GAS CHROMATOGRAPHY/MULTIPHOTON IONIZATION/MASS SPECTROMETRY OF PENTACHLORO DIBENZOFURANS IN SOILS

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Introduction

Multiphoton ionization/time-of-flight mass spectrometry (MPI/TOF-MS) is a selective, as well as sensitive analytical technique.[1] The applications of MPI/TOF-MS to the trace analysis of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/Fs) and their precursors have been reported.[2-7] Numerous congeners and isomers are present in PCDD/Fs, though only seventeen of these constituents are toxic. Among these compounds, the toxicity of samples collected from the exhaust gas from an incinerator is mainly due to pentachlorinated dibenzofurans (pentaCDFs).[3] There are two toxic pentaCDFs, i.e., 2,3,4,7,8-pentaCDF and 1,2,3,7,8-pentaCDF, and the toxic equivalency factors (TEF), are reported to be 0.3 and 0.03, respectively.[8] Thus, the quantitative analysis of pentaCDFs, especially 2,3,4,7,8-pentaCDF and 1,2,3,7,8-pentaCDF, is important to evaluate the total toxicity of exhaust gas from an incinerator. A femtosecond laser has a distinct advantage in efficient ionization of PCDD/Fs. In fact, an intense infrared femtosecond laser has been utilized for the analysis of a dibenzo-p-dioxin and polychlorinated benzenes/phenols.[9] However, more than three photons are required for resonant excitation and several additional photons are required for ionization as for the infrared laser. Consequently, ionization efficiency is rather low and such instruments are not used for trace analysis of PCDD/Fs. In this study, the ultraviolet femtosecond laser was employed for the efficient ionization of PCDD/Fs. The third harmonic emission of a femtosecond Ti:Sapphire laser emitting at 262 nm was used for efficient one-color two-photon ionization. Although, most aromatic hydrocarbons are effectively ionized at this wavelength, this wavelength-fixed laser provides poor spectral selectivity. Therefore, this technique (MPI/TOF-MS) was combined with gas chromatography (GC) for separation. In this study, we demonstrated the advantage of using femtosecond ionization in the trace analysis of PCDD/Fs based on GC/MPI/TOF-MS. In our previous work, we reported the superiority of using a femtosecond laser for ionization of PCDFs, compared to nanosecond laser, using an authentic sample.[10] In this study, this analytical system was applied to trace analysis of environmental samples.

Materials and Methods

Figure 1 shows a schematic diagram of the experimental apparatus used in this study. The third harmonic emission of a Ti:Sapphire laser (Thales, Concerto, 262 nm, 200 fs, 1 kHz) was used as the excitation/ionization source. The laser was focused into a TOF-MS using a fused-silica planoconvex lens with a focal length of 300 mm. A mixture sample, containing 1,2,4,6,8-pentaCDF, 2,3,4,6,7-pentaCDF and 1,2,3,8,9-pentaCDF with ^{13}C-1,2,3,4,6-pentaCDF
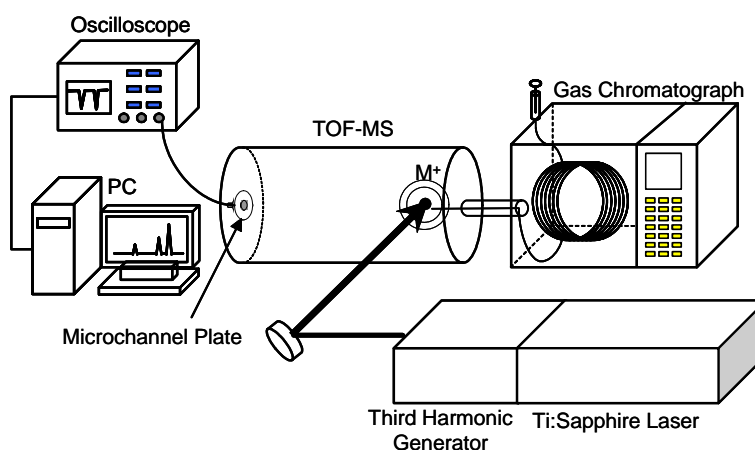

Figure 1. Schematic diagram of the apparatus used for GC/MPI/TOF-MS.

(Cambridge Isotope Laboratories Inc.), was diluted with nonane and one microliter was injected into a GC system (Agilent Technologies, 6890N). Separation was achieved using a GC column (Agilent Technologies, DB-5, i.d. 0.32 mm, 60 m) with helium as a carrier gas. The temperature of the GC oven was elevated from 130 to 300 °C at a programmed rate of 15 °C/min and then held for 5 min. A complete run required 17 min. The temperatures of the inlet and the transfer line were maintained at 300 °C. The eluted sample was directly introduced into a vacuum from the capillary, the tip of which was not restricted to allow the sample to flow continuously as an effusive molecular beam. The ions induced by multiphoton ionization were detected by a microchannel plate (Hamamatsu, F4655-10). The mass spectrum and chromatogram were recorded by using a digital oscilloscope (Tektronix Inc., DPO7104). PCDD/Fs in soil samples were extracted using an accelerated solvent extractor equipped with a solvent controller (ASE-300, Dionex) in toluene solution. After extraction, samples were concentrated and exchanged into *n*-hexane solution by an evaporator. The extract solution was cleaned up with automatic sample preparation device (SPD-600GC, Miura), and concentrated to 20 microliters for measurement by the GC/MPI/TOF-MS.

