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Detection of polychlorinated biphenyls in transformer oils in Vietnam by multiphoton ionization mass spectrometry using a far-ultraviolet femtosecond laser as an ionization source

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ABSTRACT

Polychlorinated biphenyls (PCBs) in transformer and food oils were measured using gas chromatography combined with multiphoton ionization mass spectroscopy. An ultrashort laser pulse emitting in the far-ultraviolet region was utilized for efficient ionization of the analytes. Numerous signal peaks were clearly observed for a standard sample mixture of PCBs when the third and fourth harmonic emissions (267 and 200 nm) of a femtosecond Ti:sapphire laser (800 nm) were employed. The signal intensities were found to be greater when measured at 200 nm compared with those measured at 267 nm, providing lower detection limits especially for highly chlorinated PCBs at shorter wavelengths. After simple pretreatment using disposable columns, PCB congeners were measured and found to be present in the transformer oils used in Vietnam.

Keywords:

Multiphoton ionization, Mass spectrometry, Femtosecond laser, Polychlorinated biphenyls, Transformer oil

1. Introduction

Mixtures of polychlorinated biphenyls (PCBs) have been frequently used as heat exchange oils, and they remain in some transformers, capacitors, and cables used even in modern societies. Polychlorinated dibenzodioxins and polychlorinated dibenzofurans present as impurities in these heat exchange oils can induce serious disease for human beings, often referred to as “Yusho Disease” [1,2]. The Stockholm Convention was adopted in 2001 with the participation of 172 countries [3]. Then, the transformer oil contaminated with PCBs are prohibited to be used and are kept in storage worldwide before proper processing. For this reason, the concentration level of PCBs should be measured, in order to decrease the number of oil samples to be processed. Because of the extremely high toxicities of these substances, it is required to develop an analytical method to measure these compounds at trace levels. In addition, PCB congeners have very different toxicities depending on the number of chlorine atoms present and their relative positions in the substituted benzene rings [4]. Therefore, it is necessary to selectively measure these compounds. It is, however, difficult to determine PCBs using conventional analytical equipment, such as gas chromatography (GC) combined with a quadrupole mass spectrometer. To solve this problem, high-resolution GC combined to double-sector-type high-resolution mass spectrometry has been used for trace analysis of these compounds [5]. However, this type of instrument is available only in a limited number of analytical laboratories and suffers from high maintenance costs. In addition, this approach requires a high-level of skill for operation and also for data processing. Thus, it is necessary to develop a method for rapid and comprehensive analysis of PCBs.

An alternative method would be the use of a photoionization technique. Numerous studies have been reported to date for multiphoton ionization mass spectrometry (MPI/MS) [6,7]. When the wavelength of the laser coincides with the absorption band, the analyte molecule can be efficiently ionized. The use of a narrow-band tunable laser is desirable for MPI to enhance not only the sensitivity but also the selectivity [8,9]. For this reason, trace species have been successfully measured for many samples. It is well known

that the lifetime of the electronic excited state decreases with an increase in the number of chlorine atoms in a molecule by efficient energy relaxation to triplet levels. The ionization efficiency then decreases significantly for highly chlorinated aromatic hydrocarbons when a nanosecond laser is employed. To overcome this problem, a laser with a short pulse width, e.g., a femtosecond laser emitting in the ultraviolet (UV) region, has been used [10,11]. For further enhancement of selectivity, a separation technique such as GC has been coupled with MPI/MS. Thus, GC/MPI/MS using a short laser pulse would be one potential approach for the trace analysis of highly chlorinated PCBs [12,13].

In this study, we report on the trace analysis of PCBs contained in the oils available in a factory and also in a market in Vietnam based on GC/MPI/MS using a UV femtosecond laser as an ionization source. We examined the effect of the laser wavelength (267 or 200 nm) to investigate the optimal condition for ionization and to study the ionization mechanism. We detected PCBs in the used oils, which, to our knowledge, is the first such finding in Vietnam. This result suggests the importance of further systematic studies to be performed for the protection of the environment in Vietnam.

