Ion-chromatographic study of interactions in HF–H$_3$PO$_4$–HNO$_3$ semiconductor etchants
Systematic use of statistically designed mixture experiments

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Abstract

From ion chromatography, combinations of concentrated HF, H$_3$PO$_4$ and HNO$_3$ were found to generate a fourth species, H$_2$PO$_3$F. A thorough ion chromatographic study was undertaken to determine the role of each species in the equilibrium reaction, and to quantitate the final concentrations of the acids. Mixture-design experiments were generated and conducted systematically. Statistical data analyses resulted in prediction equations for the relevant components. An additional or different parameter (possibly activity) was found to be necessary to explain the behavior completely. However, these quantities were not available and concentrations provided reasonable empirical explanations; therefore, units of weight percent were used throughout. A Dionex DX 500 ion chromatograph and JMP statistical software were used for the study. © 1998 Elsevier Science B.V.

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1. Introduction

Mixtures of concentrated acids are used throughout the semiconductor industry. These solutions, known as etchants, are used to remove unprotected areas on silicon wafers [1]. The proportion of each constituent is tightly controlled, so that the desired results are achieved.

In this paper, the etchant HF–H$_3$PO$_4$–HNO$_3$–water is considered. Preliminary chromatographic work with this combination revealed the presence of a fourth peak, which eluted shortly after phosphate under the conditions employed (see Section 2.2). Reduced amounts of fluoride and phosphate were noted as well, but neither constituent disappeared completely. Evidence of a reaction between HF and

H$_3$PO$_4$ is cited in the literature; Jacobson reports the equilibrium: HF+H$_3$PO$_4$↔H$_2$PO$_3$F+H$_2$O [2]. Shamakhova et al. performed NMR experiments to determine equilibrium constants in the HF–P$_2$O$_5$–water system [3]. No studies were found where concentrated acids were used, or where nitric acid was present as well.

The existence of an additional component (or the reduced proportions of two others) is of great concern to users of these mixes. Knowing the actual amounts of each constituent is paramount. Therefore, a simple, reliable technique was needed to study this reaction and allow quantitation of the various components; ion chromatography with conductivity detection was the logical first choice. A Dionex AS14 column was used, since it retained fluoride well out of the void volume and isocratically eluted all species in under 10 min.

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The main purpose of this paper, then, was to show the utility of ion chromatography for quantifying the final concentrations of the components. A secondary aim was to outline a detailed, systematic procedure for planning, designing, conducting and analyzing statistical mixture-design experiments. To achieve these goals, experiments were designed and data analyzed using JMP software. Analytical assays of the mixes were performed on a Dionex DX 500 ion chromatograph.

2. Experimental

2.1. Materials

For preparation of eluents, standards and acid mixes, deionized (DI) water (18 mΩ cm) was provided by a point-of-use water purification system (Ahlfinger Water, Dallas, TX, USA). Sodium carbonate and sodium hydrogencarbonate from Fluka (Ronkonkoma, NY, USA) were used to prepare individual eluent solutions of 20 mM each. The mobile phases were kept under pressure with helium throughout their life. For preparing calibration standards, the following acids were obtained from VWR Scientific (West Chester, PA, USA): Baker Analyzed 48–51% reagent HF, reagent ACS (85% by titration) H_3PO_4 and Baker Analyzed 69–71% reagent HNO_3; actual assay values were 49.1, 85.6 and 69.7%, respectively. To confirm the identity of the fourth peak, fluorophosphoric acid (70%) was purchased from Aldrich (Milwaukee, WI, USA). For preparing the various acid mixtures, the following semiconductor-grade acids were obtained from Texas Instruments (Dallas, TX, USA): 49.15% HF, 85.76% H_3PO_4 and 69.64% HNO_3.

Standards and samples were prepared and diluted out in 4-oz. polypropylene specimen containers from Fisher Scientific (Pittsburgh, PA, USA). Acids and diluents were transferred by pouring, with delivery of final weight via polyethylene transfer pipets from Fisher.

