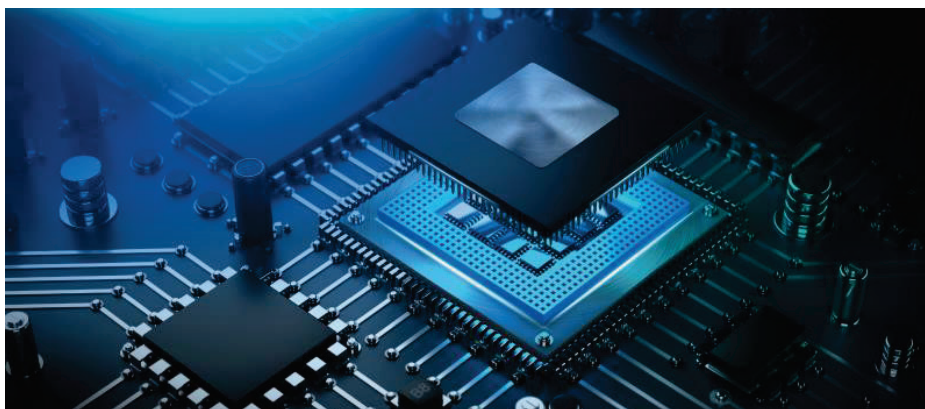**Agilent**

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Analysis of Photo Acid Generator Leaching (PAG leaching) in Photoresist using Agilent Liquid Chromatography Tandem Time-of-Flight Mass Spectrometer System (Agilent 1290 Infinity II LC/6546 Q-TOF MS)

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Abstract

In this application note, the Agilent 1290 Infinity II LC/6546 Q-TOF MS system was used for qualification and quantification on the components of photo acid generators (PAGs) leaching in photoresist. The instrument demonstrated high efficiency and excellent accuracy. Through the differential analysis workflow, sample class differences can be quickly found by using Mass ProFinder software. Either Molecular Structure Correlator (MSC) and Sirius can be used for rapid structure analysis and confirmation of unknowns.

Introduction

Lithography plays a crucial role in semiconductor fabrication. Line width limitations and accuracy determine the overall chip reliability, the degree to which components can be integrated, and costs of integrated circuits. Besides lithography machines, the property of photoresist is key to precision and yield rate. The cost of photoresist accounts for about 35% of the entire cost of IC fabrication.

The size of devices on IC chips is characterized by process nodes. Photoresists are divided into g-line (436 nm), I-line (365 nm), KrF (248 nm), ArF (193 nm), EUV (13.5 nm) according to the light wavelength. Currently ArF lithography technology (Argon fluoride laser) is the mainstream lithography technology, which includes dry lithography and immersion lithography. The latter one has been widely used in the mass production of 65 nm node or lower. It is also considered by the industry to be the most competitive technology for lithographic process of 32 nm or lower, even to 7nm node.

The main challenges of immersion lithography are defects such as bubbles and contamination generated during exposure. Thus ultrapure water is used as the liquid medium, in which both the lithography lens and the photoresist are immersed, the lithographic resolution is enhanced effectively through increasing the refractive index. But this has strict requirements on the quality of photoresist. As the main active component of photoresist — the photo acid generator (PAG) may leach into the medium then damage the lens, the lens have to be replaced frequently. The damage caused by PAG anion leaching is severe. This will increase cost and yield failure, which are undesirable in the chip fabrication. Therefore, one of the key focuses in the development of ArF photoresist is to address the issue of PAG leaching into liquid medium. The faster the PAG leaching rate, the more severe the contamination of lens. The Lithography machine suppliers have the specific requirements on the limits for their lithography machines, as shown in Table 1.

Table 1. Limits on photoresist leaching rates specified by lithography machine suppliers.