2. Experimental

2.1. Apparatus

The equipment for GC/MPI/MS has been developed in our laboratory (Japan), and the detail is reported elsewhere and is now commercially available (HGK-1, Hikari-GK, Fukuoka, Japan) [14,15]. An DB-5ms column (30 m long, 0.25 mm i.d., 0.25 mm film thickness, J&W Scientific) was used for separation of PCB congeners. The temperature of the oven in the GC was set at 80 °C and held for 2 min, and was then programmed to increase at a rate of 8 °C/min to 295 °C, and was held for 5 min. The flow rate of helium used as a carrier gas was adjusted to 1 mL/min. A deactivated silica capillary (1 m long, 0.32 mm i.d., Agilent Technologies) was connected to the separation column and was utilized as a

transfer line to introduce the analyte into the MS. Then, 1 μL volume of sample was injected into the GC (6890GC, Agilent Technologies) using an auto sampler (7683B, Agilent Technologies). Although the capillary had a greater diameter than the separation column, it provided no undesirable effect in the separation and was used in this study because of superior mechanical and thermal durability. The temperature of the inlet port of the GC and the transfer line was set at 295 $^{\circ}\text{C}$ during the experiment. The ionization sources used in the present study were the third (267 nm) and the fourth harmonic (200 nm) emissions of a femtosecond Ti:sapphire laser (800 nm, 1 kHz, 85 fs, Libra, Coherent). A fused-silica lens with a focal length of 500 mm was used to focus the laser beam into a molecular beam for MPI/MS. The induced ions were accelerated into a flight tube and were detected with an assembly of microchannel plates (F4655-11, Hamamatsu Photonics). Finally, the data were recorded and analyzed by a computer combined with a digitizer (AP240, Agilent Technologies) programmed with LabVIEW software.

2.2. Samples

A Kanechlor mixture solution (KC-mix), used as a reference sample, was purchased from GL Sciences Inc. This reagent contains many congeners of PCBs, predominately Di-CBs to Octa-CBs. A reference sample was prepared by mixing 40 μL of KC-mix (40 $\mu\text{g/mL}$), 50 μL of DLPCB-CL-A 100 (internal standard, 100 ng/mL, Kanto Chemical Co., Inc.), and 40 μL of n-hexane. We measured the reference sample prepared at a concentration of 4 $\mu\text{g/mL}$, and the S/N value was calculated from the signal intensity and the baseline drift for the PCB congeners from Di-CBs to Octa-CBs.

Five types of field samples were collected in Hanoi, Vietnam, and were measured in this study: (1) a used transformer oil derived from a factory; (2) a used transformer oil purchased from a flea market; (3) a new transformer oil derived from a factory; (4) a new transformer oil purchased from a flea market; and (5) a peanut oil purchased from a supermarket. Approximately 100 mL of each oil sample was collected in a polypropylene bottle, and the container was labeled and transported to our laboratory (Vietnam).

2.3. Pretreatment procedure

Solid phase extraction was used for cleanup of the sample because it is simpler, faster, and safer than the conventional method based on solvent extraction using concentrated sulfuric acid. Two types of columns were used in series for the solid phase extraction, namely Supelclean Sulfoxide SPE 55253-U 3 g (first column) and Sulpelcor Discovery Ag ion SPE 54225-u (second column). A unit commercially available was purchased from Sigma Aldrich Japan. First, the columns were conditioned using 10 mL of acetone and were equilibrated with 20 mL of hexane. Then, 120 μ L of sample mixed with 50 μ L of DLPCB-CL-A100 and 120 μ L of hexane were added to the first column and washed with 6 mL of hexane. The second column was then connected to the first column and they were washed with 2 mL of hexane. The PCBs were eluted with 12 mL of hexane containing 5% of dichloromethane. The sample volume was decreased to 120 μ L by evaporation of the solvent. This procedure was repeated to reduce the concentrations of the impurities, and the volume of the solution was reduced to 100 μ L by evaporation. Finally, a glass vial of the resulting sample was kept in a refrigerator before use.

