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Determination of Triacetone Triperoxide Using Ultraviolet Femtosecond Multiphoton Ionization Time-of-Flight Mass Spectrometry

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ABSTRACT

Triacetone triperoxide (TATP), an explosive compound, was measured using gas chromatography combined with multiphoton ionization time-of-flight mass spectrometry (GC/MPI-TOFMS). By decreasing the pulse width of a femtosecond laser from 80 to 35 fs, a molecular ion was drastically enhanced and was measured as one of the major ions in the mass spectrum. The detection limits obtained using the molecular ($M^{\cdot+}$) and fragment ($C_2H_3O^+$) ions were similar or slightly superior to those obtained using conventional mass spectrometry based on electron and chemical ionization. In order to improve the reliability, an isotope of TATP, i.e., TATP-d18, was synthesized and used as an internal standard in the trace analysis of TATP in a sample of human blood. TATP could be identified in a two-dimensional display, even though numerous interfering compounds were present in the sample. Acetone, which is frequently used as a solvent in sampling TATP, produced a chemical species with a retention time nearly identical to that of TATP and provided a $C_2H_3O^+$ fragment ion that was employed for measuring a chromatogram of TATP in conventional MS. This compound, the structure of which was assigned as phorone, was clearly differentiated from TATP based on a molecular ion observable in MPI-TOFMS.

Keywords:

Multiphoton ionization, Mass spectrometry, Molecular ion, Triacetone triperoxide, Explosive

1. Introduction

Triacetone triperoxide (TATP), an organic peroxide, can be produced using acetone, hydrogen peroxide, and sulfuric acid as the starting materials and is a potent explosive compound [1]. Because of its properties, it has been utilized in numerous terrorist attacks. Ion mobility spectrometry has been utilized for the analysis of TATP in practical applications [2,3]. However, it suffers from a high rate of errors, since the results can change depending on the conditions of the experiment and also on the contaminants present in the sample. For this reason, a hyphenated technique such as liquid chromatography/infrared spectrometry [4], gas chromatography/mass spectrometry (GC/MS) [5], or electrospray ionization/mass spectrometry [6] have been employed. Among them, GC/MS has been successfully used and is one of the most sensitive and reliable methods for its analysis. However, in conventional mass spectrometry based on electron ionization (EI), TATP does not provide a molecular ion [5]. In order to overcome this problem, a positive-ion chemical ionization (PICI) technique has been employed, because of its high selectivity. However, quasi-molecular ions such as $[M+H]^+$ and $[M+NH_4]^+$ are observed, but no molecular ion of $[M]^+$ is produced [5]. This results a more complicated mass spectrum consisting of numerous fragments and several quasi-molecular ions, thus making the assignment more difficult, especially in the trace analysis of TATP in a real sample containing numerous interfering compounds. It should be noted that acetone and related compounds are present even in cosmetics and human breath and provide fragment ions that are similar to those of TATP. Therefore, a selective and more reliable analytical method for measuring TATP in real samples would be highly desirable.

Gas chromatography combined with multiphoton ionization time-of-flight mass spectrometry (GC/MPI-TOFMS) can be used for a comprehensive analysis, allowing the simultaneous determination of numerous compounds from two-dimensional data. This technique has already been used in the analysis of polychlorinated dioxins and polycyclic aromatic hydrocarbons, in addition to several other organic compounds [7]. A vacuum-ultraviolet (VUV) light source is reported to be useful for single-photon

ionization of explosives, and the wavelength dependence has been studied using a synchrotron radiation source [8]. An ultraviolet (UV) femtosecond laser has also been used for the efficient ionization of TATP and provides a molecular ion, which is difficult to produce when a long pulse of nanosecond laser is used. In a previous study, a UV femtosecond laser with a short pulse width was found to be preferred for suppressing fragmentation [9,10].

In this study, a high-power UV laser with a shorter pulse width was employed to efficiently ionize TATP in a complex matrix, human blood, which contains numerous interfering species. In order to improve the reliability of the method, an isotope of TATP, i.e., TATP-d18, was synthesized for use as an internal standard. In chemical analyses associated with criminal activities, the residue of the explosives derived from human fluids or tissues, e.g., blood, related tissue, etc., has been measured after extracting the explosive for identification [11]. Due to the redox nature of blood, TATP would be expected to rapidly disappear. To address this issue, the stability of TATP in a sample of human blood was investigated, in order to demonstrate the applicability of this method to the analysis of a real sample. On the other hand, acetone has been employed as a solvent for sampling TATP, and is also one of the chemicals for synthesizing TATP. It is therefore possible that TATP, derived from acetone, might be detected because of the redox properties of blood. In fact, a chemical species that elutes from GC with a retention time that is nearly identical to that of TATP was found in this study. In order to demonstrate superior performance of GC/MPI-TOFMS especially in the practical trace analysis of TATP, this technique was applied to the determination of TATP in human blood, which contains numerous interfering species.

