Waters™

Nota applicativa

Routine High Resolution Mass Spectrometry (HRMS) for the Screening of Per- and Polyfluoroalkyl Substances (PFAS) Using the Waters ACQUITY™ RDa™ Mass Detector

Chris Henry, Ashley Sage

Waters Corporation

Questa relazione è un Application Brief e non contiene una sezione dettagliata sull'esperimento.

Abstract

This technical brief highlights a targeted workflow for routine HRMS screening using the ACQUITY RDa Mass Detector with UNIFI™ software for PFAS analysis. To demonstrate this a standard mix of thirty-three known PFAS and PFAS precursors were analyzed at a concentration of 10 ng/mL.

Combining the ACQUITY RDa with the UNIFI screening workflow, identification and characterization of the sample components and the associated fragments generated, were carried out automatically using libraries within the processing method. All components were detected and identified with mass measurements less than or equal to 3.2 ppm accuracy without the need for manual interpretation. This demonstrates a platform capable of providing robust PFAS screening and characterization for a wide range of analytical expertise.

Benefits

- Routine acquisition of sub 5 ppm mass accuracy for PFAS compounds
- Simultaneous acquisition of fragmentation data for additional confidence in compound identification
- Accurate mass screening workflow with waters_connect™ enables automatic screening of PFAS libraries for simplified data analysis
- *In Silico* generation and visualization of fragment data for increased confidence in PFAS assignment
- Automatic setup and calibration with no manual intervention required
- Access to HRMS data for non-expert users
- Compliant ready software UNIFI software as part of the waters_connect informatics platform

Introduction

PFASs are a group of diverse chemicals that are widely used in industry to produce fluoropolymer coatings and products resistant to heat, stains, grease, and water. The wide range of applicability of these compounds has resulted in ubiquity throughout a multitude of commercial and industrial processes.

However, these same properties also confer characteristics that are non-biodegradable, result in bioaccumulation in soil and aquatic life, contaminate groundwater, and surface water while also being linked to negative effects on human health.[1,2]

With increasing regulation around the monitoring and characterization of PFAS and associated precursors and intermediates, the need for access to instrumentation that provides the necessary selectivity to confidently identify these compounds has grown.[3] HRMS provides compound characterization capability, but can be expensive and require high levels of expertise to operate and for data interpretation. With the ACQUITY RDa Mass Detector (Figure 1), HRMS analysis is accessible to both experts and non-experts alike, with automatic set-up and calibration requiring no manual optimization. In combination with the compliant ready UNIFI screening application within the waters_connect™ software platform this provides a robust, easy to adopt route to routine accurate mass measurements for PFAS analysis with minimal MS expertise required.

Figure 1. The ACQUITY Premier LC system coupled to the ACQUITY RDa Mass Detector.

Results and Discussion

The ACQUITY RDa Detector was set up automatically, including detector, auto-tune, and mass calibration with no requirement for manual intervention enabling the analyst to focus solely on sample analysis and result generation. Following this routine set up, full scan accurate mass data were acquired in negative mode incorporating the 'Scheduled Lockmass' function to mitigate any potential mass accuracy shifts due to laboratory environment changes such as temperature changes. This feature runs a lockmass correction once per hour providing stable mass accuracy with a significant reduction in lockmass solution usage.

A 10 ng/mL sample of the standard solution was injected using the ACQUITY Premier System coupled to the ACQUITY RDa System with all 33 compounds being successfully detected and identified using a PFAS screening library as part of the UNIFI processing method (Figure 2).