2.4. Quantum chemical calculations

A molecule can be efficiently ionized when it is excited to a singlet excited state by the first photon and then ionized by the subsequent second photon in the MPI process. Thus, information concerning the spectral properties and molecular structure is important to find optimum conditions for analysis. In this study, a density functional theory (DFT) was used to study the molecular geometry and the energy of electronic transitions [16]. The ionization energy (*IE*) was calculated for PCBs with different numbers of chloride atoms from Di-CB to Deca-CB at the B3LYP/cc-pVDZ level [17]. No restriction was imposed during optimization, and the harmonic frequency was calculated to ensure the optimized geometry

provided an energy minimum. The transition energies and the oscillator strengths were calculated for lowest 40 singlet electronic states by time-dependent DFT (TD-DFT) to obtain the absorption spectrum down to ca. 150 nm. All calculations were carried out using the Gaussian 09 program suite [18]. The profile of the absorption spectrum was generated using the Gauss View Ver. 5 software package by assuming a Gaussian-profile peak with a half width at half maximum of 0.333 eV [19].

3. Results and discussion

3.1. Quantum chemical calculation of PCBs

The calculated absorption spectra of some illustrative PCB examples are shown in Fig. 2. The absorption maximum is located at around 200 nm (6.26 eV) in most cases and the ionization energy at around 150 nm (8.33 eV). The spectral data calculated for 10 PCBs are summarized in Table 1. The *IE* values for the PCB congeners with different numbers of chlorine atoms ranged from 8.10 to 8.59 eV. The *IE* increased with an increase in the number of chlorine atoms in a molecule. For example, the *IE* of 2,2',3,6'-Tetra-CB (8.46 eV) was much higher than the energy of one photon (4.65 eV at 267 nm or 6.20 eV at 200 nm) of the laser used in this study. Therefore, when using a laser emitting at 267 nm, the first photon can be used for excitation and the second photon for subsequent ionization for larger PCBs (*EE* = 4.53–4.66 eV). When measuring smaller PCBs (*EE* = 4.77–4.99 eV), two photons would be necessary for excitation due to a large excitation energy and PCB molecules would be ionized through a nonresonant process. When a laser emitting at 200 nm is used, all PCBs can be ionized using two photons through a resonance-enhanced two-photon ionization process.

3.2. Analysis of PCBs

A two-dimensional display of GC/MS for a KC-mix sample measured at 267 nm (72 ± 4 mW) is shown in Fig. 3(A). The congeners from Di-CBs to Octa-CBs are clearly observed for the reference sample. Fig. 3(B) shows an expanded view of the two-dimensional display and the mass chromatogram in the region where Tri-CBs appear in Fig. 3(A). Numerous isomers from 2,2',6-Tri-CB to 3,4,4'-Tri-CB were observed, in which there are no significant changes in the signal intensities when the signals are calibrated against the concentrations of PCBs contained in the KC-mix. The limits of detection were 3.22, 0.21, 0.45, 0.43, 0.84, 0.03, 0.11, 0.21, and 0.13 ng for the isomers from 2,2',6-Tri-CB to 3,4,4'-Tri-CB, respectively. The limits of detection were higher than the values of several pg reported in the previous study [13], which would be due to insufficient optimization of the mass spectrometer used in this study.

Two-dimensional displays for (1) a used oil sample from a factory and (2) a used oil purchased from a flea market are shown in Fig. 4(A) and 4(B), respectively. The signals arising from PCBs were observed in both samples (1) and (2). Conversely, no PCB signals were observed for new transformer oils obtained from the factory (3) or those purchased in the flea market (4); the data are not shown here. In addition, no signals of PCBs were observed for the peanut oil purchased in the supermarket (5).

