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APPLICATION NOTE 119

Determination of an anionic fluorochemical surfactant in a semiconductor etch bath

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Introduction

Perfluorinated surfactants are used as wetting agents in semiconductor acid etching solutions. Acid etching engraves fine patterns in silicon dioxide. Poor wetting of the wafer surface by the acid etchant during semiconductor device fabrication can result in air entrapment through the formation of small bubbles. These bubbles can mask a portion of the area to be etched, which can result in bridging over of the fine openings in the resistor surface. This can create electrical shorts in the device. The addition of a small amount of surfactant can eliminate air entrapment by improving the wetting properties of the solution.

An anionic fluorochemical surfactant (FC-93), stable in both acidic and alkaline solutions, was analyzed in this Application Note. Solutions containing perfluorocarbon surfactants have very low surface tensions. A uniform etch with sharp detail can be made using this type of surfactant. The elimination of air entrapment and the stability of the surfactant leads to an extended life of the etch solution. Due to the high price of fluorinated surfactants, it is important to have an analytical method that can measure these surfactants at low mg/L (ppm) concentrations.

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This Application Note describes the techniques, instrumentation, and method for determining low mg/L (ppm) amounts of the fluorochemical surfactant FC-93 in an etch bath (1 part hydrofluoric acid/6 parts ammonium fluoride) by ion chromatography. The surfactant is removed from the HF matrix by passing the sample through a Thermo Scientific™ Dionex™ IonPac™ NG1 column. The Dionex IonPac NG1 column is a polymeric, reversed-phase column that quantitatively retains the surfactant but does not retain inorganic anions. The concentrated surfactant is then eluted from the Dionex IonPac NG1 column onto a Thermo Scientific™ OmniPac™ PAX-500 column set. The OmniPac PAX-500 column contains a polymeric anion-exchange stationary phase that exhibits both reversed-phase and ion-exchange retention characteristics.[1] The surfactant is separated using the OmniPac column set with an eluent containing sodium hydroxide and acetonitrile. The surfactant is detected by chemically-suppressed conductivity detection.

Esperimental

Equipment

- Thermo Scientific™ Dionex™ DX-500 Ion Chromatography system* consisting of:
  - GP40 Gradient Pump
  - CD20 Conductivity Detector
  - LC20 Chromatography Enclosure equipped with a rear-loading injection valve
  - Rinsing Pump, DQP
  - LC10 Chromatography Organizer equipped with a rear-loading injection valve

* Equivalent or improved results can be achieved using the Thermo Scientific™ Dionex™ ICS-5000+ HPIC™ system.

- 4 L Plastic bottle (for DI water rinsing solution)
- 4 L Plastic bottle assemblies (for external water mode)
- Thermo Scientific™ Dionex™ PeakNet™ Chromatography Workstation

Reagents and standards

- Deionized water (DI H_2O), Type I reagent grade, 18 MΩ·cm resistance or better
- Sodium hydroxide, 50% (w/w) aqueous solution (Fisher Scientific™ or equivalent)
- Acetonitrile, HPLC grade (OmniSolv® or equivalent)
- Fluorochemical surfactant FC-93 (3M® Corporation)
- Etch bath (HF/NH_4F) (Ashland™ Chemical)

Conditions

Concentrator Column:	Dionex IonPac NG1 Guard, 4 × 50 mm (P/N 39567)
Analytical Columns:	OmniPac PAX-500 Analytical, 4 × 250 mm (P/N 042152) OmniPac PAX-500 Guard, 4 × 50 mm (P/N 042153)
Eluents:	A: 20 mM Sodium hydroxide B: Acetonitrile
Eluent Composition:	55% A/45% B
Eluent Flow Rate:	1 mL/min
Rinsing Reagent:	Deionized water
Rinsing Flow Rate:	2 mL/min
Rinse Time:	20 min
Total Run Time:	30 min
Sample Volume:	100 µL
Detection:	Suppressed conductivity, Thermo Scientific™ Dionex™ ASRS™ (4 mm), AutoSuppression™ external water mode
System Backpressure:	1500–2000 psi (10.3–13.8 MPa)
Conductivity Background:	0.3–3 µS

Pump Program:

Time	*%A*	*%B*	*Valve 1*	*Valve 2*	*Remarks*
Initial	55	45	load	inject	
0.0	55	45	load	load	Fill sample loop
1.1	55	45	inject	load	Sample to NG1
20.5	55	45	load	inject	Begin sampling*
30.0	55	45	load	inject	Finish sampling

* Begin sampling refers to data collection (the NG1 column is switched in-line with the OmniPac columns).

