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Analysis of Pesticides by Gas Chromatography/Multiphoton Ionization/Mass Spectrometry Using a Femtosecond Laser

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ABSTRACT

Gas chromatography/multiphoton ionization/time-of-flight mass spectrometry (GC/MPI/TOFMS) was utilized for analysis of a standard mixture sample containing 49 pesticides and 4 real samples using the third-harmonic emission (267 nm) of a femtosecond Ti:sapphire laser (100 fs) as the ionization source. A sample of a standard mixture of *n*-alkane was also measured for calibration of the retention time indices of the pesticides. Two photons are required for the excitation of *n*-alkane due to an absorption band located in the far ultraviolet region (140 nm). The *n*-alkane molecule in the excited state was subsequently ionized either directly or by absorbing another photon because of a high ionization potential. Due to a large excess of energy, the molecular ion was decomposed and formed many fragment ions. Compared to *n*-alkanes, most of the pesticides were softly ionized by the femtosecond laser; one photon was used for excitation and another was used for the subsequent ionization. The pesticides with no conjugated double bond had a lower ionization efficiency. The present analytical instrument was applied to several samples prepared from a variety of vegetables and a single fruit after pretreatment with solid-phase extraction. Three pesticides were found in these samples, although some of them were not detected by conventional GC/EI/MS-MS due to insufficient sensitivity and selectivity.

Keywords:

Femtosecond laser; Gas chromatography; Multiphoton ionization; Time-of-flight mass spectrometry; Pesticides; Density functional theory

1. Introduction

During the past century, more than 1,000 pesticides have been used in the production of crops, and many of them linger in the environment though they are no longer being utilized. For the protection of human health and the environment, several analytical instruments have been developed for the evaluation of pesticide residues in the food supply chain - water, soil, agricultural chemicals, food, etc. A gas chromatograph (GC) with high separation resolution has been coupled with a variety of sensitive detectors such as an electron capture detector (ECD) [1,2], a nitrogen phosphorus detector (NPD) [3], a flame ionization detector (FID) [4,5], and a flame photometric detector (FPD) [6]. In addition, mass spectrometers such as the quadrupole mass spectrometer (QMS) or the tandem mass spectrometer (MS-MS) have been successfully employed because of superior identification capability [7-11]. In addition to GC/MS, liquid chromatography/ultraviolet absorption spectrometry (LC/UV), liquid chromatography/mass spectrometry (LC/MS), and LC/MS-MS are also in common use, particularly for pesticides with high polarities and high boiling points [12-15]. However, GC/MS coupled with electron ionization (EI), often encounter interference that arises from a complicated matrix due to non-specific "hard" ionization by EI. In fact, a molecular ion is easily decomposed and forms many fragment ions that are troublesome in the determination of pesticides with a low molecular weight, although hard ionization by EI is useful for substance identification from the fragmentation pattern. Therefore, the conventional technique of EI/MS sometimes fails to determine the analytes present at low concentrations in the sample containing interference species at high concentrations.

A laser ionization technique has been developed to overcome the problem arising from EI. In this case, the wavelength of the laser can be optimized to excite the analyte molecule to intermediate levels to enhance both ionization efficiency and spectral selectivity. This technique, referred to as resonance enhanced multiphoton ionization (REMPI), is useful for "soft" ionization

and produces fewer fragments. Numerous investigations have chronicled the successful use of a variety of lasers for the measurement of aromatic hydrocarbons [16-24]. For example, the advantages of multiphoton ionization (MPI) with respect to sensitivity and selectivity were reported by Rhodes et al. and Bente et al. for the analysis of PAHs [17,18], and by Lubman et al. and Matsumato et al. for the analysis of some halogenated hydrocarbons [19,24]. A laser with a different pulse width has been utilized to ionize some organic compounds, and the ionization efficiencies has been compared with each other [20,22-24]. The studies of femtosecond ionization date from the 1990's that characterize fragmentation and dissociation pathways and their influence on the analytical capabilities of laser mass spectrometry in the gas phase [20-24]. To our knowledge, only one paper reported the analysis of a pesticide using a femtosecond ionization technique; laser desorption/multiphoton ionization/time-of-flight mass spectrometry (LD/MPI/TOFMS) was applied a metal organic compound of phenyl mercury chloride that is categorized as one of the pesticides [23]. In addition, a few pesticides have been measured based on nanosecond and picosecond ionization in LD/MPI/TOFMS [25,26,27], and based on thin layer chromatography/matrix-assisted laser desorption ionization/time-of-flight mass spectrometry (TLC/MALDI/TOFMS) [28].

In the present study, a femtosecond laser was utilized to analyze 49 pesticides, and the factors influencing ionization efficiency were investigated. Several samples extracted from a variety of vegetables and a single fruit were examined, and the high sensitivity and selectivity of GC/MPI/TOFMS were compared with those of GC/EI/MS currently used for analysis of pesticides.

2. Experimental

2.1. *Reagents and Analytes*

Standards of *n*-alkanes and pesticides were purchased from Hayashi Pure Chemical Ind., Co., Ltd. (Osaka, Japan). The *n*-alkane sample contained aliphatic hydrocarbons from C_7 to C_{33}. The concentrations were 10 μg mL^{-1} for C_7-C_{14} and C_{16}-C_{29} congeners and 20 μg mL^{-1} for C_{15} and C_{30}-C_{33} congeners (in hexane). The pesticide sample was dissolved in acetone and consisted of 49 pesticides, the concentration of each component was adjusted to an average of 20 μg mL^{-1}. Samples consisting of 20 g of either a vegetable or a fruit were homogenized with a 100 mL solution of acetonitrile-water (1:1, v/v). After filtration, 2 mL of phosphate buffer (pH = 7) and 10 g of sodium chloride were added to the filtrate and were centrifuged for 5 min. Then, 20 mL of the supernatant was taken and dried with anhydrous sodium sulfate, followed by concentration under a nitrogen flow. A mixed solvent of 2 mL acetonitrile-toluene (3:1, v/v) was added to dissolve the constituents using ultrasonic agitation. The sample solution was passed through an Envi-Carb + NH_2 solid-phase extraction (SPE) cartridge. Before loading the sample solution, the cartridge was conditioned with 10 mL acetonitrile-toluene (3:1, v/v). The analyte extracted in the cartridge was eluted 3 times using the above solvent. The solvent was evaporated under reduced pressure. The residue was reconstituted with the mixed solution containing 1 mL of chrysene-d_{12} and anthracene-d_{10} (0.5 μg mL^{-1}) for use as international standards in GC/MPI/TOFMS.

