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Esterification of perfluorinated carboxylic acids with bromomethyl aromatic compounds for gas chromatography combined with laser ionization mass spectrometry

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ABSTRACT

Perfluorinated carboxylic acids (PFCAs) were derivatized with two types of aromatic compounds that contained a bromomethyl group, i.e., 2-(bromomethyl)naphthalene (BMN) and benzyl bromide (BB). The conditions for derivatization were optimized in terms of reaction temperature and time and the concentration of derivatizing reagent. Using these optimal conditions, the PFCAs-MN and PFCAs-B derivatives were measured by gas chromatography (GC) combined with mass spectrometry using an ultraviolet femtosecond laser (267 nm) as the ionization source. The efficiency of derivatization for PFCAs-B was higher than that for PFCAs-MN because of the smaller size of the chromophore (benzene). The ionization efficiency of PFCAs-MN, however, was better than PFCAs-B, since a larger sized chromophore (naphthalene) and then a larger molar absorptivity was preferable for resonance-enhanced two-photon ionization. Due to superior GC separation, BB was successfully used as the derivatizing agent for the trace analysis of PFCAs, with detection limits of 6, 8.4, and 9.5 ng/mL for perfluoroheptanoic, perfluorooctanoic, and perfluorononanoic acids, respectively. The other bromomethyl aromatic compounds were evaluated for use as a derivatization reagent in future studies.

Keywords: Perfluorinated carboxylic acids, Derivatization, Gas chromatography, Mass spectrometry, Femtosecond laser.

1. Introduction

Perfluorinated carboxylic acids (PFCAs) are listed as persistent organic pollutants (POPs) in the Stockholm Convention, since they have emerged as worldwide pollutants in the past 60 years [1,2]. Because of their high chemical and thermal stabilities, oleophobic, hydrophobic, and other unrivalled characteristics, PFCAs and their salts have been employed as lubricants, paints, polishing agents, fire-fighting foams, and materials for food packaging in industrial and household consumables [3]. Due to their widespread use, persistency, and global distribution, PFCAs have been identified in a variety of environments, including in surface water [4,5], wildlife [6,7], and even in the human body [8]. Perfluorooctanoic acid (PFOcA) is particularly in widespread use as a material for water-repellent non-stick coatings and is well known as a representative of this entire class of pollutants. Therefore, it is used as an indicator for increasing the awareness of such compounds and their impact on animals and humans [9-11].

A wide variety of analytical methods have been developed for measuring PFCAs. Among them, gas chromatography combined with mass spectrometry (GC-MS) is one of the most commonly used techniques because of the excellent resolving power of GC and the high sensitivity/selectivity associated with MS. However, in electron ionization mass spectrometry (EIMS), the molecular ion is weak, since the energy of the electron used for ionization is typically 70 eV and frequently results in the decomposition of the molecular ion. To avoid this, several photoionization techniques have been developed for soft ionization. For example, a vacuum-ultraviolet (VUV) light source can be used for single-photon ionization, in which only molecules with ionization energies (*IEs*) lower than the VUV photon energy can be ionized and this approach provides a molecular ion [12,13]. An ultraviolet (UV) laser can also be used for two-photon ionization (2PI) in MS (LIMS), in which the analyte molecule can be efficiently ionized by absorbing the first photon for excitation and by absorbing the second photon for subsequent ionization. This technique, which is referred to as resonance-enhanced two-photon ionization (RE2PI), has been utilized for determining aromatic hydrocarbons. For example, environmental pollutants such as polychlorinated dioxins and polybrominated biphenyls [14,15], polycyclic aromatic hydrocarbons [16,17], nitrated polycyclic aromatic hydrocarbons [16-18], and pesticides [19] have been measured using a femtosecond laser as the ionization source in MS.

There are many polar POPs that cannot be vaporized for measurement by GC. Therefore, it is necessary to use a derivatization technique to increase the volatility of the analyte. It should be noted here that the analyte can be separated by liquid chromatography (LC) and then directly measured by MS (LC-MS) without using a derivatization technique [20]. However, the resolving power of LC is

limited, although it is partly compensated for by using a triple-stage MS (LC-MS/MS). In this case, the molecular ion separated in the first MS is trapped in the second MS, where it is decomposed by a collision with an inert gas, and the fragment ions are measured by the third MS. Accordingly, a comprehensive analysis of unknown samples is difficult using this approach. Many derivatizing reagents for use in GC procedures have been reported. For example, trimethylsilylation is well known and is widely used to increase the volatility of organic compounds that contain -OH or -COOH groups. On the other hand, 2,3,4,5,6-pentafluorobenzyl bromide has been utilized in LIMS for derivatizing nerve agent metabolites (NAMs), since it has a benzene chromophore for efficient 2PI in LIMS [21,22]. However, a pentafluorobenzyl group, which is useful for negative chemical ionization, is not suitable for RE2PI, since the substitution of fluorine atoms shifts the absorption spectrum toward wavelengths shorter than 267 nm and decreases the ionization efficiency. To avoid this undesirable effect, 2-(bromomethyl)naphthalene (BMN) has been employed to improve the ionization efficiency based on RE2PI, thus permitting NAMs to be detected at the sub picogram levels [23].

PFCA is a carboxylic acid with a long aliphatic chain, in which all the hydrogen atoms are substituted with fluorine atoms. A series of these compounds with different chain lengths are present at trace levels in the environment, thus requiring a sensitive analytical method with high resolving power for their measurement. In order to increase the volatility of the analyte for a GC analysis, a carboxyl group in PFCA is converted into a non-polar group by esterification [24,25]. It should be noted that benzyl bromide (BB) was examined as a potential derivatizing agent in a round robin test of PFCAs [26].

