



ELSEVIER

Journal of Chromatography A, 884 (2000) 151–159

JOURNAL OF
CHROMATOGRAPHY A

www.elsevier.com/locate/chroma

Ion-chromatographic assay of chromium(VI)-containing semiconductor etchants Statistical comparison of two columns

L.E. Vanatta^{a,*}, D.E. Coleman^b

^a*Air Liquide America, Box 650311, M/S 301, Dallas, TX 75265, USA*

^b*Alcoa Technical Center, AMCT-D-10, 100 Technical Drive, Alcoa Center, PA 15069, USA*

Abstract

Semiconductor etchants are concentrated-acid mixtures that are prepared under tight specifications. Assay procedures are needed to ensure that the proportion of each component is within a small percentage (usually 10 relative percent or less) of the target concentration. One such etchant class contains chromium trioxide, usually in combination with HF and HNO₃. While several ion-chromatographic columns can be used to analyze most mineral acids, chromium(VI) presents a problem. This latter species is highly retained by many separators and may also degrade the resins. This paper compares two columns that showed potential for success with these assays: the AS11 and the AS16 separators (both from Dionex). These columns permit elution of chromium(VI) as chromate in 25 min or less. A representative mixture of HF, HNO₃ and CrO₃ was used in the research. Simultaneous calibration studies were conducted and the data sets analyzed statistically. Also investigated was the effect on the columns of repeated exposure to chromate. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Etchants; Statistical analysis; Calibration curves; Chromate

1. Introduction

Etchants are mixtures of concentrated acids and are used in the manufacture of semiconductors. These solutions remove unwanted layers from the wafers during processing. Because the proportion of each acid is subject to tight specifications (usually within a few relative percent of the target concentration), assay methods must have good precision and be able to discriminate among a few tenths of a percentage point. Typical acids used in these etchants are HF, HNO₃, H₃PO₄ and CH₃COOH. Ion chromatography with conductivity detection is a logical choice for assay procedures, since the anionic

species of each of these acids is readily analyzed by the technique.

One class of specialized etchants contains chromium trioxide (CrO₃) in combination with HF and HNO₃. Hexavalent chromium can be determined by ion chromatography and post-column reaction with 1,5-diphenylcarbohydrazide [1], but this procedure is specific for the chromium. The CrO₃ can be detected as chromate, using conductivity detection and an alkaline eluent; several researchers have investigated the analysis of chromate and other anions in various media [2–6]. No one, though, has attempted to assay chromium-containing acid mixtures on any of the currently available hydroxide-selective anion-exchange columns.

Consequently, this research was undertaken to evaluate two such separators from Dionex: the AS11

*Corresponding author. Tel.: +1-972-995-7541.

E-mail address: lynn.vanatta@airliquide.com (L.E. Vanatta)

and the AS16. Calibration studies were conducted, using both salt-based and acid-based standards. Then both columns were subjected to 200 injections of chromate (which is highly oxidative and will attack some resins) that was ten times normal concentration. The performances of the two columns under these various conditions were studied statistically and compared with each other. A Dionex DX500 microbore system with PeakNet software was used for this project. Statistical analyses were performed with JMP software.

2. Experimental

2.1. Materials

For all eluent and standard preparations, deionized (DI) water was provided by a point-of-use water-purification system (Ahlfinger Water, Dallas, TX, USA). Sodium hydroxide (50% w/w with $\leq 0.10\%$ sodium carbonate) from Fisher Scientific (Pittsburgh, PA, USA) was used to prepare 40 mM eluent solutions for both columns. The eluent and DI-water reservoirs were purged with helium via a "homemade" degas system; after preparation, all mobile phases were kept under pressure with helium throughout their life. For calibrations with salt-based standards, 1000-ppm (w/w) solutions of fluoride, nitrate and phosphate were obtained from National Institute of Standards and Technology (NIST) (Gaithersburg, MD, USA). For the calibration runs with acid-containing standards, Baker Analyzed 48–51% reagent HF and Baker Analyzed 69–71% reagent HNO₃ were obtained from VWR Scientific (West Chester, PA, USA); 10% (w/w) chromium trioxide in water was obtained from Lab Chem (Pittsburgh, PA, USA). Actual assay values of the acids were 49.0, 69.6 and 10.0%, respectively.

