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Determination of chloride and sulfate in semiconductor-grade etchants comprised of acetic acid, nitric acid and phosphoric acid

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Abstract

The variable-capacity Dionex Cryptand A1 column was used for the determination of low-ppm levels of chloride and sulfate in etchants comprised of acetic acid, nitric acid and phosphoric acid. All possible ratios of the three acids could be analyzed for chloride and sulfate, if the samples were first diluted 1:100. However, a suitable eluent program was found to be needed for each mixture. A proprietary formulation was chosen to undergo this suitability determination. The resulting gradient was 10 mM KOH with a step to 30 mM NaOH at 15 min, flow-rate=0.5 ml/min; column temperature=29 °C; sample loop=7.5 µl. Under these conditions, a low-ppm calibration study (using the proprietary mix as the matrix) was performed and the associated prediction intervals were determined. At 50 ppm (in the original etchant), the \pm prediction interval was ± 7 ppm for chloride and ± 20 ppm for sulfate, both at the 95% confidence level. This step gradient was found to be a good starting place for separating the five components in all other ratios of these three acids.

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1. Introduction

In the electronics industry, wafer contamination can lead to high failure rates for devices. Therefore, it is necessary to control unwanted species in all process chemicals. One such problem area is trace anions in concentrated acids. Currently, specifications for these analytes are in the low-ppb (w/w) range. Wet-chemistry techniques have been the traditional methods of choice, but these procedures have several disadvantages. First, each test quantifies only one anion, so multiple analyses must be made on each sample. Second, uncertainties associated with

results are typically high. Third, each protocol is time-consuming and labor-intensive.

In recent years, concentrated weak acids (e.g., hydrofluoric, acetic and phosphoric acids) have been analyzed for anions via ion chromatography (IC) [1]. In this arrangement, undissociated acid is retained by an ion-exclusion column. The trace anions elute and are trapped on a concentrator column, which subsequently is placed in line with an anion-exchange separator for chromatographic analysis.

On the other hand, strong acids have continued to present a challenge. Since these acids are totally ionized, the predominant anions cannot be eliminated by ion exclusion. Until recently, the only ion-chromatographic approach has been to dilute the sample sufficiently so that the analytes are resolved from the

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predominant ion and the run time is acceptable. The unfortunate consequence is that the desired detection limits usually cannot be achieved for the trace anions [2]. Some strides have been made in the past few years, but these methods are complicated, involving steps such as extensive sample preparation, multiple detectors and/or heart-cutting IC [3–8].

If the sample contains multiple acids, the situation is even more difficult; no literature references were found for the ion-chromatographic determination of anions in etchants, which are mixtures of two or three concentrated acids and are used in the semiconductor industry to etch wafers. Although there are no anion specifications in the SEMI document for phosphoric etchants [9], semiconductor manufacturers are beginning to set low-ppm (w/w) limits for chloride and sulfate for this type of blended chemical. These purity requirements mean that a precise, sensitive method is needed for the determination of contaminant anions in etchants.

A recently introduced column, the Dionex Cryptand A1, theoretically shows promise for anion determination in etchants. The capacity of this separator can be changed, depending on the counter cation [10]. Capacity is highest with KOH, lower with NaOH, and lowest with LiOH. By starting in the potassium form and then stepping later to the sodium form, it is possible to chromatograph much higher concentrations of samples than can be analyzed on traditional IC separators. This variability suggests that this column might be suitable for etchants, without requiring excessive dilution.

A commonly used etchant contains acetic, nitric and phosphoric acids; the proportions are varied depending on the etching capabilities desired. Chloride and sulfate levels ideally are held to the low-ppm range. This research investigated the behavior of this type of mixture on the Cryptand column. The goals of this study were: (1) to determine if this separator could resolve the three etchant anions, chloride and sulfate for all possible combinations of the three component acids, (2) to find a suitable eluent program for a proprietary etchant, (3) to conduct a calibration study, using the proprietary matrix, and determine prediction intervals (in the low-ppm range) for chloride and sulfate, using the suitable eluent program (from goal 3), and (4) to evaluate the performance of this gradient for all other resolvable etchant formulations.