2.2. *Apparatus*

The laboratory-made linear time-of-flight mass spectrometer used in the present study has been reported in detail elsewhere and is now commercially available (HGK-1, Hikari-GK, Fukuoka) [2-31]. The third harmonic emission of a Ti:sapphire laser (wavelength, 267 nm; energy, 150 μJ; repetition rate, 1 kHz; pulse width, 100 fs; Libra, Coherent Inc., CA) was utilized as an ionization source. A 1-μL sample solution was injected into a GC system (6890N, Agilent Technologies) using an auto sampler (7683B, Agilent Technologies). The constituents in the samples were separated using a DB-5 ms capillary column (length, 30 m; i.d., 0.25 mm; film

thickness, 0.25 μm) and a carrier gas of helium at a constant flow-rate of 1 mL min^{-1}. The temperature program for the DB-5 ms column was set to increase from 50 (held for 1 min) to 125 °C at a rate of 25 °C min^{-1} and was then increased to 280 °C and held for 13.5 min. The temperatures of the injection port and the transfer line were maintained at 250 °C. The analyte eluting from the GC was introduced into a linear-type TOFMS. The induced ions were measured using a microchannel plate detector (F4655-11, Hamamatsu). The voltages applied to the electrodes in the MS were optimized by monitoring the mass spectrum of the chemical species bleeding from a GC capillary column (HP-5) using a digital oscilloscope (1 GHz, 20 GS s^{-1}, DPO7104, Tektronix), the observed mass resolution was 1040. Finally, the signal was recorded using a digitizer (1 GHz, 1 GS s^{-1}, Acqiris AP240, Agilent Technologies). The data were analyzed using LabVIEW software.

2.3. *Computational method*

The ionization energy (IE) was calculated for five *n*-alkanes and five pesticides by density functional theory (DFT) at the B3P86/cc-pVDZ level [32-33]. No restriction was imposed during optimization, and the harmonic frequency was calculated to ensure an optimized geometry providing a global energy minimum. The energy for a singlet-excited state (Es) was also calculated using time-dependent DFT (TD-DFT) [34]. All the calculations were performed using a Gaussian03 program (Gaussian, Inc., Wallingford CT, 2004) [35].

3. **Result and discussion**

3.1. *Standard sample of n-alkane*

Before analysis of the pesticides, a standard mixture sample of *n*-alkanes (C_7-C_{33}) was measured using GC/MPI/TOFMS for calibration of the retention time index (RT index) for pesticides, according to the protocol provided by the Ministry of Health, Labor and Welfare of Japan [36]. For example, when the RT index is 1,509 for one pesticide, it means that the retention time of this pesticide lies at a retention time 9 % apart from C_{15} to C_{16}. Thus, the RT index is very important in GC and is treated as a scale for calibration of the RT values. Figure 1 shows a two-dimensional display and a mass chromatogram of the standard mixture sample of *n*-alkanes. The signals for C_9-C_{33} *n*-alkanes were clearly observed in the present study. The signals for C_7 and C_8 were not measured, since their RTs were too close to that of the hexane that was used as the solvent; a large signal arising from a solvent could damage a microchannel plate detector. As mentioned, MPI is a technique of "soft" ionization. However, numerous intense peaks arising from fragment ions are observed in Figure 1 (a), and the molecular ion peaks are relatively small. The IEs for *n*-alkanes from C_9H_{20} to $C_{15}H_{30}$ ranged from 9.87 to 9.68 eV (Table 1) with the calculation at the B3P86/6-31++G(d,p) level [37], which was larger than the energy of two photons (9.30 eV) used in the present study. The IEs for a homologous series of organic compounds are known to decrease with an increase in molecular mass [38]. However, the specific values of IEs for molecules larger than $C_{16}H_{34}$ have seldom been reported in the reference. In order to investigate the character of photon absorption by *n*-alkanes, the IE and the $S_0 \rightarrow S_1$ transition energy were calculated for several *n*-alkane molecules using density functional theory (DFT). The results are summarized in Table 1. The calculated IE decreased with an increase in the number of carbons in a molecule, as predicted. For molecules smaller than $C_{15}H_{32}$, the IE was larger than the energy of two photons (9.30 eV), and the energy for excitation to the S_1 state (ca. 9 eV) was much higher than the energy of one photon (4.65 eV, 267 nm) of the laser used in the present study. Therefore, at least 2 photons were required in the first excitation step of $S_0 \rightarrow S_1$, and subsequent ionization occurred either directly or with another photon. This result suggests that *n*-alkane is ionized through the two-photon or three-photon process using a laser emitting at

267 nm. For molecules larger than $C_{15}H_{32}$, the IEs are lower than those for $C_{15}H_{32}$, in which case the energy of two photons would be sufficient for direct ionization from the ground state. A laser with a high peak power is required for non-resonant two-photon ionization, providing many fragments by "hard" ionization and a poor limit of detection (LOD). In fact, the LOD values (S/N = 3) were 0.26-1.9 ng for C_9H_{20}-$C_{33}H_{68}$ in the present study; the largest signal of $C_4H_9^+$ was used in both MPI and EI [39]. Thus, the LODs of *n*-alkanes were much poorer than those of polycyclic aromatic hydrocarbons with $S_0 \rightarrow S_1$ transition energy almost equal to the one-photon energy of the laser [40]. However, *n*-alkanes were measured for calibration of the RT indices, and the sensitivity achieved in the present study was sufficient for this purpose. Moreover, poor sensitivity for *n*-alkanes is favorable for selective as well as sensitive determination of pesticides, some of which can be resonantly ionized via a singlet-excited state. As far as can be ascertained, this is the first study to report the multiphoton ionization efficiency for a series of *n*-alkane molecules.

3.2. *Standard sample of pesticide*

Figure 2 shows the mass chromatogram obtained by accumulating the total of the ions from the data of a two-dimensional display measured for a standard mixture sample containing 49 pesticides prepared at a concentration of 20 μg mL^{-1}. All pesticide molecules were assigned from the data of the RT indices and from the mass spectrum in the reference due to similarity in the fragmentation pattern [36]. Although the experimental conditions were not exactly identical to those in the reference, the difference in the RT index was negligibly small. For example, the RT index of chloroneb was 1,509 in the reported data [36], but the value obtained in the present study was 1,516. Thus, the difference in elution time was only 4 s for this compound. Thus, the RT indices reported in the reference were successfully utilized for assignment of the pesticides in the standard mixture sample. The LODs measured for the pesticides in the present study are

summarized in Table 2, wherein the RT indices are also listed in the third column. Two series of LODs were measured by MPI; one was calculated from the intensity of the molecule ion $[M]^+$ and the other was from the fragment ion $[F]^+$. Although the fragment ion $[F]^+$ was not necessarily the strongest, it was used as a diagnostic peak according to the reference of EI mode [33]. The LODs obtained using GC/EI/MS are also listed in Table 2. The LODs achieved by GC/MPI/TOFMS were in the subpicogram/picogram range for most pesticides, which is superior to those obtained by the other methods with some minor exceptions; MPI is superior to EI for 55 % (18 pesticides/33 pesticides), inferior for 15 % (5/33), and nearly the same for the other pesticides. It should be emphasized that molecular ions are mostly observed with MPI/TOFMS and can be used for identification of the pesticides due to soft ionization in the MPI process relative to EI. However, some of the pesticides have poor LODs in MPI/TOFMS, which could be explained by the light absorption character of the pesticide molecule. In fact, pesticides with no conjugated double bond, e.g., chlorethoxyphos, di-allate, spiroxamine, endosulfansulfate, and disulfoton sulfone, the chemical structures of which are shown in Figure 3 (a)-(e), have LODs of several hundred pg. These poor LODs would be ascribed to small absorptivities at 267 nm. Unfortunately, no spectral data were available for these molecules in the reference, and the energy for excitation to the S_1 state and the ionization potential were calculated theoretically by means of the DFT method. The results are shown in Table 3. The energy of 1 photon (267 nm) is apparently insufficient for excitation of these molecules to the S_1 state, although 2 photons of the laser used in the present study were adequate for excitation to the S_1 and higher electronic states. Therefore, poor LODs would be drastically improved using a laser emitting at shorter wavelengths, e.g., the fourth harmonic emission (200 nm) of a Ti:sapphire laser.