2.2. Apparatus and columns

A Dionex (Sunnyvale, CA, USA) DX500 microbore ion chromatograph with a rear-loading 9126 Rheodyne injection valve (Rheodyne L.P., Rohnert Park, CA, USA) was utilized for all work. Unless otherwise noted, all instrument modules and consumables were from Dionex Corporation. Two column

sets were employed: (1) an IonPac AG11 (50 mm \times 2 mm) with AS11 (250 mm \times 2 mm) and (2) an IonPac AG16 (50 mm \times 2 mm) with AS16 (250 mm \times 2 mm). A GP40 Gradient Pump mixed the eluent constituents (40 mM NaOH and DI water) for the gradient program (see Table 1) used with the AS11 column. A GP50 Gradient Pump mixed the eluent constituents (40 mM NaOH and DI water) in the ratio of 60:40 for the isocratic work on the AS16. The flow rate was 0.25 ml/min and the sample-loop size was 25 μ l on both columns. On both systems, post-column eluent suppression was accomplished with an Anion Self-Regenerating Suppressor (ASRS-Ultra, 2 mm) in the recycle mode; detection was via CD20 Conductivity Detectors at an output range of 10 μ S. Samples were introduced into the instruments via AS40 Automated Samplers, using 5-ml PolyVials with plain caps. All tubing in the chromatography path was polyether ether ketone (PEEK) (0.005 in (0.125 mm) I.D.).

Instrument control and data collection were performed with a personal computer and Dionex PeakNet software. Statistical calculations were carried out using JMP (SAS Institute, Cary, NC, USA) software.

2.3. Standards preparation

2.3.1. General

Polyethylene transfer pipets from Fisher were used to weigh out the various standards and to deliver small volumes of water. A Sartorius BP301S Analytical Balance (Sartorius, Edgewood, NY, USA) was used to prepare the sodium-containing standards; a Sartorius RC210D analytical balance (Sartorius), which was in a hood, was used to weigh out all acid-containing solutions. With both balances, masses were recorded to four decimal places. Each day

Table 1
Gradient program for AS11 column^a

Time (min)	Eluent 1 (%)	Eluent 2 (%)
0.0	25	75
3.6	25	75
5.6	50	50
15.2	25	75

^a Eluent 1: 40 mM NaOH. Eluent 2: Deionized water. Flow rate = 0.25 ml/min.

that standards were prepared and analyzed, they were done so in random order.

Dilution errors in the daily working standards were estimated by conducting a Monte Carlo simulation. This exercise was based on the upper bounds on the magnitude of weighing error for the scales (0.0001 g in each case). 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.

2.3.2. Salt-based standards

Salt-based standards were prepared in 4-oz (120 ml) polypropylene specimen containers from Fisher. Each day, a mixed standard (20 ppm in each analyte) was prepared from the individual NIST stock solutions and used to make 20 g of each working standard; see Table 2 for concentrations.

2.3.3. Acid-based standards

For this research, a simulated etchant–component ratio was used. For simplicity, roughly equal proportions of each bulk acid (i.e., the actual amount of the purchased acid, without regard to assay value) were chosen. Such a simulation would result in a mixture that contained approximately 16%, 23% and 3.3% of HF, HNO₃ and CrO₃, respectively, depending on the actual assay values.

All acid-based standards were prepared in HDPE narrow-mouth bottles (125 ml) (Nalge Nunc, Rochester, USA). (To guard against any light-induced degradation of solutions, brown bottles were used for the stock standards.) Stock standards (100 g of each, in DI water) were prepared in separate containers. These HF, HNO₃ and CrO₃ solutions contained 1.6716 g, 1.6587 g and 1.5121 g of the bulk acids, respectively; actual concentrations of each acid were 0.819%, 1.15% and 0.151%, respectively. Each day, a mixed standard was prepared by diluting 1.0054, 0.9849 and 0.9938 g of the HF, HNO₃ and CrO₃ stocks, respectively, to 100 g with DI water. From this solution, 20 g of each working standard was made, as shown in Table 2. The analyte concentrations in these 11 final preparations were typical of the working standards used in actual assay procedures. This dilution scheme was such that the numerical value of each concentration also equaled the percentage of the respective acid in a simulated etch.

