Accurate Mass Library for PFAS Analysis in Environmental Samples Using High Resolution GC/Q-TOF

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Per- and polyfluoroalkyl substances (PFAS) are emerging contaminants of increasing concern due to their environmental persistence, toxicity, and capability of bioaccumulation. There are currently thought to be over 6,000 PFAS that have been commercially produced and recent studies have shown that many emerging PFAS that have been detected in the environment can be volatile or semi-volatile in nature. Therefore, a variety of analytical techniques are necessary for their detection. GC/MS is typically used for detecting volatile and non-polar PFAS compounds. In this study we used GC/Q-TOF system to take advantage of high resolution for detecting compounds with mass defect that is different from that of complex environmental matrices. For specific and sensitive PFAS detection in soil and drinking water, we have created an accurate mass GC/MS library for PFAS. We have also identified other contaminants in drinking water such as disinfection byproducts, industrial chemicals originated from personal care products, drugs, and pesticide residues.

Figure 1. Agilent 7250 GC/Q-TOF

GC-amenable PFAS standards have been used to obtain accurate mass spectra. Soil was sampled from two fields in California that have historically received biosolids and extracted with methylene chloride. The drinking water samples were collected at two different locations in California and represented two different water source categories: a small surface water (Weaverville) and a mixed surface and ground water (Irvine). Water samples (2.4 L) were extracted on a multi-mode SPE (HLB, WAX, WCS, Isoelut ENV) and eluted with 5% MTBE in MeOH, DCM, 0.5% NH_4OH in 1:1 EtAC:MeOH, and 1.7% formic acid in 1:1 EtAC:MeOH. The combined extracts were concentrated, solvent exchanged to EtAc and diluted 10x. GC/MS analysis was performed using an Agilent 8890 GC coupled to an Agilent 7250 high resolution Q-TOF (Figure 1) using the following the data acquisition parameters (Table 1).

Table 1. GC/Q-TOF Acquisition Parameters

GC and MS Conditions	DB-5MS	DB-624
MS	7250 Q-TOF	
GC	7890	
Inlet	MMI, 4-mm UI liner single taper with wool	
Inlet temperature	70 °C for 0.01 min; 300 °C/min to 250 °C	
Injection volume	1 µL	
Columns	DB-5MS UI, 30 m x 0.25 mm x 0.25 µm	DB-624 UI, 30 m x 0.25 mm x 1.4 µm
Oven temperature program	35 °C for 2 min; 7 °C/min to 210 °C, 20 °C/min to 300 °C, 4 min hold	30 °C for 2 min; 3 °C/min to 75 °C, 2 °C/min to 110 °C, 10 °C/min to 210 °C, 20 °C/min to 240 °C, 2 min hold
Column flow	1.2 mL/min constant flow	1 mL/min constant flow
Carrier gas	Helium	
Transfer line temperature	250 °C	
Quadrupole temperature	150 °C	
Source temperature	200 °C	
Electron energy	70 eV	
Emission current	Variable by time segment, 0.01 to 5 µA	
Spectral acquisition rate	5 Hz	
Mass range (Tune)	50 to 1200 m/z	

The chromatographic deconvolution and library search were performed in the MassHunter Unknowns Analysis 11.1. Accurate mass EI fragments were converted to the theoretical m/z using MassHunter Qualitative Analysis software version 10.0, and the spectra were exported into the accurate mass Personal Compound Database and Library (PCDL) Manager version 8.0. The PCDL for PFAS, PCDL for Pesticides and Environmental contaminants, as well as NIST 20 were used to perform initial compound identification. Retention Indices and accurate mass information were utilized to confirm the compound ID. Statistical analysis was performed in Mass Profiler Professional (MPP) 15.1.

