DIONEX

Application Update 139

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Determination of an Anionic Fluorochemical Surfactant (FC-95) in a Steel Bath

INTRODUCTION

In the chemical milling process, perfluorinated surfactants are used as wetting agents in acid etching solutions. Chemical milling is a method of processing metal parts by controlled chemical etching. This process either thins the metal in specific areas or removes the metal from all surfaces. Poor wetting of the metal by the acid etchant during milling can result in the formation of small bubbles that trap air or hydrogen. These bubbles cause the surface of the metal part to become rippled and irregular, and can ultimately result in the rejection of the part. The addition of a small amount of surfactant can eliminate gas entrapment by improving the wetting properties of the solution.[1]

FC-95 is an anionic fluorosurfactant of exceptional chemical and thermal stability, and is particularly useful as a wetting and anti-foaming agent in acidic solutions. FC-95 is also stable and effective in strongly oxidizing and reducing media. This type of surfactant is unique in that it is stable and active in environments that destroy conventional surfactants. Due to the high price of fluorinated surfactants, it is important to have an analytical method that can measure them at low part-per-million (ppm) concentrations.

This Application Update describes a method for determining low ppm amounts of FC-95 in a steel bath (concentrated hydrofluoric, hydrochloric, and nitric acids with 200 g/L each of iron, chromium, and nickel) by ion chromatography. The method described in this Update is similar to that described in AN 119.[2] The surfactant is removed from the acidic matrix and concentrated on an IonPac® NG1 column. The concentrated surfactant is then eluted from the IonPac NG1 column onto an OmniPac® PAX-500 column set and detected by suppressed conductivity.

EQUIPMENT

Dionex DX-500 Ion Chromatography system consisting of:
- GP40 Gradient Pump
- CD20 Conductivity Detector
- LC20 Chromatography Enclosure equipped with a rear-loading Rheodyne injection valve
- Rinsing Pump, DQP (P/N 35250)
- LC10 Chromatography Organizer equipped with a rear-loading Rheodyne injection valve

2-L Plastic bottle (for the 20 mM sodium hydroxide rinsing solution)

4-L Plastic bottle assemblies (for external water mode)

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 other)

Acetonitrile, HPLC grade (OmniSolv® or other)

Fluorochemical surfactant, FC-95 (3M Corporation)

Steel Bath: concentrated hydrofluoric, hydrochloric, and nitric acids with 200 g/L each of iron, chromium, and nickel (Aerochem, Inc.)

CONDITIONS

Concentrator Column:	IonPac NG1 Guard, 4 x 50 mm (P/N 39567)
Analytical Columns:	OmniPac PAX-500 Analytical, 4 x 250 mm (P/N 42152) OmniPac PAX-500 Guard, 4 x 50 mm (P/N 42153)
Rinsing Reagent:	20 mM Sodium hydroxide
Eluents:	A: 20 mM Sodium hydroxide B: Acetonitrile
Eluent Composition:	55% A/ 45% B
Rinse Time:	20 min
Rinse Flow Rate:	2 mL/min
Total Run Time:	35 min
Flow Rate:	1 mL/min
Sample Volume:	100 µL
Detection:	Suppressed conductivity, ASRS®-II (4 mm), AutoSuppression® external water mode
System Backpressure:	10.3–13.8 MPa (1500–2000 psi)
Background Conductance:	1–4 µS

PREPARATION OF SOLUTIONS AND REAGENTS

Standard Solutions

Stock surfactant solution (100 mg/L)

Dissolve 0.6725 g of surfactant in 1 L of deionized water.

Calibration Standards

Prepare calibration standards as shown in Table 1.

Table 1 Preparation of surfactant standards in steel bath

Concentration (mg/L)	Stock Solution (mL)	Steel Bath (mL)
10	10	90
25	25	75
50	50	50

Rinsing Solution

20 mM Sodium hydroxide

Weigh out 998.4 g of deionized water in the eluent container and vacuum degas for 5 min. Add 1.6 g of 50% sodium hydroxide concentrate and blanket under helium at 8 psi.

Eluent Solutions

Eluent A: 20 mM Sodium hydroxide

Weigh out 998.4 g of deionized water in the eluent container and vacuum degas for 5 min. Add 1.6 g of 50% sodium hydroxide concentrate and blanket under helium at 8 psi.

Eluent B: Acetonitrile

Add 1 L of acetonitrile into an eluent bottle and degas for approximately 5 min. 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 a shut down that will be longer than one night.

Steel Bath Composition

Hydrofluoric, hydrochloric, and nitric acids with 200 g/L each of chromium, iron, and nickel.