Two-dimensional displays measured at 200 nm for the KC-mix and the used oil from the factory are shown in Fig. 5(A) and 5(B), respectively. The signals occurring from PCB congeners from Di-CBs to Nona-CBs were observed more clearly for the KC-mix measured at 200 nm, even at low laser pulse energies (18 ± 2 mW), than those observed at 267 nm (72 ± 4 mW); cf. Fig. 3(A). The limits of detection were 0.82, 0.06, 0.13, 0.19, 0.47, 0.02, 0.06, 0.14, and 0.17 ng for the congeners from 2,2',6-Tri-CB to 3,4,4'-Tri-CB, respectively (see Fig. 3(B)), suggesting superior sensitivity at 200 nm. This favorable result would be obtained by larger molar absorptivities at shorter wavelengths for PCBs (see Fig. 2). This trend is more pronounced for highly chlorinated PCBs (cf. Figs. 3(A) and 5(A)). The PCB congeners in the used oil from the factory are more clearly observed up to Hexa-CBs, again suggesting superior sensitivity at 200 nm. A few lasers emitting in the deep-ultraviolet region, e.g., an ArF excimer laser at 193 nm or the fifth harmonic emission of a Nd:YAG laser at 213 nm, could be used for the present

purpose. However, these lasers are usually operated at a nanosecond or picosecond pulse width. Thus, it is desirable to use a femtosecond laser such as a Ti:sapphire laser for the efficient ionization of highly-chlorinated biphenyls having extremely-short excited-state lifetimes.

Although GC/MPI/TOFMS using a femtosecond laser especially the fourth harmonic emission is not common in the standard analytical laboratory, this technique can be applied to many types of organic compounds not only PCBs but also dioxins, pesticides, and even explosives [11]. For this reason, this technique can be widely used in the future for comprehensive analysis of trace components in industrial materials and also in the environment.

4. Conclusion

The ionization energies of PCB congeners from Mono-CB to Deca-CB were calculated by the TD-DFT method. The *IEs* were 8.10–8.59 eV for the PCB congeners, suggesting that they would be ionized either by a process of nonresonant (Mono-CB to Penta-CB, *EE* = 4.77 to 4.99 eV) or resonant (Hexa-CB to Deca-CB, *EE* = 4.53 to 4.66 eV) two-photon ionization at 267 nm (4.65 eV). Five field samples were measured in this study and two of them contained PCBs (in the used oils derived from the factory and the oil purchased from a flea market in Vietnam). No PCBs were detected from the new transformer oils or the food (peanut) oil. Owing to larger molar absorptivities at shorter wavelengths, it is recommended to use a femtosecond laser emitting at 200 nm as an ionization source. This provides better sensitivity and lower detection limits, especially for highly chlorinated PCBs, although the laser system is slightly more complicated to operate.

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Table 1

Calculated excitation and ionization energies for PCB congeners.

Compound	Excitation energy		Ionization energy	<i>IE</i> /2
	λ (nm)	<i>EE</i> (eV)	<i>IE</i> (eV)	(eV)
Biphenyl	250	4.96	7.95	3.97
3-Mono-CB	259	4.79	8.10	4.05
2,4'-Di-CB	256	4.83	8.13	4.06
2,3',4-Tri-CB	259	4.78	8.29	4.14
2,2',3,6'-Tetra-CB	248	4.99	8.46	4.23
2,3',4,4',6'-Penta-CB	260	4.77	8.45	4.22
2,3'4,4'5,5'-Hexa-CB	273	4.53	8.38	4.19
2,2',3,4,4',5,5'-Hepta-CB	266	4.66	8.52	4.26
2,2',3,4,4',5,5',6-Octa-CB	271	4.57	8.54	4.27
2,2',3,3',4,4',5,5',6-Nona-CB	271	4.57	8.59	4.29
2,2',3,3',4,4',5,5',6,6'-Deca-CB	272	4.55	8.57	4.29

Photon energy: 4.65 eV at 267 nm and 6.20 eV at 200 nm.

Figure Captions

- Fig. 1 Experimental setup of GC/MPI/MS. He, helium; GC, gas chromatograph; TOF-MS, time-of-flight mass spectrometer; MCP, microchannel plate detector.
- Fig. 2 Absorption spectra calculated for 2,3',4-Tri-CB (A) 2,3',4,4',6'-Penta-CB (B) 2,2',3,4,4',5,5',6-Octa-CB (C). *EE*, excitation energy; *IE*, ionization energy; *IE/2*, a half value of ionization energy.
- Fig. 3 (A) Two-dimensional display for KC-mix measured at 267 nm (72 ± 4 mW). (B) Expanded view and chromatogram of the region corresponding to Tri-CBs ($m/z = 256$). The assignments of the signal peaks are indicated in the figure.
- Fig. 4 Two-dimensional displays for the field samples measured at 267 nm (72 ± 4 mW). Sample (A) used transformer oil obtained from the factory and (B) used transformer oil purchased from a flea market.
- Fig. 5 Two-dimensional displays for (A) KC-mix and (B) used transformer oil obtained from the factory measured at 200 nm (18 ± 2 mW).