	ASML	Nikon
PAG leaching rate	1.6×10^{-12} mol/cm^2/s	5×10^{-12} mol/cm^2/s
Amine leaching rate	-	2×10^{-12} mol/cm^2/s

The PAG leaching test aims to simulate the types of components and their migration rates from photoresist to water in a short period under ultrapure water immersion during the actual lithography process. Different methods can be used to collect dynamic water samples, but the principles are basically similar. Currently, the mainstream approaches include the water-extraction-and-analysis apparatus (WEXA) proposed by William Hinsberg, and the dynamic leaching procedure (DLP). Since the immersion ArF photoresist formula is highly confidential and has few leaching components at low concentrations, this experiment requires highly sensitive testing methods and powerful data mining tools to complete the qualification and quantification of unknown leaching components.

In this study, water leachates of the ArF immersion photoresist leaching experiment were identified based on the Agilent 1290 Infinity II LC/6546 Q-TOF MS system. The leached substances were identified as PAG triphenylsulfonium perfluoro-1-butanesulfonate (CAS No. 144317-44-2), and its concentration was accurately determined. The method detection limit (MDL) achieves at ppt level which meets the requirements on the limit of photoresist leaching rate by the suppliers of lithography machine suppliers.

Experiment

Instruments and equipment

Agilent 1290 Infinity II liquid chromatographic system was used with the following configuration: binary pump (G7120A), autosampler (G7167B), thermostatted column compartment (G7116B), and diode array detector (G7117B).

Agilent 6546 Q-TOF MS system was used, which was controlled by MassHunter software version 10.1 for acquisition.

Data analysis was processed by MassHunter Quantitative Analysis 10.1, MassHunter Qualitative 10.0, MassHunter Profinder 10.0, Molecular Structure Correlator 5.00, and Sirius 5.5.7.

Samples

Two types of immersion ArF photoresists were selected for leaching experiment, and two groups of leaching samples were analyzed (Group A and Group B).

Calibration Curve Preparation

The stock solution of PFBS at 100 µg/mL was accurately prepared in methanol. The stock solution was diluted sequentially with methanol: water (1:1) to prepare a series of calibration solutions at 0.005, 0.01, 0.05, 0.10, 0.50, 1, 5, 10, 50, and 100 ng/mL.

LC Conditions

Chromatographic column:	Agilent InfinityLab Poroshell 120 SB C18, 3.0 × 150 mm, 1.9 µm (p/n 683675-302)	
Column temperature:	40 °C	
Mobile Phase A:	Ultrapure water	
Mobile phase B:	ACN	
Flow rate:	0.3 mL/min	
Gradient elute:	Time (min)	B (%)
	0.0	5.00
	1.0	5.00
	7.0	95.0
	9.0	95.0
Stop time:	12 min	
Injection volume:	2 µL	

MS parameters

Ion source :	Dual AJS-ESI
Drying gas temperature:	300 °C
Drying gas flow rate:	10 L/min
Nebulizer:	45.0 psi
Sheath gas temperature:	350 °C
Sheath gas flow rate:	11 L/min
Fragmentor voltage:	160
Capillary voltage:	4.0/3.5 KV (positive/negative)
Nozzle voltage:	500/1500 V (positive/negative)
Polarity:	positive/negative
Scan mode:	Full scan and targeted MS/MS

Experiment process

Figure 1. workflow of ArF photoresist leaching experiment based on Agilent hardware and software platform

Results and Discussion

Compounds differential analysis

- Differential analysis on unknown compounds with Agilent Profinder software, Mass Profile Professional software
- Differential analysis on target compounds