2. Experimental

2.1. *GC/MPI-TOFMS*

The TOFMS instrument used in this study has been reported in detail elsewhere [12] and is commercially available (HGK-1, Hikari-GK, Fukuoka, Japan). An aliquot of the sample was injected into a GC system (6890GC, Agilent Technologies, CA) using an auto sampler (7683B, Agilent Technologies). Helium was used as the carrier gas, at a flow rate of 1.2 mL min^{-1}. A DB-5ms capillary column (30 m long, 0.25 mm i. d., 0.25 μm film thickness, J&W Scientific, Folsom, CA, USA) was employed for the separation of the analytes and an HP-5 capillary column (30 m long, 0.25 mm i. d., 0.25 μm film thickness, J&W Scientific, Folsom, CA, USA) for comparison with the DB5-ms column. The temperature of the GC oven was set at 50 °C for 3 min, and then increased at a rate of 8 °C min^{-1} to 130 °C, and subsequently increased at a rate of 40 °C min^{-1} to 210 °C, and then held for 5 min. The injection port was maintained at 110 °C, and the transfer line was set at 100 °C for 10 min and was then set at 210 °C. The fundamental beam of a Ti:sapphire laser (Elite, 800 nm, 35 fs, 4.5 mJ, 1 kHz; Libra, 800 nm, 80 fs, 1 mJ; Coherent Inc., CA, USA) was converted into the third harmonic emission (0.7 mJ for Elite and 0.11 mJ for Libra) for ionization of the analyte molecules. The ions induced were detected by an assembly of microchannel plates (MCP, F4655-11, Hamamatsu, Shizuoka, Japan). The signal was passed through an amplifier (Timing Amplifier 574, ORTEC) and a discriminator (Constant Fraction Discriminator 584, ORTEC) to improve the sensitivity [13]. A block diagram of the experimental apparatus is shown in Supporting Information 1.

2.2. *Sample extraction procedure*

A 50-μL aliquot of human blood was placed in 24 individual vials, each of which contained 50 ng of TATP. The analyte in the sample mixture was extracted with 1 mL of dichloromethane immediately and at 1, 2, 3, 4, 5, 6, 7 days after sample preparation. A group of three vials prepared under the same conditions was used for evaluating the reproducibility of the method. After extraction and concentration of the sample, 100 μL of synthesized TATP-d18 (approximately 100 ng μL^{-1} in dichloromethane) was added to each solution for

use as an internal standard. A blank solution containing no TATP was also prepared to evaluate the contamination of the GC system.

A 50-μL aliquot of human blood was added to 12 individual vials, each of which contained 100 μL of acetone. The analyte in the sample mixture was extracted using 1 mL of dichloromethane immediately and at 1, 2, 3, 4, 5, 6, 7 days after sample preparation. A pair of samples was simultaneously prepared to confirm the reproducibility of the method. After concentrating the sample, 100 μL of TATP-d18 (approximately 100 ng μL^{-1} in dichloromethane) was added to each sample solution. A sample containing no acetone was prepared for use as a blank.

2.3. *Chemical regents*

A standard solution of TATP dissolved in acetonitrile was purchased from Accustandard (New Haven, CT, USA). The concentration was 100 ng μL^{-1} and was sufficiently low to assure its safety. An internal standard of TATP-d18 was synthesized in our laboratory. The procedure for the syntheses followed a protocol reported in a literature [14]. Briefly, sulfuric acid was added to a mixture of acetone-d6 (2.7 μL, Wako Pure Chemical industries, Ltd, Osaka, Japan) and 30% w/v hydrogen peroxide (4.6 μL, Wako Pure Chemical industries, Ltd, Osaka, Japan) and the resulting solution was stored at 2 °C. After 1 hour, TATP-d18 was extracted from the reaction mixture using 100 μL of dichloromethane (Wako Pure Chemical industries, Ltd, Osaka, Japan). After concentration, 100 μL of dichloromethane was added to the sample. This isotope (TATP-d18) was used as an internal standard in the measurement of TATP. The concentration was calibrated against the concentration of the standard TATP purchased from the manufacturer. Because only a small amount of TATP-d18 was used, the solution can be safely handled in the experiment. Phorone, purchased from Matrix Scientific (SC, Columbia, USA), was used in assigning the GC peak. A sample of venous blood was obtained from T. I. (the last author of this paper) at the Institute of Health Science, Kyushu University.

2.4. *Quantum chemical calculations*

We examined TATP to evaluate its spectral properties, i.e., excitation and ionization energies. The electronic ground state geometry was fully optimized using the density functional theory (DFT) at the level of Beck's three-parameter hybrid exchange functional and the Lee-Yang-Parr correlation functional (B3LYP) [15] with Dunning's correlation consistent triple zeta (cc-pVTZ) [16] basis set. No restrictions were imposed during the optimization, and the harmonic frequency was calculated to ensure an optimized geometry for achieving a global energy minimum. The energies of the ground and ionic states were calculated using B3LYP with the AUG-cc-pVTZ [17] basis set, in which diffuse functions were added to the cc-pVTZ, at the optimized geometry of the ground state at B3LYP/cc-pVTZ. The lowest 40 singlet excitation energies were calculated using time-dependent (TD) DFT [18-20] at the level of B3LYP/AUG-cc-pVTZ//B3LYP/cc-pVTZ. The oscillator strengths (OSs) and the vertical absorption energies were fit with a series of Gaussian peaks with a half-width at a half-maximum of 0.333 eV and were summed to generate a predicted spectrum. All computations were performed with the Gaussian09 program package [21].