2.2. Apparatus and columns

A Dionex (Sunnyvale, CA, USA) DX 500 ion chromatograph was utilized for all work. Unless otherwise noted, all instrument modules and consumables were from Dionex. Analytical columns used were an IonPac AG14 Guard (50 mm×4 mm) with AS14 Analytical (250 mm×4 mm). A GP40 Gradient Pump mixed the eluent constituents (20 mM Na_2CO_3, 20 mM $NaHCO_3$ and DI water) in the ratio of 12.5:17:70.5; final composition was 2.5 mM Na_2CO_3–3.4 mM $NaHCO_3$. Delivery of the eluent was at a flow-rate of 1.5 ml/min. Postcolumn eluent suppression was accomplished with an anion self-regenerating suppressor (ASRS-I, 4 mm) in the recycle mode; detection was via a CD20 conductivity detector at an output range of 10 μS. A 10-μl sample loop was employed. Instrument control and data collection were performed with a personal computer and Dionex PeakNet software. Statistical analyses and calculations were carried out using JMP software (SAS Institute, Cary, NC, USA).

2.3. Preparation of samples and standards

All samples were prepared so that each concentrated starting acid was present at a specific percentage by mass (hereafter known as %, w/w). To facilitate calculations, 100-g samples were generated in all cases. It should be emphasized that the weights of the starting acids were actual grams of the liquid that were in the reagent bottle; no adjustments for assay values were made. (In the initial experiments, water also was allowed as a fourth component; total mass of final mix remained at 100 g.) When all weighings were complete, containers were capped, swirled and allowed to stand for 51–53 h before analysis. Although no light sensitivity was observed, samples were kept in darkness when not in use. In each set of experiments, mixes were prepared in random order and analyzed in that same order.

For analysis, each sample was diluted 4 g to 100 g with deionized water; immediately thereafter, the resulting solution was further diluted 3 g to 100 g with 3.5 mM Na_2CO_3–2.0 mM $NaHCO_3$. This buffer was used to optimize the chromatography of this final solution, which was stable for at least several days. However, the first dilution was not as well behaved; the monofluorophosphoric acid disappeared with time, but the kinetics appeared to be quite slow.

To evaluate the short-term stability of Dilution 1,

four mixtures were selected (original ratios of HF–H_3PO_4–HNO_3 were: (1) 99:1:0; (2) 1:99:0; (3) 40.2:40.2:19.6 and (4) 40.2:59.8:0). With each, Dilution 2 was prepared in a one-step procedure; i.e., 0.12 g of the original mixture was taken to 100 g with eluent. Each of these solutions chromatographed the same as the corresponding Dilution 2 from the original protocol, indicating no short-term degradation of Dilution 1. Consequently, the two-step process was used here to avoid the problem of weighing 0.12 g accurately.

To calibrate the instrument for the three starting acids, the following levels (all in %, w/w) were chosen: (1) for HF and H_3PO_4, 1, 2, 4, 8, 16.66, 25, 33.33, 50, 66.66, 75, 83.33 and 98; (2) for HNO_3, 1, 2, 4, 8.33, 16.66, 25, 33.33, 41.66, 50, 58.3, 66.66, 75, 83.33 and 98. Stock standards were prepared from the VWR concentrated acids as follows (dilutions were with deionized water and each preparation was in a separate specimen cup). Concentrations less than 10% were prepared from the starting acids; each was then diluted 2 g to 100 g to form the stock standard. The remaining levels were prepared at the stock (i.e., 2–100 g) level directly from the starting material. To prepare mixed working standards for injection into the ion chromatograph, 6 g of each appropriate stock standard were combined in a specimen cup; 82 g of the diluent buffer were added to reach 100 g. Throughout the entire study, suites of working standards were prepared and analyzed in random order; each of these solutions was prepared fresh each day of analysis. A total of 200 data points was collected for each anion; no drift in instrument response was detected for any species. Therefore, calibration curves were generated from the entire set of values. (No standards were analyzed for H_2PO_3F, since it was not available at high purity. The response factor for this compound was assumed to be that of H_3PO_4, and the phosphoric curve was used for H_2PO_3F quantitation.)