2. Experimental

2.1. Materials

Sodium hydroxide (50%, w/w, with $\leq 0.10\%$ sodium carbonate) and potassium hydroxide (45%, w/w) from Fisher Scientific (Pittsburgh, PA, USA) were used to make concentrated (200 and 100 mM, respectively) eluent solutions. Stock standards (1000 ppm each) of chloride and sulfate were purchased from Spex (Metuchen, NJ, USA). For eluent preparation and dilution of standards, deionized (DI) water (18 m Ω cm) was delivered by a point-of-use water-purification system (Ionics-Ahlfinger, Dallas, TX, USA). Semiconductor grades of acetic acid (100%, w/w), nitric acid (69%, w/w) and phosphoric acid (85%, w/w) were obtained from Air Liquide America (Dallas, TX, USA).

Water for eluents was sparged with helium before use. Subsequently, the DI water (for diluting the eluent concentrates), NaOH and KOH reservoirs were kept under pressure with helium throughout their life.

2.2. Apparatus and columns

Unless otherwise noted, all instrument modules and supplies were from Dionex (Sunnyvale, CA, USA). A DX 500 microbore ion chromatograph was used for all analyses. Analytical columns were an IonPac Cryptand G1 5 μ m Guard (30 mm \times 3 mm) with Cryptand A1 5 μ m Analytical (150 mm \times 3 mm). Post-column eluent suppression was achieved using an Anion Self-Regenerating Suppressor (ASRS-Ultra, 2 mm) in the external-water mode. To maintain constant equilibrium [11], water was allowed to flow continuously through the regenerant chamber, even when the chromatograph was not in use. Water flow-rate (with ASRS current off) was approximately 15 ml/min. The columns and suppressor were housed in an LC25 Chromatography Oven with a rear-loading 10-port Rheodyne (Rohnert Park, CA, USA) valve. The column temperature was held at 29, 33, or 37 $^{\circ}$ C, depending on the experiment. All tubing in the chromatography paths was PEEK (polyether ether ketone) [0.005 in (0.125 mm) I.D.].

A GP40 Gradient Pump was used to deliver eluent to the system. The concentration and form of the eluent varied, but always involved starting with

KOH and stepping later to NaOH. Eluent flow-rate was always 0.50 ml/min. To trap any contaminant anions remaining in the mobile phase, an IonPac ATC (2 mm) was installed immediately after the pump transducer. A 7.5- μ l sample loop was loaded via an AS40 Automated Sampler, using PolyVials (5 ml) and plain caps. Before use, all vials were rinsed 20 times with running DI water from the tap; each rinsing consisted of filling the vial completely and then pouring out the water. Detection was via a CD20 Conductivity Detector at an output range of 10 μ S.

Instrument control and data collection were accomplished using a personal computer and PeakNet 5.1 software. JMP 4.0 software (SAS Institute, Cary, NC, USA) was used to design experiments and carry out statistical calculations.

2.3. Preparation of etchants and standards

All solutions were prepared in new high-density polyethylene (HDPE) narrow-mouth bottles (125-ml capacity) (Nalge Nunc, Rochester, NY, USA). Vinyl gloves (Oak Technical, Stow, OH, USA) were worn at all times when handling standards and samples. Disposable polyethylene transfer pipets (Fisher Scientific) were used to deliver small volumes of liquids.

Etchants were mixed at full strength, using the proportions desired in each case. Percentages were always of the bulk acid, without regard to assay value. These preparations were diluted 1:100 for injection into the ion chromatograph. For all design-of-experiments work, these final dilutions were also spiked at 10 ppm each of chloride and sulfate.

For the calibration study, a mixed standard (100 ml, in water) containing 10 ppm each of chloride and sulfate was prepared from the corresponding 1000-ppm stock standards. Six working standards (blank; 100, 200, 300, 400 and 500 ppb) were formed by diluting 1 g of the etchant, plus the appropriate mass of the mixed standard, to 100 g with DI water. These spike concentrations corresponded to 10, 20, 30, 40 and 50 ppm in undiluted etchants.

All masses were determined using a Sartorius MC1 Analytical Balance (Sartorius, Edgewood, NY, USA) and were recorded to 0.0001 g. This balance was located in a fume hood suitable for acids. Dilution errors in the daily working standards were

estimated by conducting a Monte Carlo simulation [12]. This exercise was based on the upper bound (0.0001 g) on the magnitude of weighing error for the balance. In the simulation, weighing errors were randomly drawn from a Normal distribution with mean equal to zero and standard deviation equal to the upper bound. The distribution of these relative concentration errors was found never to exceed 0.1% relative error, which was considered negligible.