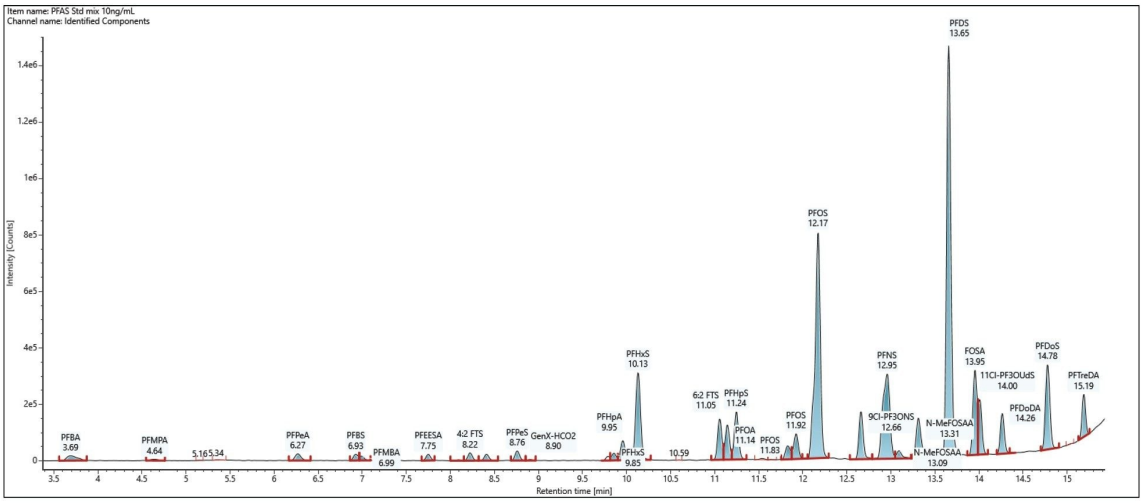

Figure 2. Extracted ion chromatogram (XIC) of all the identified PFAS standard mix.

All compounds were detected and identified with mass accuracy measurements ranging between -2.9 and 3.2 ppm, providing high confidence in correct compound assignments, with lowest levels of quantitation (LLOQ's) ranging between 1.0 pg/mL and 9.18 ng/mL (Table 1).

Component name	Observed neutral mass (Da)	Observed *m/z*	Mass error (ppm)	Observed RT (min)	LLOQ (ng/mL) s/n *10
11Cl-PF3OUdS	631.8957	630.8884	-1.3	14.01	0.06
4:2 FTS	327.9813	326.9740	-0.9	8.23	0.04
6:2 FTS	427.9753	426.9680	0.3	11.06	0.04
8:2 FTS	527.9701	526.9628	2.4	12.91	0.06
9Cl-PF3ONS	531.9031	530.8958	0.5	12.66	0.13
ADONA	377.9766	376.9693	1.2	10.12	0.43
FOSA	498.9532	497.9459	-0.5	13.95	0.03
GenX-HCO2	285.9853	284.9781	0.6	8.91	0.40
N-EtFOSAA Branched Isomer 1	584.9901	583.9828	-0.3	13.35	9.18
N-EtFOSAA Branched Isomer 2	584.9897	583.9825	-0.9	13.67	5.94
N-EtFOSAA Linear	584.9908	583.9835	0.9	13.47	0.69
NFDHA	295.9729	294.9657	-0.6	8.10	0.47
N-MeFOSAA Branched Isomer 1	570.9740	569.9668	-1.0	13.31	0.88
N-MeFOSAA Branched Isomer 2	570.9762	569.9689	2.8	13.09	0.37
N-MeFOSAA Linear	570.9764	569.9692	3.2	12.98	0.06
PFBA	213.9861	212.9789	-1.6	3.69	0.52
PFBS	299.9502	298.9429	-0.3	6.93	0.33
PFDA	513.9676	512.9604	0.6	12.94	0.35
PFDoDA	613.9595	612.9522	-2.3	14.26	0.51
PFDoS	699.9243	698.9170	-0.6	14.77	0.04
PFDS	599.9310	598.9237	-0.2	13.66	0.06
PFEESA	315.9460	314.9387	2.7	7.75	0.001
PFHpA	363.9772	362.9699	0.8	9.96	0.07
PFHpS	449.9410	448.9337	0.8	11.25	0.11
PFHxA	313.9799	312.9726	-0.7	8.41	0.23
PFHxS Branched Isomer	399.9443	398.9370	1.1	9.86	2.00
PFHxS Linear	399.9448	398.9375	2.3	10.14	0.14
PFMBA	279.9782	278.9709	0.0	7.00	0.30
PFMPA	229.9812	228.9740	-0.7	4.64	0.27
PFNA	463.9711	462.9638	1.3	12.12	0.11
PFNS	549.9345	548.9272	0.4	12.97	0.21
PFOA	413.9743	412.9671	1.6	11.14	0.10
PFOS Branched Isomer 1	499.9381	498.9308	1.1	11.82	1.20
PFOS Branched Isomer 2	499.9386	498.9313	2.2	12.17	0.47
PFOS Linear	499.9374	498.9301	-0.3	11.92	0.04
PFPeA	263.9825	262.9752	-2.9	6.27	0.23
PFPeS	349.9471	348.9398	0.0	8.76	0.16
PFTreDA	713.9536	712.9463	-1.3	15.19	0.10
PFTnDA	663.9566	662.9494	-1.6	14.79	0.16
PFUnDA	563.9640	562.9567	-0.2	13.65	0.24