A Sartorius LC 3201D analytical balance was used to weigh out concentrated acids. This balance was used because it was in a hood; masses were recorded to three decimal places. All other weighings (each to four decimal places) were made on a Sartorius MC1 analytical balance.

Dilution errors in the daily working standards were estimated by conducting a Monte Carlo simula-

tion. This exercise was based on the upper bounds on the magnitude of weighing error for the scales (0.001 g for the LC balance and 0.0001 g for the analytical 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.

3. Results and discussion

3.1. Preliminary work

At the beginning of this study, very little was known about this combination of acids, except that a fourth component was seen under some circumstances (see Fig. 1). Identity of this compound was established by matching its ion chromatographic retention time with that of fluorophosphoric acid standard. If the three concentrated, starting acids (HF, H_3PO_4 and HNO_3) were mixed in some ratio, and no additional water was included, then an additional peak occurred. The amounts of HF and H_3PO_4 decreased, but the level of HNO_3 remained the same. However, if the individual acids were at the stock-standard level (see Section 2.3) before mixing, no extra peak was seen; responses for the three starting acids were the same as when the acids were analyzed individually. To investigate this equilibrium reaction in greater detail, various mixes were designed statistically and assayed by ion chro-
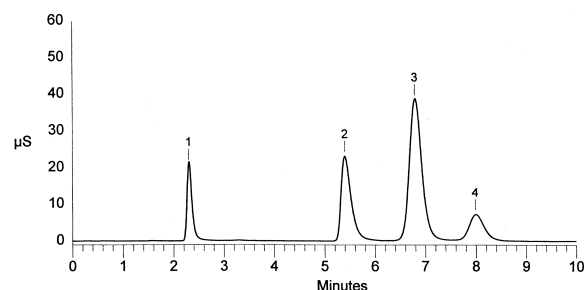

Fig. 1. Chromatogram of the components seen in the equilibrated four-acid mixture. Acid peak identities are: 1=hydrofluoric; 2=nitric; 3=phosphoric; 4=fluorophosphoric.

matography; data were then subjected to regression analysis.

With statistically designed experiments, the preliminary planning is a crucial step, and often determines whether the data collected are meaningful and appropriate [4]. During this phase, all parties involved meet for a structured 'brain-storming session' to identify the problem and the objectives specifically, and to determine what control (or *x*) variables and response (or *y*) variables are to be included. In addition, design preferences are determined, and duties of individual researchers are assigned. As experiments progress, participants meet frequently to discuss data, draw conclusions and revise objectives.

For this study, the results of the initial planning were as follows:

(1) Objectives: (a) determine if nitric acid is necessary for the reaction; (b) investigate the effect of additional water on the amount of product formed; (c) determine general conditions for maximum production of product; (d) generate a formula to predict the amount of product formed in a specific mix of starting acids; (e) generate formulas to quantitate the amounts of the acids remaining at equilibrium for each mix.

(2) Control variables: starting amounts (%, w/w) of HF, H_3PO_4, HNO_3 and added water.

(3) Response variables: amount (chromatographic peak area) of product formed.

(4) Design preferences: mixture design [5].

The control variables should have been expressed in units of activity, since molarity and ionic strength were quite high in these samples. However, the appropriate activity coefficients were not available and measurement of them was outside the scope of this project. Thus, the mass percents were utilized. It still was reasonable to seek an empirical product-prediction equation (objective d) using concentration, since the activity of each acid should be a small, monotonic function of concentration.

Mixture design was chosen because it mimicked the preparation protocol used in the semiconductor industry. (Etchants are always mixed on a percent-by-mass basis.)

3.2. Experiment 1

The first experiment was designed to obtain a general overview of the reaction process, and to address objectives a to c. The following steps in JMP were used to generate a possible design. Factors were four in number: the three starting acids and water. Levels (in %, w/w) were defined as follows: (1) 1–98 for the three starting acids and (2) 0–97 for water. Then, Mixture Design was chosen, using four Factors and Extreme Vertices with Degree=3.