In the calibration study, the set of standards was run in quadruplicate and all analyses were made on the same day. Designed experiments were each run in duplicate, with each replicate performed on a different day. In all work, solutions were randomized within each replicate. Peak areas (PAs) were used to measure each analyte's response.

3. Results and discussion

3.1. Initial considerations

Since this column had not been used previously to study trace anions in etchants, a starting eluent program had to be developed. One related investigation had been performed with the Cryptand column: the determination of trace anions (fluoride, acetate, formate and chloride) in 2% sulfuric acid. This separation was conducted at 35 °C, using 10 mM KOH initially and stepping to 50 mM NaOH after 10 min [10]. Under these conditions, all anions were resolved adequately. Therefore, it was decided to begin this research using 10 mM KOH at a flow-rate of 0.5 ml/min and with the oven temperature held at 33 °C. When desired, late-eluting peaks were removed quickly by stepping from KOH to 50 mM NaOH and remaining in the NaOH form until all anions had eluted. Woodruff et al. [10] had found that 5 min was sufficient for subsequent reequilibration to KOH; as a precaution, 10 min was allowed in this study.

In this research, the peak shapes, which are an indication of column overloading, for the matrix ions were not of interest. Thus, neither a column-capacity study nor a thorough evaluation of various dilution factors was undertaken. Woodruff et al. [10] showed that their analytes of interest could be resolved adequately from sulfate if the total sample concentration was under ca. 2%. Thus, a 1:100 dilution

was tried in this research and found to be a workable compromise between sensitivity for the two analytes of interest, and adequate resolution of both chloride and sulfate from the matrix ions. Under the above starting conditions for this study (and with all gradients tried throughout this project), the elution order of the anions was acetate (first), chloride, nitrate, sulfate and phosphate (last).

3.2. Mixture experiments

The first goal of this research was to determine if all possible ratios of acetic, nitric and phosphoric acids could be resolved from each other (at 1:100 dilution), and from trace levels of chloride and sulfate, using the Cryptand column. An experiment was designed via JMP's "Mixture Design" option, using three factors and extreme vertices with degree=3 [13]. The three factors were acetic, nitric and phosphoric acids. Concentrations of each component were allowed to range from 1 to 98%. The final design contained 10 mixtures, as depicted in Fig. 1.

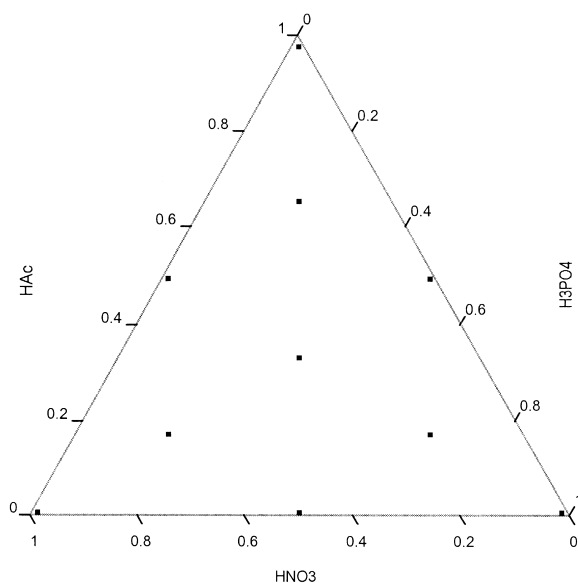


Fig. 1. Ternary plot showing the various ratios (expressed as decimal fractions) of acetic (100%, w/w), nitric (69%, w/w) and phosphoric (85%, w/w) acids used for the mixture experiment (see Section 3.2 for details). Legend: HAc=acetic acid; HNO3=nitric acid; H3PO4=phosphoric acid.

It was expected that each mixture would require a different run time. Therefore, all mixes were analyzed using the eluent program designed in Section 3.1 (i.e., 10 mM KOH; oven temperature=33 °C; flow-rate=0.5 ml/min) until the last (phosphate) peak had begun eluting. Then, the eluent was stepped to 50 mM NaOH to drive off the remaining anions more quickly. If the PO_4^{3-} had not eluted by 60 min, the step was initiated at that time.