Results and Discussion

The performance of the GC/MPI/TOF-MS was confirmed by quantification of pentaCDF standards. One microliter of calibration standard solution was injected into the system several times, and the instrumental detection limit, response factors (RFs), relative response factor (RRFs), and calibration curves were estimated.

Figure 2 shows two dimensional display of the data obtained by GC/MPI/TOF-MS. The sample was a mixture solution, which contained 100 pg for each of 1,2,3,8,9-pentaCDF, 2,3,4,6,7-pentaCDF, and 1,2,4,6,8-pentaCDF. As shown in figure 2, three native-pentaCDFs are

Figure 2. Two-dimensional display of the data obtained by GC/MPI/TOF-MS. Sample; 100 pg for each pentaCDF isomer.

completely separated by the DB-5 column and also isotopes of each pentaCDF can be seen clearly. For 1,2,3,8,9-pentaCDF, six peaks were observed in figure 2, which were as follows: $C_{12}H_3O^{35}Cl_5$, m/z = 338, $^{13}C^{12}C_{11}H_3O^{35}Cl_5$, m/z = 339, $C_{12}H_3O^{35}Cl_4^{37}Cl$, m/z = 340, $^{13}C_2^{12}C_{10}H_3O^{35}Cl_4^{37}Cl$, m/z = 341, $C_{12}H_3O^{35}Cl_3^{37}Cl_2$, m/z = 342, and $^{13}C_3^{12}C_9H_3O^{35}Cl_3^{37}Cl_2$, m/z = 343. From shape of the peaks, hence pentaCDFs were easily determined. Moreover, the detection limit (S/N = 3) for 1,2,3,8,9-pentaCDF, 2,3,4,6,7-pentaCDF and 1,2,4,6,8-pentaCDF were lower than the value of 100 fg required for dioxin analysis by Japan Industrial Standard (JIS).[11]
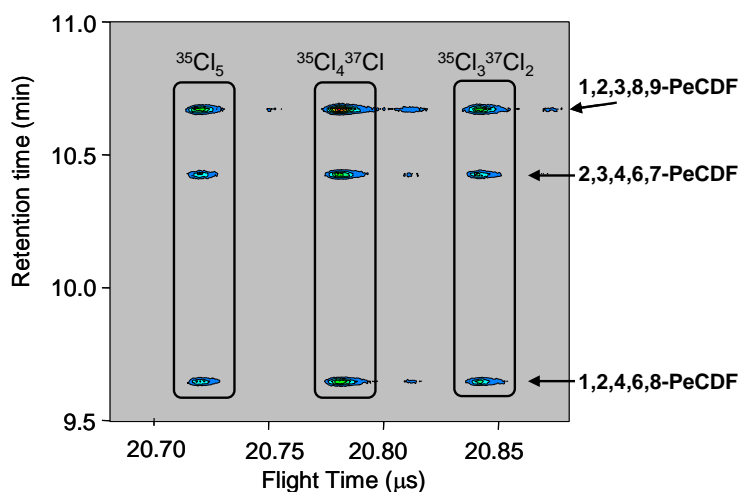
Figure 3 shows the mass spectrum for native and labeled pentaCDF, respectively. Shapes of both native and labeled pentaCDF were clearly observed, and make it easy to determine the isomers of pentaCDFs. Incidentally, the gate of the mass chromatogram was adjusted to the largest isotope peak whose abundance ratio was the highest among the isotope peaks: $C_{12}H_3O^{35}Cl_4^{37}Cl$, m/z = 340 for native pentaCDF and $^{13}C_{12}H_3O^{35}Cl_4^{37}Cl$, m/z = 352 for labeled pentaCDF. In the relative calibration method, linearity was observed in the relation between the signal response and the amount injected for pentaCDFs in the range investigated (from 0.5 to 100 pg per microliter), whereas the determination coefficients (r^2) are larger than 0.99 for 1,2,4,6,8-pentaCDF, 2,3,4,6,7-pentaCDF and 1,2,3,8,9-pentaCDF, respectively. The RRF was calculated by dividing the ratio of the signal response of one pentaCDF to the ^{13}C-labeled 1,2,3,4,6-pentaCDF by the ratio of the amount of the pentaCDF to that of the ^{13}C-labeled 1,2,3,4,6-pentaCDF. The relative standard deviations (RSDs) of the RFs and

RRFs of each pentaCDF ranged less than 10% and 6%, respectively. The fluctuation of the RFs and RRFs is less than 15% and 10%, respectively, which prescribed in standard methods such as JIS.[11] Also, the fluctuation of the retention time for 1,2,4,6,8-pentaCDF, 2,3,4,6,7-pentaCDF and 1,2,3,8,9-pentaCDF, in each concentration of the calibration were less than 5%, which was prescribed in JIS.[11] These results suggest that the GC/MPI/TOF-MS is a suitable analytical system for determining PCDD/Fs isomers amounts.