3. Results and discussion

3.1. *Spectral properties of TATP*

Figure 1 shows an electronic (absorption) spectrum of TATP obtained using quantum chemical calculation. The first and second electronic excited states were located at 223 and 222 nm, respectively. Their wavelengths are apparently shorter than the laser wavelength of 267 nm, and the OSs were 0.0000 and 0.0003 at these wavelengths, respectively. A strong absorption line appeared in the vicinity of 192 nm (OS =

0.0135). Thus, TATP cannot be excited using a photon emitting at 267 nm. However, the ionization energy was calculated to be 8.88 eV, which corresponds to 140 nm. Therefore, two-photon ionization can be achieved at wavelengths below 279 nm, which is slightly longer than the one-photon energy of the laser emitting at 267 nm. These results suggest that TATP can be non-resonantly ionized through a two-photon process and that the excess energy of the ion would be small (0.44 eV), thus minimizing fragmentation and efficiently producing a molecular ion.

3.2. *Effect of laser pulse width*

Figure 2 shows the mass spectra of TATP measured using a Ti:sapphire laser with different pulse widths of 35 and 80 fs, respectively. The ratio of the intensities for the molecular ion and the fragment ions ($M\cdot^+/C_2H_3O^+$) increased from 8% to 60% with a decrease in the pulse width, although the output energy remained unchanged (0.11 mJ). This result suggests that a shorter pulse width and a high peak power of the laser would produce a molecular ion more efficiently. It is interesting to note that the molecule is ionized with a minimal excess energy through a non-resonant two-photon process under present conditions as suggested from the data obtained using quantum chemical calculation. The remaining excess energy in the ion would be immediately lost as a translational energy of an electron. As demonstrated herein, an ultrashort laser pulse would be useful for observing a molecular ion, which is one of the major advantages of UV femtosecond ionization in mass spectrometry.

3.3. *Effect of laser pulse energy*

Figure 3 shows the effect of laser pulse energy on the signal intensity of the molecular and fragment ions. The slope of the signal for a molecular ion was 1.4, which is in contrast to a slope of 2.1 for the fragment ion.

These results suggest that a molecular ion is formed through a process of non-resonant two-photon ionization and the fragment ions would occur more efficiently at high pulse energies due to a three-photon process that provided a larger excess energy and accelerated the fragmentation. It should be noted that a space charge effect would decrease the slope of the curve for both the molecular and fragment ions, which would explain the decrease in the slopes (2.0 →1.4, 3.0 →2.1). It is apparent that a laser with a larger pulse energy and a shorter pulse width, i.e., a high-peak-power, would be useful for the sensitive detection of TATP especially for observing a molecular ion, although the beam diameter at the molecular beam should be optimized (expanded) to observe a molecular ion more efficiently.

3.4. *Detection limits*

The limit of detection (LOD) obtained for TATP using GC/MPI-TOFMS was compared with data reported using GC/MS based on MPI, EI, and PICI [5,7,22]. The results are shown in Table 1. The LOD calculated using a molecular ion was improved 16-fold using a discriminator/amplifier system based on ion counting (Method 1) than the LOD obtained in the previous study (MPI) and was lower than the reported data obtained using PICI. This approach using ion counting, however, provides saturated signals due to a low repetition rate (1 kHz) of the laser for a large peak such as $C_2H_3O^+$. In order to avoid such signal saturations, removing a discriminator for analog measurement (Method 2) is proposed. In this case, the LOD obtained using the fragment ion was similar to that obtained using the method based on EI [22]. Thus, the present approach can be used for the detection of TATP using a fragment ion as well as a molecular ion, making the finger-printing determination of TATP feasible.

3.5. *Internal standard*

An internal standard was utilized to improve the reliability in identification and also the quantitative analysis of the sample. In a previous study, diphenyl sulfone was employed for this purpose [10]. The chemical structure is, however, very different from that of TATP, and this molecule would be ionized through a one-photon excitation process and subsequent one-photon ionization. In addition, as reported in the reference, its GC retention time is very different from that of TATP. Such large differences in spectrometric and thermodynamic properties would induce inevitable errors in the identification and quantitative analysis of TATP. This is particularly a serious issue in the measurement of TATP in a real sample containing numerous interfering species. In order to avoid such difficulties, TATP-d18 was synthesized and used as an internal standard in this study. As shown in Fig. 4, the difference in retention time for TATP and TATP-d18 was small (only 9 s), which is due to the similarity in boiling point and polarity for such isotopes. Thus, TATP-d18 would be useful in terms of compensating for the changes in GC retention time as well as in signal intensity arising from the drift in laser power.

