INVESTIGATING FIRE FIGHTER AND E-WASTE HANDLERS EXPOSURE TO PFAS USING LIQUID CHROMATOGRAPHY AND CYCLIC ION MOBILITY MASS SPECTROMETRY

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INTRODUCTION

Polyfluorinated alkyl substances (PFAS) exposure is a potential contributor to increased cancer and disease in the human population. Firefighters, shown in Figure 1 (Fire categories: Gas, bush, industrial, basement, trees, domestic, factory, commercial, electrical), and E-waste handlers (categories: electrical wires, mobile phones, hair dryers, refrigerators, washing machine, open air burning, dump with other wastes) have a high exposure to PFAS due to their occupational demands. Monitoring of PFAS levels in human biofluids helps to gain understanding into exposure levels and pathways. PFAS isomeric compounds can be challenging to efficiently separate using liquid chromatography (LC). The SELECT SERIES™ Cyclic™ Ion Mobility Mass Spectrometer provides an added dimension of separation (see Figure 2).

***Figure 1**. Ghana national fire service.*

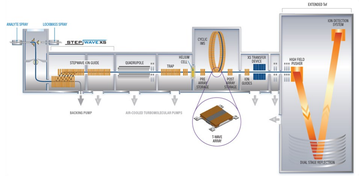


Figure 2. SELECT SERIES Cyclic IMS System.

METHODS

Using a 22 min reversed phase separation gradient, LC-cIM-MS (ion mobility resolution (R)~65 and 145) non-targeted analysis has been performed to analyse anonymised human serum samples of Ghanaian firefighters and E-waste handlers. Human serum sample extraction was performed using SPE 96-well µElution plates, containing a polymeric reversed-phase, weak anion exchange mixed-mode sorbent. Full experimental conditions and ethical statement have previously been described.[1,2]

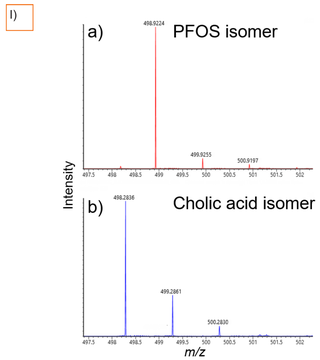
RESULTS

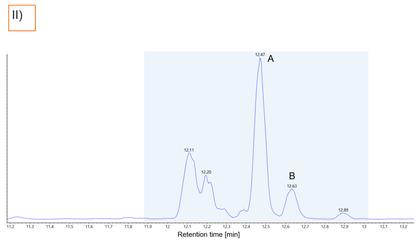
The Cyclic Ion Mobility System enhances peak capacity (see Figure 3) and provides collision cross section (CCS) values, which serve as a complementary identification descriptor (see Figure 3).

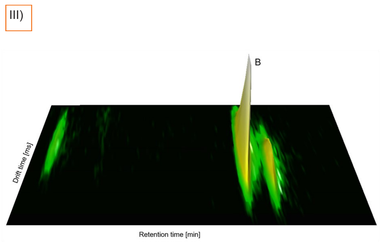
Δ CCS < 1% have been observed compared to the PFAS library CCS values. For E-waste handler serum samples, PFAS, including, PFOA, PFOS and 6:2 FTS have been identified. In firefighter serum samples, PFAS, including, PFHxS, PFOS, PFHpS and PFNA have been identified (see Figure 3 sample F12).

LC-cIM-MS has been used to analyse a series of PFAS analytical standards comprised of structurally equivalent PFOA and PFOS branched isomers. Characteristic CCS values have been determined for branched PFOS and PFOA isomers, this enabled identification of branched PFAS in human serum samples.[3] Figure 3 shows identification of linear PFOS, branched P6MHpS and P5MHpS. For a comparison between br-PFAS travelling wave ion mobility (TWIM) CCS values, drift tube and trapped ion CCS measurements, Δ CCS <0.6% has been obtained.[2]

Additionally, we present identification of perfluoroalkyl carboxylic acids (PFCA) in human serum using ion mobility PFCA conformeric profile specificity, enabling highly specific identification at low intensities where product ions may be absent (Figure 5).







