Poster Reprint

ASMS 2024
Poster number WP 496

Quantitative Analysis of Legacy & Emerging PFAS in Semiconductor Lubricant using Triple Quadrupole LC/MS

Aimei Zou, Stephan Baumann, Cleyde Helena

Agilent Technologies, Inc.

Introduction

Per- and polyfluoroalkyl substances (PFAS) are known to play an important role in the semiconductor industry. For example, PFAS-containing lubricants used in manufacturing processes mainly include perfluoropolyether (PFPE), polytetrafluoroethylene (PTFE) and others that are believed to be of very low toxicity.[1] With environmental regulations & manufacturing restrictions continuing to expand in their scope, the semiconductor industry is facing the challenge of sustainability.[2] Reliable workflows are needed to ensure effective monitoring and control of PFAS in upstream processes. This study established a workflow based on solid phase extraction (SPE) and LC/MS/MS for analyzing over 100 PFAS from semiconductor lubricant matrix.

Experimental

Instrumentation

Agilent 1290 Infinity II LC system (fitted with a PFC-Free Conversion Kit to minimize background) interfaced with a 6475 triple quadrupole mass spectrometer was used for the analysis (Figure 1). The chromatographic separation was on a ZORBAX RRHD Eclipse Plus C18 column with ammonium acetate and methanol mobile phase system.

Figure 1. The 1290/6475 LC/TQ instrumentation

Methodology

The LC/TQ acquisition method used in the application note is built based on the commercial Agilent PFAS MRM Database (part number G1736AA) and is also available as an electronic eMethod (part number G5285AA). Data acquisition and processing were performed using MassHunter Acquisition software (v: 12.0) and Quantitative Analysis software (v:12.0).

Experimental

Sample Extraction

The lubricant liquid sample was from a semiconductor manufacturer. Organic solvent (methanol/dichloromethane, 50/50, v/v) extraction was applied to remove fat content in the lubricant sample before SPE.[3] Figure 2 illustrates the sample preparation in detail. [4]

1 Solvent Extraction	Weigh 1±0.1 g of lubricant sample into tube; add 3 mL of methanol/DCM; gino grinder for 10 mins; centrifuge for 10 mins; transfer the supernatant to a new sample tube; repeat the above solvent extraction three times; combine the extract into the same sample tube
2 Dryness and Reconstitution	Dry the sample tube under a gentle nitrogen stream; redissolve into 5 mL of water and mix well
3 Setup SPE	Connect SPE manifold to the vacuum trap; place sample tube in the collection rack; assemble stopcock, WAX cartridge, adaptor and sample reservoir
4 Condition SPE	5 mL of 0.1% methanolic ammonium hydroxide; 5mL of methanol; 5mL of water
5 Load Sample	Pour the samples into the reservoir; adjust vacuum and stopcock to flow rate at ~2 mL/min
6 Rinse Sample Tube and Reservoir	5 mL of water; dry the cartridge under vacuum for 2 mins
7 Elute Sample	Rinse sample tube & reservoir with 2.5 mL of methanol and transfer to SPE cartridge; Rinse sample tube & reservoir with 2.5 mL of 0.1% methanolic ammonium hydroxide and transfer to SPE cartridge; Flute the cartridge by gravity and dry it.
8 Concentrate the Eluate	Concentrate the eluate to near-dryness under gentle nitrogen stream
9 Reconstitute and add IPS	Reconstitute with methanol/water and spike IPS; vortex well
10 Analyze Sample	Transfer an aliquot into poly ALS vial for LC/TQ analysis; store any remaining solution at -20 °C

Figure 2. Lubricant sample extraction procedure

Calibration Performance and Method Sensitivity

In this study, 71 native PFAS were target analytes and the other 37 compounds were used as surrogates or internal standards. All 71 analytes demonstrated a wide analytical range of at least three orders of magnitude with good linear or quadratic fit of R2 ≥0.99. Figure 3A and 3B show the calibration curves for PFHpS and PFNA, respectively.