3.6. *Stability of TATP in human blood*

Figure 5 (a) shows an expanded view of the two-dimensional display obtained for a sample of human blood containing TATP. A molecular ion of TATP can be clearly observed, in addition to several fragment ions such as $C_2H_3O^+$. It should be noted that an interfering species was observed even between the retention times for TATP and TATP-d18. Therefore, the use of an internal standard is desirable for the reliable determination of TATP in a real sample. Figure 6 shows the change in the concentration of TATP in a human blood. The ordinate represents a peak area of TATP that was calibrated against the area of TATP-d18. This result suggests that TATP is quite stable in human blood, although it undergoes some decomposition in a week. The concentration of TATP was fitted to a first-order decay curve, i.e., 68 exp (-x/4.7) + 33, suggesting that some fraction of the TATP would be present on the surface of the blood plasma sample and can be

decomposed (time constant, 4.7 days) and that a fraction (33/68) would be present inside the plasma and would be more stable.

3.7. *Reaction products of acetone in human blood*

Acetone was added in a human blood sample to determine whether TATP is formed as a spontaneous reaction product or not. Figure 5 (b) shows a two-dimensional display obtained using GC/MPI-TOFMS. No signal, assignable to TATP, was observed. This suggests that TATP is not produced from acetone, even though a redox reagent such as hemoglobin is present in the blood sample. This result can be attributed to a lack of acid in the reaction mixture. However, we observed a large GC peak with a retention time very near that of TATP. This compound produced a fragment peak at m/z = 43, corresponding to $C_2H_3O^+$, which is currently used in the identification and quantitative analysis of TATP in conventional mass spectrometry based on EI. In organic chemistry, acetone is known to form phorone by self-aldol condensation under basic conditions [23]. Supporting information 2 shows a scheme for a synthesis of phorone [24-27]. The pH of human blood is weakly alkaline, condition that are favorable for the production of phorone. Furthermore, the molecular weight of phorone is 138, which coincides with the peak observed at m/z = 138. Moreover, a mass spectrum obtained from the NIST database strongly suggests that this peak can be assigned to phorone [28].

In order to verify the above assignment, a standard sample of phorone was purchased and was measured using GC/MPI-TOFMS. Figure 7 shows a mass spectrum and a mass chromatogram of the chemical species produced in human blood and corresponding data for a standard sample of phorone. The fragment pattern in the mass spectrum, and the retention time in the chromatogram are nearly identical. Thus, the product can be assigned to phorone, and the slight difference in the mass spectrum can be attributed to interfering species in the human blood sample. Supporting information 3 shows the mass chromatogram for a mixture of the product and TATP measured using two types of GC columns, i.e., DB-5ms and HP-5. The difference in

retention time for TATP and phorone is quite small (only 4 s) for the HP-5 column, although the properties of the columns are nearly identical to each other. Thus, the GC signal should be carefully evaluated, especially when a flame ionization detector or even a conventional mass spectrometer is utilized for measuring TATP.

4. Conclusion

The use of an ultrashort laser pulse emitting at 267 nm drastically enhanced a molecular ion for TATP, and this method has a distinct advantage for achieving a more reliable analysis. The detection limit using GC/MPI-TOFMS was compared with those obtained using mass spectrometry based on EI and PICI. Even when a non-resonant process was employed in two-photon ionization, it provided similar or slightly superior LODs. The reliability was significantly improved by synthesizing and using TATP-d18 as an internal standard in the measurement of TATP. This approach using an isotope internal standard was useful, especially when an interfering species with a retention time close to TATP is present, and provides a similar pattern in the mass spectrum. In fact, phorone was formed from acetone that is currently used for sampling TATP in human blood. This compound, the properties of which are similar to TATP in GC separation, provides several fragment ions including $C_2H_3O^+$. This compound can, however, be clearly differentiated from TATP by using a molecular ion that is observable in MPI-TOFMS, which is in contrast to conventional mass spectrometry in which $C_2H_3O^+$ is produced as a major fragment ion for use in quantitative analysis. As demonstrated herein, multiphoton ionization mass spectrometry using a UV ultrashort laser has superior performance than conventional mass spectrometry using an electron ionization source for more reliable trace analysis of TATP especially in a real sample such as human blood. It should be noted that a reliable analytical method is important to avid misjudgment in the court, and the instrument based on GC/MPI-TOFMS, although it is rather complicated and expensive, would be essential to protect human rights.

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Table 1. Detection limits for TATP measured using GC combined with MPI-TOFMS, EI-MS, and PICI-MS

Ionization method	*m/z*	Ions	LOD (pg)
MPI (Method 1)	222	$M\cdot^{+}$	43
	43	$C_2H_3O^{+}$	(4)
MPI (Method 2)	222	$M\cdot^{+}$	140
	43	$C_2H_3O^{+}$	12
MPI* [9]	222	$M\cdot^{+}$	670
	43	$C_2H_3O^{+}$	83
EI* [22]	43	$C_2H_3O^{+}$	10
PICI (NH_3)* [5]	240	$[M+NH_4]^{+}$	100

The LOD was calculated as a concentration, at which the signal is three times larger than the noise of the base line in the chromatogram.