Chemical stability at an elevated temperature would be one of the other reasons for low LODs. For example, the LOD of oryzalin with a chemical structure shown in Figure 3 (f) was relatively poor, as shown in Table 2, probably due to poor chemical stability arising from the hydrogen bonding of a sulfonamide group [42]. Therefore, oryzalin was measured by LC rather

than by GC to avoid thermal decomposition [43]. In fact, relatively poor LODs were obtained with both GC/MPI/TOFMS and GC/EI/MS. A slightly poorer result obtained in the present study with MPI/TOFMS could be attributed to the high temperature of the transfer line (250 °C), since this temperature is appreciably higher than the decomposition temperature of oryzalin (213 °C). A similar case would be imazamethabenz-methyl (Figure 3 (g)), which is more amenable to the use of LC rather than GC [44]. Therefore, the use of LC/MPI/TOFMS is desirable for the measurement of such thermally labile pesticides. Another reason for poor LOD could be fast photolysis of a pesticide molecule. For example, only 20 % of the chlozolinate shown in Figure 3 (h) is reported to remain after the irradiation of sunlight for one hour [45]. For the furilazole shown in Figure 3 (i), a poor LOD would be ascribed to poor thermal/photochemical stability and/or a low absorptivity at 267 nm.

3.3. *Real samples*

The pesticides extracted from several real samples were measured for the performance evaluation of GC/MPI/TOFMS. A two-dimensional display of the data for a cucumber is shown in Figure 4. The pesticides in the sample were assigned from the data of the RT indices in GC and the *m/z* values in MS obtained for the standard chemicals. The cucumber sample yielded 3 species of pesticides, 2-(1-Naphthyl)acetamide, thiabendazole, and tricyclazole, although none of these compounds were detected by conventional GC/EI/MS-MS [46]. For a more careful check of the above assignment, expanded views of the two-dimensional display and the mass spectrum corresponding to the regions of a molecular ion and a fragment ion of 2-(1-Naphthyl)acetamide ($C_{12}H_{11}NO$) are shown in Figure 5. The intensity distribution of the isotope peaks for $[M]^+$ (*m/z* = 185), $[M+1]^+$ (*m/z* = 186), and $[M+2]^+$ (*m/z* = 187) can be calculated to 100 : 14 : 0.2, owing to a natural abundance of C, O, H, and N atoms. As shown in Figure 5 (a), the isotope peaks were well-resolved for a molecular ion, and the intensity distribution was in reasonable agreement

with that expected above. The assignment was confirmed by comparing the data obtained for the standard chemical (Figure 5 (b)). The isotope peaks are poorly resolved in the mass spectrum for a fragment ion of $[M-44]^+$. The result obtained for the real sample was, however, in reasonable agreement with those obtained for the standard chemical. Thus, the presence of 2-(1-Naphthyl)acetamide was confirmed in the cucumber from both the retention time in GC and the isotope pattern in the mass spectrum. It should be noted that the advantage of GC/MPI/TOFMS over GC/EI/MS is not only higher sensitivity, i.e., 118 (13 pg/0.11 pg) times for 2-(1-Naphthyl)acetamide (shown in table 2), but also superior reliability in the assignment provided by a single data set from a two-dimensional display.

The results for the assignment of thiabendazole ($C_{10}H_7N_3S$) are shown in Figure 6. The intensity distribution of the isotope peaks can be calculated to 100 : 13 : 4.5 for $[M]^+$, $[M+1]^+$, and $[M+2]^+$ from the natural abundance of C, H, N, and S atoms. The experimental results obtained for the real sample were consistent with the predicted intensity distribution of the isotope peaks and were also in reasonably good agreement with those obtained for the standard chemical. The isotope peaks for the fragment ions, $[C_9H_6N_2S]^+$, were not resolved for either standard or real samples, although the resolution of the mass spectrometer was sufficient ($m/\Delta m$ = 1040). It should be noted that the peak width of the mass spectrum was much larger than that of 2-(1-Naphthyl)acetamide, as shown in Figure 5. Thus, poor resolution for the fragment isotope peaks cannot be ascribed to the performance of the analytical instrument. A possible explanation could be the increased initial velocity distribution by fragmentation, suggesting that a thiabendazole molecule has a larger internal energy before dissociation/ionization and produces fragment ions with larger velocities. Such an initial velocity distribution is cancelled in a reflectron-type TOFMS but can be measured using a linear-type TOFMS. Thus, the linear-type instrument used in the present study has the potential for use in the differentiation of a molecular ion against a fragment ion having the same *m/z* value occasionally produced from a chemical species having the same RT value in GC. Thus, the present approach using a linear-type TOFMS has an

advantage over a reflectron-type TOFMS, although the latter has a relatively higher mass resolution.

Similar work has been conducted for a signal assigned to tricyclazole ($C_9H_7N_3S$). The results obtained in the present study were similar to those in the previous section, but are not shown here. The only difference is a lack of fragments, probably due to the more rigid structure of tricyclazole compared with that of thiabendazole.

A two-dimensional display of the data measured for a lemon sample is shown in Figure 7. In this case, only thiabendazole was found and confirmed according to the procedure described in the previous sections, although this compound could not be detected by conventional GC/EI/MS-MS [46]. This fact suggests a superior sensitivity/selectivity for GC/MPI/TOFMS. We also measured pesticides in the other vegetables. For example, thiabendazole was found in a tomato and thiabendazole in green pepper and chrysanthemum coronarium using GC/MPI/TOFMS, although these three pesticides were not detected by GC/EI/MS-MS. Thus, the approach based on GC/MPI/TOFMS was sufficient for the determination of pesticides in the real samples, because of a high sensitivity as well as a high selectivity arising from the process of MPI providing suppressed signals for aliphatic hydrocarbons and less fragmentation.

