 0.061
Nitrate	0.9997	0.00995 ± 0.00010	-0.0113 ± 0.0107

^a Calibration curves based on linear regression for mixed anion standard solutions in DIW. Concentration levels: 10, 20, 50, 100 and 200 $\mu\text{g}/\text{l}$ with one replicate at each level. Peak area is in the unit of $\mu\text{S min}$. Values after the \pm sign are standard deviations based on a 95% confidence interval.

Table 7
Method performance of chloride and nitrate analysis in 49% (w/w) hydrofluoric acid

Anions	MDL ($\mu\text{g}/\text{l}$) ^a	Recovery (%) ($n=6$) ^b	SEMI maximum impurity limits ($\mu\text{g}/\text{l}$) ^c
Chloride	2.8	91 ± 8	200
Nitrate	6.8	83 ± 10	100

^a MDLs were determined with the SEMI guidelines [11], using OLS regression (confidence level=99.87%) of triplicate measurements of two levels of standards in DIW at 20 and 40 $\mu\text{g}/\text{l}$ each. The calculated MDL values are multiplied by 2 for the dilution factor of 49% (w/w) hydrofluoric acid.

^b The tests were performed by spiking 50 $\mu\text{g}/\text{l}$ of each anion into six 1:1 diluted 24.5% (w/w) hydrofluoric acid. The values after the \pm sign are standard deviations of % recovery.

^c SEMI C28-0699 Specifications and Guidelines for Hydrofluoric Acid, Tier B [1].

rized in Table 7. It can be seen that the accuracy of this method is good with average spike recoveries of chloride and nitrate of $91 \pm 8\%$ and $83 \pm 10\%$, respectively.

To overcome the difficulty in measuring sulfate and phosphate in hydrofluoric acid by the ion-exclusion technique, a sample preparation procedure as mentioned in Section 2.3 was developed to remove the hydrofluoric acid matrix. It was found that to obtain good recovery for sulfate and phosphate ions, it was critical that the sample solution must not be allowed to dry out during the evaporation step. It was also important to prevent sulfate and phosphate contamination from the cleanroom environment and containers used in sample preparation. In practice, duplicate sample preparation controls were performed by evaporation with DIW at the same time as the hydrofluoric samples. The sulfate and phosphate backgrounds found in these blanks were used for corrections. High concentrations of sulfate and phosphate found in sample preparation blanks were used to indicate contamination problems, and in such cases, the sample preparation was repeated.

Representative chromatograms for the analysis of sulfate and phosphate in an evaporated blank, 49% (w/w) hydrofluoric acid sample and spike are shown in Fig. 3A–C, respectively. It can be seen the residual amount of fluoride ion left after evaporation, as well as nitrate from evaporation of nitric acid on a