Preparation of solutions and reagents

Standard solutions

Stock Surfactant Standard Solution (1,000 mg/L)
Dissolve 4.15 g of surfactant in 1,000 mL of deionized water and store at room temperature.

Calibration Standard Solutions
Appropriate calibration standards are prepared from the 1,000 mg/L standard above. Select a range similar to the expected analyte concentrations in the samples. These standards can be prepared in water.

Eluent solutions

Deionized Water, Type I reagent grade, 18 MΩ·cm resistance or better
Vacuum-degas 2 L of deionized water in a clean bottle while sonicating for 5 minutes.

Eluent A: 20.0 mM Sodium Hydroxide
Weigh 998.4 g of deionized water into an eluent bottle. Degas for approximately 5 minutes. Tare the bottle and carefully add 1.6 g of 50% sodium hydroxide directly to the bottle. Mix and quickly transfer the eluent bottle to the instrument and pressurize the bottle with helium.

Eluent B: Acetonitrile
Add 1 L of acetonitrile into an eluent bottle and degas for approximately 5 minutes. Quickly transfer the eluent bottle to the instrument and pressurize the bottle with helium.

Note: Because acetonitrile is not stable for more than a day in base (it forms ammonia and acetate), the sodium hydroxide and acetonitrile should be kept in separate bottles and mixed by the pump. Wash the system for 30 minutes with water prior to shutting down the system or longer than one night.

Caution: Exercise extreme caution when handling HF samples. Always wear gloves and a lab coat. To dilute the sample, add acid to water. If contact is made, a 2.5% calcium gluconate gel should be applied to affected skin areas.

System operation

System configuration and operation parameters for this application are outlined in previously published documents.[2,3]

The sensitive analysis of the fluorochemical surfactant in an acid (HF) etch bath is accomplished in four steps: (1) fill the sample loop, (2) load the concentrator column, (3) eliminate the HF matrix, and (4) separate the surfactant. Figure 1 shows how the system performs these tasks. In Figure 1A, the system is in the standby mode, ready for sample analysis. In Figure 1B, Rheodyne® Valve 2 is switched to the load position. The sample is loaded with a syringe into the 100 µL sample loop on Rheodyne Valve 1.

Sample handling

When using a syringe, the black rubber plunger in disposable plastic syringes can be a source of contamination. To minimize the introduction of sample contamination, pull rather than push the sample into the loop, as shown in Figure 1A. Be sure to pull slowly so that bubbles will not be introduced. The loop should be overfilled by at least 3 times its capacity (> 300 µL) to ensure reproducible results.

Matrix elimination

After the sample loop is filled, deionized water from the DQP transfers the sample out of the loop and onto the NG1 concentrator column in the opposite direction of the eluent. Surfactant is retained on the concentrator column.

The HF matrix is removed from the Dionex NG1 column by rinsing with deionized water from the DQP at 2 mL/min (DQP head pressure should be at least 100 psi.) for 20 minutes (See Figure 1C). Finally, activating the Rheodyne Valve 2 to the inject position switches the Dionex NG1 column in-line with the eluent stream and the analytical columns. The surfactant is then eluted from the Dionex NG1 cplumn in the reverse direction of the concentration step and separated on the Dionex OmniPac columns, as shown in Figure 1D.

Special care should be taken to minimize contamination. The deionized water used for preparing the rinse solution, eluent, and standards should be free of measurable levels of ionic impurities, organics, microorganisms, and particulate matter larger than 0.2 µm.