Accurate Mass Library for PFAS

In order to create an accurate mass GC/MS PCDL, the spectra have been collected for over a hundred PFAS compounds. Accurate mass fragment ions have been automatically annotated with formulas based on accurate mass information and isotope ratios using MassHunter Qualitative Analysis software (Figure 2). The fragment formula annotations were manually verified, corrected when necessary and automatically converted to the theoretical m/z.
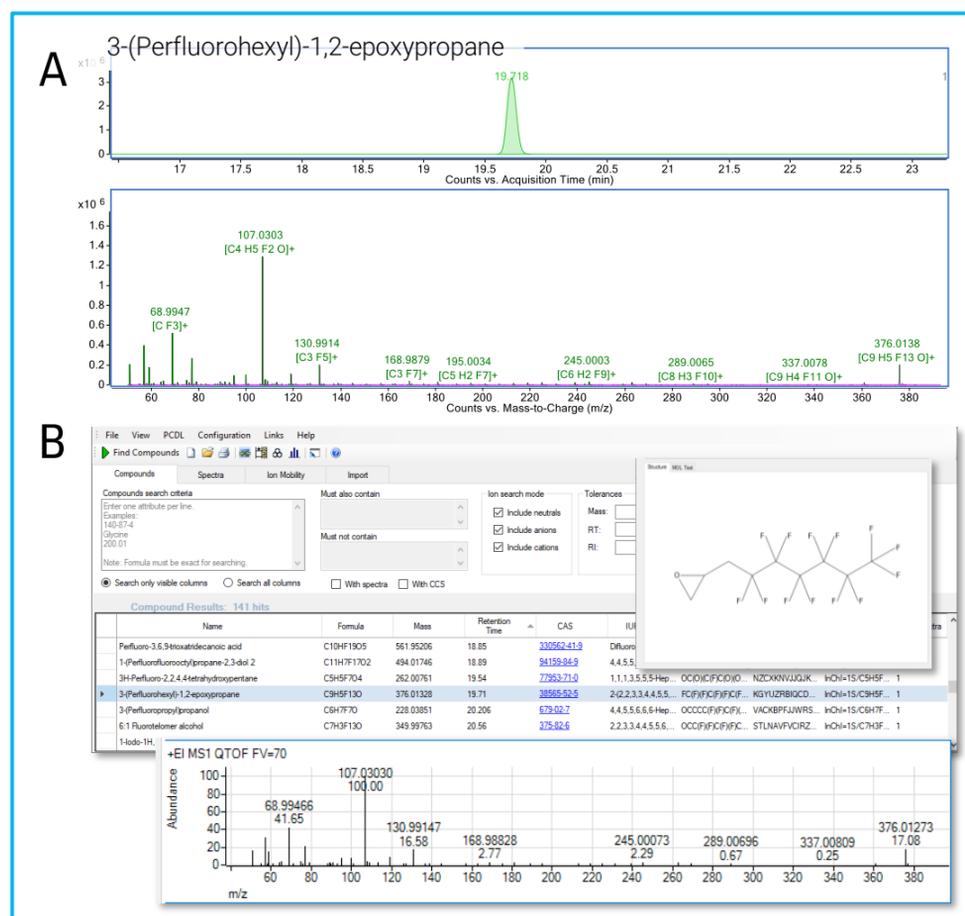
Figure 2. (A) EIC of the molecular ion and fragment formula annotation of spectrum for one of the PFAS compounds in MassHunter Qualitative Analysis software. (B) The PFAS PCDL contains EI spectra as well as the metadata including molecular structure and database identifiers.

The PFAS compound classes include perfluoroalkyl iodides (PFAIs), fluorotelomer iodides (FTIs), fluorotelomer alcohols (FTOHs), fluorotelomer olefins (FTOs), fluorotelomer acrylates (FTACs), fluorotelomer methacrylates (FTMACs) and perfluoroalkyl carboxylic acids (PFCAs) among others (Figure 3).
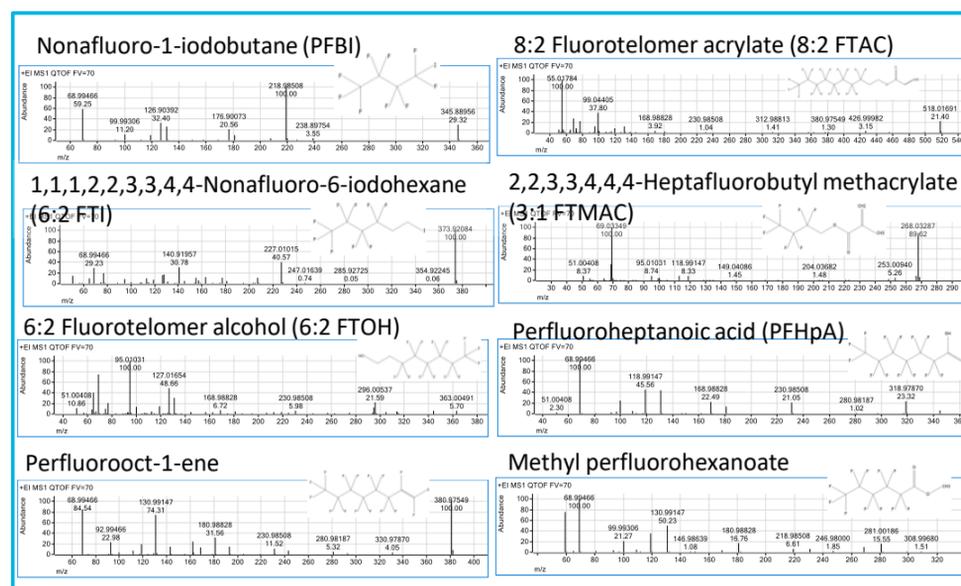
Figure 3. Examples of spectra in PFAS PCDL from different PFAS compound classes.