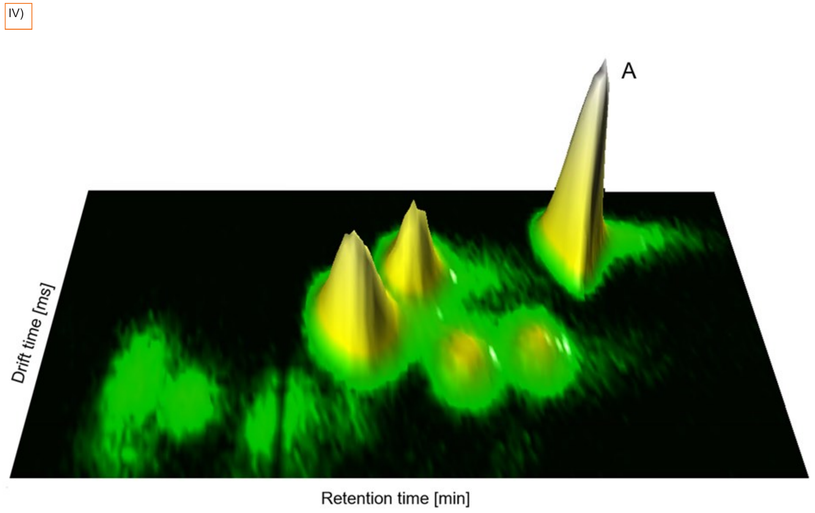


***Figure 3.** I). Isobaric mass spectra of a) linear PFOS and b) taurodeoxycholic acid cholic. Using targeted analysis, the potential exists for false PFOS detections or erroneous quantified calculated concentrations, the nominal MRM transitions, precursor m/z 499 > m/z 80 would not be differentiated, unless cholic acid biomarkers and PFOS isomers are fully resolved. II) Base peak ion chromatogram of coeluting isobaric branched PFOS isomers and cholic acid isomers detected in human serum of fire fighters (Sample F12). III) Ion mobility separation of coeluting cholic acid isomer biomarkers. IV) Nine ion mobility resolved branched and linear PFOS isomers (R~145).*

References

1. McCullagh M, Lioupi A, Theodoridis G, Plumb R, Wilson I and Adams S. Enhanced Identification Confidence and Specificity for PFAS Analysis Using Cyclic Ion Mobility Mass Spectrometry Collision Cross Sections. 2025. Waters Application Note 720008536.
2. McCullagh M, Adams S, Tudor A, Goshawk J, Mortishire-Smith R, Megson D, Ansong Asante K and Bruce-Vanderpuije P. Combining Pattern Analysis and Cyclic Ion Mobility Mass Spectrometry to Research Per-and Poly Fluoroalkyl substances (PFAS) Exposure in E-waste Handlers. 2025. Waters Application Note 720008784.
3. McCullagh M, Marsden Edwards E and Adams S. Illustrating the Use of Cyclic Ion Mobility to Enhance Specificity for branched-PFAS Isomer Analysis. 2025. Waters Application Note 720007823.

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Ethical Approval: This study received ethical approval from the Ghana Health Service Ethics Review Committee (ref: GHS-ERC 023/01/25) on February 9th, 2025.
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9	13C8-PFOS	[13C]8HF17O3S	506.9584	12.52	167.4	166.54	0.52	43004 -H
10	6:2 FTS	C8H5F13O3S	426.9689	11.43	167.1	166.41	0.42	305 -H
11	9Cl-PF3ONS	C8HClF16O4S	530.8960	12.94	171.2	169.58	0.94	1015 -H
12	D3-MEFOSAA	C11H3[2H]3F17NO4S	572.9872	13.65	192.2	190.94	0.64	27201 -H
13	D5-ETFOSAA	C12H3[2H]5F17NO4S	589.0159	13.99	195.9	194.85	0.53	18442 -H
14	P4SDMHxS	C8HF17O3S	498.9317	11.84	162.6	161.50	0.66	740 -H
15	P5SDMHxS	C8HF17O3S	498.9317	11.93	162.1	162.70	-0.36	359 -H
16	P5MHpS	C8HF17O3S	498.9317	12.15	164.4	163.50	0.55	20382 -H
17	P6MHpS	C8HF17O3S	498.9315	12.25	166.2	165.40	0.46	11263 -H
18	PFDA-HCO2	C10HF19O2	468.9718	13.31	156.5	155.87	0.41	839 -HCO2
19	PFecHS	C8HF15O3S	460.9349	11.39	155.2	153.77	0.91	154 -H
20	PFHpS	C7HF15O3S	448.9341	11.57	159.0	157.99	0.65	1721 -H
21	PFNA-HCO2_1	C9HF17O2	418.9749	12.47	148.4	147.81	0.38	978 -HCO2
22	PFOS	C8HF17O3S	498.9316	12.52	167.4	166.44	0.58	59150 -H
23	PFUnDA-HCO2	C11HF21O2	518.9693	14.01	164.8	164.03	0.49	956 -HCO2
24	taurochenodeoxycholic acid	C26H45NO6S	498.2896	12.67	207.5	206.70	0.40	33976 -H
25	taurodeoxycholic acid	C26H45NO6S	498.2893	12.94	206.6	205.90	0.34	4070 -H
26	tauroursodeoxycholic acid	C26H45NO6S	498.2900	10.62	208.4	207.30	0.52	1135 -H

***Figure 4**. Component summary for labelled PFAS internal standards and identified PFAS in human serum resulting from environmental exposure, detected in the anonymised fighter sample F12 (RMS Δ CCS =0.6%).*

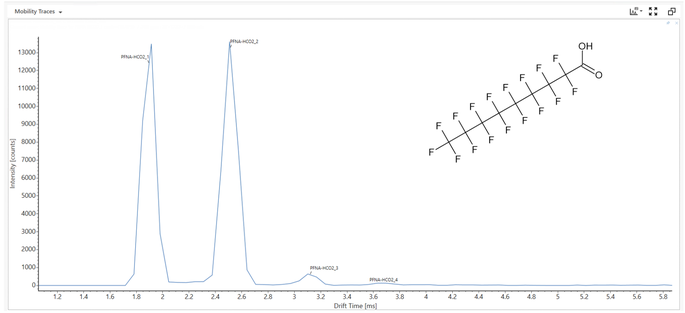

***Figure 5**. Ion mobility conformeric profile for PFNA identified in E-waste handler sample 28.*

CONCLUSION

- **Enhanced identification specificity of PFAS achieved using LC-cIM-MS can form a critical part of analytical strategy.**
- **Known and unknown PFAS in complex samples can be identified using a highly specific LC-cIM-MS non-targeted analysis.**

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