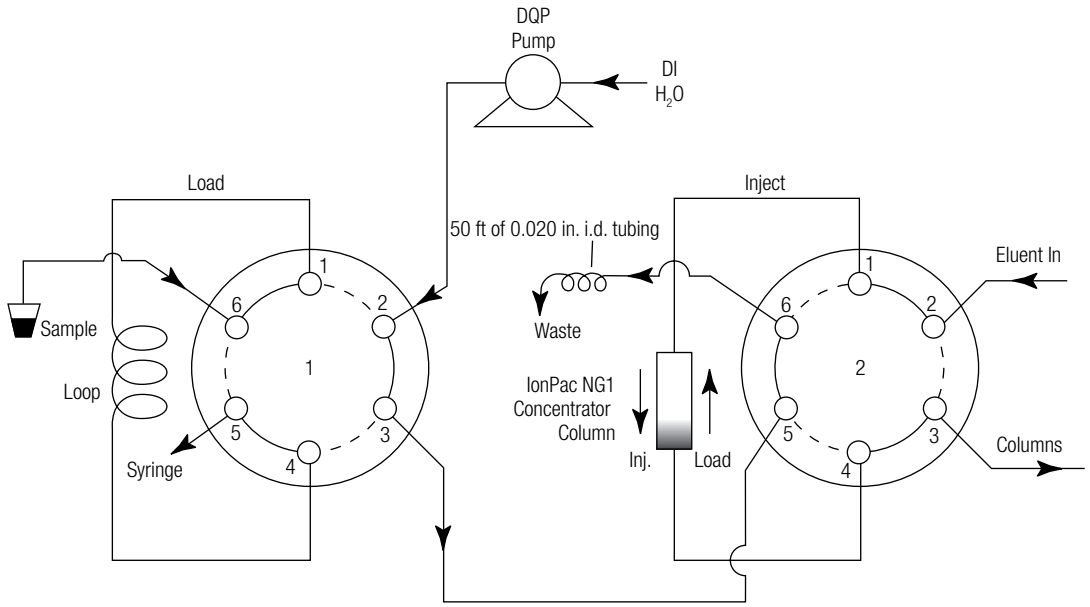

Figure 1A. Initial conditions.

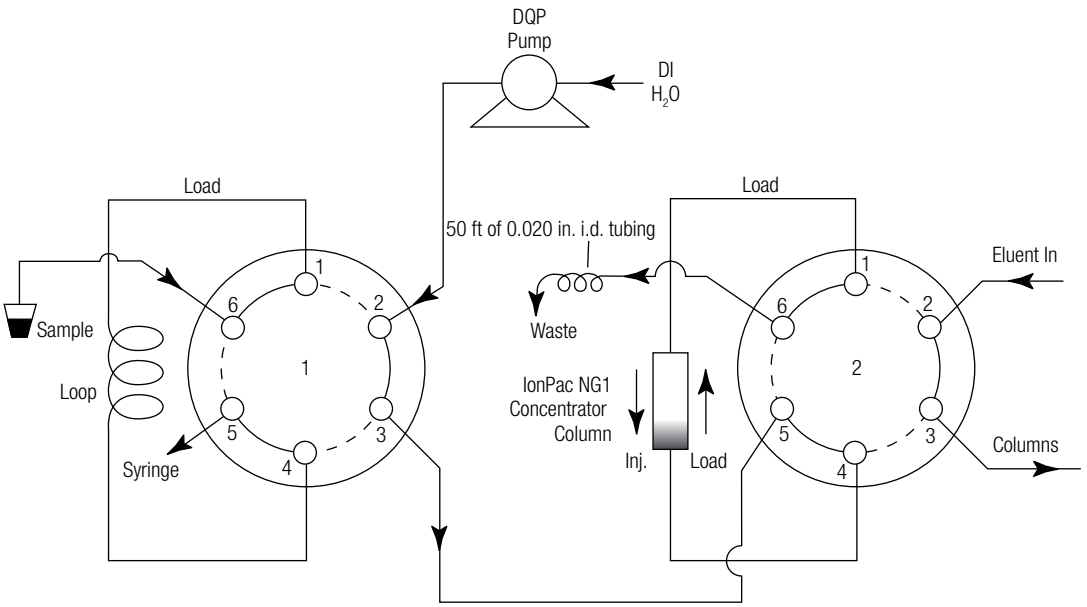

Figure 1B. Loading the sample loop. Time: 0–1.10 min.