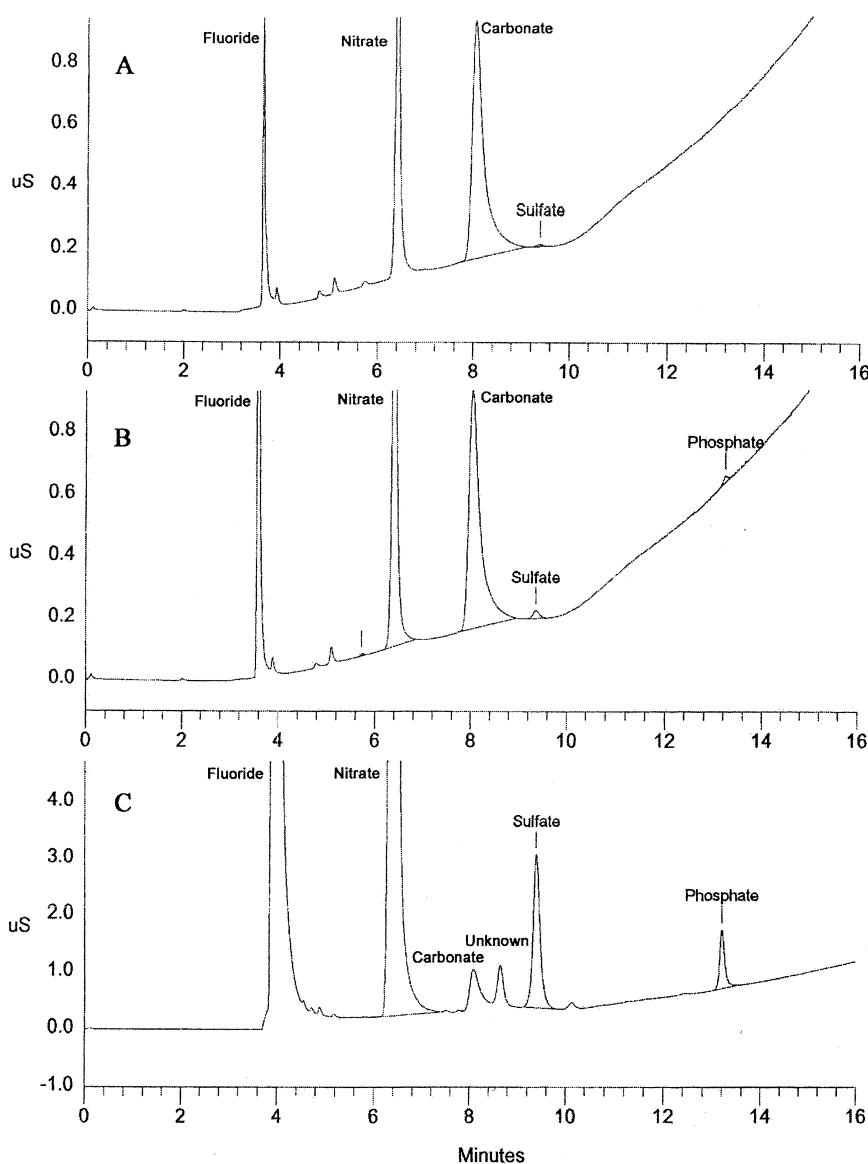


Fig. 3. Analysis of sulfate and phosphate in 49% (w/w) hydrofluoric acid by evaporation. Nitrate was contaminant from evaporation of nitric acid in the same hood. (A) Sample preparation blank; sulfate: 1.4 $\mu\text{g}/\text{l}$. (B) A 49% (w/w) hydrofluoric acid sample after evaporation; sulfate: 5.2 $\mu\text{g}/\text{l}$, and phosphate: 6.2 $\mu\text{g}/\text{l}$. (C) Spike of 150 $\mu\text{g}/\text{l}$ sulfate and phosphate in the 49% (w/w) hydrofluoric acid; sulfate: 294 $\mu\text{g}/\text{l}$, and phosphate: 266 $\mu\text{g}/\text{l}$. Sample preparation: 10-g hydrofluoric acid sample was evaporated on hotplate then diluted with 5 ml of DIW. Sample: 375 μl . Analytical column: IonPac AS11 (250 \times 4 mm). Guard column: IonPac AG11 (50 \times 4 mm). Detection: conductivity. Suppression: ASRS-Ultra with recycle water mode. Gradient conditions: see Table 2.

nearby hotplate in the same hood, did not interfere with chromatographic separation and detection of sulfate and phosphate. The average recovery values for sulfate and phosphate in five 49% (w/w) hydro-

fluoric acid samples spiked with 150 $\mu\text{g}/\text{l}$ of these anions were $103\pm 13\%$ and $88\pm 12\%$, respectively. These results are tabulated in Table 8.

The calibration curves for each anion were calcu-

Table 8
Method performance of sulfate and phosphate in 49% (w/w) hydrofluoric acid

Anions	MDL ($\mu\text{g/l}$) ^a	Recovery (%) ($n=5$) ^b	SEMI maximum impurity limits ($\mu\text{g/l}$) ^c
Sulfate	1.3	103 \pm 13	200
Phosphate	1.4	88 \pm 12	100

^a MDLs were determined with the SEMI guidelines [11], using OLS regression (confidence level=99.87%) of triplicate measurements of two levels of standards in DIW at 10 and 20 $\mu\text{g/l}$ each. The MDL values listed above are divided by a concentration factor 2 to account for the concentration of the sample to half of its original mass.

^b The tests were performed by spiking 150 $\mu\text{g/l}$ of each anion into 49% (w/w) hydrofluoric acid. The values after the \pm sign are relative standard deviations of % recovery.