An amplifier and a discriminator were used in Method 1. The LOD obtained using the fragment ion was calculated from the ratio of the signal intensities for the molecular and fragment ions.

Figure Captions

Figure 1 UV spectrum of TATP obtained by quantum chemical calculations. The lowest excitation and ionization energies are shown in the figure. The broken line shows the wavelength used for MPI.

Figure 2 Mass spectra measured using GC/MPI-TOFMS for a standard sample containing 100 ng of TATP. The pulse width of the laser; (a) 35 fs (b) 80 fs.

Figure 3 Dependence of signal intensity on laser pulse energy. (a) linear plot (b) logarithmic plot. (1) $C_2H_3O^+$, m/z = 43 (2) $M\cdot^+$, m/z = 222.

Figure 4 Mass chromatogram measured by monitoring the molecular ion. A sample solution contains 50 ng of TATP and ca. 100 ng of TATP-d18.

Figure 5 Two-dimensional display obtained using GC/MPI-TOFMS. Either (a) TATP or (b) acetone was added to the human blood sample and was measured 3 days after the sample preparation. Lines appearing at flight times of 4.7 and 6.2 μs are due to the presence of oxygen and water that are present in the mass spectrometer, respectively. A small amount of TATP-d18 was added to the sample solution before a sample injection into GC for calibration.

Figure 6 Dependence of the concentration of TATP in human blood on the day after sample preparation. Three samples prepared under the same conditions were measured and the results were averaged. The standard deviation is shown as a bar in the graph.

Figure 7 Mass spectra for (a) the product produced from acetone and (b) a standard sample of phorone. Mass chromatograms for (c) the product produced from acetone and (d) after adding a standard sample of phorone. TATP-d18 was added as an internal standard.

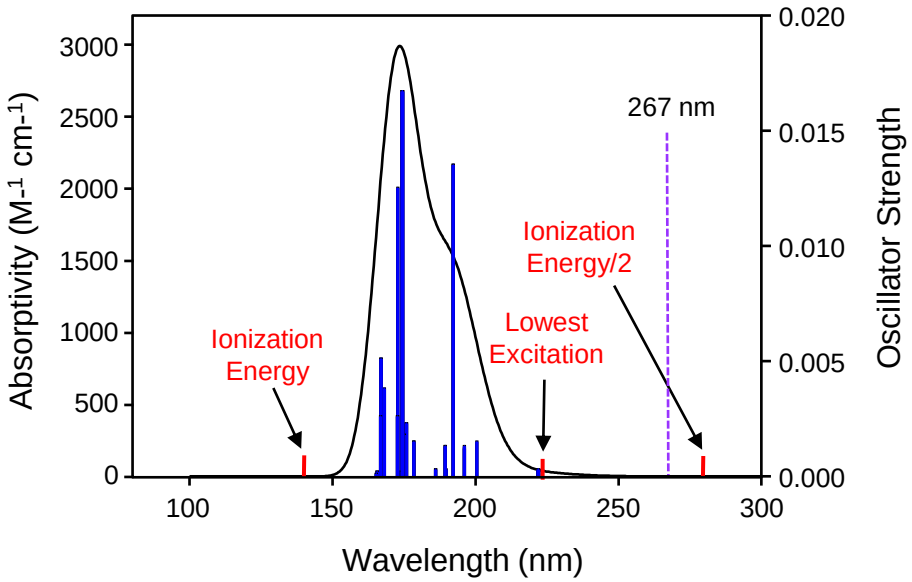

Fig. 1 R. Ezoe, et al.