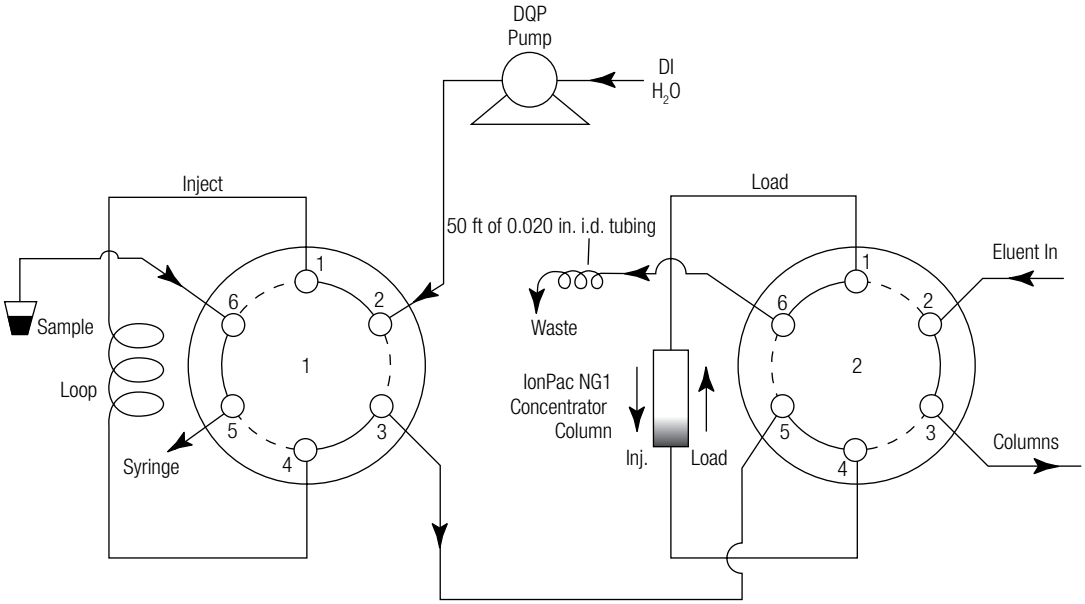

Figure 1C. Loading the concentrator column and eliminating the matrix. Time: 1.10–20.5 min.

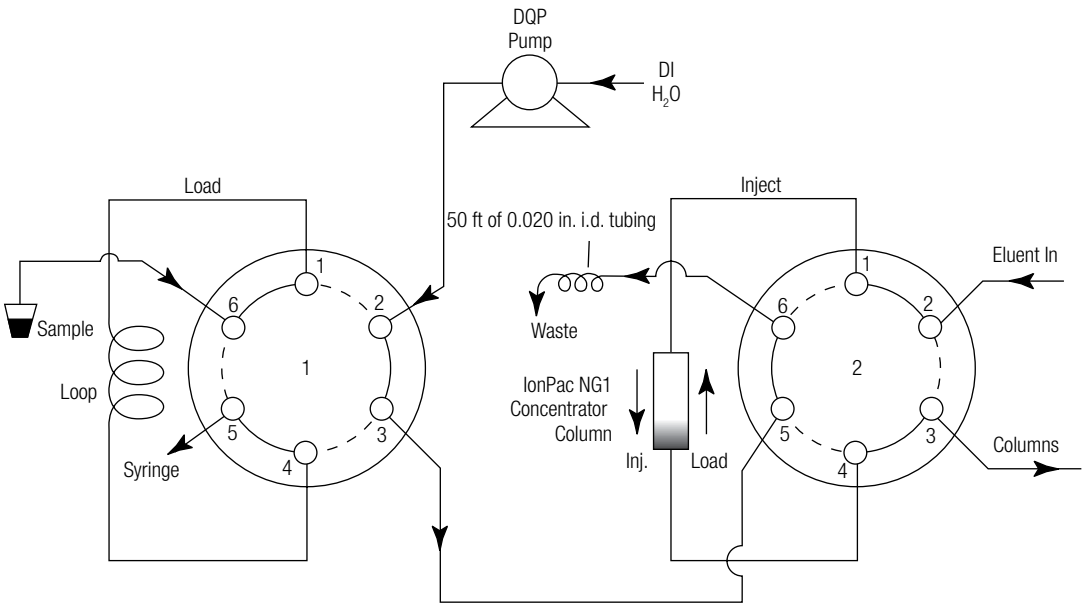

Figure 1D. Chromatography of the retained surfactant. Time: 20.5–30.0 min.

Results and discussion

For the best performance at low mg/L levels, it is critical that baseline noise be kept to a minimum. An equilibrated system will demonstrate a conductivity background between 0.3–3 µS. Peak-to-peak noise is typically 10 nS and system backpressure is 1,500–2,000 psi (10.3–13.8 MPa). A system blank is determined by using deionized water as the sample. The blank establishes the baseline and confirms the lack of contamination in the system. It is especially important to ensure that the system is free of carryover after multiple sample injections containing high concentrations of surfactant.