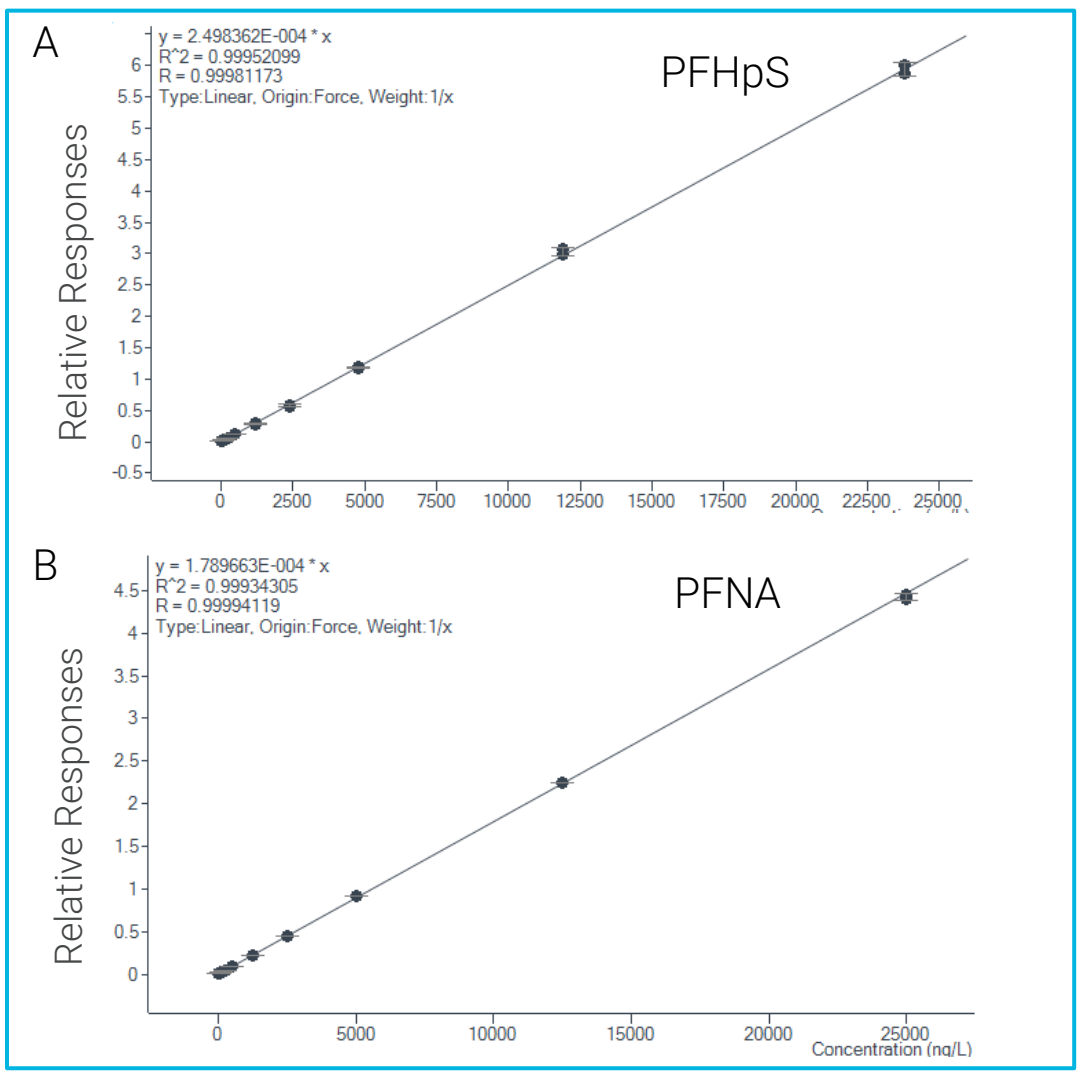

Figure 3. Calibration curves for PFHpS (A) and PFNA (B)

The LOQ distribution for 71 PFAS analytes is mapped in Figure 4. LOQ for 14 compounds were not determined due to the challenges associated with sample preparation.