2.3.4. Stress-testing solutions

For the stress testing, a 30-ppm solution of CrO₃ was prepared as needed from the 0.151% stock described in the previous section. Also prepared on Monday of the stress-testing week were the 11 working standards, both salt- and acid-based. These solutions were tested just before and just after the 200 concentrated chromate samples were chromatographed.

Table 2
Concentrations of working standards

Level	Salt-based standards		Acid-based standards			
	g mixed std ^a	ppm of each ion	g mixed std ^a	HF (ppm)	HNO ₃ (ppm)	CrO ₃ (ppm)
1	0.7	0.7	3.2	13.18	18.19	2.40
2	0.9	0.9	3.4	14.00	19.33	2.55
3	1.0	1.0	3.5	14.41	19.90	2.63
4	1.1	1.1	3.6	14.82	20.47	2.70
5	1.3	1.3	3.8	15.65	21.60	2.86
6	1.5	1.5	4.0	16.47	22.74	3.00
7	1.7	1.7	4.2	17.29	23.88	3.16
8	1.9	1.9	4.4	18.12	25.01	3.31
9	2.0	2.0	4.5	18.53	25.58	3.38
10	2.1	2.1	4.6	18.94	26.15	3.46
11	2.3	2.3	4.8	19.76	27.29	3.61

^a All dilutions were to 20 g. See Sections 2.3.2 and 2.3.3 for details on mixed-standard preparations.

3. Results and discussion

3.1. Calibration design

On each column, two calibration studies were conducted; each design contained 11 concentrations (or levels), which were prepared and analyzed on eight separate days. The first study utilized the common, salt-based, NIST-traceable standards and was conducted to assess the performance of the columns under typical conditions. The second evaluation used acid-based solutions and was performed to simulate a calibration curve for assaying etchants. Three anions were included in both studies: fluoride, nitrate and either phosphate (salt-based work) or chromate (acid-based tests). Phosphate was used in the initial study since it is a common anion with response and elution characteristics similar to those of chromate.

The various components of acid etches are held to tight specifications, usually to within 5% of the target (or within a few tenths of an absolute percentage, if the concentration itself is less than about 10%). To be able to detect small changes in concentration, any calibration curve must contain a sufficient number of levels, none of which exceeds the specification limits by very much. For both of these studies, the 11 dilutions were made from the appropriate mixed stock (see Table 2 for numbering scheme and actual concentrations). The design was a modified equi-spaced arrangement. Levels 3 and 9 represented the “specification limits” and were each in between two equally spaced concentrations. Since the specification limits are critical when assaying etchants, this design was chosen to allow more precise quantitation in those two regions. Level 6 represented the “target” concentration and was the mid-point of the design. Levels 1, 2, 10 and 11, which were outside the low and high limits, respectively, were included to allow determination of concentrations slightly below and above specifications.

3.2. Salt-based calibration studies

The studies were performed simultaneously on the AS11 and on the AS16, always using the same preparations of salt-based standards on both columns. The “target” concentration (1.5 ppm) was

chosen to assure adequate, but not undue, response from each anion. For a mid-level standard, an example chromatogram is shown in Fig. 1a for the AS11 column and in Fig. 1c for the AS16 column. Fluoride is retained longer on the AS16, while nitrate and phosphate elute in similar times, respectively, on the two separators.

Before the study was conducted, a model and a fitting technique were proposed for each anion's curve. Past experience suggested that a straight line with ordinary-least-squares (OLS) fitting was appropriate for nitrate and phosphate, but that a quadratic with OLS would be needed for fluoride.

After the chromatographic work was completed, statistical analysis of the data was conducted. The techniques used have been detailed earlier [7,8] and are not repeated here. However, terms and symbols are defined in Appendix A. Initial inspection of the scatterplots showed no irregularities, so all 88 points were used in each instance.

To determine the appropriateness of OLS fitting, a plot of standard deviation (of responses) vs. concentration was constructed for each anion on each column. The slope had a significant p -value for fluoride on both columns, and for phosphate on the AS11. Therefore, weighted least squares (WLS) was needed in those three cases. When the proposed model was tested with the appropriate fitting technique, the model was found to be adequate in all cases. R_{adj}^2 was above 0.997 for all plots and the p -values of each curve's coefficients were significant. The next-higher order always resulted in overfitting. Residual patterns were acceptable and a formal lack-of-fit test revealed no significant p -values. For the various analytes, the prediction intervals (for $\alpha = \beta = 0.025$) were similar (see Table 3). However, the values were slightly better for the AS11.