In this study, we report on the derivatization of PFCAs for measurement by GC combined with time-of-flight mass spectrometry (TOFMS) using a UV femtosecond laser as the ionization source. Two different types of derivatizing reagents, i.e., BMN and BB, were evaluated (the reaction scheme is shown in Figure 1) in terms of derivatization and ionization efficiencies as a basic feasibility study to examine a possibility for use in practical trace analysis in the future. A sample comprised of a mixture of PFCAs-B was separated from each other by GC and the side-reaction products arising from the use of BB were examined. Molecular ions, in addition to several fragment ions, were clearly observed on a two-dimensional display of GC-MS, permitting a comprehensive analysis of PFCAs at trace levels. Some other aromatic compounds that contained a bromomethyl group were also considered for use as a derivatization reagent in future studies and this is also discussed.

2. Experimental

2.1. Apparatus

A schematic diagram of the experimental apparatus used in this study is shown in Figure 2. A GC analytical instrument (6890 GC, Agilent Technologies) was combined using a transfer line (fused-silica capillary tube) with the TOFMS developed in this laboratory [27]. The third harmonic emission (267 nm) of a Ti:sapphire laser (800 nm,100 fs, 1 kHz, 1 mJ, Libra, Coherent, Inc.) was used as the ionization source. An aliquot of a sample solution (1 μL) was injected into the GC by an autosampler, and the analytes were separated using a DB-5ms column (30 m in length, 0.25 mm inner diameter, 0.25 μm film thickness). A split injection method (10:1) was used for a sample of PFCAs-B prepared at high concentrations (e.g., 50 μg/mL) to avoid signal saturation. On the other hand, a splitless injection mode was used for a sample prepared at low concentrations (e.g., <1 μg/mL) to improve the sensitivity. The oven temperature program of GC was set as follows: initially held at 30 ℃ for 1 min, then increased to 80 ℃ at a rate of 15 ℃/min, followed by an additional increment to 280 ℃ (10 min hold) at a rate of 20 ℃/min. Helium gas (purity, 99.9999%) was used as the carrier gas at a flow rate of 1 mL/min. The temperatures of the sample injection port and the transfer line were maintained at 280 and 250 ℃, respectively. The analytes separated by GC were ionized by the UV pulse in the TOFMS. The ion was detected by an assembly of microchannel plates (MCP, F4655-11, Hamamatsu Photonics), and the signal was recorded by a digitizer (Acqiris AP240, Agilent Technologies). The data were processed by a home-made software programmed by Visual Basic.

2.2. Reagents

Perfluoroheptanoic acid (PFHpA), PFOcA, perfluorononanoic acid (PFNA), BB, acetonitrile (ACN, HPLC-grade), and N,N-dimethylformamide (DMF) were purchased from Wako Pure Chemical Industries. The BMN was supplied from Sigma-Aldrich. All the derivatizing reagents were dissolved in ACN. The stock solution of PFCAs was prepared at concentrations of 100 μg/mL (2.91×10^{-4} M, 2.53×10^{-4} M, 2.26×10^{-4} M for PFHpA, PFOcA, PFNA, respectively) or 300 μg/mL in ACN and were diluted stepwise for the analysis.

2.3. Procedure

Typical conditions for preparation of the sample solution were as follows. For measuring the PFCAs-MN, an 80-μL aliquot of a 300 μg/mL (1.36×10^{-3} M) stock solution of BMN and a 100-μL aliquot of a 100 μg/mL stock solution of PFCAs were transferred to a GC vial, and a 20-μL portion

of ACN was added to give a final solution of 200 μL (50 μg/mL for PFCAs). The sample solution was heated at 75 ℃ for 1.5 hr. After centrifugation of the sample solution, the supernatant was transferred to another GC vial, and a 1-μL aliquot of the sample solution was injected into the GC. For measuring PFCAs-B, a 100-μL stock solution of BB prepared at 0.1 M (1.71×10^{-2} g/mL) and a 100-μL stock solution of PFCAs prepared at 100 μg/mL were reacted in a GC vial at 75 ℃ for 1.5 hr. This sample solution was directly injected into the GC without removing the BB and its side-reaction products.

3. Results and Discussion

3.1. Spectral properties calculated for derivatized compounds

The absorption spectra and the *IE* values were calculated for the derivatized compounds of PFHpA-MN, PFOcA-MN, and PFNA-MN, based on time-dependent density functional theory (TD-DFT) using a B3LYP method and a cc-pVDZ basis set. As shown in Fig. S1(A)-(C) (see Supplementary Material), the *IEs* were calculated to be 8.0932 eV (153.20 nm), 8.0921 eV (153.22 nm), 8.0914 eV (153.23 nm), and the excitation energy (*EE*) to the first excited state was calculated to be 4.2949 (288.68 nm), 4.2946 eV (288.70 nm), 4.2966 eV (288.56 nm), for PFHpA-MN, PFOcA-MN, and PFNA-MN, respectively. The above findings suggest that these compounds can be efficiently ionized via RE2PI at the wavelength of the third harmonic emission (267 nm, 4.64 eV) of a Ti:sapphire laser. This favorable result can be attributed to the presence of a naphthalene unit with a large molar absorptivity at 267 nm as the chromophore. The data for PFHpA-B, PFOcA-B, and PFNA-B are shown in Fig. S1(D)-(F), providing *IEs* of 9.1449 eV (135.58 nm), 9.1392 eV (135.66 nm), 9.1318 eV (135.77 nm) and the *EEs* of 5.2738 eV (235.09 nm), 5.2713 eV (235.20 nm), 5.2692 eV (235.30 nm) for PFHpA-B, PFOcA-B, and PFNA-B, respectively. These data suggest the occurrence of nonresonant two-photon ionization (NR2PI) or weakly-resonant two-photon ionization (WR2PI) at 267 nm for these compounds. This unfavorable result can be attributed to the small benzene unit as a chromophore, which provides a small molar absorptivity at 267 nm. In order to suppress the background signal arising from BMN and BB, the spectral properties of these reagents were also calculated, providing *IEs* of 7.9053 eV (156.84 nm) and 8.8512 eV (140.08 nm) and *EEs* of 4.1528 eV (298.56 nm) and 5.0197 eV (247.00 nm) for these compounds. These findings indicate that BMN and BB are ionized via RE2PI and NR2PI/WR2PI, respectively.