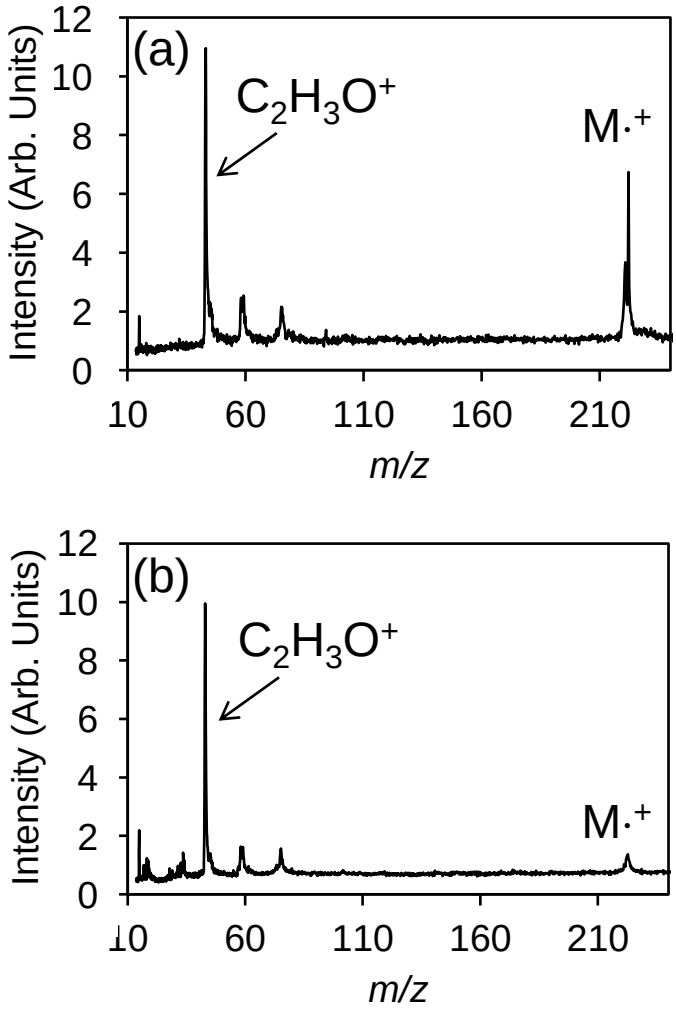

Fig. 2 R. Ezoe, et al.

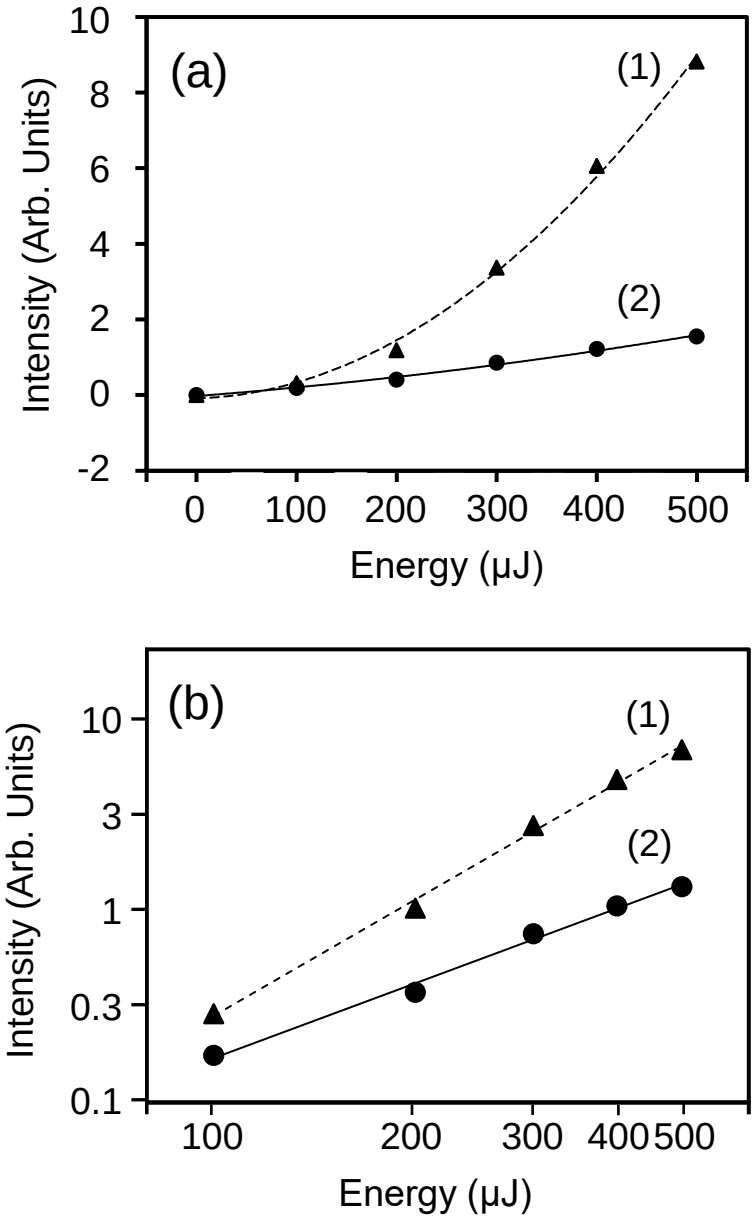

Fig. 3 R. Ezoe, et al.

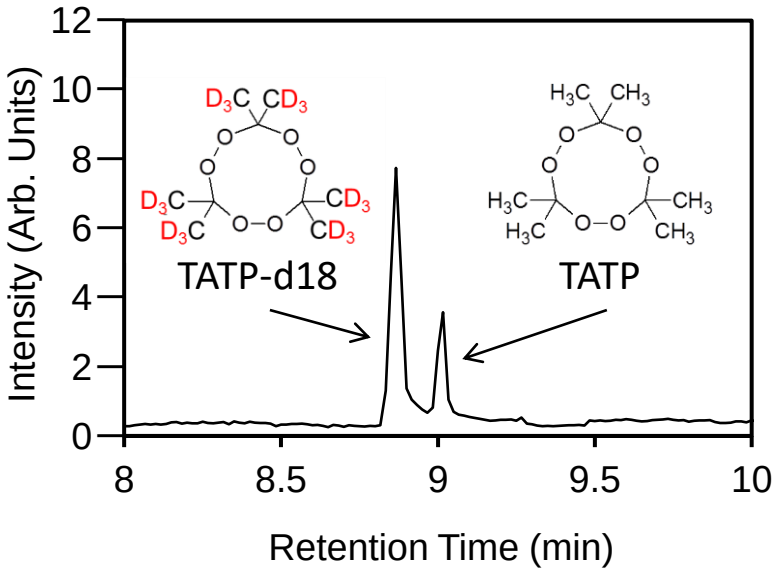

Fig. 4 R. Ezoe, et al.