^c SEMI C28-0699 Specifications and Guidelines for Hydrofluoric Acid, Tier B [1].

lated from analyzing anion standard solutions of five levels, and the results are summarized in Table 9. As shown, excellent linearity was obtained for each anion with $r^2 > 0.999$. The MDLs for sulfate and phosphate analysis were determined by triplicate analysis of two standards in DIW at 10 and 20 $\mu\text{g/l}$ each using the same SEMI guideline [11]. The MDL values were calculated to be 2.5 and 2.7 $\mu\text{g/l}$ for sulfate and phosphate, respectively. Since the hydrofluoric acid sample was concentrated by a factor of 2 after evaporation and dilution with DIW, the MDL values for sulfate and phosphate should be divided

Table 9
Calibration^a results for anions by direct injection IC analysis

Anions	r^2	Slope $\times 10^{-4}$	Intercept $\times 10^{-5}$
Fluoride	0.9998	21.7 \pm 0.17	17.4 \pm 8.58
Chloride	0.9999	12.9 \pm 0.051	-5.48 \pm 2.58
Nitrite	0.9999	8.95 \pm 0.046	1.59 \pm 2.33
Bromide	0.9998	5.22 \pm 0.024	-0.21 \pm 1.23
Nitrate	0.9999	7.34 \pm 0.045	-5.71 \pm 2.28
Sulfate	0.9998	8.47 \pm 0.068	-5.89 \pm 1.67
Phosphate	0.9992	3.16 \pm 0.053	-2.20 \pm 1.30

^a Calibration curves based on the ordinary least squares linear regression for mixed anion standard solutions in DIW. Concentration levels: 50, 100, 200, 500 and 1000 $\mu\text{g/l}$ with one replicate at each level for fluoride, chloride, nitrite, bromide and nitrate; 50, 100, 200, 300 and 400 $\mu\text{g/l}$ with one replicate at each level for sulfate and phosphate. Values after the \pm sign are standard deviations based on a 95% confidence interval.

by a factor of 2. Therefore, the MDL values calculated for sulfate and phosphate were 1.3 and 1.4 $\mu\text{g/l}$, respectively, in 49% (w/w) hydrofluoric acid (Table 9). These values are much lower than the SEMI specification limits for 49% (w/w) hydrofluoric acid [1].

With the combination of analyzing chloride and nitrate by the ion-exclusion pre-separation and sulfate and phosphate in the evaporated sample by direct injection IC, anions in 49% (w/w) hydrofluoric acid samples can be accurately determined at very low levels. Table 10 shows some examples of 49% (w/w) hydrofluoric acid samples analyzed by a combination of these two methods. For most anions, the concentrations in these high-purity hydrofluoric acid samples were very low, being less than 60 $\mu\text{g/l}$.

3.3. Chloride analysis in slurry

Most slurry samples analyzed in this study had pH in the range of 10–11. Therefore, the supernatant obtained after the centrifuge step required pretreatment with OnGuard-H pretreatment cartridge. The pH after the treatment was generally 5–6. Fig. 4 shows the chromatograms of a typical slurry analysis. In Fig. 4A, a DIW blank of the cartridge containing 1.4 $\mu\text{g/l}$ of chloride is shown. The chromatogram of a supernatant solution of a silica-based slurry after treatment with an OnGuard-H cartridge is shown in Fig. 4B. The concentration of chloride in this sample was 354 $\mu\text{g/l}$. Fig. 4C shows the chromatogram of the supernatant solution that was spiked with 500 $\mu\text{g/l}$ chloride. Average spike % recovery \pm SD for five different slurry samples of the same type was 97 \pm 7%.

For chloride analysis in slurry, the same direct injection IC set up for the evaporated hydrofluoric acid samples was employed. In the same study, the

Table 10
Anion concentration ($\mu\text{g/l}$) in 49% (w/w) hydrofluoric acid from three suppliers

Anions	Supplier A	Supplier B	Supplier C
Chloride	<2.8	17	25
Nitrate	12	16	14
Sulfate	7.9	57	45
Phosphate	<1.4	<1.4	<1.4