For all 10 mixtures in the experiment, the goal was met (i.e., all five constituents were resolved adequately from each other). Retention times are given in Table 1. (The acetate peak shape was essentially independent of the acetate concentration, and the chloride peak was always at or near the end of the acetate-peak tail. However, the nitrate and/or phosphate peaks often were quite broad. Thus for nitrate, the peak's "start" and "end" times are given instead of the retention times. This choice was made to show that this component is always well resolved from the analytes of interest; i.e., chloride and sulfate. Similarly, the "start" time was given for the phosphate peak to show its resolution from sulfate). An example chromatogram (for the ratio 33.33:33.33:33.33) is shown in Fig. 2. This diagram illustrates a situation where the phosphate cannot be eluted (using KOH alone) in a reasonable period of time.

No attempt was made to optimize the separations, since doing so was not a goal here. Because the experiment's design contained points at the extremes of the ternary plot, as well as in the middle sections, it was concluded that the Cryptand A1 column could be used to separate all five anions in any ratio of the three etchant acids.

By studying the etchant components' retention times in the 10 mixes, it was possible to see the effect of the concentration of each component on its retention time. (See Table 1, which has been sorted first by phosphoric content and then by nitric content). In all cases, the retention time of the acetate peak was essentially unchanged, ranging from 4.3 to 4.5 min. The chloride peak moved very little, varying from 5.5 min to 6.6 min. Not surprisingly, the Cl^- retention time roughly increased as the concentration of the preceding analyte (acetate) increased. The only exception was the mixture where acetic acid, nitric acid and phosphoric acid were in

Table 1
Retention times (t_R , min) measured in the mixture experiment^a

Mix	Acetic acid ^b (%)	Nitric acid ^b (%)	Phosphoric acid ^b (%)	t_R A ^c	t_R Cl	Start N ^{c,d}	End N ^{c,d}	t_R SO ₄	Start P ^{c,d}
1	98.00	1.00	1.00	4.5	6.6	16	20	38.9	>60
2	49.50	49.50	1.00	4.3	6.2	10	22	38.9	>60
3	1.00	98.00	1.00	4.5	5.9	8	23	39.1	>60
4	65.67	17.17	17.17	4.4	6.3	12	21	35.0	>60
5	17.17	65.67	17.17	4.3	6.0	9	22	34.7	>60
6	33.33	33.33	33.33	4.3	6.0	10	20	31.1	59
7	49.50	1.00	49.50	4.3	6.1	14	18	28.8	48
8	1.00	49.50	49.50	4.4	5.6	9	19	26.8	34
9	17.17	17.17	65.67	4.3	5.8	10	19	24.1	29
10	1.00	1.00	98.00	4.4	5.5	12	16	18.7	19

^a See Sections 2 and 3.2 for details.

^b All percentages are w/w and are of the bulk acid, without regard to assay value.

^c Legend: A=acetate; N=nitrate; P=phosphate.

^d The start times of the nitrate and phosphate peaks, plus the ending time of the nitrate peak, are given instead of the retention times. This decision was made to show that these two typically wide peaks were always well resolved from chloride and sulfate.

the ratio of 1:98:1; chloride's retention time was similar to mixes with 17% acetic. For the sulfate and phosphate peaks, the controlling factor clearly was phosphate; the retention time of SO₄²⁻ and PO₄³⁻ decreased steadily as the concentration of phosphoric increased. (As can be seen in the table, exact times for PO₄³⁻ were not available for the mixes with less than 33.33% phosphoric acid. In these cases, the phosphate did not begin eluting until the step to

NaOH was made at 60 min). The nitrate peak began eluting more quickly as the nitric acid concentration increased. For a given percentage of HNO₃, the elution began more rapidly as the proportion of H₃PO₄ increased.

These variations in retention behavior reflect the fact that, while the peak resolutions are adequate for the purposes of this research, the overall capacity of the column is overloaded even at a 1:100 dilution. A