4. Conclusion

An ultraviolet femtosecond laser operated at 267 nm was utilized for the trace analysis of pesticides by GC/MPI/TOFMS. An *n*-alkane standard sample was measured for the calibration of the RT indices for pesticides. The experimental data and the result of DFT calculation suggested two-photon excitation to the S_1 state for *n*-alkanes. Accordingly, the efficiencies of multiphoton ionization were three orders of magnitude lower than those for other aromatic hydrocarbons such as pesticides, resulting in several ng of LODs for *n*-alkanes. However, pesticides were efficiently ionized through a resonant process via the S_1 state, wherein the LODs

were in a subpicogram/picogram range that was superior to those obtained by GC/EI/MS in most cases; an exception was pesticides having no absorption band at the laser wavelength. The present analytical instrument was applied to the trace analysis of pesticides in a variety of vegetables and a single fruit after pretreatment with SPE. Three pesticides, which were not detected by GC/EI/MS, were clearly observed by GC/MPI/TOFMS. This favorable result was ascribed to superior sensitivity/selectivity provided by resonant MPI. Further improvement in performance could be possible by increasing the repetition rate of a laser. Thus, the present approach of using GC/MPI/TOFMS would be useful for the trace analysis of pesticides in the environment.

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Figure Captions

Figure 1 Two-dimensional display (a) and total-ion-monitoring mass chromatogram (b) of a standard mixture sample of *n*-alkanes measured by GC/MPI/TOFMS using a femtosecond laser emitting at 267 nm. Concentration: 100 μg mL^{-1} for C_7-C_{14} and C_{16}-C_{29} alkanes, 200 μg mL^{-1} for C_{15} and C_{30}-C_{33} alkanes.

Figure 2 Mass chromatogram of a standard mixture sample containing 49 pesticides (20 μg mL^{-1} for each) measured using GC/MPI/TOFMS. Large peaks are slightly saturated to enhance small signals.

Figure 3 Chemical structures of 9 pesticides: (a) chlorethoxyphos (b) di-allate (c) disulfoton sulfone (d) spiroxamine (e) endosulfansulfate (f) oryzalin (g) imazamethabenz-methyl (h) chlozolinate (i) furilazole.

Figure 4 Two-dimensional display for a cucumber sample measured using GC/MPI/TOFMS. The peaks marked with 15, 19 and 27 were assigned to 2-(1-Naphthyl)acetamide, thiabendazole, and tricyclazole, respectively. Internal standards of chrysene-d_{12} and anthracene-d_{10} were added in the sample.

Figure 5 Mass spectrum and two-dimensional display for a cucumber sample (a) and a standard mixture sample (b): The signal is assigned to molecular (right) and fragment (left) ions arising from 2-(1-Naphthyl)acetamide. RT: retention time.

Figure 6 Mass spectrum and two-dimensional display for a cucumber sample (a) and a standard mixture sample (b): The signal is assigned to molecular (right) and fragment (left) ions arising from thiabendazole. RT: retention time.

Figure 7 Two-dimensional display of a lemon sample measured with GC/MPI/TOFMS. The peak marked with 19 was assigned to thiabendazole. Internal standards of chrysene-d_{12} and anthracene-d_{10} were added to the sample.

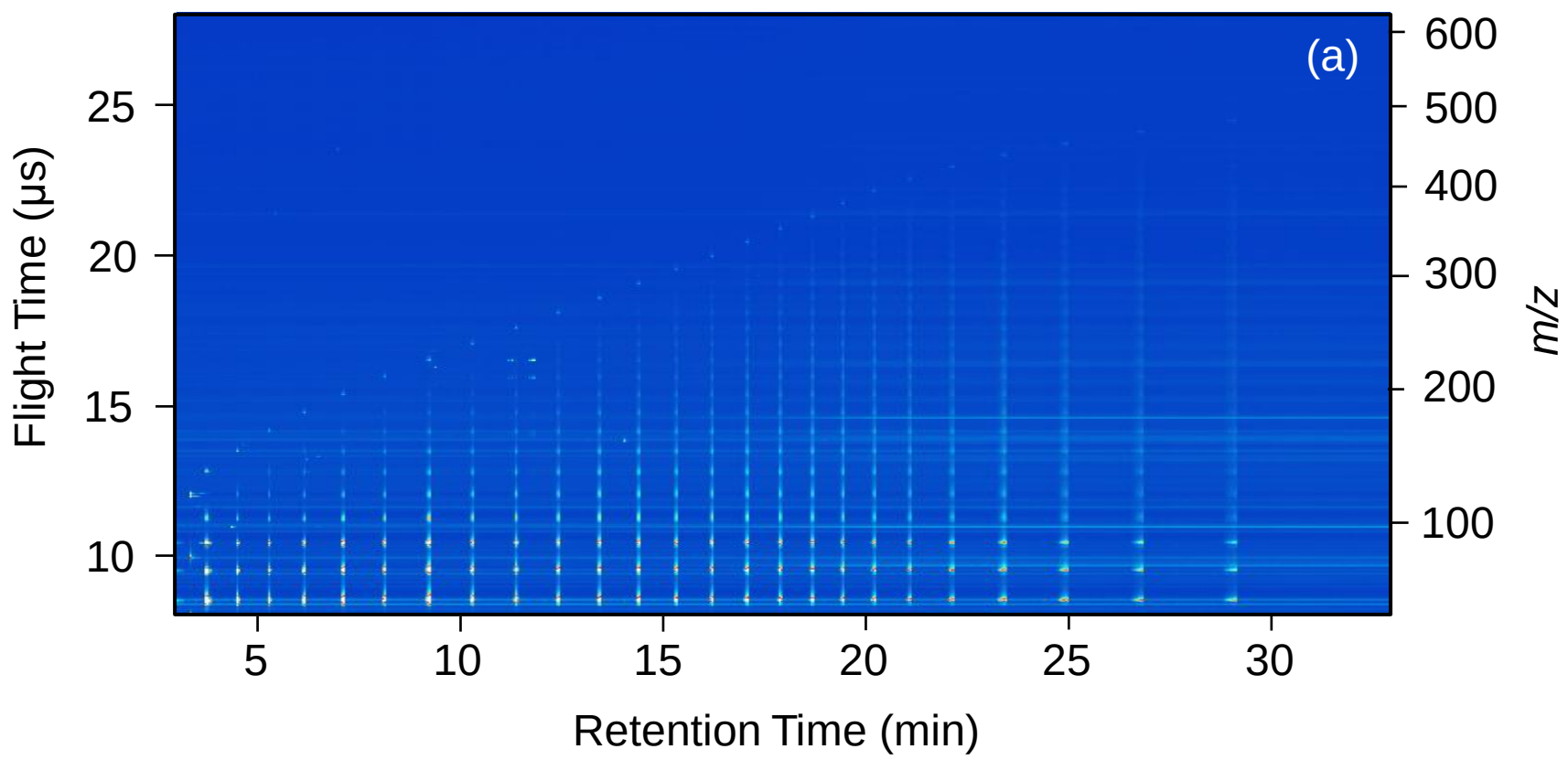

(a)
Flight Time (μs)
25
20
15
10
5
10
15
20
25
30
Retention Time (min)
600
500
400
300
200
100
m/z