The generated design and analytical results (peak areas) are shown in Table 1 (sorted by peak area). Mixture 11 was not suggested by JMP, but was added to include a center point (i.e., where all ingredients were at the same level, which here is 25%). Duplicates were added to allow for lack-of-fit testing during data analysis and to obtain a pure-error term.

Data analysis began by inspecting Table 1 for trends. Very little product resulted if either added water or nitric acid was high (Mixes 1 through 7). Highest amounts of product occurred when both hydrofluoric and phosphoric acids were high and no water was added (Mixes 14 and 15). In mixes with only 1% nitric, results indicated that product might be formed even if that acid were omitted (assuming the water content was not too high).

Although objective d was not a primary goal of this experiment, preliminary insight was gained through statistical analysis. This task was conducted using the Fit Model platform in JMP. The four initial components were highlighted and then the Mixture Response Surface Effect Macro was chosen; those four terms, plus all cross products, became *x* (or control) variables. Product peak area was used for the *y* (or response) variable. Standard least squares was chosen, the model was run and the results table investigated.

In the Parameter Estimates section, only the HF–H_3PO_4 interaction was significant (its *p* value was less than 0.0001). This finding supported the hypothesis that these two acids were interacting. The lack-of-fit test also had a *p* value less than 0.0001, showing that the model was not complete, given these data.

Next, the analysis was repeated, using the log of the product peak area for the *y* variable. This time, all three acids and the HF–H_3PO_4 interaction were significant. However, lack of fit was still a problem. Furthermore, when the model's prediction formula was used to calculate peak areas, almost all the

Table 1
Mixture design and results for experiment 1

Mix	HF (%)	H_3PO_4 (%)	HNO_3 (%)	Water (%)	Peak area of product
1	1	1	1	97	0
2	1	1	49.5	48.5	3
3	49.5	1	1	48.5	6
4	1	49.5	1	48.5	6
5	1	1	98	0	7
6[a]	1	33.3	33.3	32.3	7, 8
7[a]	33.3	1	33.3	32.3	10, 8
8	98	1	1	0	59
9	49.5	1	49.5	0	60
10	1	49.5	49.5	0	164
11[a]	25	25	25	25	245, 246
12	1	98	1	0	251
13[a]	33.3	33.3	1	32.3	321, 328
14[a]	33.3	33.3	33.3	0	1493, 1516
15	49.5	49.5	1	0	2478

See text for discussion of design and results.

Data sorted by peak areas, which are given in thousands.

[a] Sample was prepared and analyzed in duplicate.

results were in error by more than 20% ($\pm$, relative to true). A possible explanation for this situation was that the equation was trying to fit too little data over too broad a range. However, this experiment provided the desired information, screening the possibilities to give broad conclusions (discussed above). No attempt was made to quantify the acids in the mix, since this work was 'broad-brush' in nature.

3.3. Experiment 2

For this set of mixtures, additional water was omitted, since its presence hindered the product. The goal was to gather additional data for objectives a and c, with a secondary aim of addressing d. Once again, the design was created using JMP. Factors were the three starting acids. Levels (in %, w/w) ranged from 25 to 75 for HF and H_3PO_4, and from 0 to 50 for HNO_3. (Contact the authors for the transformation required on the matrix generated by JMP.)

The ion-chromatographic data are shown in Table 2, which is sorted by peak area and includes duplicates as noted. Clearly, objective a was achieved; product always was seen, even when no nitric acid was present. Maximum peak area occurred when HF–H_3PO_4 was 37.5:62.5. Also, for a given propor-

tion, more product was obtained when H_3PO_4 was the larger concentration.