PFAS in Environmental Samples

For PFAS detection, the extracts of drinking water and soil were separated on DB-624 column analyzed by the GC/Q-TOF MS. The chromatographic deconvolution was performed in the Unknowns Analysis software using a SureMass algorithm that is optimized for complex high resolution EI data. The PFAS PCDL was used to search the deconvoluted spectra with RT matching. Figure 4 shows PFAS compounds identified in soil and drinking water (one in each matrix). PFAS (a derivative of PFCAs) were detected in most drinking water samples and the soil extract from Field 1.
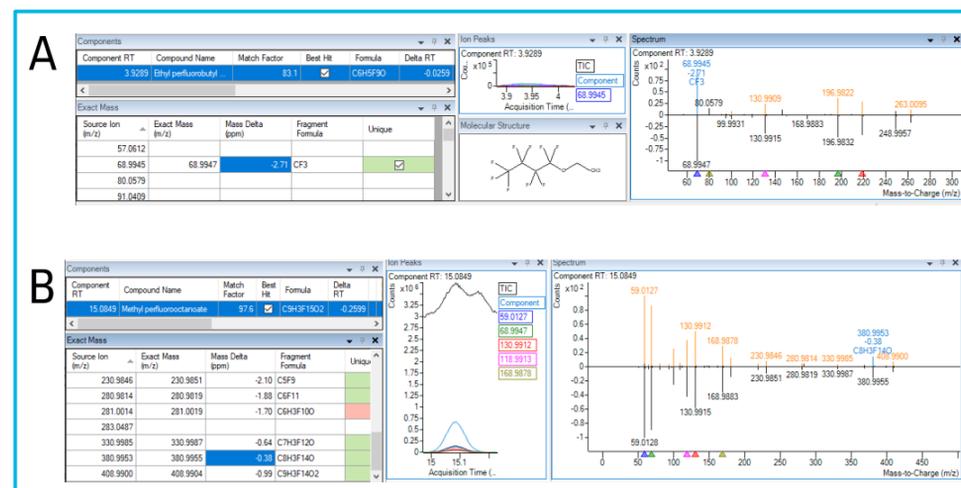
Figure 4. PFAS identified in soil Field 1 (A, ethyl perfluorobutyl ether) and drinking water Irvine (B, Methyl perfluorooctanoate) samples.

Identification of the Additional Contaminants in Drinking Water Samples

To identify other contaminants in drinking water samples the GC/Q-TOF Pesticide PCDL as well as NIST 20 library were used. Over hundred contaminants have been identified and confirmed using accurate mass information (Figure 5 and Tables 2 and 3) from sample without reinjection.

Figure 5. Examples of the contaminants identified in drinking water extracts using NIST 20 (A) and Pesticide PCDL (B). ExactMass tool (in red rectangle) helps to provide additional confirmation of unit mass library hits based on accurate mass. Compound ions are highlighted in mirror plot when m/z corresponds to the library hit formula.

Table 2. Contaminants identified in drinking water using NIST 20 library with the library match score > 75. *Denotes the cases where delta RI was calculated considering NIST estimated RIs rather than experimental (experimental not available).