Fig.1

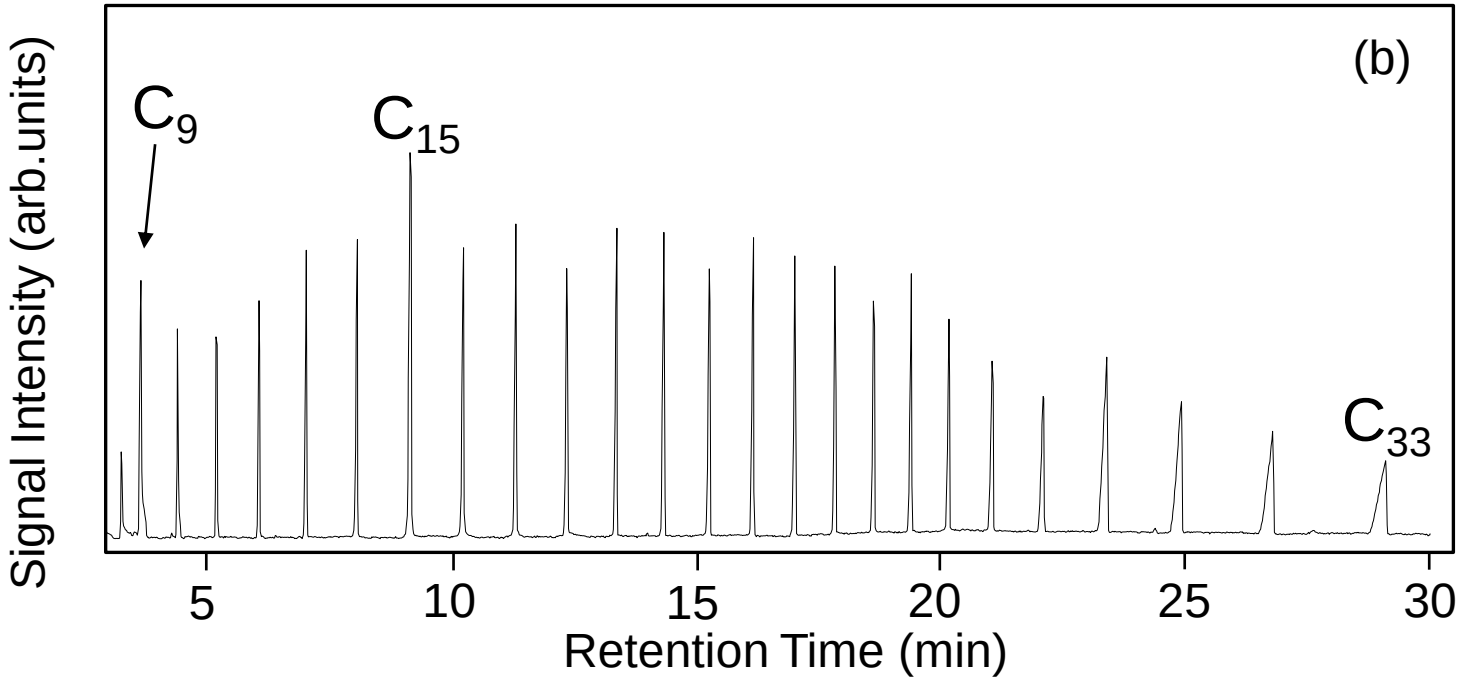

(b)
C9
C15
C33
Signal Intensity (arb.units)
5
10
15
20
25
30
Retention Time (min)

Fig.2

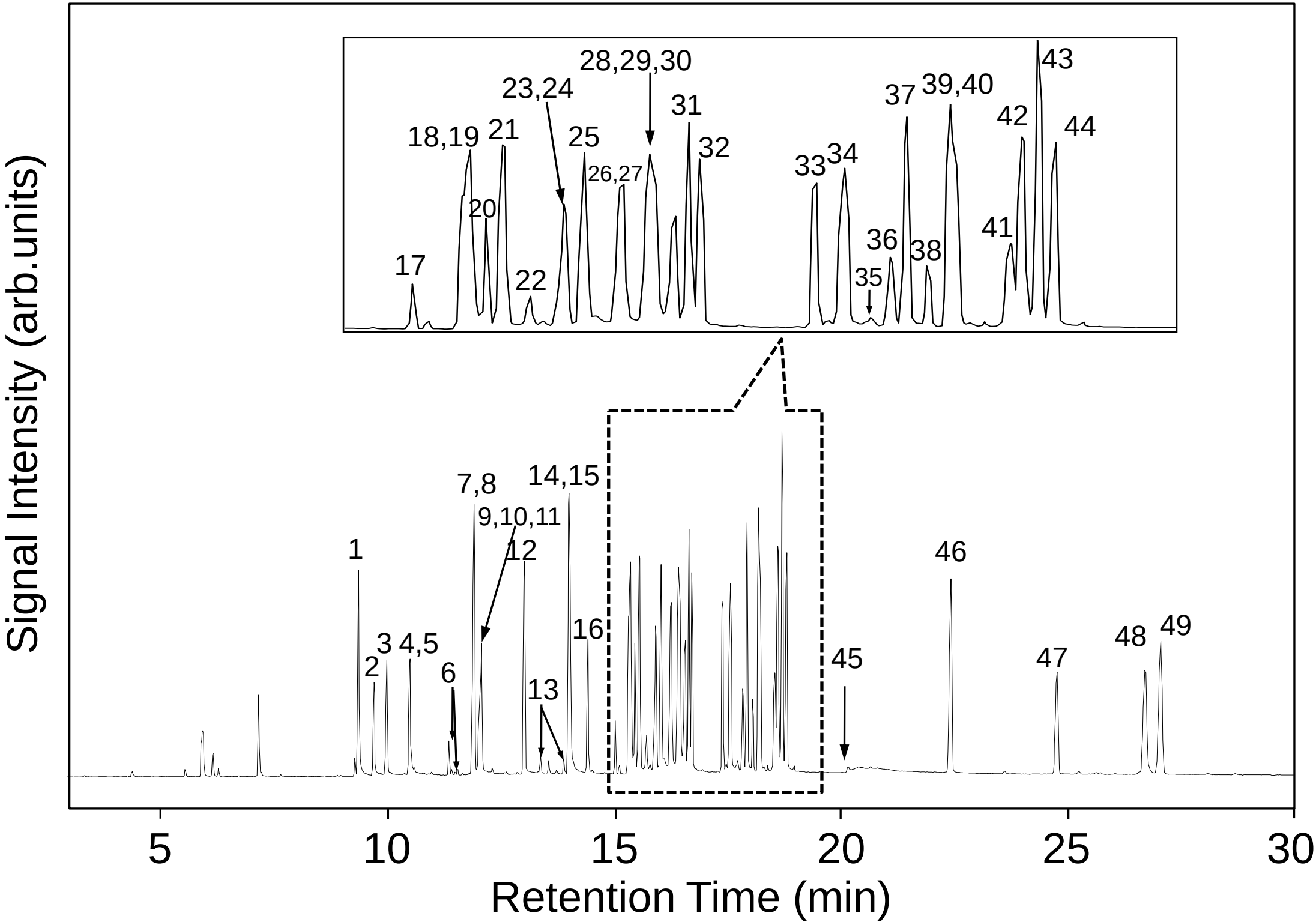

Signal Intensity (arb.units)
Retention Time (min)
5
10
15
20
25
30
1
2
3
4,5
6
7,8
9,10,11
12
13
14,15
16
45
46
47
48
49
17
18,19
20
21
22
23,24
25
26,27
28,29,30
31
32
33
34
35
36
37
38
39,40
41
42
43
44