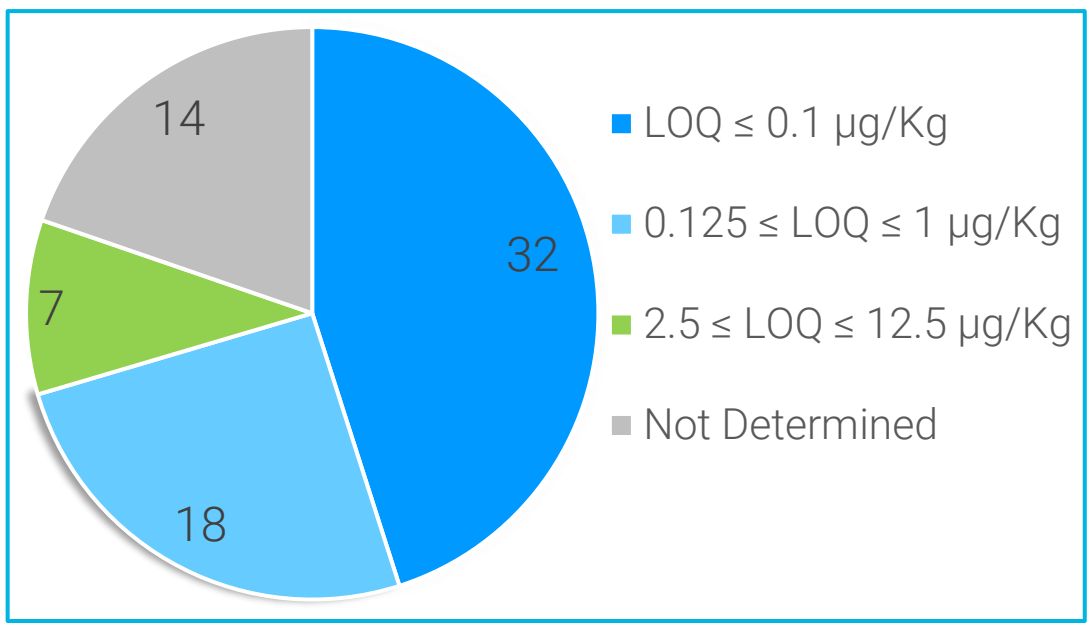

Figure 4. Distribution of LOQ for the 71 PFAS analytes in a lubricant sample

Method Recovery and Precision

Matrix spiked QCs recovery was used to evaluate the method accuracy and reproducibility in this study.

Three technical preparations were performed for both low spiked QC (LSQ) and high spiked QC (HSQ). The measured concentration of each analyte in spiked QC sample was corrected by subtracting its native level present in the un-spiked lubricant sample.

For low spiked QC samples, 42 out of 71 analytes met recovery 70-130% with %RSD≤20. Figure 5A and 5B show the chromatogram overlay of triplicate preparations of LSQ for PFOA and PFOS, respectively.