SYSTEM OPERATION

System operation parameters are described in Application Note 119.

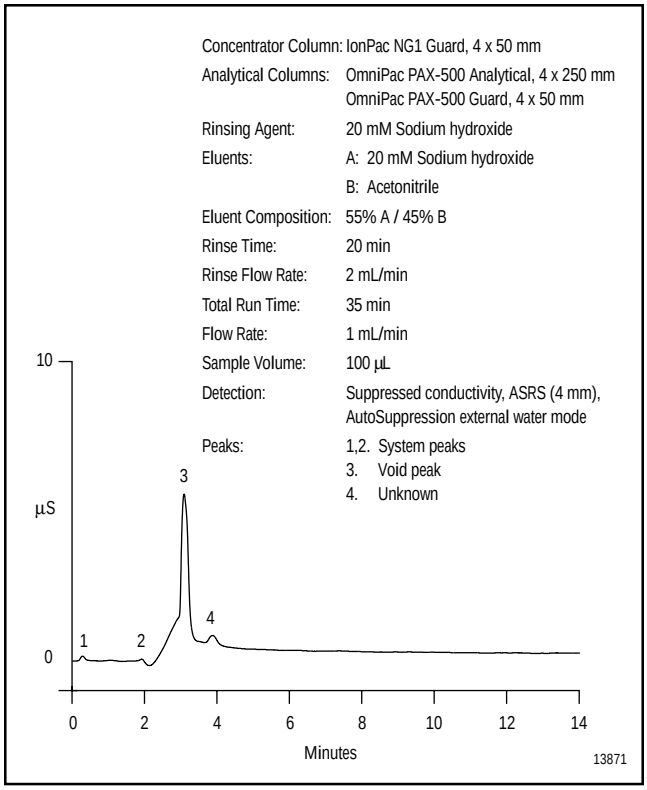

Figure 1 *Water blank*

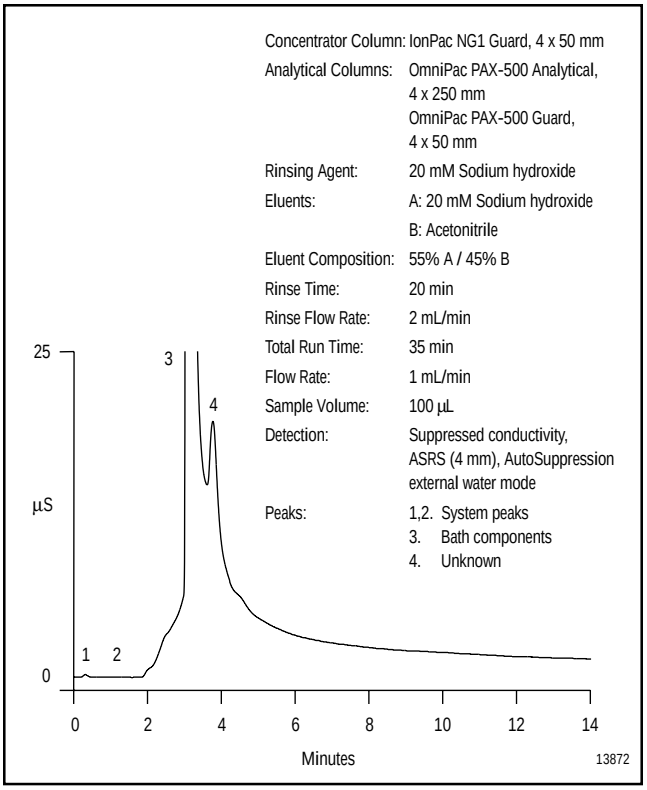

Figure 2 *Bath blank*

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 1 to 4 µS. Peak-to-peak noise is typically 5 nS and system backpressure is 1500–2000 psi. A system blank is determined by using deionized water as the sample. This blank establishes the baseline and demonstrates a lack of contamination in the system (Figure 1). It is especially important to prove that the system is free of carryover after injecting samples with high surfactant concentrations.

The IonPac NG1 is a polymeric, reversed-phase column that quantitatively retains surfactant but does not retain inorganic anions. The concentrated surfactant is then eluted from the IonPac NG1 onto an 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. The surfactant is separated using the OmniPac column set with an eluent containing sodium hydroxide and acetonitrile.