3.2. Optimization of the derivatization reaction

3.2.1 Optimal condition for derivatization *with BMN*

In the previous study of measuring NAMs, the analytes were derivatized with BMN using K_2CO_3 as a base (catalyst). However, the efficiency of reaction was low for PFCAs, probably due to a long aliphatic chain that was substituted with fluorine atoms. The analytes were then reacted without K_2CO_3 in a mixture of ACN and an aprotic solvent, DMF, to dissolve the BMN at high concentrations. However, the derivatization efficiency decreased in the mixed solvent, as shown in Fig. S3. Other solvents and bases were examined, but no suitable candidates were found in this study. Therefore, ACN was used as the solvent in the optimal condition studies related to the reaction temperature and time and the molar ratio between the PFCAs and BMN. Note that a chlorinated compound, i.e., chloromethylnaphthalene, was not examined due to lower reactivity in the derivatization reaction.

As shown in Figure 3(A), the derivatization efficiency increased with increasing temperature and was saturated at temperatures above 75 ℃. Since the boiling point of ACN is 83 ℃, the reaction temperature was set at 75 ℃ to minimize the vaporization of the solvent during the reaction. The efficiency of derivatization reached a constant value at reaction times above 1.5 hr, as shown in Figure 3(B). On the other hand, the efficiency increased with increasing concentration of BMN and reached a constant value at molar ratios of BMN:PFOcA above 3:1, as shown in Figure 3(C). Since the concentrations of BMN and the corresponding concentrations of the side-reaction products increased with increasing concentration of BMN, the ratio was set at 3:1 in this study.

3.2.2 Optimal conditions for derivatization with BB

The efficiency in derivatizing PFCAs with BB was examined using GC-FID, since the signals arising from PFCAs-B were clearly separated by GC from the background signals from BB and the side-reaction products (see Fig. S4). As shown in Figures 3(D)-(F), the derivatization efficiency reached a constant value at temperatures above 75 ℃ and 1.5 hr, in which the concentration of BB was increased to 0.05 M by following the protocol reported in reference [25]. The efficiency increased with increasing concentration of BB, and the background compounds were separated by GC even at a high concentration of 0.05 M (8.55×10^{-3} g/mL). As a result, PFCAs were derivatized at a temperature of 75 ℃, a reaction time of 1.5 hr, and a BB concentration of 0.05 M in this study.

3.3. Two-dimensional display and mass spectra measured with BMN

A standard sample mixture containing three PFCAs was measured using BMN by GC-LIMS. As shown in Figure 4, molecular ions for PFHpA-MN, PFOcA-MN, and PFNA-MN were clearly observed at *m/z* = 504, 554, and 604 at retention times of 10.5, 10.7, and 11.0 min, respectively, in the two-dimensional display. In addition, two isotopomers of BMN with nearly identical signal intensities were observed at *m/z* = 220 and 222, since there are two relatively abundant isotopes for Br (^{79}Br:^{81}Br = 50.7:49.3). The background signals arising from BMN and the side-reaction products appeared at the retention times where the PFCAs-MN was observed. This made it difficult to identify the fragment ions and to discuss the ionization/fragmentation processes. This unfavorable result can be attributed to the fact that the physical properties such as polarity and the volatility of PFCAs-MN are not determined by the aliphatic chain of PFCAs but, rather, is mainly determined by the naphthalene chromophore. The mass spectra measured at the retention time where PFHpA-MN, PFOcA-MN, and PFNA-MN appeared in the two-dimensional display, are shown in Figure 5. Molecular ions were clearly observed and the fragment ions at *m/z* > 250 were negligibly small. These data suggest that the derivatized compounds are highly stable, which can be attributed to the stable aliphatic chain substituted with fluorine atoms. The sample was measured in the 0-20 μg/mL range, and the detection limit defined as the concentration at which the signal-to-noise ratio was three was ca. 1 μg/mL for PFOcA.

3.4. Two-dimensional display and mass spectra measured with BB

A standard sample mixture containing three PFCAs was analyzed by GC-LIMS. Figure 6 shows a two-dimensional display, in which the signals arising from PFHpA-B, PFOcA-B, and PFNA-B were clearly separated from the large background signals from BB and the side-reaction products by GC. The analytes were observed at retention times of 10.6, 11.3, and 12.0 min, respectively (see the total ion chromatogram). A large signal peak appeared at a retention time of 12.6 min, which can be assigned to one of the side-reaction products appeared in the derivatization reaction or one of the thermally decomposed products of BB appeared in the sample injection port of the GC. As shown in Figure 7, molecular ions were observed in the mass spectra at *m/z* = 454, 504, 554 for PFHpA-B, PFOcA-B, PFNA-B, respectively, in addition to several fragment ions such as $C_4F_9^+$, $C_3F_7^+$, $C_3F_5^+$, $C_2F_5^+$ at *m/z* = 219, 169, 132, 120, respectively. Note that the molecular ion peak was more pronounced than the fragment ions when compared with data obtained by EIMS [26]. The peak width

of the molecular ion was slightly broadened, which would arise from a space charge effect; the initial velocity distribution of the molecular ion increased by a repulsive force induced by a charge produced by a large number of fragment ions (see Fig. 6). This undesirable effect can be reduced by decreasing the laser power or the concentration of the analyte. A linear analytical curve was constructed in the range of 0-3 μg/mL. The detection limit was calculated from the signal-to-noise ratio in the mass spectrum measured at a concentration of 0.5 μg/mL (see two-dimensional displays shown in Fig. S5). The detection limits achieved by observing a molecular ion were 6, 8.4, and 9.5 ng/mL for PFHpA, PFOcA, and PFNA, respectively. The major advantage of the present technique against EIMS would be the enhancement in the intensity of the molecular ion by LIMS. Moreover, the comprehensive analysis can be achieved by TOFMS, which is in contrast to a scanning-type quadruple MS currently used in environmental analysis [26].