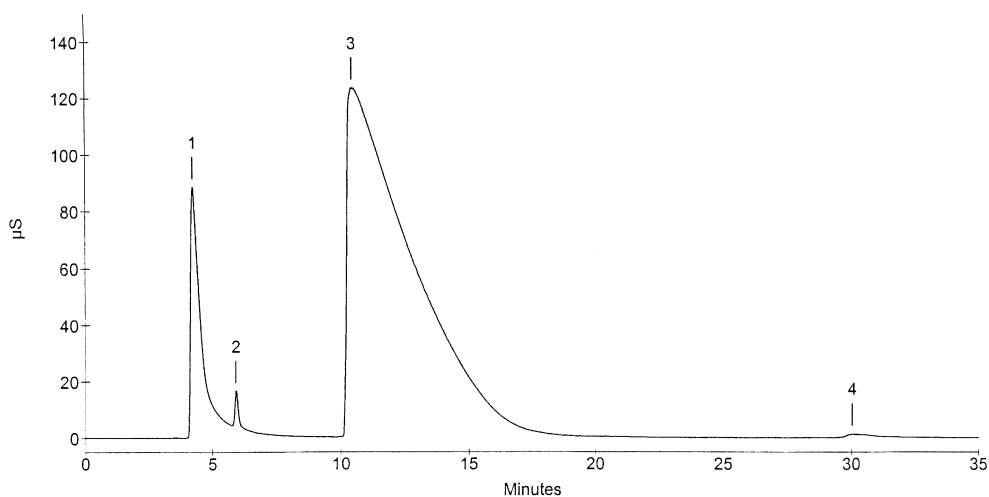


Fig. 2. Chromatogram of an etchant mixture (diluted 1:100) containing 33.33% each of acetic (100%, w/w), nitric (69%, w/w) and phosphoric (85%, w/w) acids, using conditions of: 10 mM KOH; flow-rate=0.5 ml/min; column temperature=33 °C. Diluted solution has been spiked with 10 ppm each of chloride and sulfate. See Sections 2 and 3.2 for additional details. Peak identities: (1) acetate, (2) chloride, (3) nitrate and (4) sulfate; under these chromatographic conditions, phosphate does not elute, even after 60 min.

detailed investigation of column overloading was not necessary for the development of a trace-anion procedure. Furthermore, such a study was outside the scope of this project and was not undertaken.

3.3. Gradient-determination experiments

From the results of the mixture experiments, it was clear that the analytes' relative retention times varied, depending on the ratio of the etchant acids. Consequently, a suitable eluent program would have to be determined for each etchant blend. Statistical design of experiments was used to accomplish this task. To illustrate the process, the details for the previously mentioned proprietary blend are detailed in the remainder of this section (i.e., Section 3.3).

Before the experiments were begun, considerable thought was given to the two main elements in experimental design: (1) what factors should be controlled (i.e., assigned specific values to be used within the design), and (2) what responses should be monitored and used for calculations. From preliminary work, it was decided that the main chromatographic influences (and the appropriate factors) were: (1) the concentration of KOH, (2) the concentration of NaOH, (3) the time at which KOH was stepped to NaOH and (4) the temperature of the column.

The choice of responses was driven by one of the main purposes of this research; i.e., to calibrate and quantify Cl^- and SO_4^{2-} at the low-ppm range in the etchant. To achieve this goal, it would be necessary to have sharp chloride and sulfate peaks, as well as adequate resolution of these analytes from the matrix anions. Initial work had indicated that the shape of the Cl^- peak, plus its resolution from the acetate peak, was virtually the same, no matter how the gradient program was constructed. Consequently, no chloride-related responses were chosen. The four selected responses were: (1) peak height of sulfate, (2) the peak width [in min, and defined as $(t_f - t_i)$, where t_f =time when the peak returned to baseline and t_i =time when the peak began rising from the baseline] of sulfate, (3) the time difference between the end of the nitrate peak and the start of the sulfate peak and (4) the time difference between the end of the sulfate peak and the start of the phosphate peak. The times in 2, 3 and 4 were determined manually.

The above responses were utilized because of

software limitations. Since the various eluent programs sometimes resulted in poorly resolved nitrate–sulfate and/or sulfate–phosphate peaks, the PeakNet software was not able to calculate the traditional quantities of peak width, peak efficiency, peak asymmetry, peak tailing factor, or peak resolution. Furthermore, measurements of such quantities were not ends in themselves, but simply responses for use in finding a suitable gradient. The four chosen responses were calculated in a consistent manner throughout the study. The resulting measurements provided information that was adequate for use in data analysis. As a result, the lack of traditional values was not of concern.