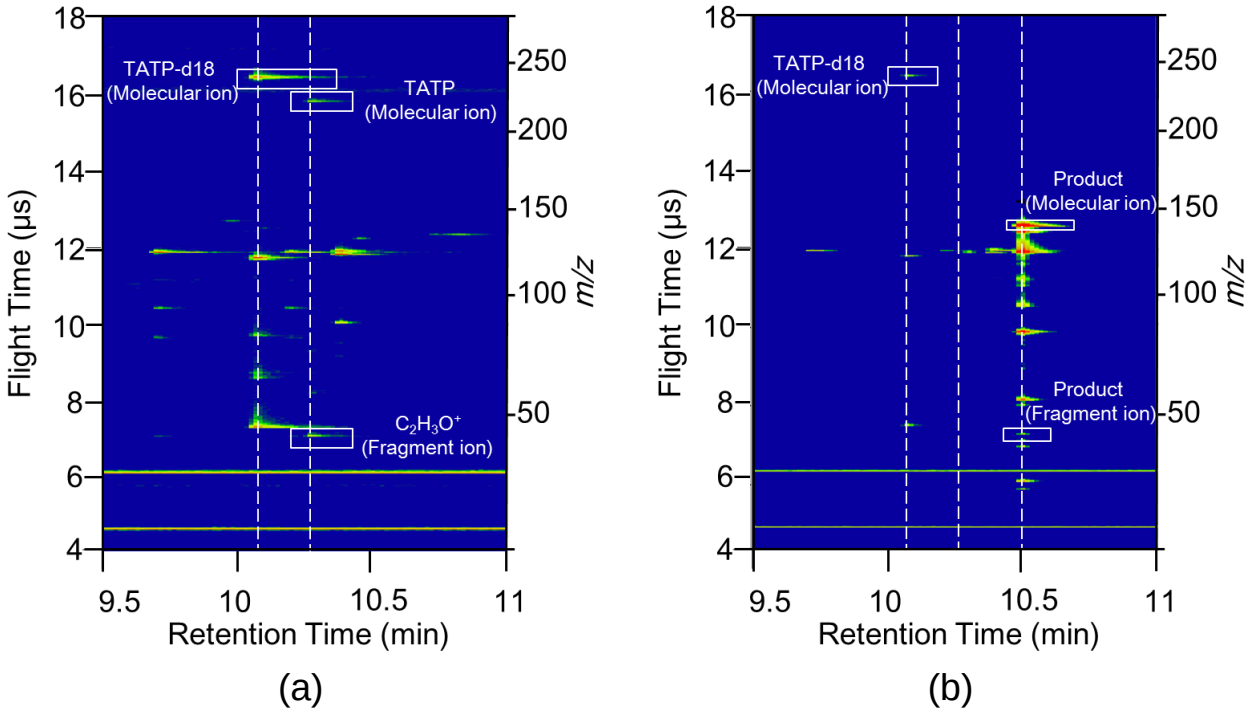

Fig. 5 R. Ezoe, et al.