3.5. Comparison of BMN and BB

As summarized in Table S1, derivatization efficiency can be calculated from the signal intensities measured by GC-FID. It should be noted that the efficiency was nearly independent of the chain length among the various PFCAs-MN and PFCAs-B. In contrast, the efficiency obtained using BMN was only 1.9-2.0% of the values obtained when BB was used, suggesting that the naphthalene chromophore decreased the rate of reaction with PFCAs because of increased chemical stabilization by a larger number of π-electrons and of the large steric hindrance conferred by the larger size of the chromophore as predicted from statistical molecular thermodynamics. Similarly, the ionization efficiency did not change significantly among the PFCAs-MN and also among the PFCAs-B, as shown in Table S2. This trend remained unchanged, even when the total ion signal was used (see Table S3). However, the ionization efficiency obtained using BB was only 1.9-2.1% of the values obtained using BMN (see Table S2). As shown in Fig. S1, the molar absorptivity of PFCAs-B at 267 nm is very (or negligibly) small, suggesting NR2PI or WR2PI as mentioned in Section 3.1. Therefore, the poor ionization efficiency of the PFCAs-B can be attributed to the small molar absorptivities of these compounds at 267 nm. As a result, the detection efficiency of the various PFCAs was nearly identical, in total, in the experiments where BMN and BB were used. Additional important factors include physical properties such as the polarity and volatility of PFCAs-MN and PFCAs-B, which affects the resolution among the analytes and also from the interference from BB and the side-reaction products. To resolve the products (derivatized compounds) from the reactant (derivatization reagent), it is desirable to use a small, non-polar molecule as a derivatizing reagent. In fact, the PFCAs-MN

derivatives were not separated from the BMN that remained in the sample solution, although optimizing the ramp rate of the column or using a different type of column, e.g., DB-1ms, cyanopropyl column, or other columns designed for separating fatty acid methyl esters, could separate BMN. In contrast, the PFCAs-B derivatives were separated from the background signals of BB and the side-reaction products, even though the a comparatively large amount of BB was injected into GC (8.6 μg/μL). For this reason, BB was considered to be more preferential for the use as a derivatizing reagent in the trace analysis of PFCAs.

3.6. Other possible derivatization reagents

Two types of derivatizing reagents with different chromophores were investigated in this study and their use was based on their optimal spectral and physical properties for measuring polar analytes of PFCAs. As summarized in Fig. S4, there are many other types of bromomethyl aromatic compounds that have the potential for use in the derivatization of PFCAs. Note that the *IE* decreases and the molar absorptivity increases by substituting -H with $-CH_3$, $-OCH_3$, $-NH_2$, and $-N(CH_3)_2$ in a benzene chromophore and, as a result, an electron donating group would be favorable for achieving a more efficient ionization. However, a hetero atom (O or N) in the molecule would serve as a reactive site and would need to be protected before the derivatization reaction. Two-ring aromatic compounds such as naphthalene, quinoxaline, quinoline, indole, and naphthylamine have larger molar absorptivities and would be useful for achieving a more efficient RE2PI. However, volatility of these materials decreases significantly (*b.p.* >200 ℃ for chromophore). It is interesting to note that aromatic amines have small *IEs* and are preferential for RE2PI, but they have poor volatility. Other compounds such as phenanthrene, anthracene, and pyrene derivatives have poor volatilities and may not be useful for GC (but, however, useful for LC).

The physical and spectral properties for benzene, toluene, and naphthalene derivatives are summarized in Table S5. The *IEs* for all these compounds are smaller than the two-photon energy at 267 nm (9.29 eV) and can be ionized via 2PI. The molar absorptivity increases in the order of molecular size (ε, ~0 for benzene, ~300 for toluene, ~3000 for naphthalene), but volatility decreases according this order (*b.p.*; 154, 176, and 274 ℃ for methoxybenzene, 1-methoxytoluene, and 2-methoxynaphthalene, respectively). As a result, the efficiency of RE2PI and volatility would be compromised for successfully using them as a derivatizing reagent in GC-LIMS. In general, the absorption spectrum tends to shift toward longer wavelengths and the *IE* decreases with an increase in the size of the chromophore (e.g., benzene → toluene → naphthalene). Because of this, it would

be desirable to find an optimal derivatizing reagent that absorbs the light at the laser wavelength. In addition, it would be more desirable for the derivatized compound to be more efficiently ionized via RE2PI than the derivatizing reagent. It should be noted here that the concentration of the derivatizing reagent in the sample solution is much higher than that of the compounds to be derivatized, resulting in large background signals in trace analysis. Unfortunately, the *EE* and the *IE* of the derivatized compound are slightly larger than those of the derivatizing reagent (see Table S5). This unfavorable result can be attributed to the strong electron attractive effect conferred by fluorine atoms in the alkyl chain. Accordingly, it would be difficult to selectively ionize the derivatized compounds against the derivatizing reagent in the measurement of PFCAs. Therefore, finding a suitable derivatizing reagent that allows the complete separation of the derivatized compounds against the derivatizing reagent by GC (like BB) is clearly needed. One of the alternative candidates that can be used for derivatization would be 4-(bromomethyl)toluene (BT) to form PFCAs-T, since it could be more efficiently ionized than BB by LIMS and has the possibility to be separated from BT and the side-reaction products by GC.

4. Conclusions

In this study, PFCAs were derivatized using BMN and BB and were comprehensively analyzed by GC-TOFMS. When BB was used for derivatization, GC allowed PFHpA-B, PFOcA-B, PFNA-B to be separated from BB and the side-reaction products, permitting a trace analysis at the ng/mL levels by LIMS. Molecular ions, in addition to several fragment ions, were clearly observed on the two-dimensional display of the GC-LIMS. Other possible candidates for use as a derivatization reagent that might lead to the more sensitive/selective detection of PFCAs and for better background suppression by GC. The approach proposed herein can be generally used for the trace analysis of polar compounds such as NAMs and pesticides that contain -OH or -COOH groups by GC-LIMS and would be useful for a comprehensive analysis of the constituents in environmental and forensic samples.