Statistical analysis was performed in JMP, using the same procedure as in experiment 1; the log of product peak area was the y variable. All coefficient estimates were significant, but poor fitting still existed ($p=0.0032$). However, the prediction equa-

Table 2
Mixture design and results for experiment 2

Mix	HF (%)	H_3PO_4 (%)	HNO_3 (%)	Peak area of product
1[a]	25	25	50	1034, 1038
2	37.5	25	37.5	1236
3[a]	50	25	25	1345, 1346
4	62.5	25	12.5	1433
5[a]	75	25	0	1481, 1499
6	25	37.5	37.5	1517
7	37.5	37.5	25	1789
8[a]	25	50	25	1932, 1954
9	50	37.5	12.5	1964
10	62.5	37.5	0	2075
11	37.5	50	12.5	2299
12	25	62.5	12.5	2371
13[a]	50	50	0	2553, 2564
14[a]	25	75	0	2766, 2769
15	37.5	62.5	0	2796

See text for discussion of design and results.

Data sorted by peak areas, which are given in thousands.

[a] Sample was prepared and analyzed in duplicate.

tion was useful; when it was applied to the data, the calculated peak areas were within $\pm 3\%$ of the actual.

3.4. Experiment 3

The preceding work successfully addressed objectives a and b, and focused in on the conditions for maximum product. In addition, experiment 2 provided an empirical prediction equation for H_2PO_3F. However, this formula was derived from a restricted set of conditions (i.e., for HF and H_3PO_4 each at $\geq 25\%$, w/w); whether the prediction would hold for the full range (1–99%, w/w) remained unanswered. Consequently, a third experiment was constructed. In JMP, allowed Factors and Levels were: (1) HF and H_3PO_4, each between 1 and 99% (w/w) and (2) HNO_3, between 0 and 98% (w/w).

Results are presented in Table 3. Further evidence is seen that more product resulted from a given proportion when the larger % (w/w) was given to phosphoric acid. The point of maximum product occurred when HF–H_3PO_4 was 40.2:59.8.

Table 3
Mixture design and results for experiment 3

Mix	HF (%)	H_3PO_4 (%)	HNO_3 (%)	Peak area of product
1	1	1	98	3
2[a]	20.6	1	78.4	41, 42
3	40.2	1	58.8	52
4[a]	59.8	1	39.2	52, 53
5[a]	99	1	0	55, 60
6	79.4	1	19.6	58
7[a]	1	20.6	78.4	73, 74
8	1	40.2	58.8	146
9[a]	1	59.8	39.2	185, 197
10	1	79.4	19.6	233
11[a]	1	99	0	255, 258
12	20.6	20.6	58.8	811
13[a]	40.2	20.6	39.2	1058, 1063
14	59.8	20.6	19.6	1194
15[a]	79.4	20.6	0	1247, 1261
16[a]	20.6	40.2	39.2	1476, 1480
17	40.2	40.2	19.6	1968
18	20.6	59.8	19.6	2109
19	59.8	40.2	0	2221
20[a]	20.6	79.4	0	2667, 2669
21	40.2	59.8	0	2780

See text for discussion of design and results.
Data sorted by peak areas, which are given in thousands.
[a] Sample was prepared and analyzed in duplicate.

The product's prediction formula from experiment 2 did not work well for these data, especially for low amounts of HF and/or H_3PO_4; errors were as high as several hundred relative percent. This situation presumably was due to the lack of low-level data in experiment 2. Statistical analysis was performed, then, on only the data in this set, using the same x and y variables as in Section 3.3. All factors were significant, but lack-of-fit remained poor. From this new equation, predicted peak areas were better. Relative errors, though, still were fairly large; the mean of the absolute values of the errors was 51%. However, considering that this experiment covered the entire range of mixtures (three orders of peak-area magnitude) with only 21 combinations, such an error was not considered unreasonable. The formula could estimate the amount of product in various regions; from that overview, the researcher could choose the areas to be examined in more detail.

3.5. Experiment 4

A final set of mixtures was analyzed to understand two regions more fully: (1) where HF and/or H_3PO_4 was less than 20% (w/w) and (2) the proportion yielding maximum product. The design matrix and results are given in Table 4. To show trends, Fig. 2 shows these data along with those from experiment 3. The product peak area of 2881 (HF–H_3PO_4 = 30:70) is the largest value obtained. Values at 35:65 and at 25:75 (from experiment 2) are below the first area, indicating that the absolute maximum is somewhere in this range.