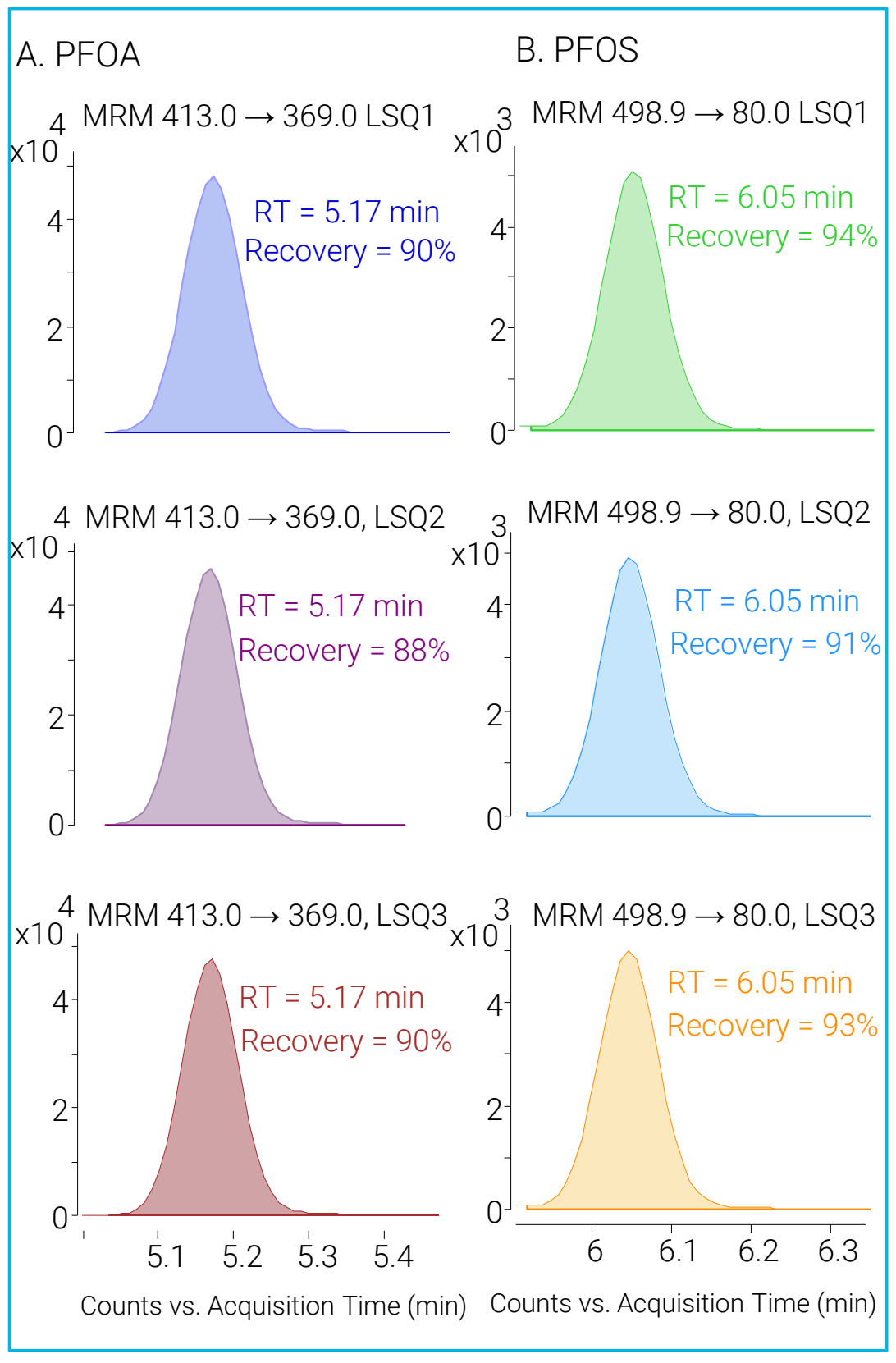

Figure 5. The chromatogram overlay of triplicate preparations of LSQ for PFOA (A left) and PFOS (B right) at 0.5 ug/kg

Results and Discussion

For high spiked QC samples, 58 compounds obtained recovery between 70-130% with %RSD ≤20, which demonstrated the excellent efficiency and reproducibility of the developed WAX based SPE protocol for PFAS extraction from oil containing lubricant samples (Figures 6 and 7).