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Figure Captions

Fig. 1. Scheme for the reaction of PFOcA with (A) BMN and (B) BB.

Fig. 2. Experimental apparatus of GC-LIMS used in this study.

Fig. 3. Optimization of the derivatization reaction. (A) (B) (C) BMN (D) (E) (F) BB. Effects of (A) (D) temperature (reaction time, 1.5 hr; molar ratio, PFOcA:BMN = 3:1) (B) (E) reaction time (temperature, 75 °C; molar ratio, PFOcA:BMN = 3:1): (C) molar ratio of PFOcA and BMN (F) concentration of BB (temperature, 75 °C; reaction time, 1.5 hr). Concentration of PFCAs; 300 μg/mL for BMN and 150 μg/mL for BB. GC-FID was used for optimization in (D) (E) (F). On the other hand, GC-LIMS was used in (A) (B) (C), since it was difficult to identify the signal peaks arising from the PFCAs-MN derivatives on the chromatogram measured by FID due to large interference signals that were observed before optimizing the reaction conditions. Note that a semi-logarithmic plot is used in (F).

Fig. 4. Two-dimensional display of GC-MS measured for a sample mixture containing PFHpA-MN, PFOcA-MN, and PFNA-MN. Analyte concentration, 50 μg/mL for each compound. Inserts show expanded views of the parts where PFHpA-MN, PFOcA-MN, PFNA-MN, and BMN appear. Concentration, 50 μg/mL for each compound. Splitless injection.

Fig. 5. Mass spectra of a sample mixture containing PFHpA-MN, PFOcA-MN, and PFNA-MN measured at retention times of (A) 10.5 (B) 10.7 (C) 11.0 min. (a) - (c), molecular ions.

Fig. 6. Two-dimensional display of GC-MS measured for a sample mixture containing PFHpA-B, PFOcA-B, and PFNA-B. Analyte concentration, 50 μg/mL for each compound. The total ion chromatogram is shown at the top of the two-dimensional data. Analyte concentration, 50 μg/mL for each compound. Split injection.

Fig. 7. Mass spectra of a sample mixture containing PFHpA-B, PFOcA-B, and PFNA-B measured at retention times of (A) 10.6 (B) 11.3 (C) 12.0 min. (a) - (c), molecular ions; (d) $C_4F_9^+$ (e) $C_3F_7^+$, (f) $C_3F_5^+$ (g) $C_2F_5^+$.

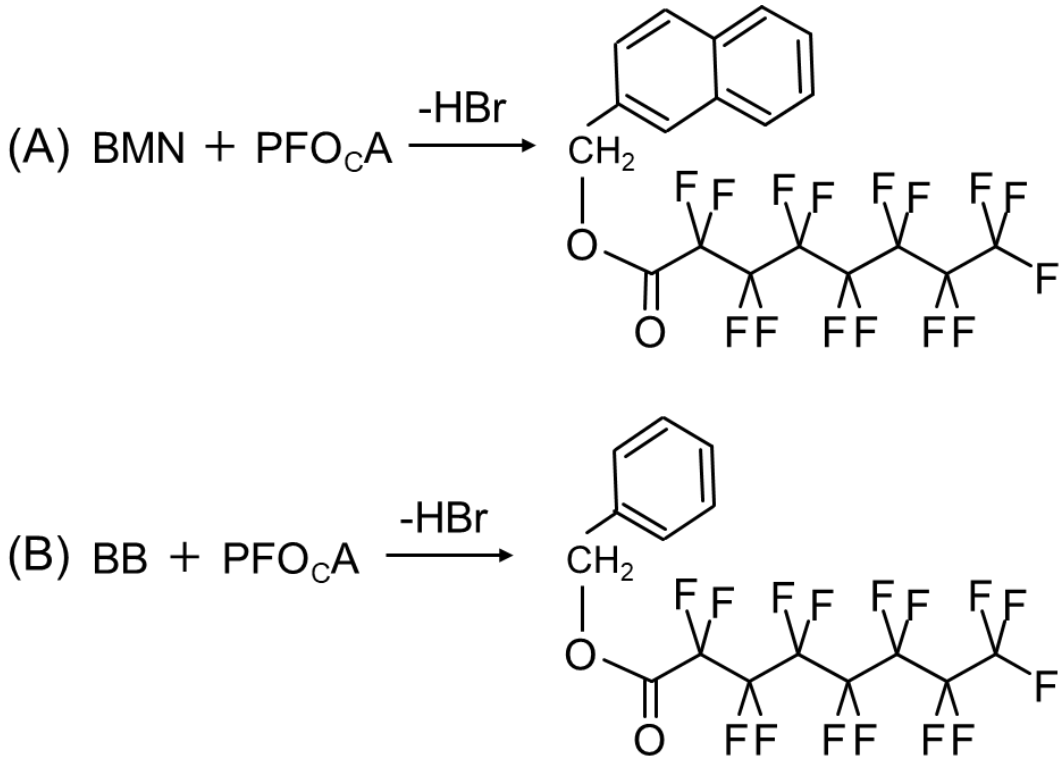


Fig. 1 Lu Wen, et. al.