RT	Compound Name	Match Score	Formula	RI delta	RT	Compound Name	Match Score	Formula	RI delta	RT	Compound Name	Match Score	Formula	RI delta
4.79	Bromodichloromethane	95.4	CHBrCl2	-56	19.96	Acenaphthene	91.2	C12H10	-4	27.31	Dibutyl phthalate	92.4	C16H22O4	9
4.81	Chloral	78.8	C2HCl3O	3	20.18	4-Methylbiphenyl	79.4	C13H12	-4	27.59	9,10-Anthracenedione	93.2	C14H8O2	-27
4.91	Dichloroacetonitrile	86.4	C2HCl2N	-76	20.28	2,4-Di-tert-butylphenol	90.2	C14H22O	10	28.21	Octachlorostyrene	88.6	C8Cl8	-7
4.95	Chloromethylmethyl sulfide	94	C2H5ClS	-59*	20.56	Dibenzofuran	92.4	C12H8O	-5	28.36	Cyclopenta(def)phenanthrene	97.2	C15H8O	-74*
5.11	Dimethyl disulfide	98.4	C2H6S2	-35	21.21	3-Bromododecane	75.7	C12H25Br	-10	28.51	Cyclic octaatomic sulfur	93.1	S8	-18
5.35	Methyldiallylamine	85.7	C7H13N	-50*	21.45	Diethyltoluamide (DEET)	78.1	C12H17NO	10	28.53	Drometrizole	82.3	C13H11N3O	-5
5.47	Bromoacetonitrile	82.8	C2H2BrN	1	21.69	Diethyl Phthalate	96	C12H14O4	8	28.54	Fluoranthene	97.8	C16H10	-12
5.95	Dibromochloromethane	95.5	CHBr2Cl	-25	21.71	Fluorene	75.3	C13H10	-4	28.57	Phenindione	79	C15H10O2	-50*
6.01	Tetrachloroethylene	96.5	C2Cl4	-12	22.01	2-(Methylmercapto)benzothiazole	77.8	C8H7NS2	2	28.71	8-Carboxynaphthalene-1-carboxamide	85.5	C12H9NO3	135*
6.04	1,1-Dimethyl-3-chloropropanol	88.4	C5H11ClO	7	22.43	Benzophenone	94.8	C13H10O	4	28.91	β-Methylanthracene	75.5	C15H10O2	33
6.34	Bromochloroacetonitrile	86.2	C2HBrClN	60*	22.60	Tributyl phosphate	93	C12H27O4P	7	28.94	Dibenzothiophene sulfide	82.2	C12H8OS	N/A
6.59	Dichloroacetic acid methyl ester	89.2	C3H4Cl2O2	-7*	23.51	Hexachlorobenzene	97.2	C6Cl6	9	29.02	Pyrene	89.3	C16H10	-25
6.84	Dimethyl Sulfoxide	93.4	C2H6OS	-42	24.19	9H-Fluoren-9-one	97.1	C13H8O	8	29.34	1-Azapyrene	78.4	C15H9N	2
7.67	Tribromomethane	98.2	CHBr3	3	24.26	9H-Fluoren-9-ol	81.5	C13H10O	9*	29.37	Biphenanthrene	84.1	C15H16O2	34*
8.24	Methyl bromo(chloro)acetate	77.4	C3H4BrClO2	-13	24.30	Anthracene	94.4	C14H10	0	29.69	2-Amino-9-fluorenone	83.3	C13H9NO	2*
8.31	Dibromoacetonitrile	86.6	C2HBr2N	64*	24.19	Methylene-fluorene	81.9	C14H10	-75	29.87	Bis(4-chlorophenyl) sulfone	77	C12H8Cl2O2S	-1
8.56	1-Bromo-2,2-dimethoxypropane	79.2	C5H11BrO2	-58	24.91	Tris(2-chloroisopropyl)phosphate	82.2	C9H18Cl3O4P	27	29.87	2,2'-Methylene-bis-(4-methyl-6-t-butylphenol)	87.5	C23H32O2	2
10.63	2,2-Dichloroacetate	83.5	C2H3Cl2NO	-4*	25.02	Benzo[h]quinoline	88.2	C13H9N	-2	30.90	Benzo[b]naphtho[1,2-d]thiophene	77.2	C16H10S	13
10.73	1,2-Dichlorobenzene	86.9	C6H4Cl2	9	25.53	2,6-Diphenyl-4-methyl-2(E)-pentene	76.5	C18H20	8	30.94	7H-Benz[de]anthracen-7-one	89.2	C17H10O	85
14.12	Naphthalene	81.9	C10H8	-4	25.55	Benzo[h]isoquinoline	91.1	C13H9N	-53*	31.04	Benzo[2,1-d]thiophene	81.3	C16H9S	57
15.45	Caprolactam	89.6	C6H11NO	3	25.73	Carbazole	76.8	C12H9N	-4	31.38	Phthalic acid, di(2-propylpentyl) ester	94.8	C24H38O4	-5
16.43	2-Methylnaphthalene	89.3	C11H10	-1	25.90	Di-sec-butyl phthalate	90.8	C16H22O4	2	31.48	Bis(3,4-dichlorophenyl)sulfone	94	C12H6Cl2O2S	3*
16.64	Phthalic anhydride	92.5	C8H4O3	5	26.09	2,3-Diphenyl-2-propenenitrile	77	C15H11N	30*	31.51	Bumetrizole	78.6	C17H18ClN3O	57
16.98	Benzamide	82.8	C7H7NO	12	26.73	4-Methyldibenzothiophene	80.8	C13H10S	-5	31.82	Benz(a)anthracene-7,12-dione	76.1	C18H10O2	-48*
18.05	Biphenyl	83.2	C12H10	-1	26.66	4-Methylphenanthrene	84	C15H12	1	32.37	Bis(2-ethylhexyl) isophthalate	84.7	C24H38O4	-35
18.18	Benzeneacetamide	84.3	C8H9NO	13	27.02	2-Methylanthracene	88.5	C15H12	-27	33.24	Decachlorobiphenyl	94.3	C12Cl10	-81
19.27	Dimethyl phthalate	75.1	C10H10O4	8										