3.3. Acid-based calibration studies

These acid-based calibrations were also conducted simultaneously on both columns and were performed to simulate curves for assaying etchants. Example chromatograms of the “target” concentrations are shown in Figs. 1b (AS11 column) and 1d (AS16 column). These standards contained chromate (instead of phosphate), which is retained longer on the AS11 than on the AS16. This finding is not surpris-

ing, since the AS16 was designed to separate polarizable anions.

Models and fitting techniques again were proposed for the data before any analyses were performed. The same choices were made here as in the initial studies.

Inspection of these scatterplots (88 data points total) revealed atypically low responses from the AS11 for Level 9 on day 5. Since the phenomenon occurred for all three anions, it was concluded that a systematic problem had occurred during that injection. Consequently, that particular analysis was dropped from that dataset and (to keep all comparisons equal) from the AS16 set as well. The standard deviation of the responses was found to be constant in all cases, so OLS was the appropriate fitting technique. As before, the proposed models

were found to be appropriate. R_{adj}^2 was at least 0.996 for all curves except the CrO_3 on the AS16; that last value was 0.987. Residual patterns and lack-of-fit p -values also were acceptable. For each analyte, the prediction intervals (for $\alpha = \beta = 0.025$) again were similar on the two columns (see Table 3). However, as with the salt-based standards, the values were slightly better for the AS11.

3.4. Stress testing with concentrated chromate

3.4.1. Study protocols

Following the completion of the two calibration studies, both columns were subjected to 200 injections/analyses of 30-ppm CrO_3 , a concentration that was ten times the “target” level. These in-