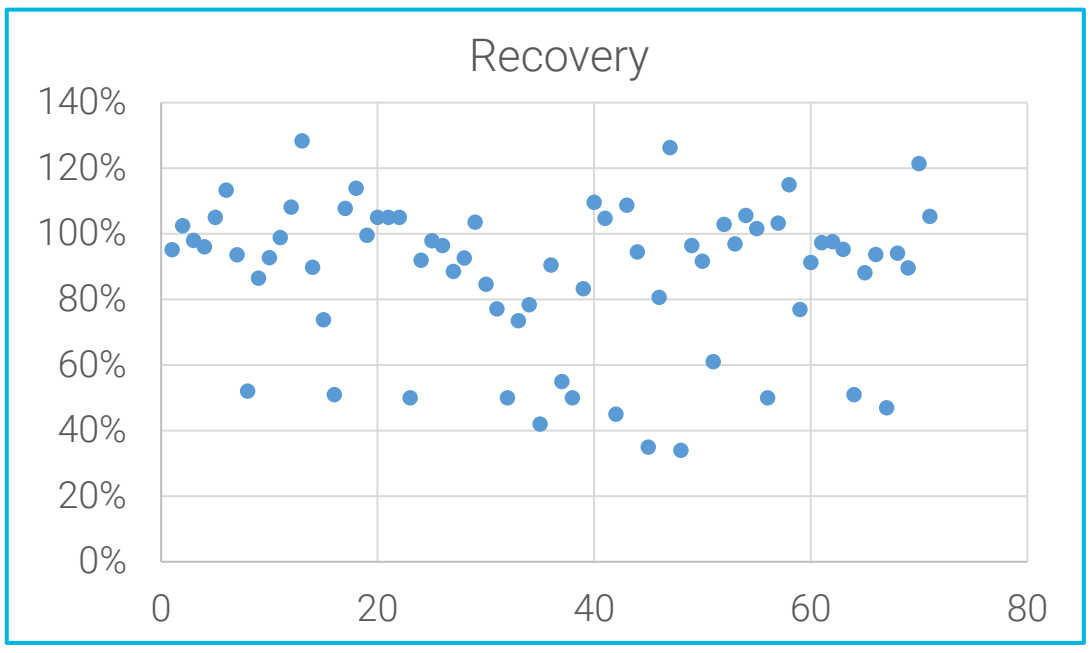

Figure 6. Recovery distribution of HSQ samples

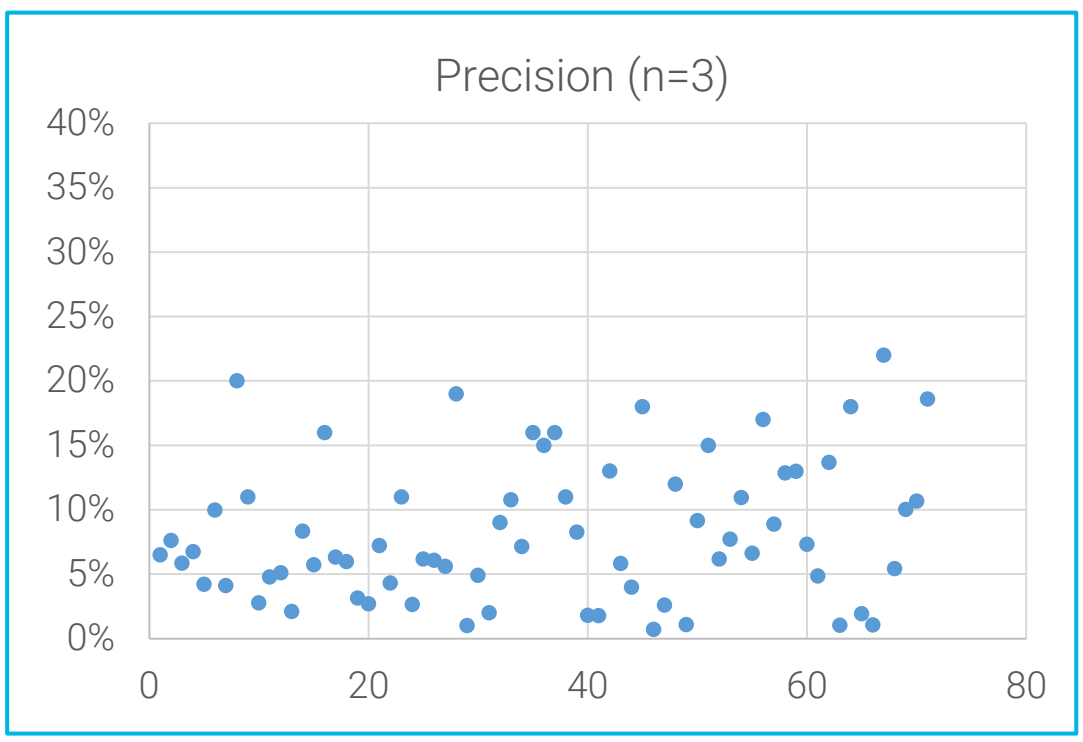

Figure 7. Recovery precision (n=3) of HSQ samples

Lubricant Sample Analysis Result

The native level of PFAS present in the lubricant sample was also studied.