Agilent MassHunter Profinder software is capable of data mining and analysis on mass spectral data of multiple sample batches, peak extraction, and recursive alignment to minimize false positive and false negative identification results. In this study, MassHunter Profinder was used for peak extraction, and recursive alignment on the three groups of dataset (Blank, Group A, and Group B). By comparing the peak results of the three groups of samples and substracting the blank, Profinder found differential substances. The results of Profinder software analysis are shown in Figure 2. In total, 13 differential features were extracted, which demonstrated the significant differences between two sample groups. Then the secondary MS data was acquired through the targeted MS/MS scan mode for further structure analysis and confirmation of these compounds.
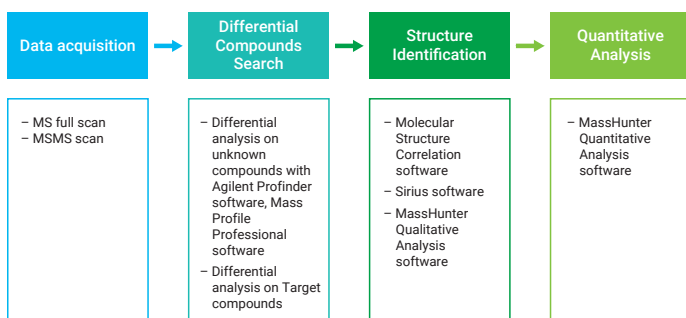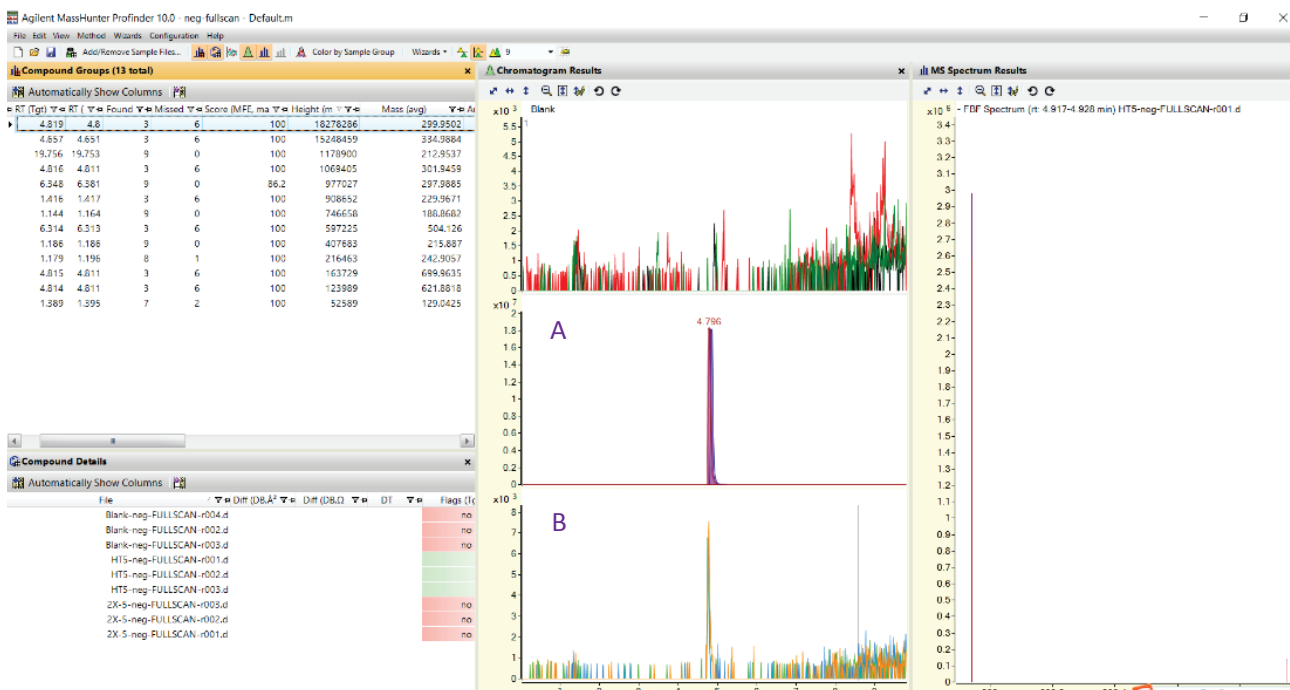

Figure 2. Blank, Group A, and Group B results extracted by MassHunter Profinder software