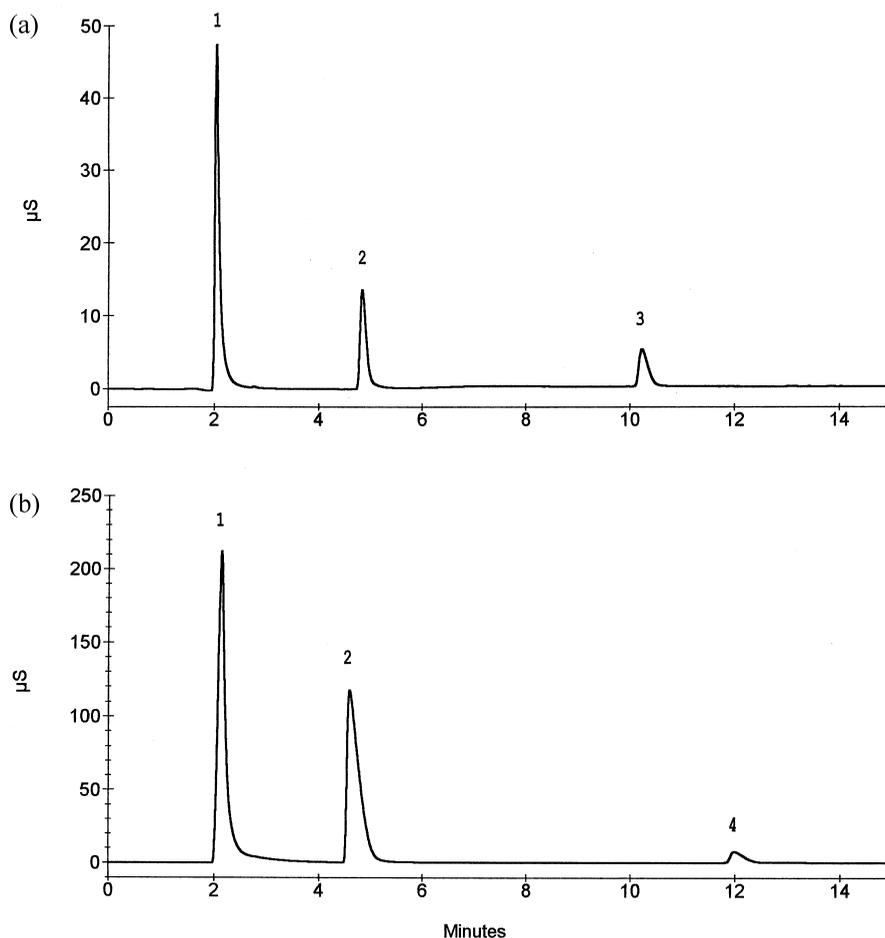


Fig. 1. Example chromatograms of mid-level standards: (a) salt-based, AS11; (b) acid-based, AS11; (c) salt-based, AS16; (d) acid-based, AS16. Peak identities: (1) fluoride, (2) nitrate, (3) phosphate and (4) chromate. Concentrations of the standards are those given for Level 6 in Table 2. Chromatographic conditions are those given in Section 2.2.

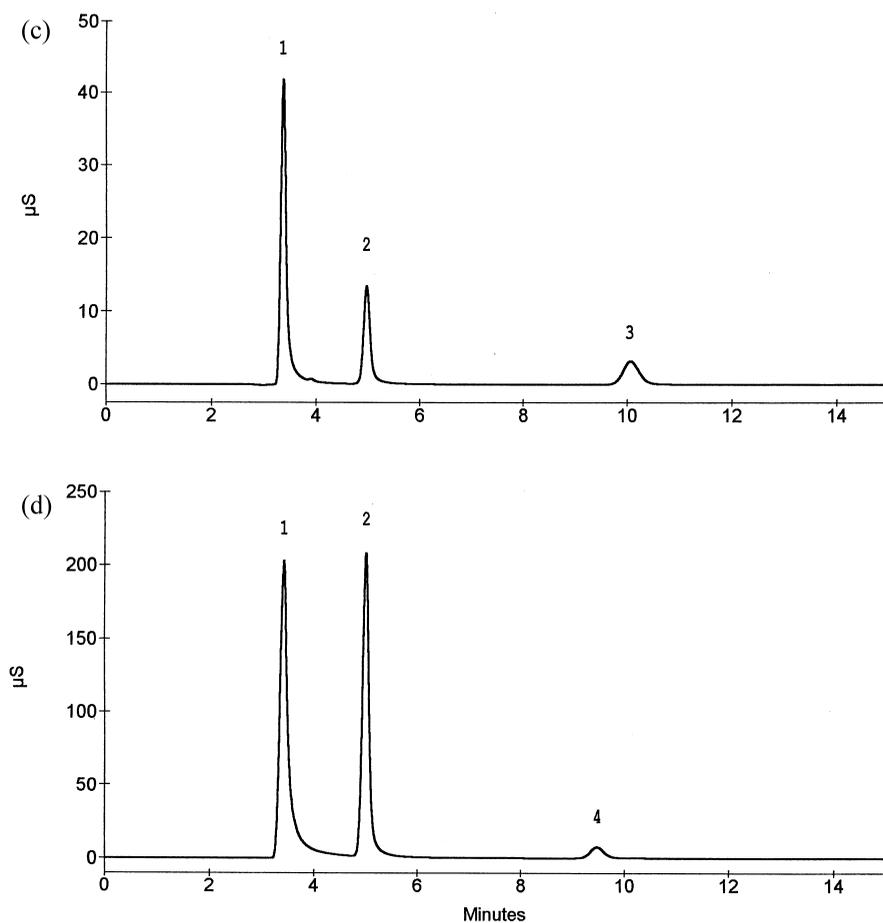


Fig. 1. (continued).

jections were made to see if either resin would degrade under such oxidative conditions. The testing began on a Monday morning and ended on the following Friday afternoon. The instruments were run continuously during that period. Both PeakNet method were set to the same run time (22 min each) so that the tests would start and end simultaneously.

At the beginning of the protocol, the 11 salt-based working standards were prepared and chromatographed, followed by the 11 acid-based working standards. These same 11 preparations were also run immediately after the stressing was completed. The “before” and “after” curves resulting from these analyses were used to evaluate the impact of the stress on the columns and their respective calibration

curves. Four different statistics were assessed: (1) prediction intervals, (2) retention times, (3) peak asymmetries and (4) peak width at half-height.