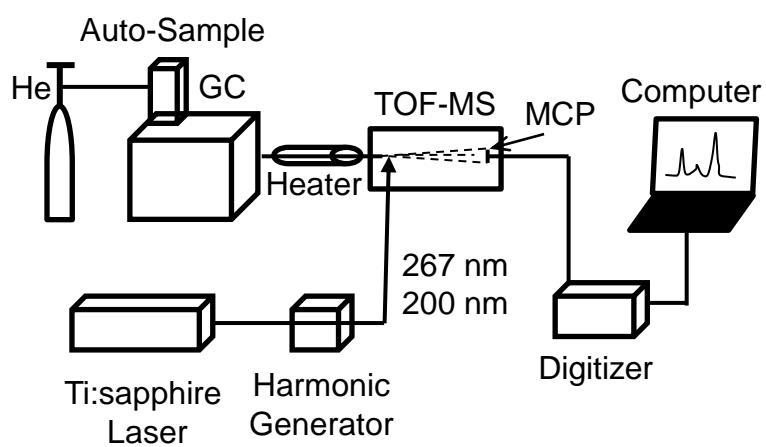


Figure 1. V.T.T. Duong et al.

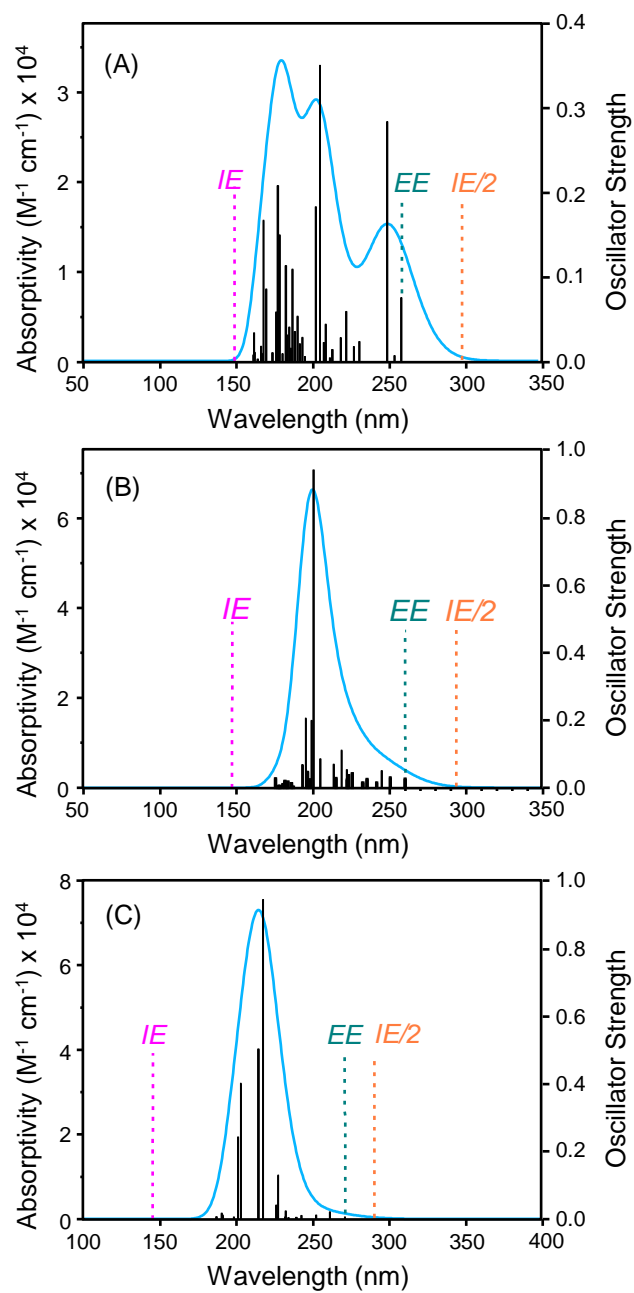