Structure Identification

– Molecular structure correlation software

– Sirius software

For structure analysis of differential substances, Agilent Molecular Structure Correlator (MSC) software can be used together with Sirius software to quickly analyze compound structural formulas based on MS/MS spectra, providing molecular formula calculations, ion fragment matching, and verification of possible structures with excellent efficiency and accuracy. In this experiment, the differential substance with retention time of 4.2 min under negative ion mode was identified as perfluorobutanesulfonate (PFBS) anion, and the differential substance with retention time of 6.33 min under positive ion mode was identified as triphenylsulfonium cation. The retention time was consistent with the standards. Based on the above experimental results, it can be inferred that the photoresist leaching component detected in the leaching sample is PAG triphenylsulfonium perfluoro-1-butanesulfonate, which is ionized into PFBS anion and triphenylsulfonium cation in aqueous solution. Figure 3 and Figure 5 are the fragmentation tree and its possible molecular formula composition analyzed by Sirius software based on the secondary fragments of the unknown, and Figures 4 and Figure 6 are the secondary ion fragments patterns matched by the MSC software based on the possible structures.
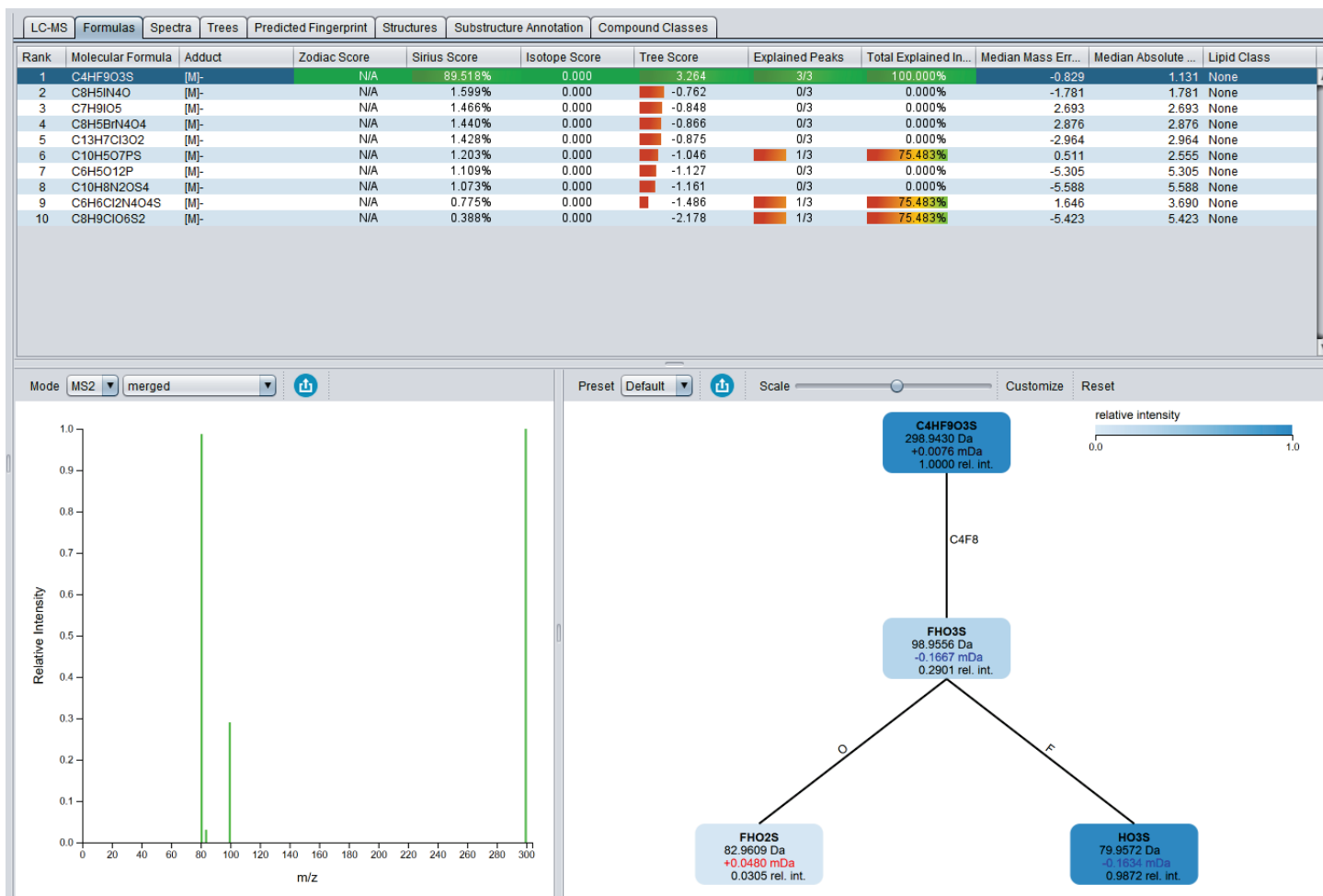