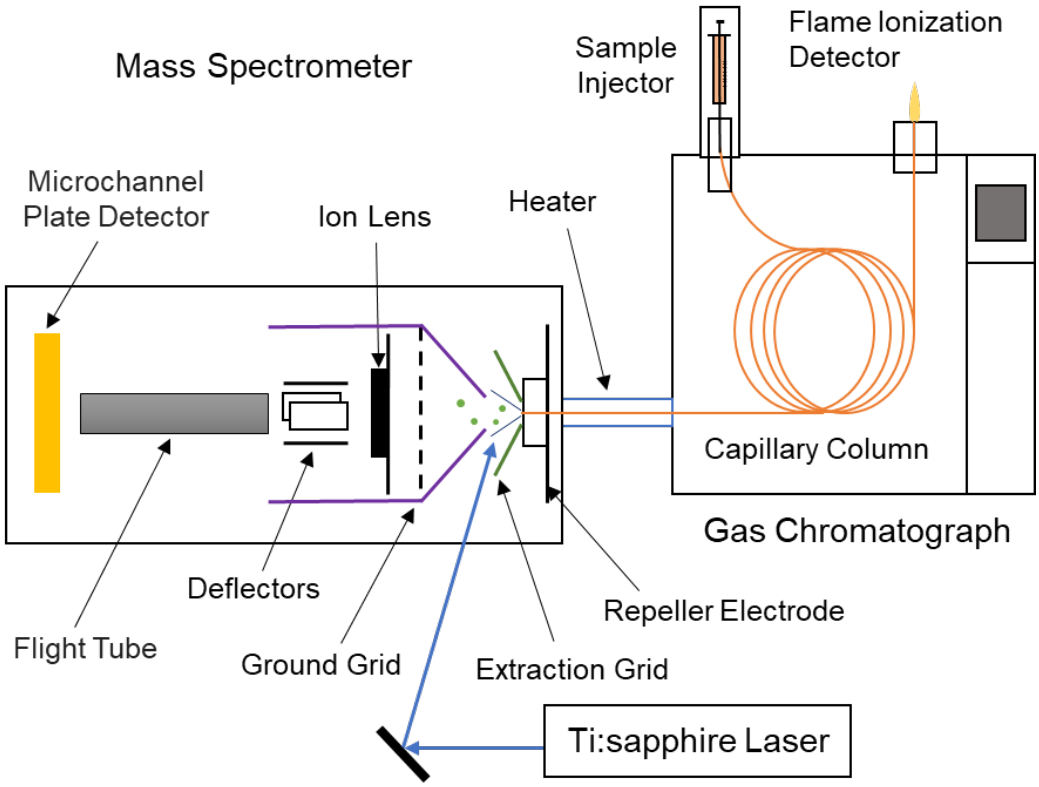
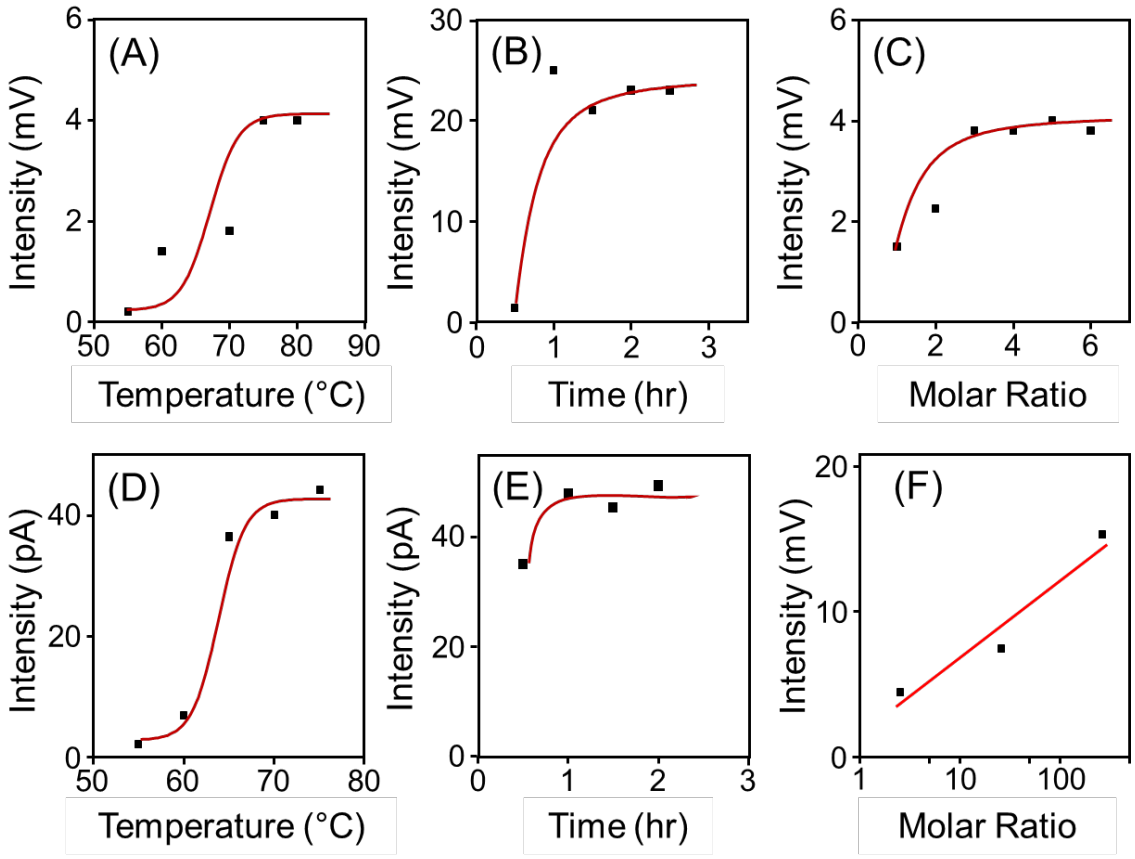


Fig. 2 Lu Wen, et. al.