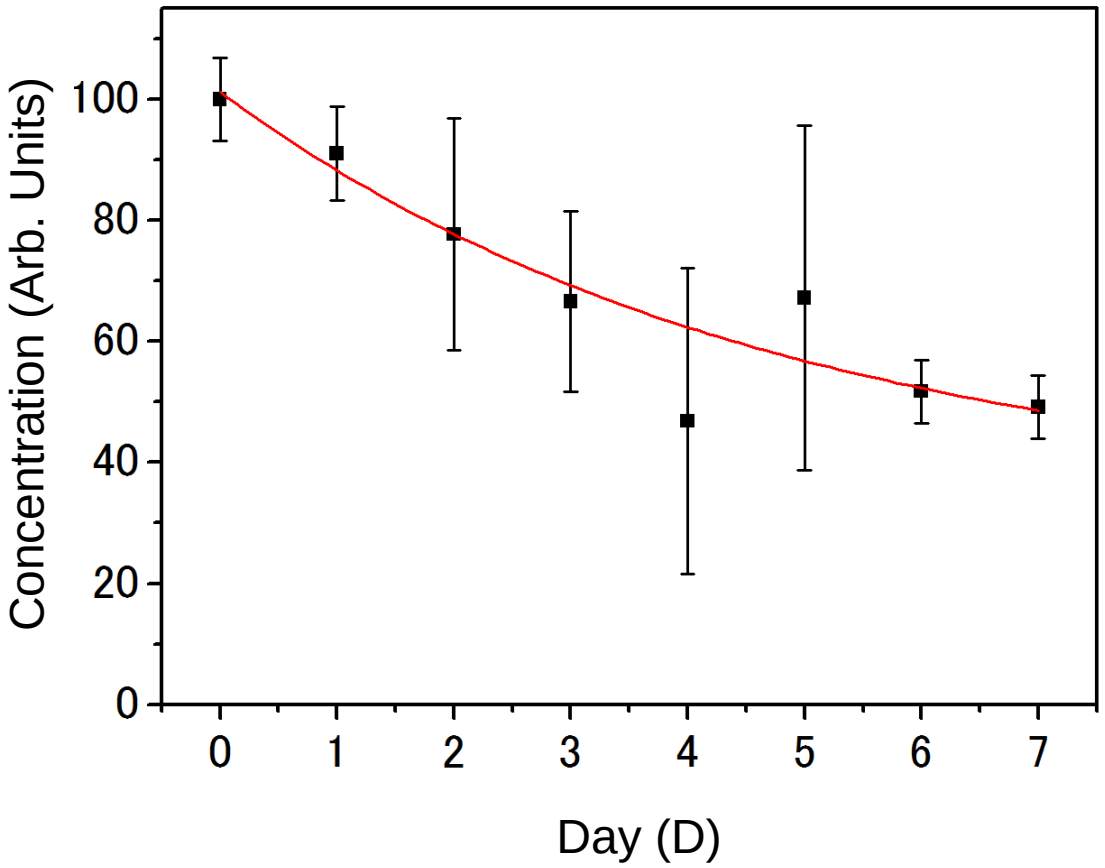

Fig. 6 R. Ezoe, et al.

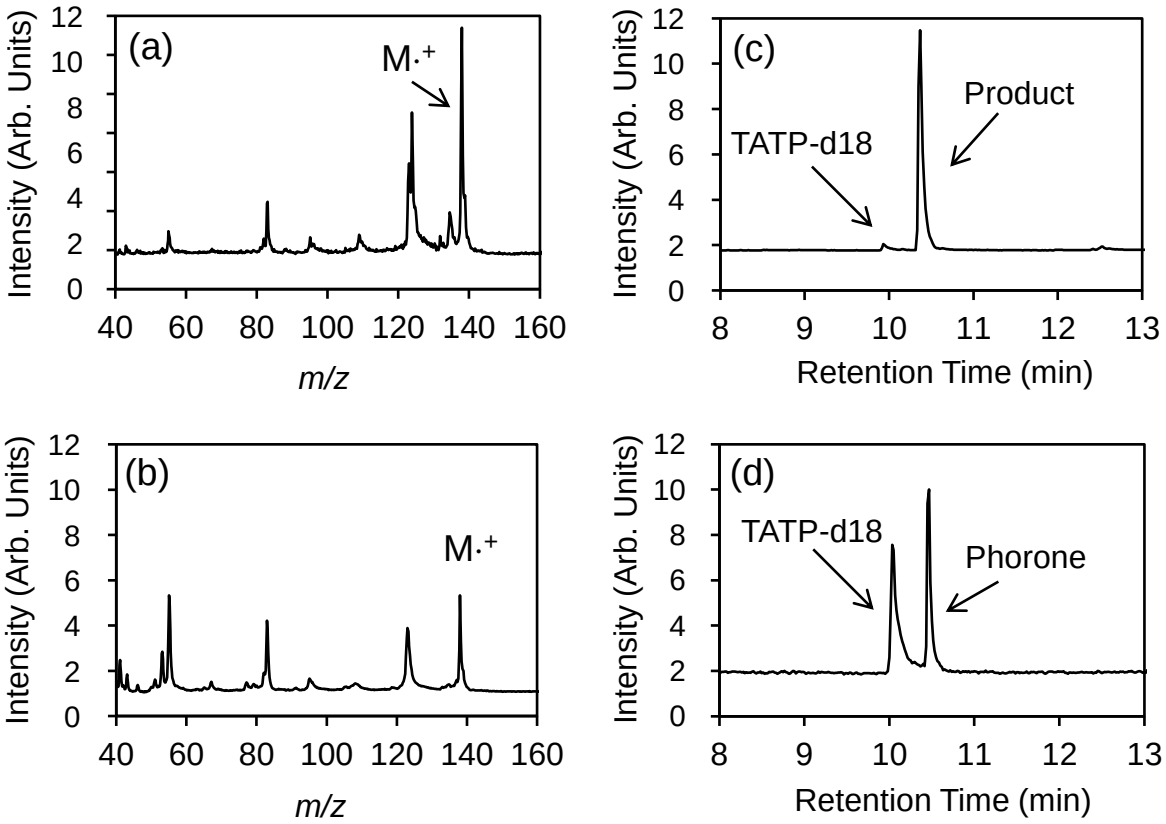

Fig. 7 R. Ezoe, et al.