Fig.3

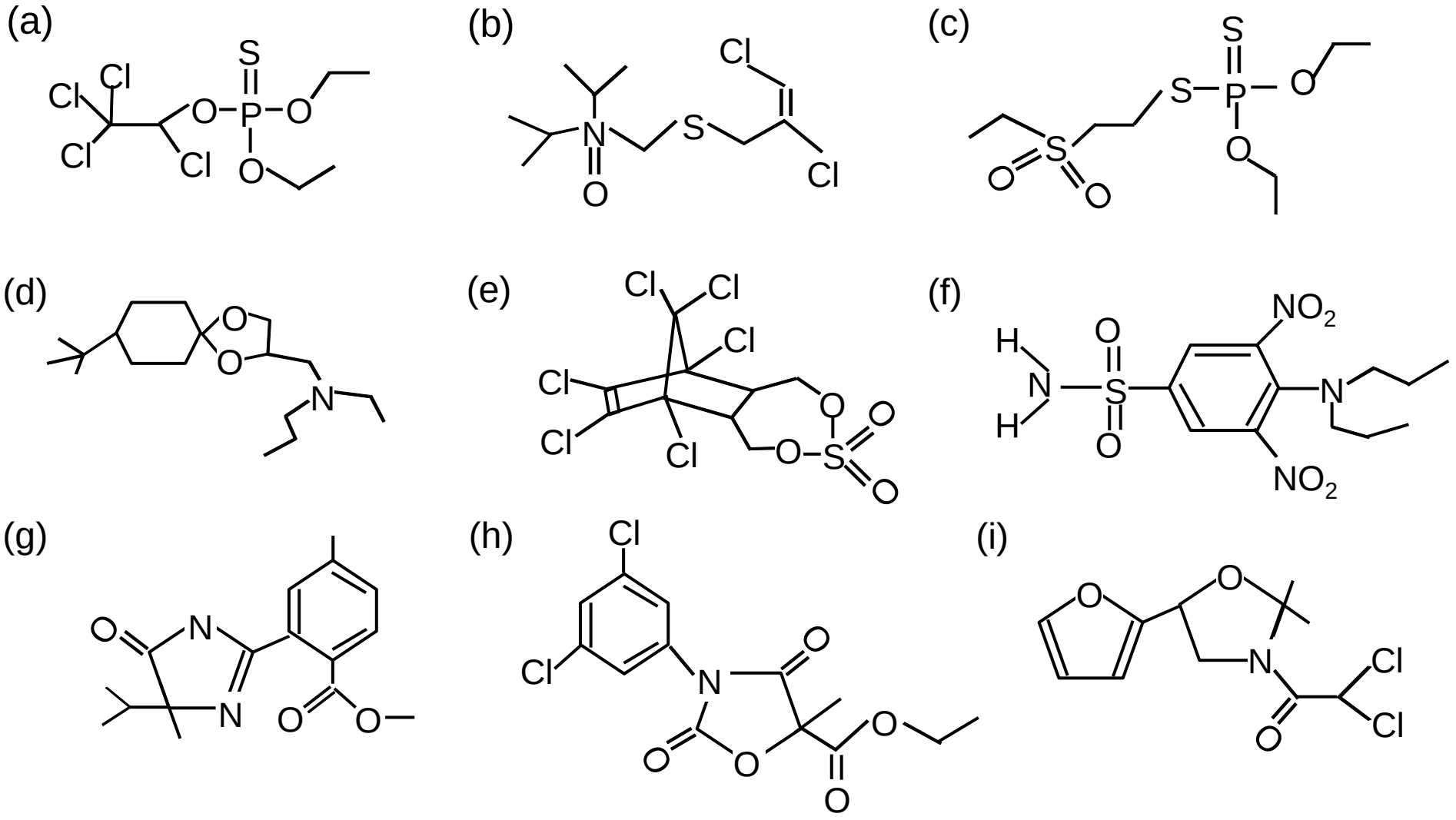


Fig.4

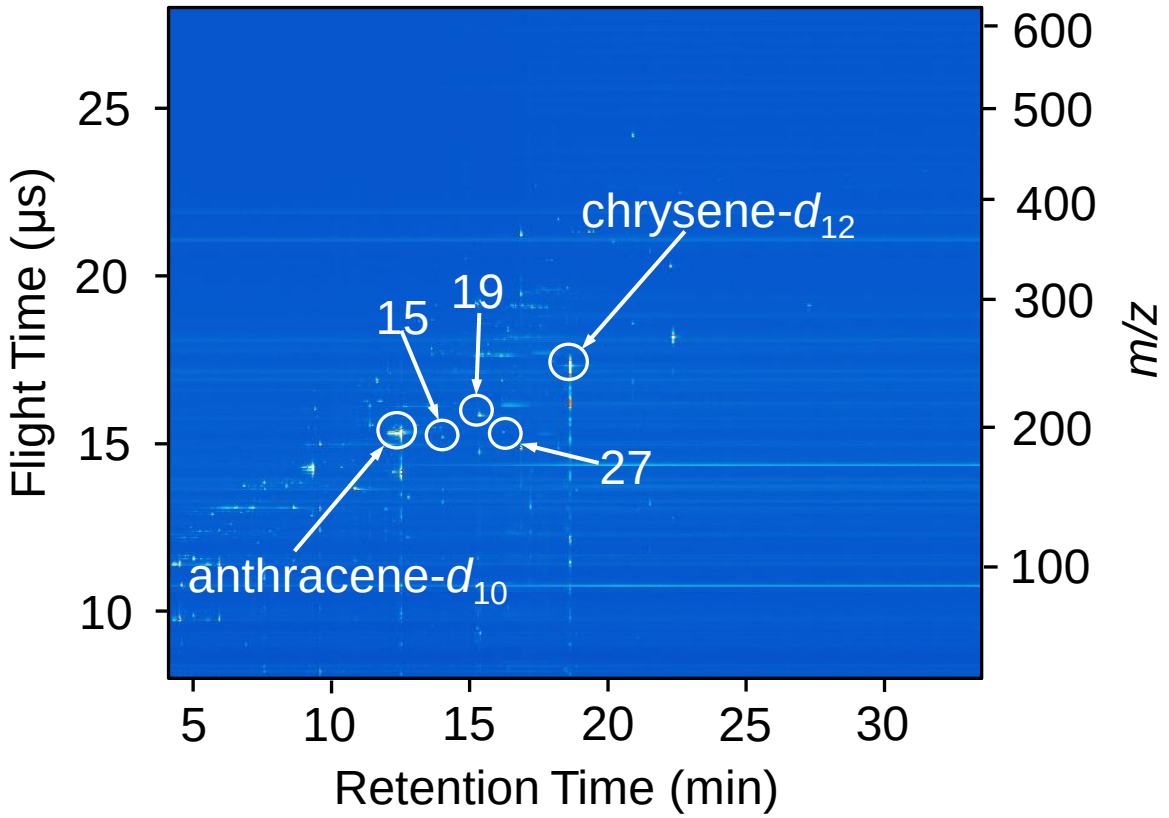

Flight Time (μs)
25
20
15
10
5
10
15
20
25
30
Retention Time (min)
600
500
400
300
200
100
m/z
chrysene-d_{12}
19
15
27
anthracene-d_{10}