Figure 8 shows the MRM overlay of blank lubricant sample. Approximate 15 native PFAS in sub-ppb level were detected from lubricant samples, such as PFBA, PFBS, PFDA, HFPO-TA, PFOA, PFNA, PFHxA, PFHpA, PFPeA, etc., which are substances of concern in global regulations including EPA 1633, EPA 533, EPA537.1, ASTM, ISO 21675, SW-846 8327 and EU 2022/2388.

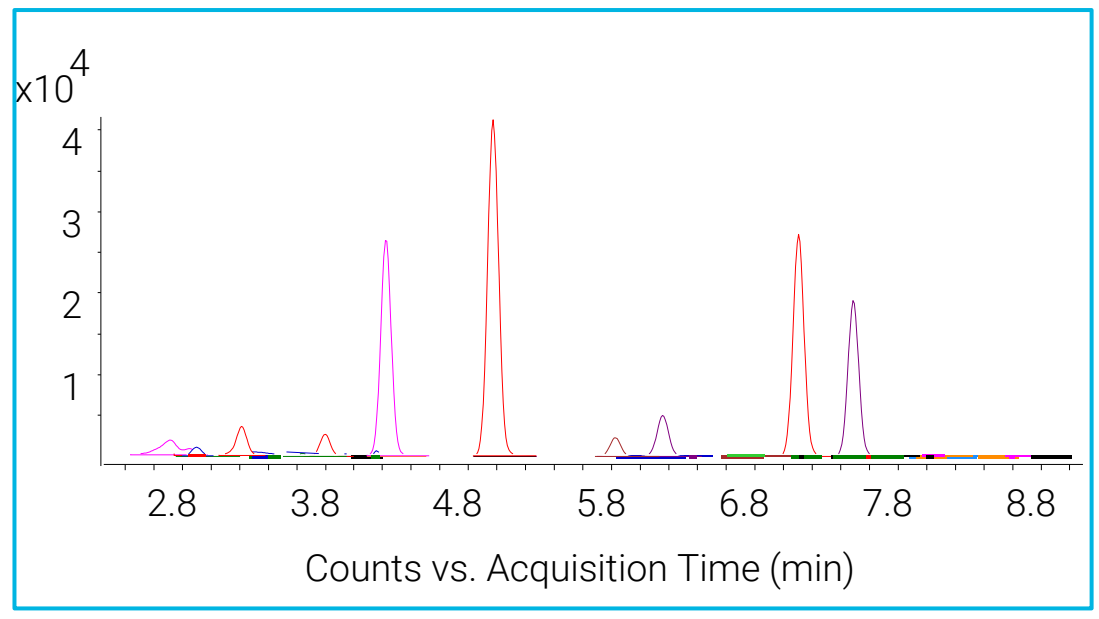

Figure 8. MRM chromatogram of the matrix blank

Conclusions

- A reliable workflow for quantitation of trace levels of PFAS in semiconductor lubricant, based on SPE cleanup and LC/MS/MS was developed.
- The Agilent Bond Elut PFAS WAX cartridge offered selective and effective extraction for matrix cleanup and preconcentration of PFAS analytes in lubricant.
- The workflow performance confirmed the applicability of the Agilent PFAS MRM Database and eMethod, for quantitation of PFAS using the Agilent 6475 LC/TQ system.
- This workflow enables a ready-to-use protocol for lubricant suppliers and semiconductor manufactures to monitor trace levels of critical PFAS in lubricants.

References

1. Linda G. T. Gaines, Historical and current usage of per- and polyfluoroalkyl substances (PFAS): A literature review. Am J Ind Med. 2023; 66:353–378.
2. European Commission, Chemicals Strategy for Sustainability. October 2020.
3. Hongkai Zhu et al., A pilot study of per- and polyfluoroalkyl substances in automotive lubricant oils from the United States. Environmental Technology & Innovation 19 (2020) 100943.
4. Aimei Zou, Quantitative Analysis of Legacy and Emerging PFAS in Semiconductor Lubricant Using Agilent 6475 Triple Quadrupole LC/MS. Agilent Publication 5994-7246EN.

https://www.agilent.com/en/promotions/asms

DE21748365

Published in USA, May 31,2024

Agilent
Trusted Answers