Table 3. Additional contaminants identified in drinking water using Pesticide PCDL for GC/Q-TOF.

RT	Compound Name	Match Score	Formula	RT	Compound Name	Match Score	Formula	RT	Compound Name	Match Score	Formula
6.17	2-Picoline	96.7	C6H7N	9.17	Benzaldehyde	98.5	C7H6O	22.29	DPA / Diphenylamine (DFA)	84.7	C12H11N
6.90	Methanesulfonate-methyl	79.6	C2H6O3S	9.52	Phenol	89.6	C6H6O	22.64	Isoxadifen	93.3	C16H13NO3
8.17	PPD / p-Phenylenediamine	80.0	C6H8N2	11.46	Acetophenone	94.3	C8H8O	24.64	Benzylbenzoate	83.0	C14H12O2
8.40	o-Toluidine	82.3	C7H9N	11.99	2,4,5-Trimethylaniline	82.7	C9H13N	25.96	DIBP / Diisobutyl phthalate	86.1	C16H22O4
8.93	Thanite	83.9	C13H19NO2S	12.90	2-Nitrophenol	77.1	C6H5NO3	27.00	Methylphenanthrene	85.3	C15H12

Statistical analysis was performed in the MPP where the differences between Weaverville and Irvine water sources (n=5/group) have been evaluated (Figure 6).

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Figure 6. Comparison of water sourced in Irvine vs Weaverville using Volcano plot, showing log2 of Fold Change (FC) vs −log10 of p-Value (p). Compounds on the right part of the plot (red squares) present at higher concentrations in Irvine water extracts, those on the left (blue squares) are present at higher concentrations in Weaverville extracts.

Additionally, contaminants with high response have been reprocessed using targeted approach, and the results are shown in Figure 7.

Figure 7. High abundance contaminants identified in drinking water(n=5 for each group). IR: Irvine; WV: Weaverville.

Conclusions

- PFAS accurate mass library containing over 100 EI spectra has been created for high resolution GC/Q-TOF including several emerging volatile PFAS

- PFAS compounds have been identified in soil and water extracts using PFAS PCDL

- Additional contaminants have been identified in drinking water from two different source categories and included disinfection byproducts, chemicals from personal care products, drugs, pesticides and other industrial contaminants without re-injecting the sample