Fig.5

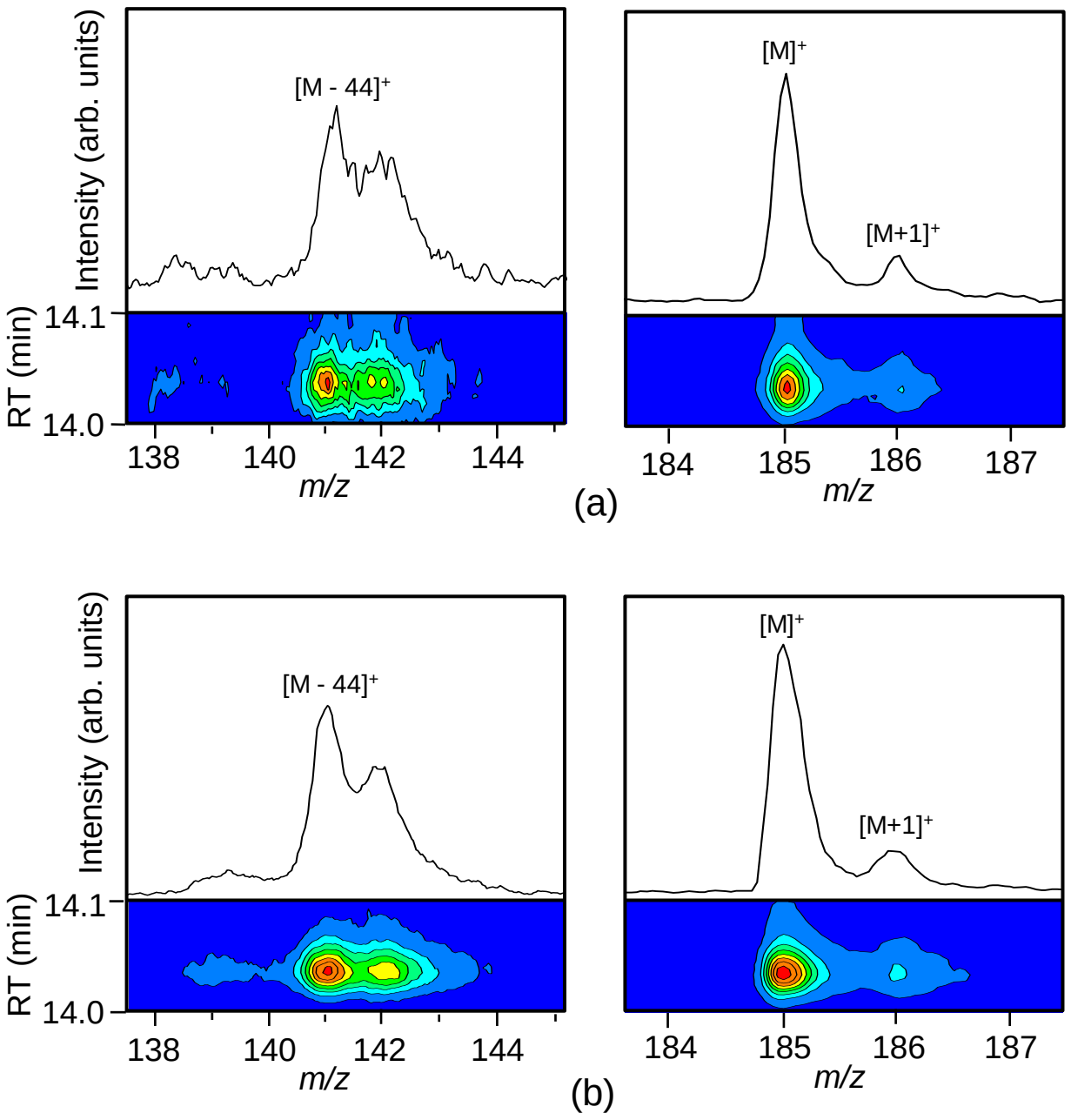
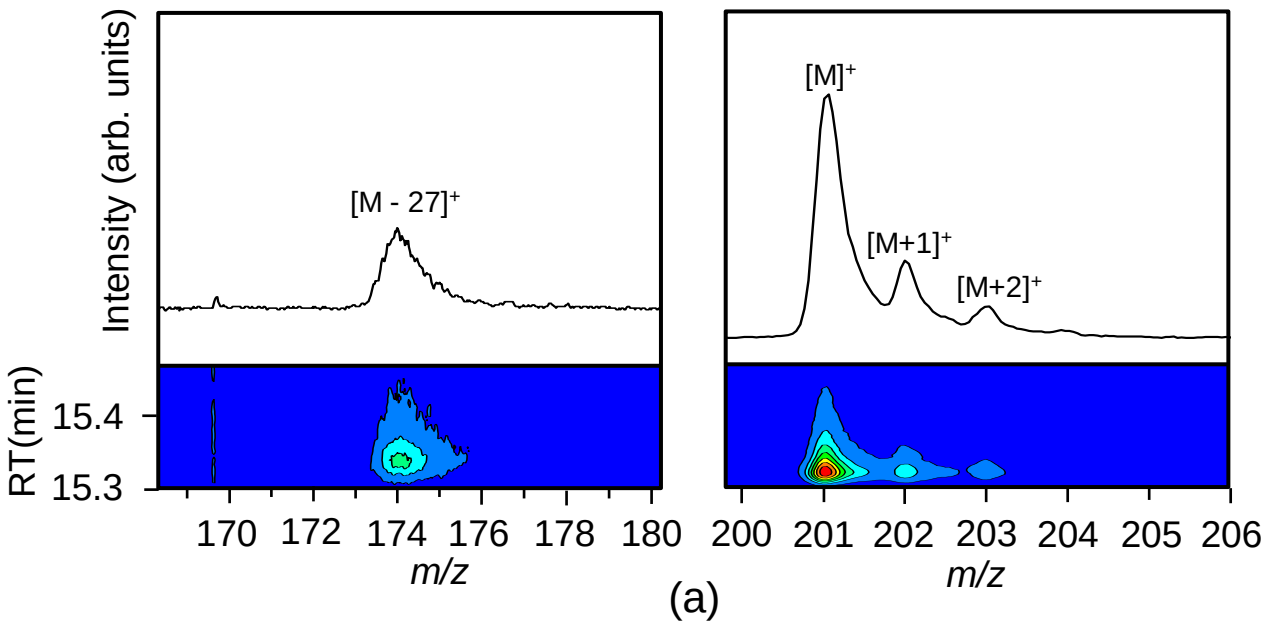
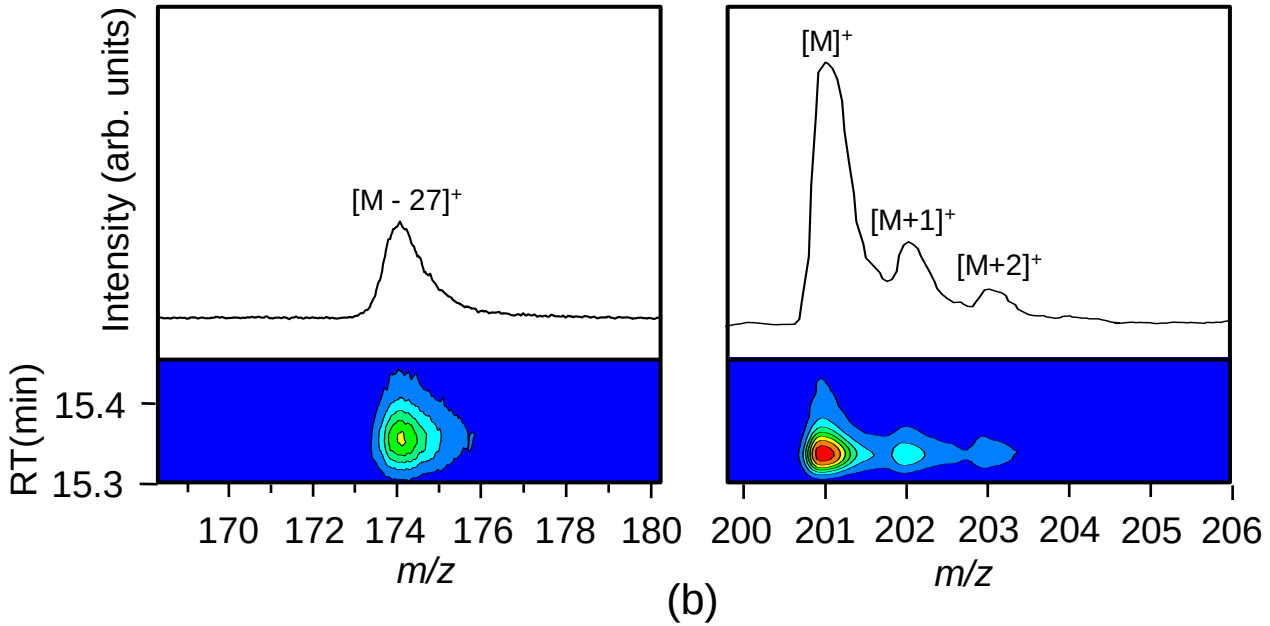