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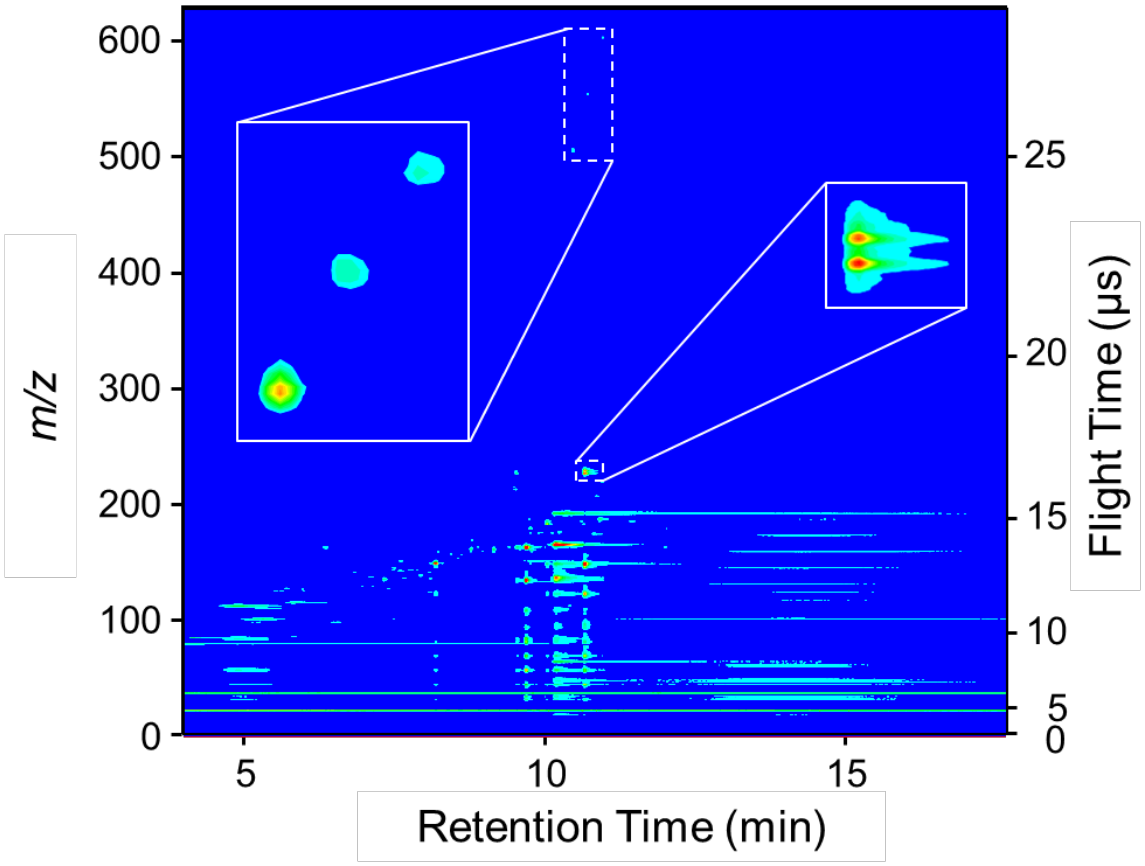

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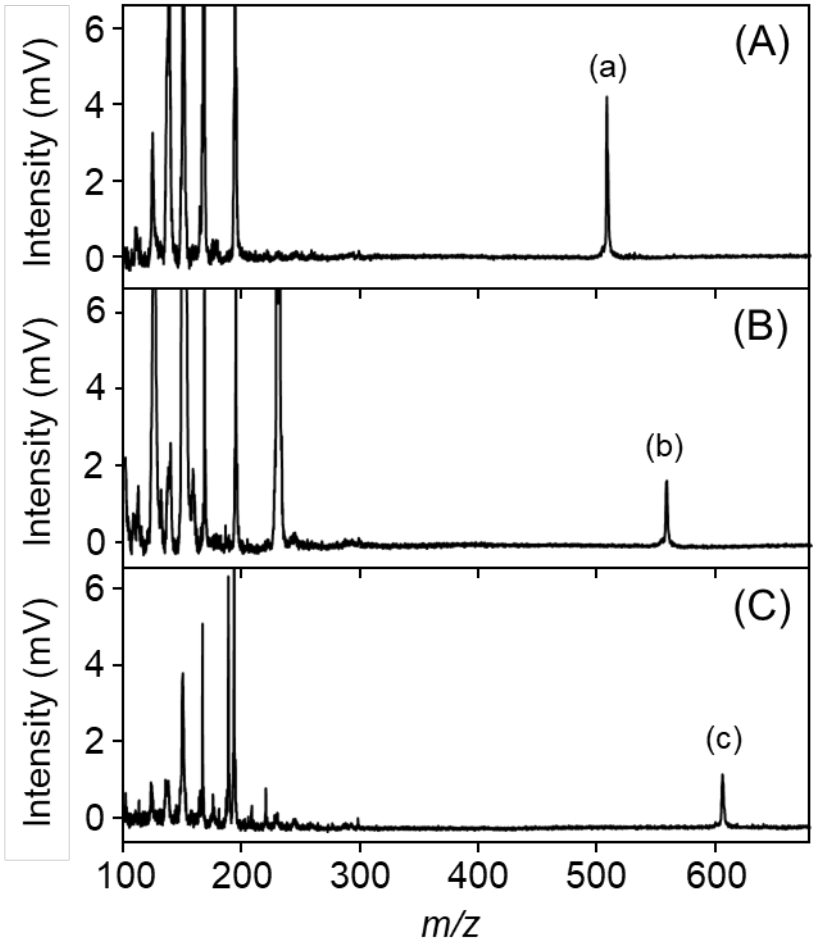

Fig. 5 Lu Wen, et. al.