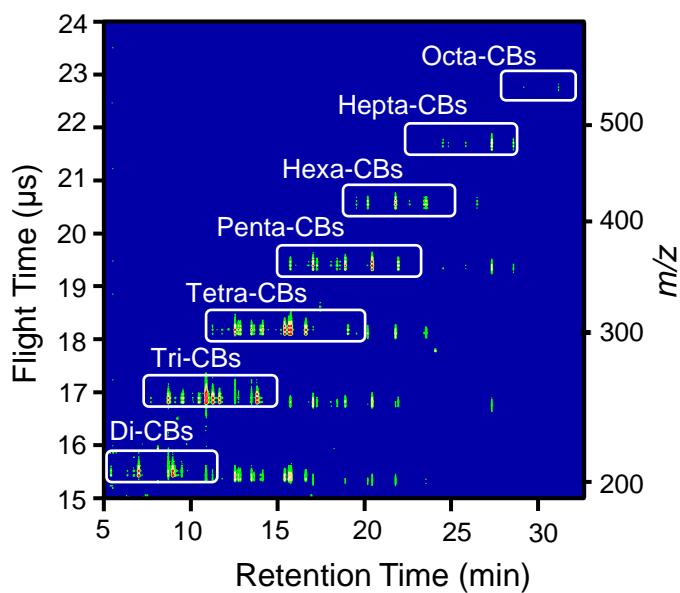
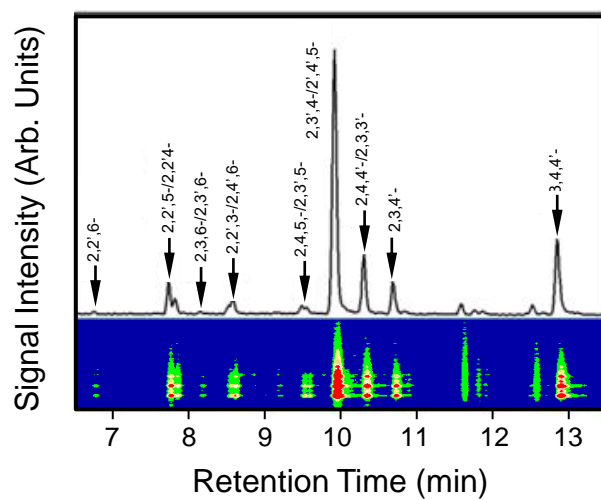


Figure 2. V.T.T. Duong et al.