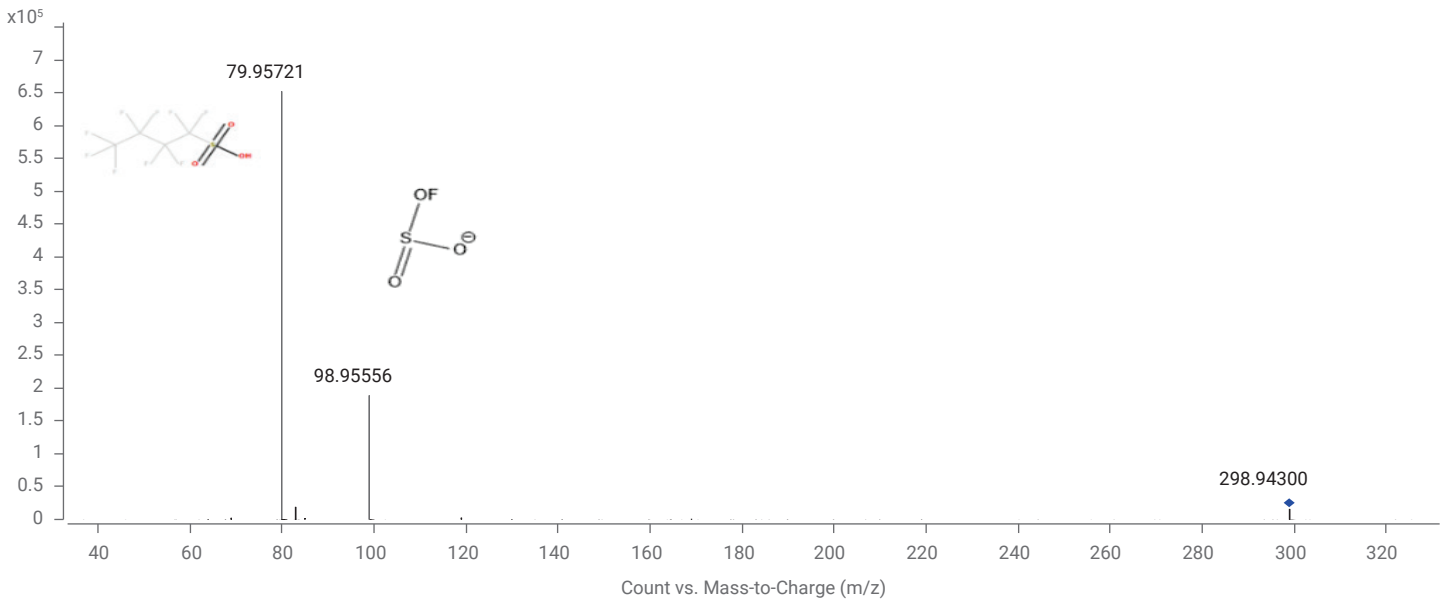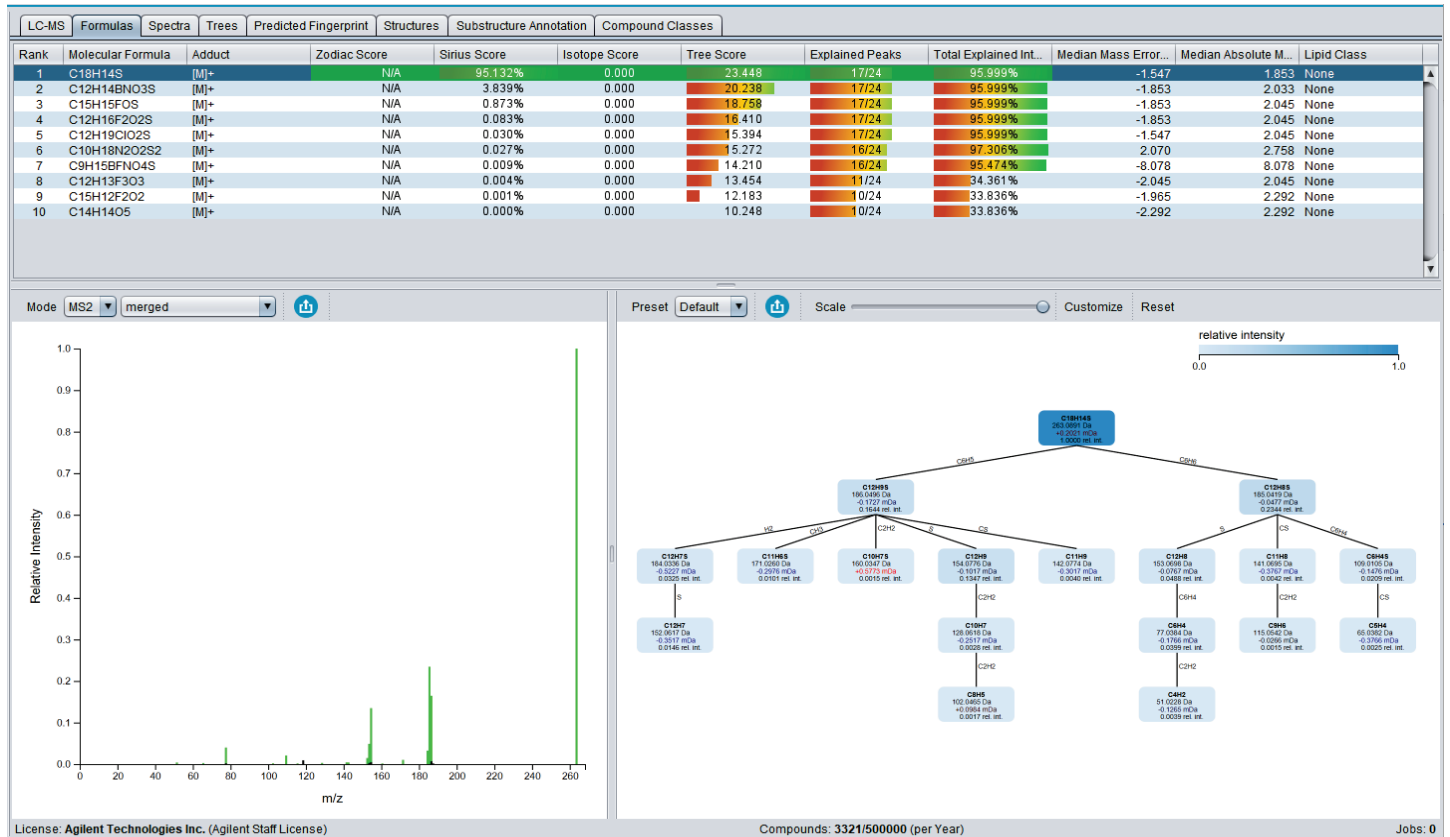**Figure 3.** Interface overview of PFBS identification with Sirius software