Sodium hydroxide (20 mM) was used to wash the NG1 column, reducing the amount of bath components that eluted onto the OmniPac columns. Despite washing the NG1 column for 20 minutes with a 20 mM sodium hydroxide solution to eliminate the steel bath matrix, some components of the bath may break through to the OmniPac columns and elute in the void volume (Figure 2). During a long wash, the amount of components in the void volume is greatly reduced so they do not interfere with surfactant detection. Shorter wash times (less than 20 minutes) were investigated, but proved to be insufficient for rugged chromatography. Seven injections of the steel bath sample with 10 ppm of FC-95 were made to determine area count and retention time reproducibility (see Table 2). No significant variation in retention time or peak area were observed, indicating that 10 ppm of surfactant can be easily detected and quantified in the steel bath.

Figure 3 shows a typical chromatogram of 25 ppm of surfactant detected in the steel bath. A linear concentration range was established to accurately quantify the low ppm range of surfactant in the steel bath. Figure 4 shows the results of linearity analyses. Detection of FC-95 in the steel bath is linear between 10 to 50 ppm.

Table 2 Area count and retention time reproducibility

Injection #	Area	Retention Time
1	590329	7.43
2	581930	7.57
3	585159	7.55
4	584119	7.52
5	588249	7.60
6	591020	7.52
7	589390	7.57
Average	587175	7.54
SD	3454	0.06
% RSD	0.59	0.73

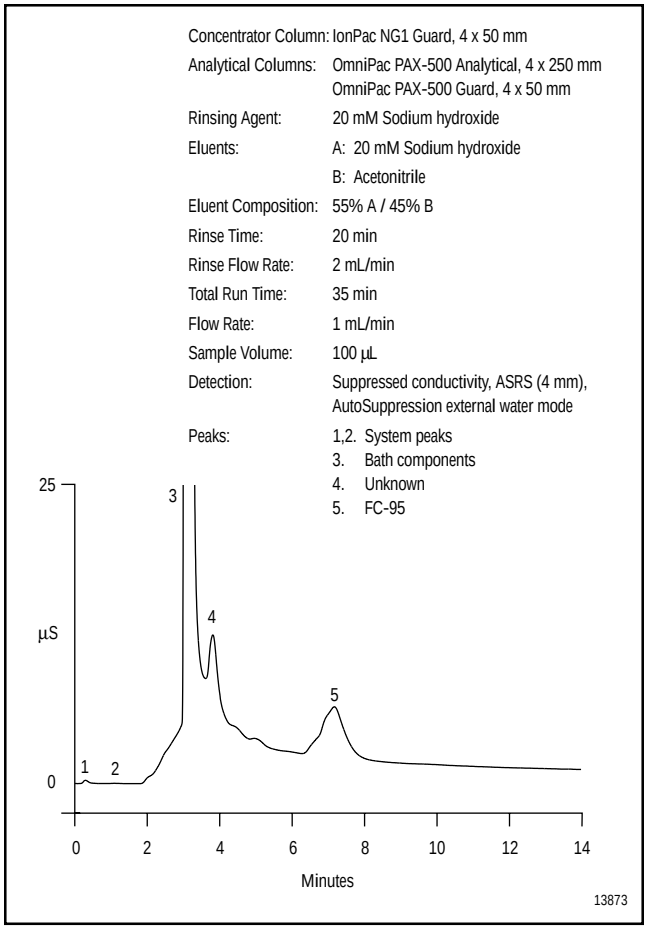

Figure 3 *25 ppm FC-95 in steel bath*

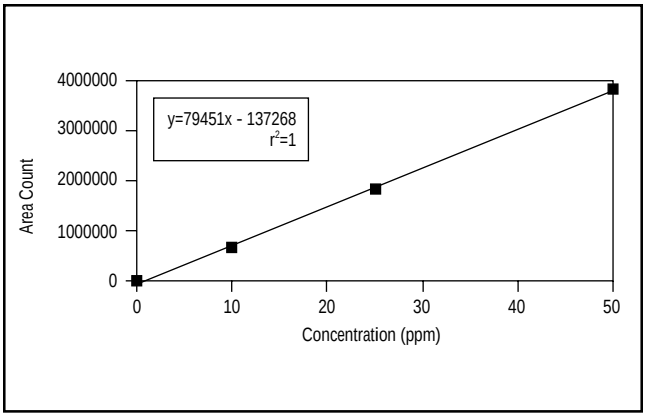

Figure 4 *Linear concentration study of FC-95 in steel bath*

REFERENCES

1. Eugene M. Langworthy, Aerochem, Inc. Metals Handbook, AS for Metals, 9th Ed., Volume 16.
2. Dionex Corporation, Application Note 119, "Determination of an Anionic Fluorochemical Surfactant in a Semiconductor Etch Bath".

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