A Box–Behnken design [14] was chosen, since it requires only three settings per factor and permits estimation of response–surface terms; i.e., curvature. A response surface is defined mathematically as follows:

$$\text{response} = \text{straight-line terms} + \text{quadratic terms} \\ + \text{cross-product terms}$$

For a four-factor design, which was used in this research:

$$\text{response} = a_0 + a_1(\text{factor 1}) + a_2(\text{factor 2}) \\ + a_3(\text{factor 3}) + a_4(\text{factor 4}) \\ + a_{11}(\text{factor 1})^2 + a_{22}(\text{factor 2})^2 \\ + a_{33}(\text{factor 3})^2 + a_{44}(\text{factor 4})^2 \\ + a_{12}(\text{factor 1})(\text{factor 2}) \\ + a_{13}(\text{factor 1})(\text{factor 3}) \\ + a_{14}(\text{factor 1})(\text{factor 4}) \\ + a_{23}(\text{factor 2})(\text{factor 3}) \\ + a_{24}(\text{factor 2})(\text{factor 4}) \\ + a_{34}(\text{factor 3})(\text{factor 4})$$

where all “a” terms are coefficients.

3.3.1. Screening design

Because four factors were involved and little was known about the relative influence of each factor on the chromatography, this first set of experiments was designed and conducted for screening purposes. In other words, the ranges for each of four factors were set to be fairly wide. These range assignments would

help ensure that an important response region was not overlooked. Settings are given in Table 2.

To evaluate the sulfate separation, a qualitative approach was sufficient. With the exception of gradients numbered 11 and 12, the sulfate peak shape was poor (i.e., too broad and/or showing too little response) in all programs and poorly resolved in several. It was decided that these two acceptable gradients would be the basis of a second Box–Behnken experiment. This design would concentrate on a more narrowly defined response surface and allow further refinement of the gradient.

To set the new factor levels, the results were reviewed in more detail. This additional analysis revealed two main observations. First, the conditions for gradients 11 and 12 were the same except for temperature; one factor combination was with the column temperature at the minimum (29 °C) and the other at the maximum (37 °C). However, the sulfate peak was only marginally better at the lower setting.

Consequently, in the second round of experiments, the temperature was held at 29 °C.

Second, it was clear that 15 mM KOH was too high for the starting concentration; in all six of those screening settings, the sulfate peak coeluted with the tail of the nitrate peak. Because of this fact, plus the fact that 10 mM KOH was used in gradients 11 and 12, KOH was limited to 11 mM maximum in the second design.

The ranges of choices for the NaOH concentration and for the time of the eluent step change were not as obvious. Therefore, some additional gradient programs were tested. It was not possible to narrow the range for the step-change time, and 30 mM appeared to be a reasonable maximum for the NaOH concentration. The final design is given in Table 3.

It should be emphasized that the new settings for each factor were not the only possibilities. Ranges could have been widened to avoid missing possible suitable portions of the response surface. Alternative-

Table 2
Factor settings in the initial (screening) Box–Behnken experimental design^a

Gradient	KOH (mM)	NaOH (mM)	<i>t</i> of step ^b	Temperature (°C)
1	5	10	20	33
2	5	30	15	33
3	5	30	20	29
4	5	30	20	37
5	5	30	25	33
6	5	50	20	33
7	10	10	15	33
8	10	10	20	29
9	10	10	20	37
10	10	10	25	33
11	10	30	15	29
12	10	30	15	37
13	10	30	20	33
14	10	30	25	29
15	10	30	25	37
16	10	50	15	33
17	10	50	20	29
18	10	50	20	37
19	10	50	25	33
20	15	10	20	33
21	15	30	15	33
22	15	30	20	29
23	15	30	20	37
24	15	30	25	33
25	15	50	20	33

^a See Sections 2 and 3.3.1 for details.

^b Legend: *t* of step = time (in min) of the eluent step from KOH to NaOH.

Table 3
Factor settings in the refined Box–Behnken experimental design^a

Gradient	KOH (mM)	NaOH (mM)	<i>t</i> of step ^b
1	5	10	20
2	5	20	15
3	5	20	25
4	5	30	20
5	8	10	15
6	8	10	25
7	8	20	20
8	8	30	15
9	8	30	25
10	11	10	20
11	11	20	15
12	11	20	25
13	11	30	20

^a Column temperature was 29 °C throughout. See Sections 2 and 3.3.2 for additional details.

^b *t* of step=time (in min) of the eluent step from KOH to NaOH.

ly, the spans could have been restricted further to focus more precisely on an area that looked promising. The above choices were made because they seemed a reasonable compromise between the two alternatives. These range limitations also made it likely that the statistical software could be used to generate a more suitable eluent program.