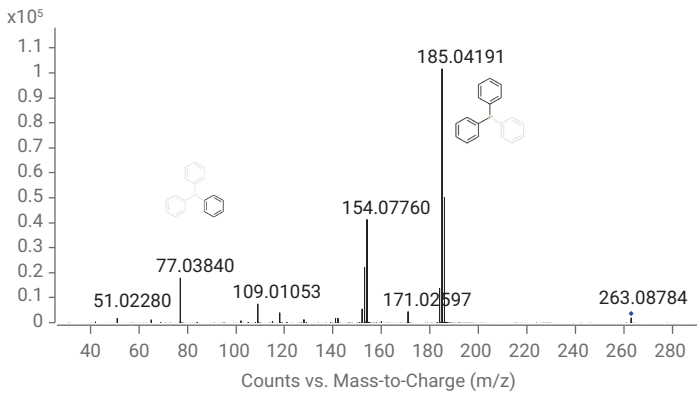**Figure 4.** PFBS matched by secondary ion fragments analysis with MSC software

Figure 5. Diagram of triphenylsulfonium cation identification with Sirius software

Figure 6. Triphenylsulfonium cation matched by secondary ion fragments analysis with MSC software

– MassHunter Quantitative Analysis Software

The sample quantification results are shown in Figure 7. In the concentration range of 0.005-100ng/mL, the great linearity with the correlation coefficient $R^2 \geq 0.99$, and the accuracy within 91.0%−110.5%. The signal-to-noise ratio for PFBS at a concentration of 0.005 ng/mL is 3.8 (Figure 8).
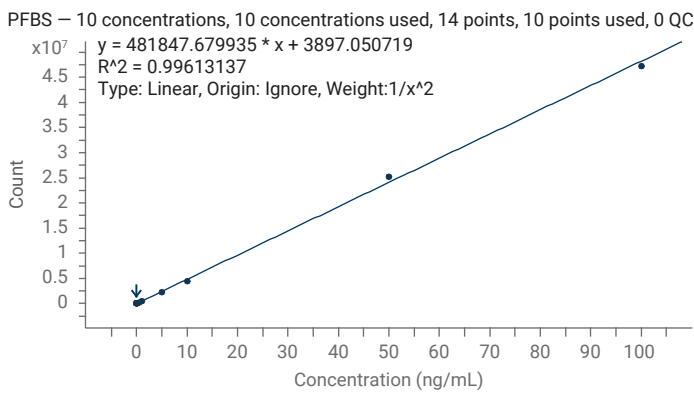
PFBS — 10 concentrations, 10 concentrations used, 14 points, 10 points used, 0 QC

y = 481847.679935 * x + 3897.050719
R^2 = 0.99613137
Type: Linear, Origin: Ignore, Weight:1/x^2

Figure 7. PFBS calibration curve (concentration range 0.005–100 ng/mL)
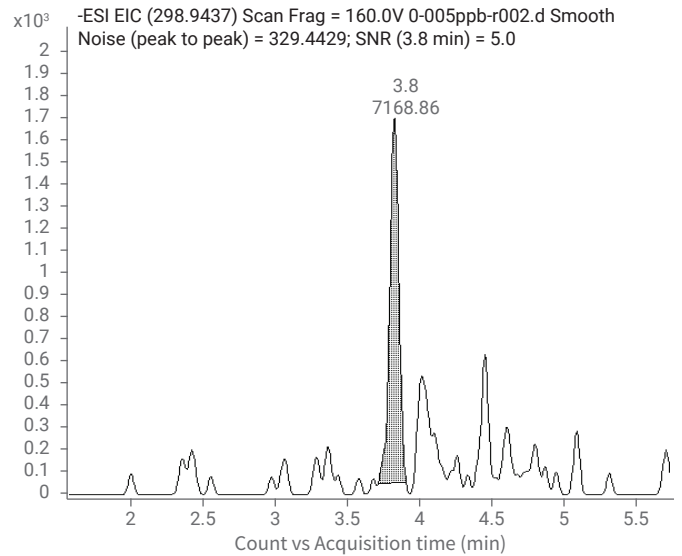

Figure 8. Diagram of 0.005 ng/mL PFBS (S/N = 3.8)