As a check, the 'entire-range' prediction equation from experiment 3 was applied to these new data, and percent deviations from true were calculated. These results (absolute values) were greater than 60% for mixtures that were at or near 0% (w/w) for one or more acid. However, this situation is not unusual for mixture models. To obtain more accurate estimates of the extreme regions, designs such as experiment 2 are needed.

3.6. Calibration-curve evaluation and quantitation of final concentrations

All of the above work centered on exploring, describing and predicting the formation of H_2PO_3F,

Table 4
Mixture design and results for experiment 4

Mix	HF (%)	H_3PO_4 (%)	HNO_3 (%)	Peak area of product
1	5	15	80	242
2[a]	10	10	80	248, 280
3[a]	30	10	60	471, 474
4	5	35	60	540
5[a]	50	10	40	548, 559
6[a]	70	10	20	602, 606
7[a]	90	10	0	625, 633
8	25	15	60	655
9[a]	10	30	60	748, 770
10	5	55	40	802
11	15	25	60	823
12	5	75	20	1009
13	5	95	0	1171
14[a]	10	50	40	1194, 1212
15	35	25	40	1208
16	30	30	40	1358
17	15	45	40	1385
18	15	50	35	1577
19[a]	10	70	20	1587, 1593
20	15	65	20	1914
21[a]	10	90	0	1914, 1932
22[a]	35	45	20	2042, 2066
23	30	50	20	2143
24	25	55	20	2171
25	15	85	0	2403
26[a]	35	65	0	2765, 2859
27	30	70	0	2881

See text for discussion of design and results.

Data sorted by peak areas, which are given in thousands.

[a] Sample was prepared and analyzed in duplicate.

Fig. 2. Plot showing H_2PO_3F peak areas (in thousands) for the various mixtures in experiments 3 (data are in boxes) and 4. Where necessary, nitric acid was used to bring the mixture to 100% (w/w). Maximum product occurred for HF–H_3PO_4 between 35:65 and 25:75. Because of space considerations, the mixture of HF–H_3PO_4–HNO_3=15:50:35 (experiment 4) was not plotted.

as summed up in objectives a to d. The final goal, e, was addressed last, after all calibration data had been collected. For each of the three starting acids, a curve was generated using all 200 points (see Section 2.3). (No fluorophosphoric-acid standards were prepared and analyzed, since this compound cannot be obtained in pure form, see Section 2.3.)

Inspection of the scatter plots showed curvature for each graph. Therefore, a quadratic model was proposed, with ordinary least squares as the fitting technique. For HF, H_3PO_4 and HNO_3, regression results were, respectively: (1) adjusted $r^2=0.9996$, 0.9992 and 0.9996 and (2) 95% confidence interval=±1.3, 1.7 and 1.2% (w/w). The p value for lack-of-fit was less than 0.0001 for all three curves, indicating that the model was missing one or more terms. However, from a pragmatic standpoint, the
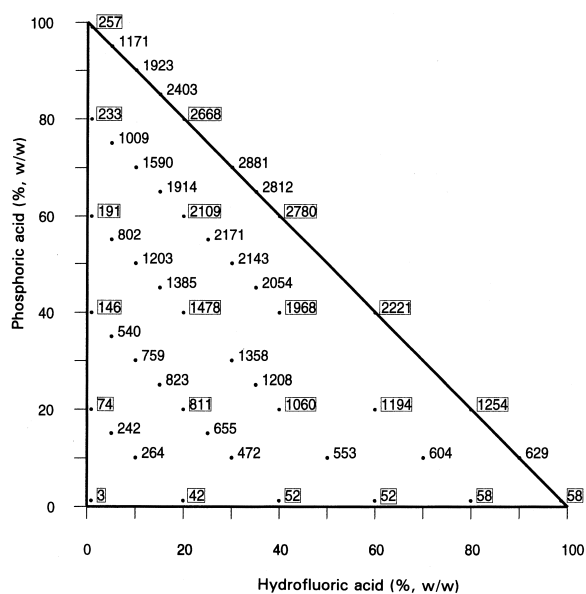
other statistics indicated that this deficiency was unimportant. Therefore, these curves were used to quantitate the acids remaining in each mix's reacted state; the phosphoric equation was used for the product.