Since the entire objective of an assay method is to report measurements and their uncertainties, the width of the prediction interval is the most important of the four criteria. The other three statistics are more classical indicators of the condition of a column and are the basis of other evaluations (e.g., efficiency).

3.4.2. Effect of concentrated CrO_3 on the columns

As detailed in Table 4, the prediction interval was either unchanged or slightly less after the 200 concentrated injections. These data indicated that the

Table 3
Prediction intervals from the 88-point calibration studies

Column	Standard	Analyte	ppm ^a	±p.i. ^b
AS11	Salt	F	1.5	0.03
AS16	Salt	F	1.5	0.03
AS11	Salt	NO ₃	1.5	0.03
AS16	Salt	NO ₃	1.5	0.05
AS11	Salt	PO ₄	1.5	0.04
AS16	Salt	PO ₄	1.5	0.05
AS11	Acid	F	16.47	0.19
AS16	Acid	F	16.47	0.25
AS11	Acid	NO ₃	22.74	0.18
AS16	Acid	NO ₃	22.74	0.26
AS11	Acid	CrO ₃	3.00	0.05
AS16	Acid	CrO ₃	3.00	0.09

^a ppm: concentration of the middle standard (Level 6).

^b ±p.i.: the width of the plus-or-minus prediction interval (in ppm) at Level 6, with $\alpha = \beta = 0.025$. See Sections 3.2 and 3.3 for discussion of calibration models and diagnostics.

precision had not been affected adversely on either column.

Retention-time, peak-asymmetry and peak-width values are shown in Table 5. Post-stress retention times were either unchanged or within approximately 0.1 min of the initial averages; these differences were considered negligible.

All but one of the stress-related asymmetry values were within one standard deviation of the respective means from the large studies. The “outlier” was the “after” salt-based nitrate on the AS16; its asymmetry was 0.032 units greater than the one-standard-deviation limit of 1.432. All these data indicated that asymmetry was not affected adversely by the chromate stress.

As seen in Table 5, the peak widths remained virtually constant. These data also indicated that column performance was not degraded for either separator.

A small-scale stability study of acid-based working standards was performed to see if any changes occurred over a two-week period. Old and new solutions of four levels (1, 4, 6 and 9) were tested, each in triplicate. Fluoride showed no differences in any of the levels. However, nitrate and chromate peak areas rose in standards 4 and 6; the *p*-values for a *t*-test were less than 1% in each case. These findings indicated that the *y*-intercepts should not be compared for the “before” and “after” curves. For a particular application, either column might or might not have a different bias after long-term chromate exposure, and therefore might need recalibrating. However, the precisions remained acceptable and stable.

4. Conclusions

This research showed that the AS11 and AS16 columns are comparable for assaying HF/HNO₃/CrO₃ etchants. The peak shapes were more Gaussian for the AS16. However, the corresponding prediction intervals were essentially the same for the two columns. Such findings emphasize the importance of conducting statistically sound calibration studies. Lack of “pristine” chromatography does not necessarily mean that a particular method will afford

Table 4
Comparison of prediction intervals for calibrations performed before and after stress testing^a

Column	Std. type	Calibration	Fluoride ±p.i. ^b	Nitrate ±p.i.	Phosphate or chromate ±p.i.
AS11	Salt	Before	0.05	0.09	0.08
		After	0.05	0.04	0.02
AS16	Salt	Before	0.08	0.04	0.03
		After	0.01	0.04	0.02
AS11	Acid	Before	0.23	0.27	0.05
		After	0.17	0.14	0.02
AS16	Acid	Before	0.23	0.29	0.05
		After	0.23	0.15	0.04

^a Calibrations are the 11-point designs performed both before and after stress testing.

^b ±p.i.: the width of the plus-or-minus prediction interval (in ppm) at Level 6, with $\alpha = \beta = 0.025$.