Despite washing the Dionex NG1 column for 20 minutes with deionized water to eliminate the etch bath matrix, detectable levels of fluoride elute from the NG1 to the Dionex OmniPac columns (see Figure 2). This amount of fluoride is greatly reduced during the long wash so that it does not interfere with surfactant detection. Shorter wash times (less than 20 minutes) were investigated and proven to be insufficient for rugged chromatography. The best way to control the retention time of the surfactant is by small adjustments to the percentage of acetonitrile in the eluent. Lowering the amount of acetonitrile by 5% will add at least 5 minutes to the surfactant retention.

Concentrator Column:	Dionex IonPac NG1 Guard, 4 × 50 mm
Analytical Columns:	Dionex OmniPac PAX-500 Analytical, 4 × 250 mm Dionex OmniPac PAX-500 Guard, 4 × 50 mm
Eluents:	A: 20 mM Sodium hydroxide B: Acetonitrile
Eluent Composition:	55% A/45% B
Eluent Flow Rate:	1 mL/min
Rinsing Reagent:	Deionized water
Rinsing Flow Rate:	2 mL/min
Rinse Time:	20 min
Run Time:	10 min
SampleVolume:	100 µL
Detection:	Suppressed conductivity, Dionex ASRS (4 mm), Dionex AutoSuppression external water mode
Peaks:	1.System peak 2. System peak 3. Fluoride 4. Unknown

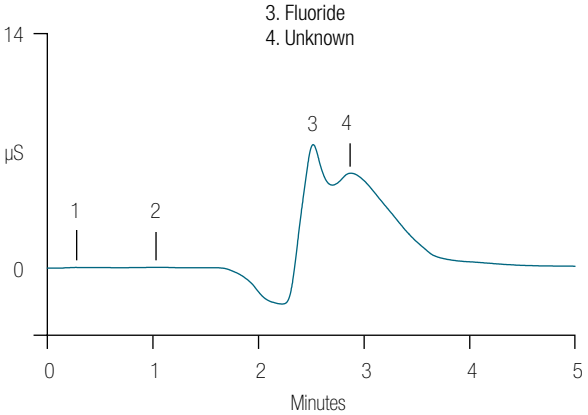

Figure 2. Etch bath blank.

In order to minimize peak broadening and maximize peak efficiency, it is advisable to separate the surfactant on the analytical column in the first 10 minutes of the run. In order to achieve the 5 mg/L (ppm) detection limit, a 100 µL sample volume is concentrated on the Dionex NG1 concentrator column (see Figure 3). Lower detection limits are possible with increased loop size. This change may require a longer wash time to minimize the break through of fluoride.

Concentrator Column:	Dionex IonPac NG1 Guard, 4 × 50 mm
Analytical Columns:	Dionex OmniPac PAX-500 Analytical, 4 × 250 mm Dionex OmniPac PAX-500 Guard, 4 × 50 mm
Eluents:	A: 20 mM Sodium hydroxide B: Acetonitrile
Eluent Composition:	55% A/45% B
Eluent Flow Rate:	1 mL/min
Rinsing Reagent:	Deionized water
Rinsing Flow Rate:	2 mL/min
Rinse Time:	20 min
Run Time:	10 min
SampleVolume:	100 µL
Detection:	Suppressed conductivity, Dionex ASRS (4 mm Dionex AutoSuppression external water mode
Peaks:	1.System peak 2. System peak 3. Fluoride 4. Unknown 5. Surfactant

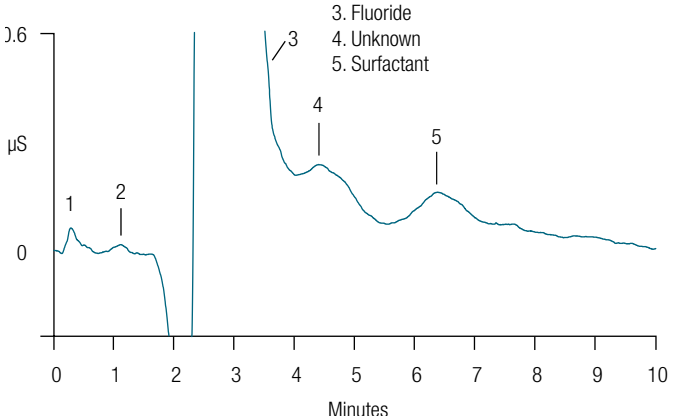

Figure 3. 5 mg/L (ppm) surfactant in an etch bath.