Intensity (arb. units)
[M - 44]+
[M]+
[M+1]+
RT (min)
14.1
14.0
138
140
142
144
184
185
186
187
m/z
(a)
(b)

Fig.6

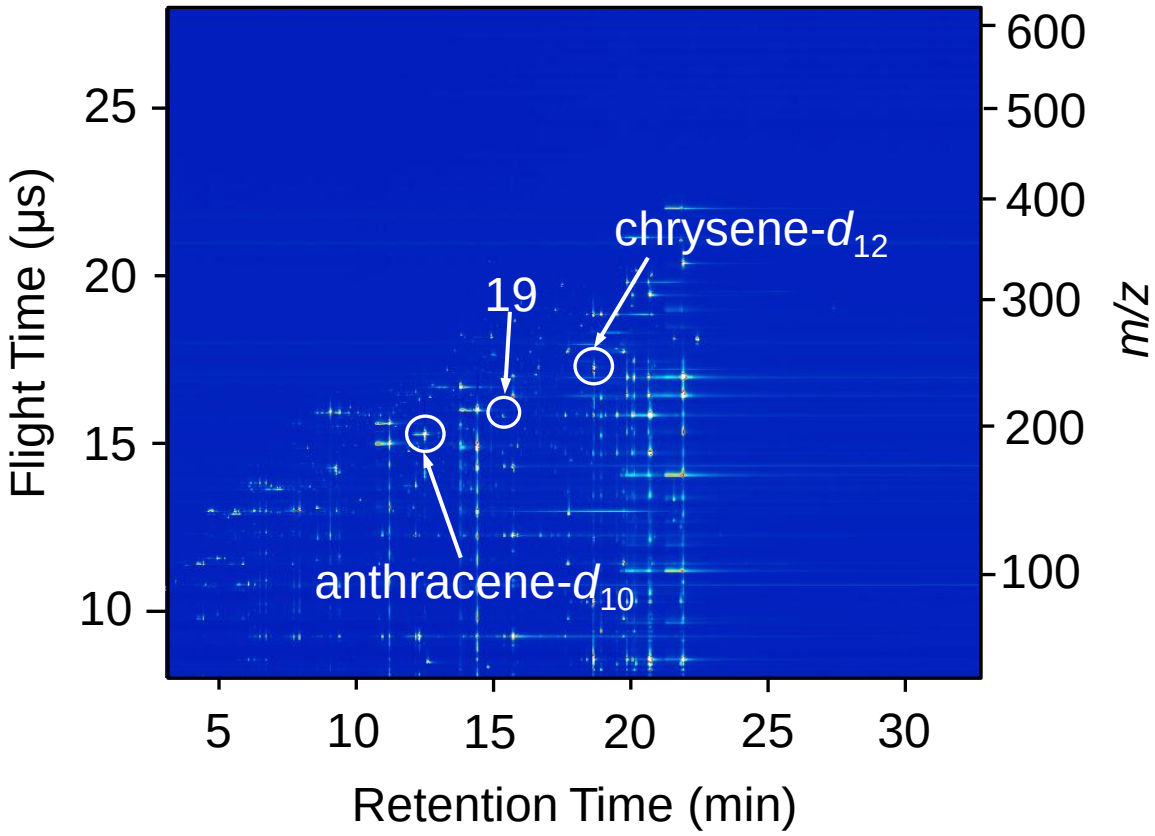

Intensity (arb. units)
[M - 27]+
[M]+
[M+1]+
[M+2]+
RT(min)
15.4
15.3
170 172 174 176 178 180
200 201 202 203 204 205 206
m/z
m/z

(a)


Intensity (arb. units)
[M - 27]+
[M]+
[M+1]+
[M+2]+
RT(min)
15.4
15.3
170 172 174 176 178 180
200 201 202 203 204 205 206
m/z
m/z

(b)

Fig.7


Flight Time (μs)
25
20
15
10
5
10
15
20
25
30
Retention Time (min)
600
500
400
300
200
100
m/z
chrysene-d_{12}
19
anthracene-d_{10}