Sample A3 was diluted 100 times, and injected 6 times continuously for the reproducibility analysis. The EICs of the target compounds are shown in Figure 9, with peak area RSD at 2.1%, demonstrating good reproducibility of the method.
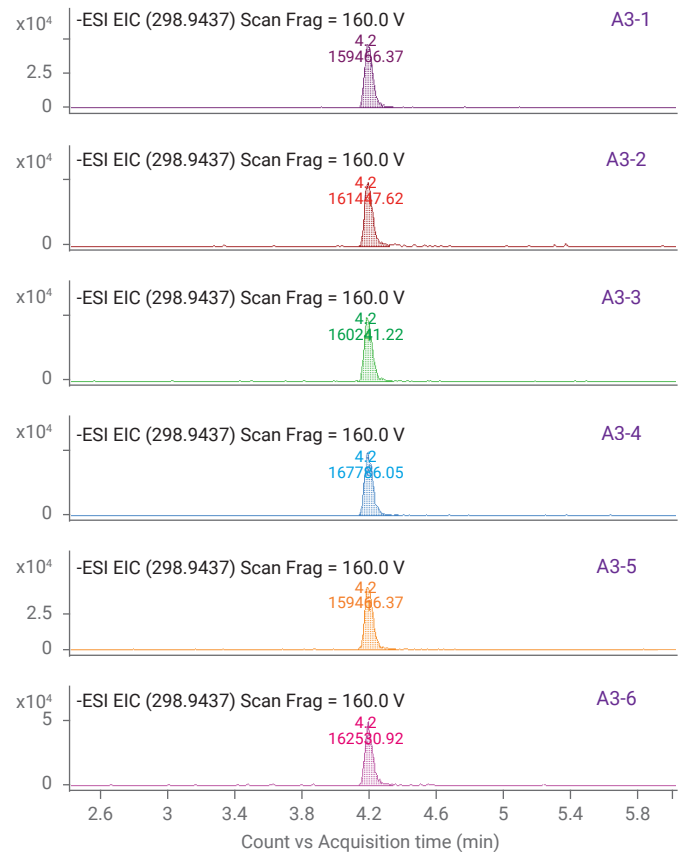

Figure 9. The results of 6 consecutive injections of A3 sample which diluted 100 times

The above quantitative method was used to determine PFBS contents in photoresist leaching samples (Group A and Group B) from two suppliers. The results showed the different leaching pattern of PFBS content from the photoresist samples. The leaching content of the B series samples series achieved highest at the first sampling timepoint, then decreased and reached a steady state over time; while for the A series samples, the leaching content continued increasing. The leaching content from the two photoresist samples did not show linear relationship with time.

Table 2. Analysis results of immersion ArF photoresist PFBS leaching

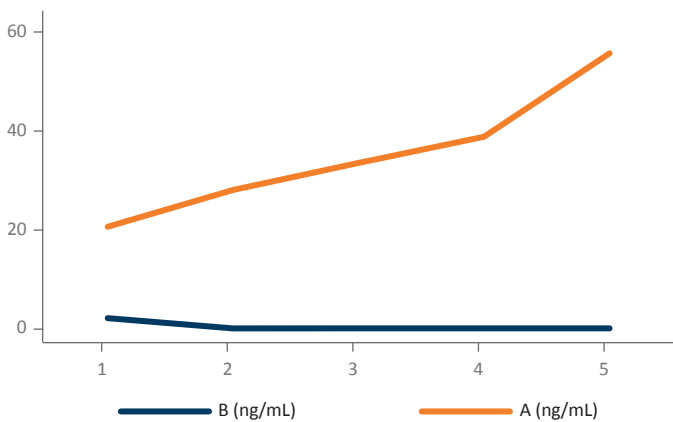| Sample	B (ng/mL)	A (ng/mL)
1	2.08	20.61
2	0.003	28.04
3	0.009	33.54
4	0.01	38.86
5	0.01	55.76

Figure 10. Trend of PFBS leaching from Immersion ArF photoresist

Conclusions

In this application note, a method of identification and quantification on PAG leaching components (anion and cation components) from immersion ArF photoresist was investigated by using Agilent 1290 Infinity II LC/6546 Q-TOF combined with MassHunter Profinder, Sirius and MSC software. Triphenylsulfonium perfluoro-1-butanesulfonate leaching from the real samples was successfully identified and quantitatively analyzed. The method provides the support on R&D and accreditation for the suppliers of immersion ArF photoresist, and photoresist quality monitoring in advanced semiconductor manufacturing.

References

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2. A. Sekiguchi, Y. Matsumoto, K. Okubo, Study of Leaching Analysis of Immersion Resist Components using the WEXA-2 System, J. of Photopolymer Science and Technology, Vol 23, PP 427–433, 2010

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