Calibration results indicated that nitric acid remained virtually unchanged in all cases, while the % (w/w) of both hydrofluoric and phosphoric acids dropped as product was formed. When final concentrations were added together, the total averaged 97.7% (w/w) for all mixes (ones with added water were not included). Additionally, a small amount of water ($<4\%$, w/w) was formed from each mixture's reaction. This essentially complete accounting for all species indicated that the calibration curves were appropriate and that it was acceptable to use the phosphoric curve to quantitate fluorophosphoric acid.

Equations were found to predict the final concentrations of HF and H_3PO_4 from their starting amounts and the percentage (w/w) of H_2PO_3F produced. When the values calculated from these two formulas were compared with those via calibration

curves, the mean absolute deviation was 0.44% (w/w) for HF and 0.58% (w/w) for H_3PO_4.

4. Conclusions

Ion chromatography and statistically designed experiments were used successfully to study mixtures of concentrated HF, H_3PO_4 and HNO_3. In stages, efficient designs were developed and executed to investigate this matrix. Unless the solution was diluted with additional water, fluorophosphoric acid was formed in an equilibrium reaction. Nitric acid was not involved in the reaction.

When the first two acids ranged from 1 to 99% (w/w) and the nitric from 0 to 98% (w/w), maximum product was found to occur at HF–H_3PO_4 ratios between 35:65 and 25:75. Despite the fact that concentrations were used instead of activities, useful prediction equations were generated for the amount of product.

Quadratic calibration curves were established for HF, H_3PO_4 and HNO_3, and were used to quantitate the % (w/w) of all four acids in the equilibrated mixture. (The phosphoric plot was applied to the fluorophosphoric acid data.) These curves all had good statistical performance (high adjusted r^2 and narrow confidence intervals). Equations also were found to predict the final concentrations of HF and H_3PO_4 from their starting amounts and the % (w/w) of H_2PO_3F. The results from these two approaches agreed well for each mix.

Thus, ion chromatography was found to be a fast, reliable technique for investigating this acid system. In addition, mixture–design experiments provided an efficient method for planning the study. The overall result was knowledge of all final concentrations, which are needed to determine the correct proportions for a given etchant application.

5. Terms used

Confidence interval: a pair of confidence limits (an upper and a lower) used to bracket the true value of a statistic.

Control variable: an x variable, the range of which is set or controlled in a designed experiment.

Empirical: based on relationships observed in data, rather than theory.

Factor: in JMP software, the term for a control variable.

Lack-of-fit: the difference between residual sum of squared deviations and the sum of squared deviations of replicates, usually divided by the latter, and standardized for a statistical test. A large lack-of-fit results in a low p value from the statistical test, and indicates that one (or more) term is missing from the model.

Level: a value assigned to a factor in JMP software.

Mean absolute deviation: the mean of the absolute value of the quantity 'true minus predicted'.

Mixture design: an experimental design in which all of the control variables are given in percentages and their sum is 100%.

Monotonic function: a function that consistently increases or consistently decreases with respect to its variable(s), such as log x or exp x, but not $x(x-3)$.

p value: the probability value associated with a statistical test, representing the likelihood that a test statistic would assume or exceed a certain value given chance behavior (and other null-hypothesis assumptions). A low p value indicates statistical significance at a level of confidence equal to 1.0 minus the p value; e.g., a p value of 0.01 is statistically significant at 99% confidence.

Pure error (also called 'pure experimental error'): (estimated) error that is not confounded with possibly missing terms in a model, hence only obtainable by including experimental replicates.

% (w/w): a concentration unit. It is the weight–weight percentage of a species in a final solution. (Here, the mass of an acid is of the liquid as it comes from the reagent bottle; the assay value is not taken into account.)

Relative %: the quantity 'true minus predicted', divided by the true and multiplied by 100.

Response variable: y variable in designed experiments.

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