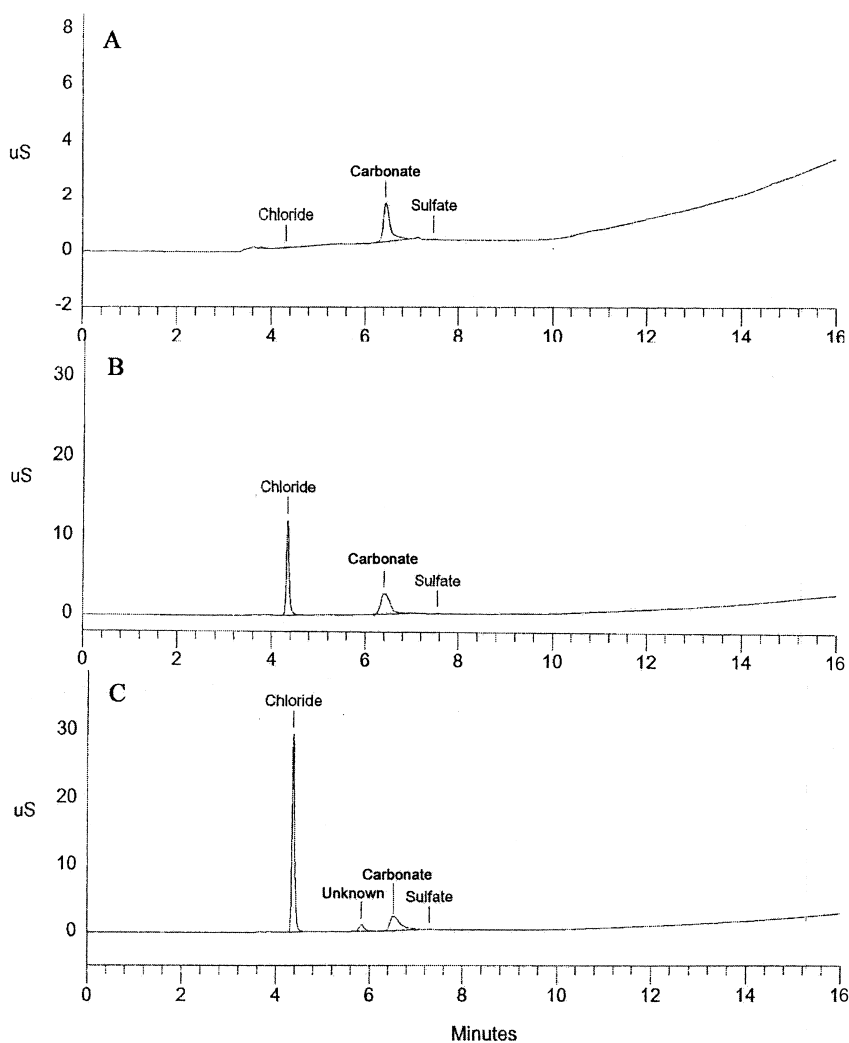


Fig. 4. Chloride in silica slurry: (A) DIW OnGuard-H cartridge blank; chloride: $1.2 \mu\text{g/l}$, and sulfate: $2.4 \mu\text{g/l}$. (B) Supernatant of a slurry sample after centrifugation and pretreatment; chloride: $354 \mu\text{g/l}$, and sulfate: $5.2 \mu\text{g/l}$. (C) Spike of $500 \mu\text{g/l}$ chloride in the slurry sample; chloride: $870 \mu\text{g/l}$, and sulfate: $6.8 \mu\text{g/l}$. Sample preparation: basic slurry was centrifuged and the supernatant was neutralized by being passed through an ion-exchange OnGuard-H cartridge, then directly injected. Chromatographic conditions as in Fig. 3.

MDL for chloride was determined to be $1.4 \mu\text{g/l}$ following the SEMI guideline. Incidentally, it was observed that other anions such as nitrate, sulfate and phosphate in slurry samples could be analyzed by

this method. Finally, Table 11 shows the chloride concentrations of several different types of slurries. The chloride concentrations varied greatly from 0.13 to 200 mg/l for different kinds of slurries.

Table 11
Chloride concentration in five different slurry samples (in mg/l)

Anion	Slurry A	Slurry B	Slurry C	Slurry D	Slurry E
Chloride	51	2000	37	0.35	13

4. Conclusions

The use of an SP10 AutoNeutralization sample pretreatment module in conjunction with a standard ion chromatographic set-up allowed easy and accurate analysis of a wide range of anions at low- $\mu\text{g}/\text{l}$ levels in 29% (w/w) ammonium hydroxide. For the analysis of hydrofluoric acid, the use of ICE-AS6 ion-exclusion sample pretreatment separated the anions of interest from the hydrofluoric acid matrix. Although the method provides much-improved analysis of chloride and nitrate in 24.5% (w/w) hydrofluoric acid, it is not feasible for analyzing sulfate and phosphate ions due to the excessive bleeding of sulfate from the column and unacceptable recovery of phosphate. However, a sample preparation method followed by direct injection IC separation was successfully implemented to overcome this problem for the analysis of sulfate and phosphate in 49% (w/w) hydrofluoric acid. Finally, chloride was successfully determined in the supernatant solutions of slurries by IC at low- $\mu\text{g}/\text{l}$ levels.

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