3.3.2. Refined design

With this refined design, the same responses were monitored as in the screening work. First, the data from this design were evaluated qualitatively. With the KOH concentration set at 8 mM, two programs (i.e., one with a step to 20 mM NaOH at 20 min and the other with a step to 30 mM NaOH at 25 min) gave a sulfate peak similar to that seen with gradient 11 in the previous design.

Next, the data were analyzed statistically to see if a more suitable eluent program could be found. The procedure involved the use of JMP software, specifically the “Fit Model” platform, and the “Maximize Desirability” option in the “Profiler” platform. (Interested readers should contact the authors for details on these procedures, since details in the JMP manuals are sketchy). The resulting program called for 7.6 mM KOH and a step to 30 mM NaOH at 25 min. This program was in essence the second one mentioned in the preceding paragraph, and, for all

analytes, did indeed give almost identical peak shapes and retention times.

The similarity of the chromatograms from these four gradients (i.e., the above two at 8 mM, the 7.6 mM, and number 11 in Table 2) suggested that further refinement was not warranted. Gradient 11 was selected, since it had the advantage of the shortest run time (a response that was not used in the statistical analyses) and thus was used for the calibration work.

3.4. Calibration study

Once a suitable eluent program had been selected (i.e., 10 mM KOH, stepping to 30 mM NaOH at 15 min; column temperature=29 °C; flow-rate=0.5 ml/min; sample loop=7.5 μl), the final research objective was undertaken; i.e., estimating the prediction interval associated with low-ppm determinations of chloride and sulfate in the etchant. This goal was achieved by conducting a brief calibration study, using the proprietary mixture as the matrix. A straight line with ordinary-least-squares (OLS) fitting was proposed for both analytes. Peak area (PA) was used as the response.

This equi-spaced calibration design (six levels and four replicates, for a total of 24 data points; see Section 2.3 for details) allowed for modeling the standard deviation and testing the proposed model. In both cases, the standard deviation was found not to increase with concentration. Thus OLS fitting was appropriate. In addition, a straight line was adequate in both cases, since no lack of fit was seen in either test. Furthermore, the residual plots showed no systematic departure from a straight line. The prediction interval [15] was determined at the 95% confidence level ($\alpha = \beta = 2.5\%$). For both chloride and sulfate, these lines were essentially parallel to the calibration line. In the undiluted proprietary etchant, uncertainties were ± 7 and ± 20 ppm, respectively, at all points along the curve. The Hubaux–Vos detection limits [16] were 14 and 39 ppm, respectively, again at 95% confidence. R_{adj}^2 was 0.9648 for chloride and 0.7892 for sulfate. While the latter value is not particularly high, it did not cause concern, for two reasons. First, although a low R_{adj}^2 can sometimes indicate a departure from linearity, this situation was not the case (as explained above). Second,

in this study, the prediction intervals were the desired summary measure for evaluating precision.

The equations for the chloride and sulfate calibration curves were, respectively:

$$PA_{Cl} = 2935.4 + 81.9 \text{ ppb}$$

$$PA_{SO_4} = 9314.5 + 26.0 \text{ ppb}$$

For both analytes, there were traces of the analytes in the unspiked etchant, resulting in the positive y -intercepts listed above. To use these equations for prediction purposes, the average of the blank responses should be subtracted from the calculated y -intercept. The resulting value should be used as the value for “ a ” in $x = (y - a)/b$.

3.5. General evaluation of the suitable eluent program

Although the suitable eluent program was developed using only one etchant mix, it was hoped that this gradient would be a reasonable starting place for analyzing any ratio of these three acids. To make this evaluation, the 10 etchants from the mixture experiment (see Table 1) were chromatographed under the new conditions. In all cases, the

separations of the five components were adequate enough to be a starting point for experimental-design work on any etchant comprised of acetic acid, nitric acid and phosphoric acid. An example chromatogram (for the ratio 33.33:33.33:33.33) is shown in Fig. 3. With any etchant proportions, beginning here should allow a suitable eluent program to be found in only one experimental-design cycle.

4. Conclusions

For all possible etchants comprised of acetic acid, nitric acid and phosphoric acid, the Cryptand A1 column was able to resolve the major constituents from each other, and from traces of chloride and sulfate. This separation was accomplished using a KOH/NaOH capacity gradient. The results were achieved with minimal sample preparation (i.e., a 1:100 dilution of the etchant). Through the testing of a proprietary mix, it was shown how statistically designed experiments can be used to find a suitable eluent program. Besides being suitable for this etchant, the conditions were found to be a good starting place for chloride/sulfate determinations in any mix of these three acids.