Table 1. Compounds detected with mass accuracy, LLOQ's and retention times listed.

Using the *Full Scan with Fragmentation* function allows cone voltage ramping to simultaneously acquire high and low energy spectra. The high energy data function, containing fragment ion information, was assigned automatically providing further confidence for compound identification with visual assignations to aid in speedy data appraisal (Figure 3).

Figure 3. Screenshot of UNIFI sample review table featuring simultaneously acquired low and high energy spectral data visualizing structures of the intact ADONA (3H-perfluoro-3-[(3-methoxy-propoxy)propanoic acid]) and fragment information.

Conclusion

The ACQUITY RDa has demonstrated the ability to detect and identify all the components of the screening standard. All compounds were identified with mass accuracy measurements of less than or equal to 3.2 ppm. Creation of PFAS libraries allows for routine screening of samples using accurate mass, fragments, and retention times for confident component identification significantly reducing analyst burden for data interpretation. With the ACQUITY RDa and UNIFI as part of waters_connect providing simple intuitive workflows, HRMS

measurements for PFAS are achievable for novice users and ms experts alike.

References

1. Current Review of Increasing Animal Health Threat of Per- and Polyfluoroalkyl Substances (PFAS): Harms, Limitations, and Alternatives to Manage Their Toxicity. Peritore FA, Gugliandolo E, Cuzzocrea S, Crupi, Rosalia, Britti, D; *Int. J. Mol. Sci.* 2023, *24*(14), 11707. https://doi.org/10.3390/ijms241411707 < https://doi.org/10.3390/ijms241411707>

2. Directive (EU) 2020/2184 of the European Parliament and of the Council of 16 December 2020 on the Quality of Water Intended for Human Consumption (Recast) [Online]. https://eur-lex.europa.eu/eli/dir/2020/2184/oj < https://eur-lex.europa.eu/eli/dir/2020/2184/oj>

3. Total Oxidizable Precursor (TOP) Assay- Best Practices, Capabilities and Limitations for PFAS Site Investigation and Remediation". Ateia M., Chiang D, Cashman M., and Acheson C. *Environmental Science and Technology.* https://pubs.acs.org/action/showCitFormatsdoi=10.1021/acs.estlett.3c00061&ref=pdf < https://pubs.acs.org/action/showCitFormats?doi=10.1021/acs.estlett.3c00061&ref=pdf>

Featured Products

ACQUITY Premier System <https://www.waters.com/waters/nav.htm?cid=135077739>

ACQUITY RDa Detector <https://www.waters.com/waters/nav.htm?cid=135077027>

UNIFI Scientific Information System <https://www.waters.com/waters/nav.htm?cid=134801359>

waters_connect Software Solutions <https://www.waters.com/nextgen/us/en/products/informatics-and-software/waters_connect.html>

720008362, May 2024