Table 5

Comparison of retention time, peak width at half-height and peak asymmetry for calibrations performed before and after stress testing^a

Column	Std. type	Calibration	Fluoride			Nitrate			Phosphate or Chromate		
			Avg. t_R^b	Avg. Asy. ^c	Avg. PW ^d	Avg. t_R	Avg. Asy.	Avg. PW	Avg. t_R	Avg. Asy.	Avg. PW
AS11	Salt	Before	2.03	3.138	0.087	4.82	2.521 ^e	0.129	10.21	2.459	0.195
		After	2.06	2.755	0.085	4.82	2.604	0.133	10.14	2.547	0.193
AS16	Salt	Before	3.37	1.855	0.113	4.98	1.392	0.140	10.10	1.266	0.342
		After	3.37	1.937	0.113	4.99	1.464	0.140	10.22	1.274	0.340
AS11	Acid	Before	2.12	2.019	0.145	4.57	5.118	0.251	12.01	3.272	0.288
		After	2.13	1.895	0.143	4.56	4.969	0.251	11.90	3.255	0.283
AS16	Acid	Before	3.43	1.950	0.154	5.01	1.272	0.140	9.52	1.232	0.298
		After	3.43	1.942	0.152	5.01	1.287	0.140	9.44	1.241	0.290

^a Calibrations are the 11-point designs performed both before and after stress testing.^b t_R = average retention time for the 11 standards used in each calibration set.^c Avg. Asy. = average peak asymmetry for the 11 standards used in each calibration set.^d Avg. PW = average peak width at half-height for the 11 standards used in each calibration set.^e For Avg. Asy. and Avg. PW, emboldened numbers indicate "After" value was greater than "Before" value.

unacceptable results. Conversely, "textbook" chromatography alone does not assure superior precision.

Additionally, both columns were able to withstand repeated (200) chromate injections of 30 ppm, which was ten times normal concentration. Prediction intervals, retention times, peak asymmetries and peak widths for all analytes remained basically unchanged after such exposure. Both columns were found to be rugged enough for long-term tolerance of these oxidative etchants.

Acknowledgements

The authors would like to acknowledge Ruthann Kiser and Navette Shirakawa of Dionex Corporation for their advice regarding column selection; Nancy Grams, Ray Maddalone, Robert Gibbons and Jim Rice for their useful contributions in developing the interdisciplinary analytical–statistical methods.

Appendix A

Mathematical symbols used

α : average probability of false positives.

b : slope of calibration curve.

β : average probability of false negatives.

R_{adj}^2 : 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 used

Lack-of-fit (LOF) test: a test of the statistical significance of the residual variation that is above and beyond that attributable to pure error.

Null hypothesis: usually, the hypothesis that the investigator is attempting to disprove, at a specified level of confidence. Note that lack of rejection does not prove the hypothesis.

OLS: ordinary least squares. A fitting technique that minimizes the sum of squares of the residuals.

Peak asymmetry at 10%: a measure of the quality of peak shape. Is calculated as width of the back of the peak divided by width of front of the peak. To measure widths, draw a line from the top of the peak perpendicular to the baseline; draw a horizontal line at 10% peak height; from the intersection of these two lines, measure the horizontal distance to the back and to the front of the peak. Also known as skew factor.

Peak width at half height: the width of the peak at a distance that is halfway up the height of the peak.

Prediction interval (p.i.): a pair of limits that bracket the uncertainty in one future measurement.

p-value: the probability value associated with a statistical test, representing the likelihood that a test statistic would assume or exceed a certain value, if the null hypothesis is true.

Residual: the actual (measure) value minus the predicted value.

Statistically significant: causing a null hypothesis to be rejected at some accepted confidence level.

WLS: weighted least squares. Same methodology as OLS, except weights are incorporated to account for non-constant response variation.

References

- [1] Technical Note No. 26, Dionex, Sunnyvale, CA, 1988.
- [2] Technical Note No. 24, Dionex, Sunnyvale, CA, 1987, p. 5.
- [3] A.V. Pirogov, O.N. Obrezkov, O.A. Shpigun, J. Anal. Chem. (Transl. of Zh. Anal. Khim.) 52 (1997) 152.
- [4] C. Umile, J.F.K. Huber, Talanta 41 (1994) 1101.
- [5] D. Cao, Sepu 8 (1990) 56.
- [6] S. Sopok, J. Chromatogr. A 671 (1994) 265.
- [7] L.E. Vanatta, D.E. Coleman, J. Chromatogr. A 770 (1997) 105.
- [8] L.E. Vanatta, D.E. Coleman, J. Chromatogr. A 850 (1999) 107.