Once a suitable gradient program for this pro-

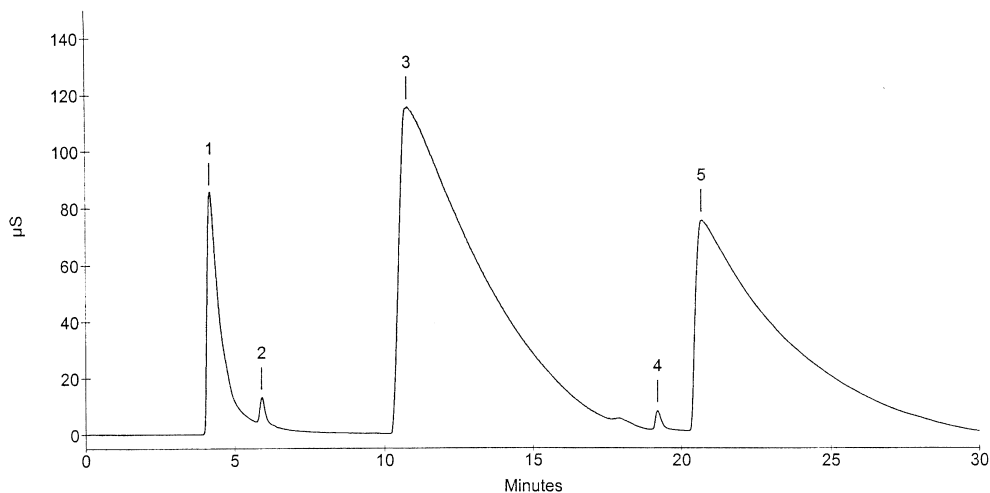


Fig. 3. Chromatogram of an etchant mixture containing 33.33% each of acetic (100%, w/w), nitric (69%, w/w) and phosphoric (85%, w/w) acids, using suitable eluent program from experimental-design work. Conditions are: 10 mM KOH with step to 30 mM NaOH at 15 min; flow-rate=0.5 ml/min; column temperature=29 °C. For analysis, the mixture has been diluted 1:100; diluted solution also contains 10 ppm each of chloride and sulfate. See Sections 2 and 3.5 for additional details. Peak identities: (1) acetate, (2) chloride, (3) nitrate, (4) sulfate and (5) phosphate; small peak before sulfate is carbonate.

prietary etchant mixture was established, it was shown that low-ppm levels of chloride and sulfate can be detected with high confidence (95%). At this same confidence level and at 50 ppm (the highest standard used in the calibration study), the relative uncertainty is an acceptable $\pm 14\%$ for chloride and a marginal $\pm 40\%$ for sulfate. If the prediction-interval widths are maintained at higher concentrations, the sulfate uncertainty would drop to an acceptable $\pm 20\%$ at 100 ppm. More generally, these intervals can also serve as a guide to the uncertainties that could be anticipated for other ratios of the three etchant acids. The results also show that with minimal sample preparation (i.e., a 1:100 dilution of the etchant), chloride and sulfate can be detected and possibly quantitated at low-ppm levels.

In conclusion, all four goals of the research were achieved. Furthermore, no degradation of the Cryptand A1 was seen even after over 350 injections of 1:100 etchant. Thus, the separator was found to be a reliable, rugged column for the low-ppm detection of chloride and sulfate in etchants comprised of acetic acid, nitric acid and phosphoric acid.

5. Nomenclature

Mathematical symbols used

α	Average probability of false positives
β	Average probability of false negatives
R^2_{adj}	A version of R^2 , “penalized” for each independent variable used in the regression (R^2 measures the amount of total variation in the response “explained” by the dependent variable)

Terms and abbreviations used

DL	Detection limit. The concentration below which the analytical method cannot reliably detect a response
OLS	Ordinary least squares. A fitting technique that minimizes the sum of squares of the residuals

Prediction interval	A range of values defined by a pair of limits that bracket the uncertainty in one future measurement
PA	Peak area
PH	Peak height
PW	Peak width (in min). Here, measured manually and defined as $(t_f - t_i)$, where t_f = time when the peak returned to baseline and t_i = time when the peak began rising from the baseline
t_R	Retention time (in min).

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