Five injections of the same 5 mg/L (ppm) concentration standard in the etch bath were made to determine area counts and retention time reproducibility.

The data presented in Table 1 show that 5 mg/L (ppm) of surfactant can be easily detected and quantified in an etch bath. No significant variation in retention time was observed.

Table 1 Area counts and retention time reproducibility.

Injection #	Area	Retention Time (min)
1	29,699	6.37
2	29,580	6.27
3	29,516	6.20
4	29,492	6.42
5	29,839	6.08
Average	29,625	6.27
%RSD	0.49	2.16

A linear concentration range was established to accurately quantify the surfactant in the 5–15 mg/L (ppm) range. Figure 4 shows a representative chromatogram for a 15 mg/L (ppm) surfactant. Figure 5 shows the results of linearity analysis.

Concentrator Column:	Dionex IonPac NG1 Guard, 4 × 50 mm
Analytical Columns:	Dionex OmniPac PAX-500 Analytical,4 × 250 mm Dionex OmniPac PAX-500 Guard, 4 × 50 mm
Eluents:	A: 20 mM Sodium hydroxide B: Acetonitrile
Eluent Composition:	55% A/45% B
Eluent Flow Rate:	1 mL/min
Rinsing Reagent:	Deionized water
Rinsing Flow Rate:	2 mL/min
Rinse Time:	20 min
Run Time:	10 min
SampleVolume:	100 µL
Detection:	Suppressed conductivity, Dionex ASRS (4 mm), Dionex AutoSuppression external water mode
Peaks:	1.System peak 2. System peak 3. Fluoride 4. Unknown 5. Surfactant

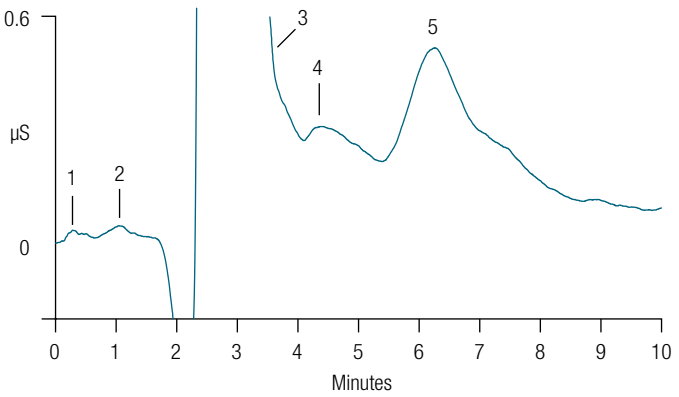

Figure 4. 15 mg/L (ppm) surfactant in an etch bath.

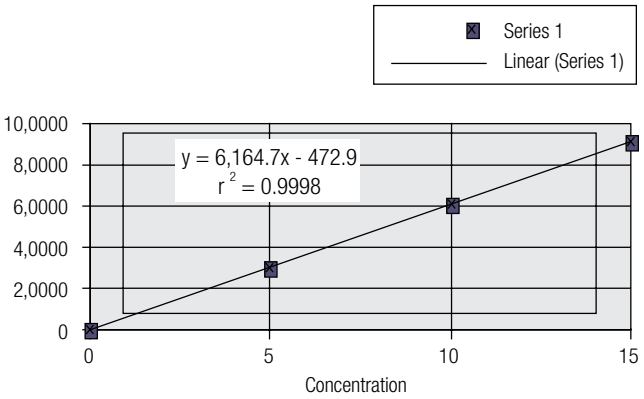

Figure 5. Linear concentration study of surfactant in an etch bath.

Detection of this surfactant is linear in the low-ppm (mg/L) range. The same response factor was demonstrated for standards prepared in etch bath or deionized water. Similar results were obtained for an etch bath composition of 1 part HF to 500 parts NH_4F.

Summary

The method outlined in this Application Note accurately quantifies low mg/L (ppm) amounts of an anionic fluorochemical surfactant in acid etch bath samples by using an on-line matrix elimination technique.

References

1. Thermo Scientific, OmniPac Guidebook (P/N 34517).
2. Thermo Scientific, "Determination of Trace Anions in Isopropyl Alcohol", Application Note 85.
3. Kaiser, E.; Wojtusik, M. J. *J. Chromatogr. A.* **1994,** *671,* 253–258.

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