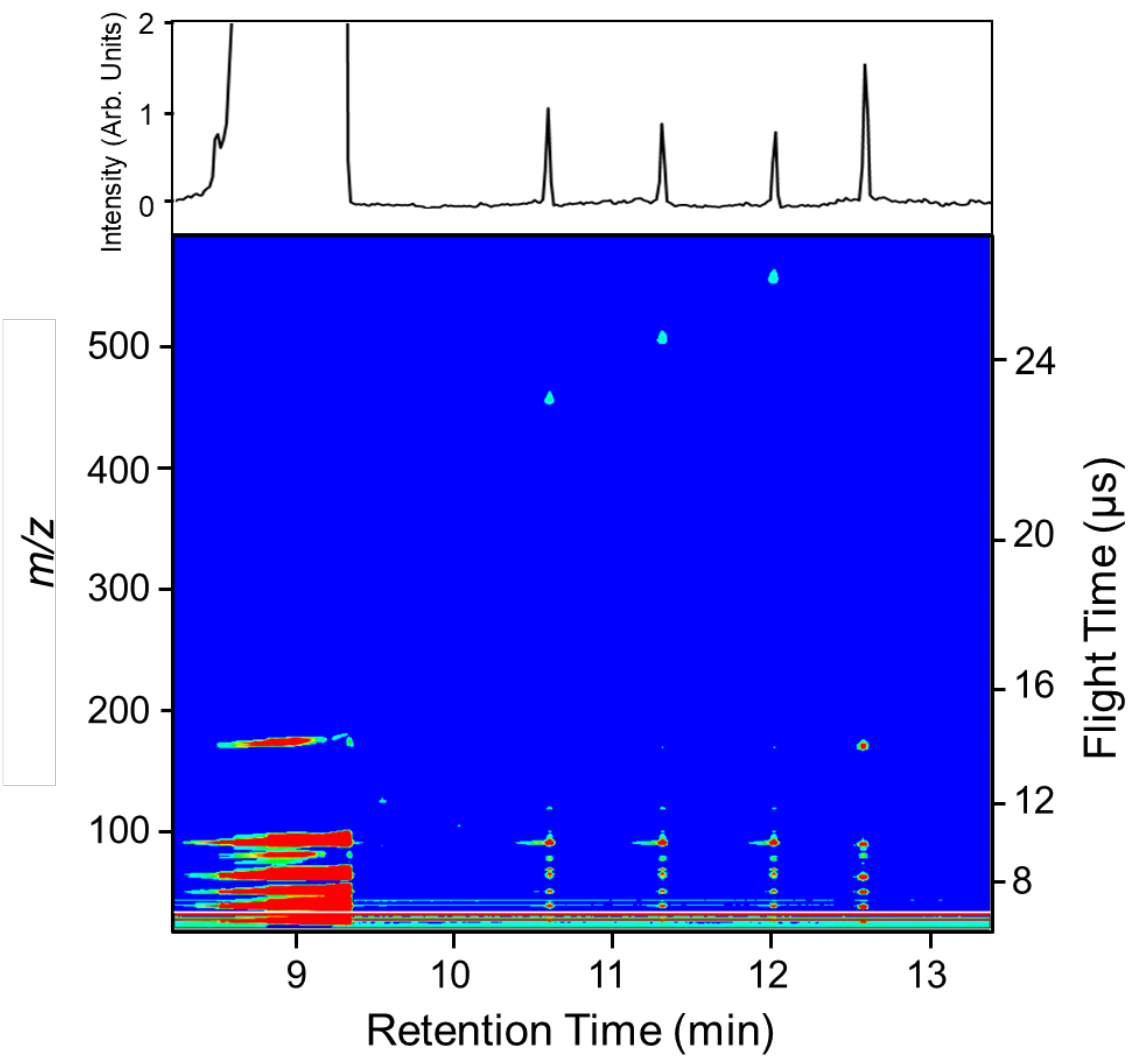

Fig. 6 Lu Wen, et. al.

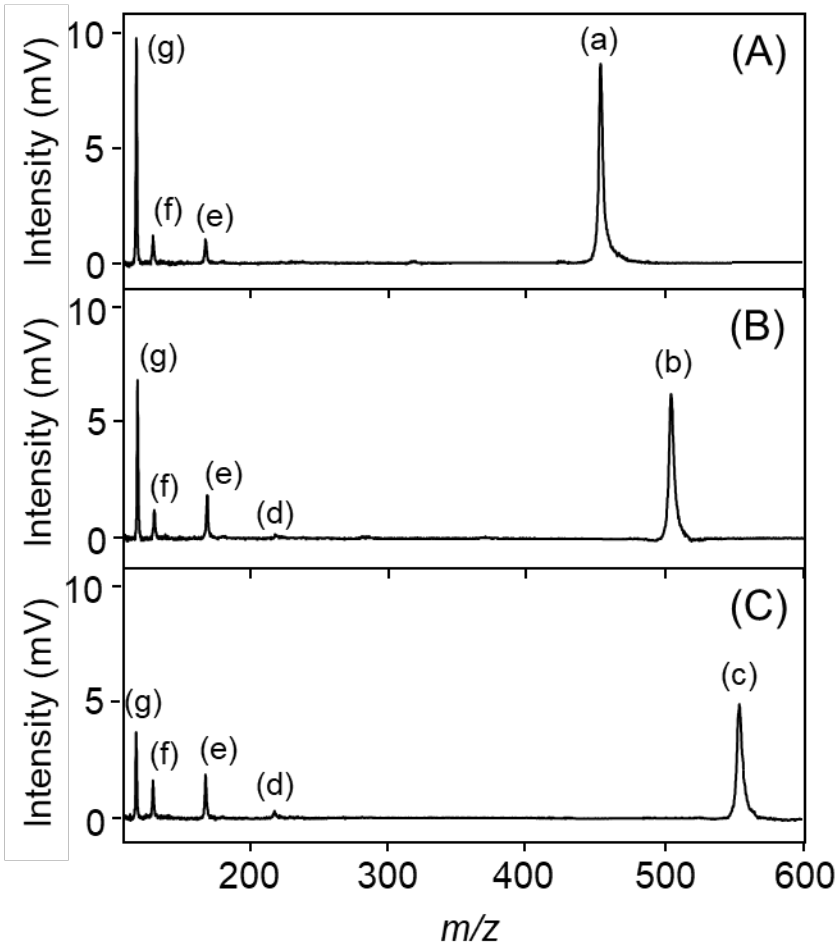

Fig. 7 Lu Wen, et. al.