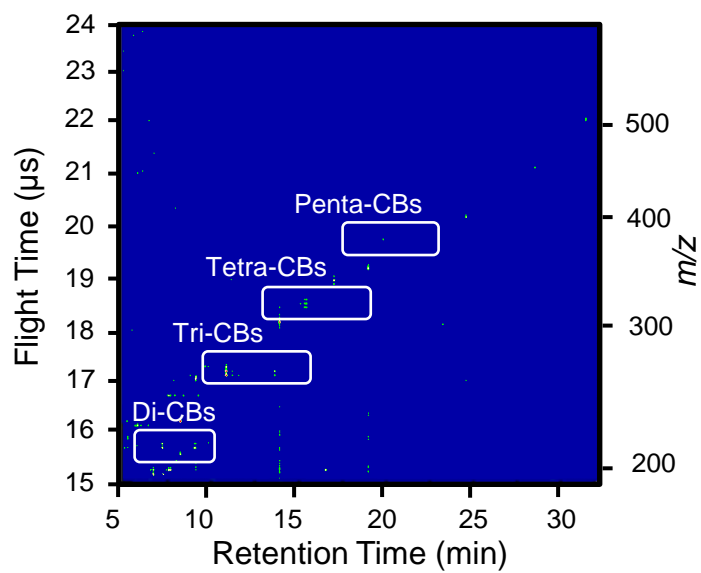


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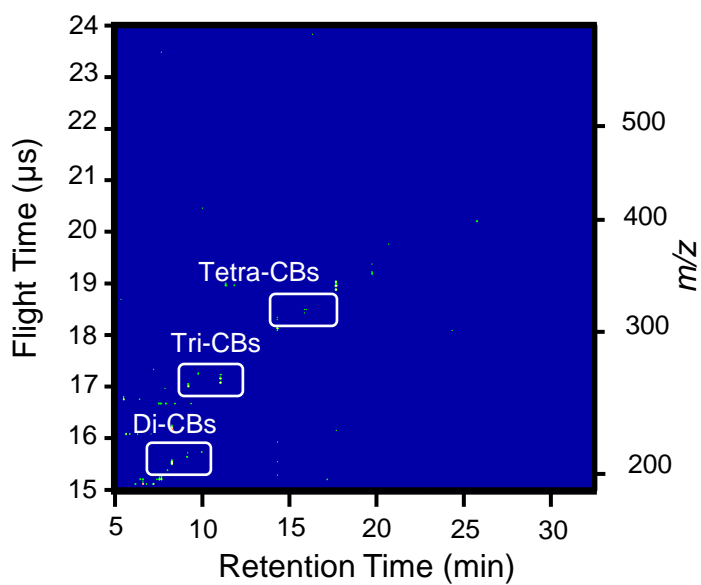


(B)

Figure 3. V.T.T. Duong et al.

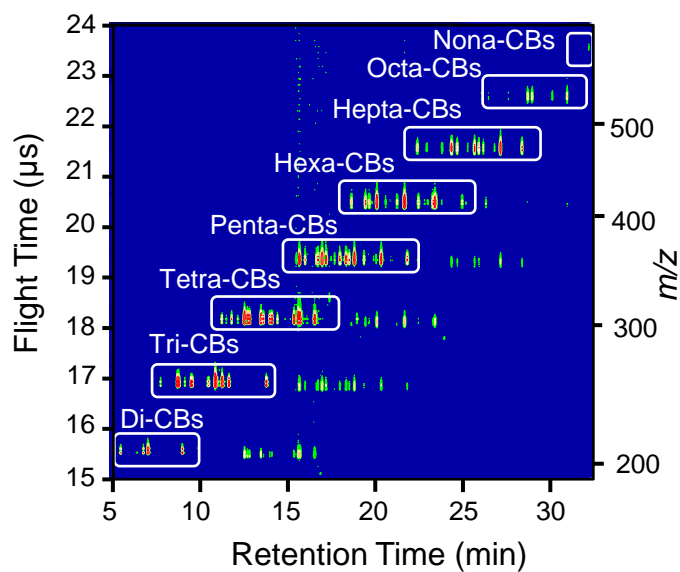


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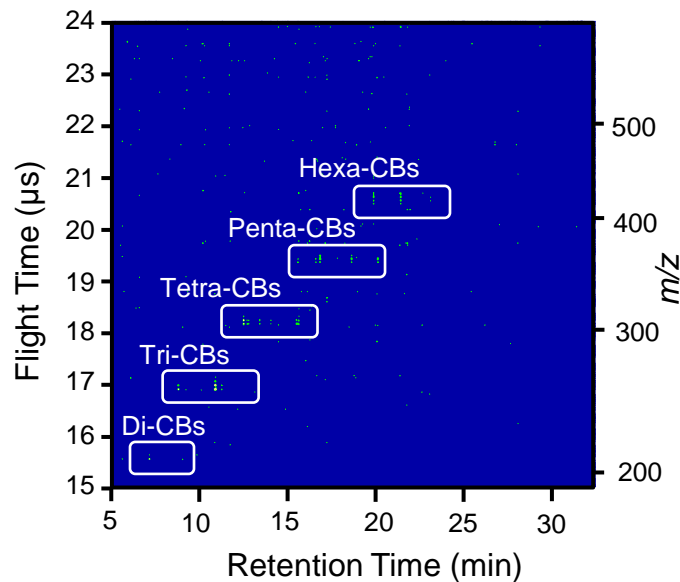


(B)

Figure 4. V.T.T. Duong et al.



(A)



(B)