We measured pentaCDFs in the extract from the soil using GC/MPI/TOF-MS. The soil samples used in this study were collected at the industrial waste disposal landfill in Fukuoka prefecture, Japan. For comparison, the same soil sample was extracted according to the JIS[11] and measured by GC/high-resolution MS (GC/HRMS) in Fukuoka Institute of Health and Environmental Sciences. Figure 4 shows the two-dimensional display of the data obtained by GC/MPI/TOF-MS from the soil sample. As

Figure 3. Mass spectrum of native and labeled 2,3,4,6,7-pentaCDF in the soil.

shown in figure 4, not only native-pentaCDF, labeled-^{13}C-pentaCDF and pentaCDD but also haxachloronaphthalene was observed. Thus, using this system, interferences can be seen at once. Therefore, pentaCDFs are quantified by the GC/MPI/TOF-MS, even in the simple cleanup procedure such as SPD-600GC. The results of measurements by GC/MPI/TOF-MS and GC/HRMS for 2,3,4,6,7-pentaCDF agreed quite well with each other. Unfortunately, some pentaCDF isomers are superimposed on others. For example, three pentaCDFs, i.e., 1,2,4,8,9-pentaCDF, 1,2,6,7,9-pentaCDF, and 1,2,3,6,9-pentaCDF, are superimposed on 2,3,4,7,8-pentaCDF on the chromatogram using DB-5 column.[12,13] Therefore, it is difficult to determine 2,3,4,7,8-pentaCDF selectively using GC/MS. In fact, this compound is responsible for one-third of the TEQ value and shows high correlation between the concentration and the TEQ value (correlation coefficient, 0.99).[14] In this study, the wavelength of the femtosecond laser (262 nm) was fixed and used for MPI, and provide no or little spectral selectivity for pentaCDF isomers. However, it is possible to resonantly excite and ionize 2,3,4,7,8-pentaCDF selectively in the vicinity of the 0-0 transition. For this purpose, the analyte molecules should be expanded from the restrictor into a vacuum to form a supersonic jet (SSJ) for spectral line narrowing. A combination of the spectral selectivity given by SSJ/MPI/TOF-MS and the separation selectivity by GC is useful to determine the toxic pentaCDFs isomer-specifically at ultratrace levels.

The advantage of ultraviolet femtosecond ionization in the determination of PCDD/Fs, especially pentaCDFs having short singlet-excited-state lifetimes, is applied to the measurement of the environmental sample. The detection limits of pentaCDFs were less than 0.1 pg, the fluctuations of the RFs and RRFs were less than 15% and 10%, respectively, which are prescribed in the standard method in JIS.[11] Thus, GC/MPI/TOF-MS based on ultraviolet femtosecond laser ionization has a potential as a powerful tool for use in environmental analysis of, e.g., soils, even after simple clean-up procedure.
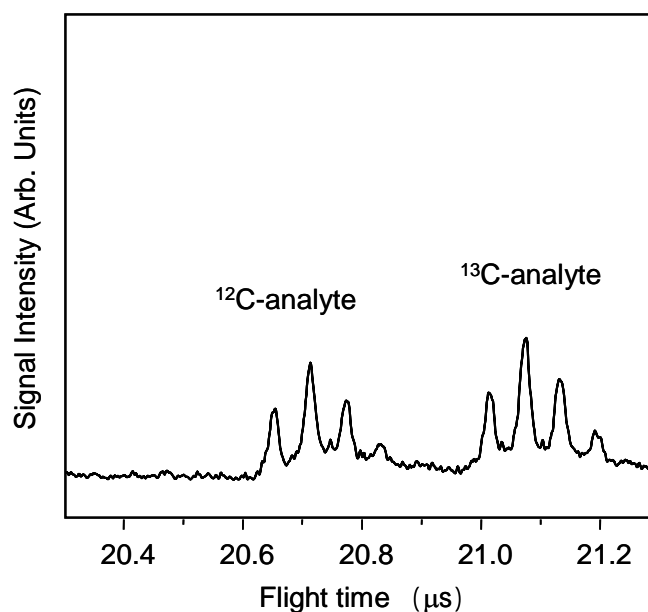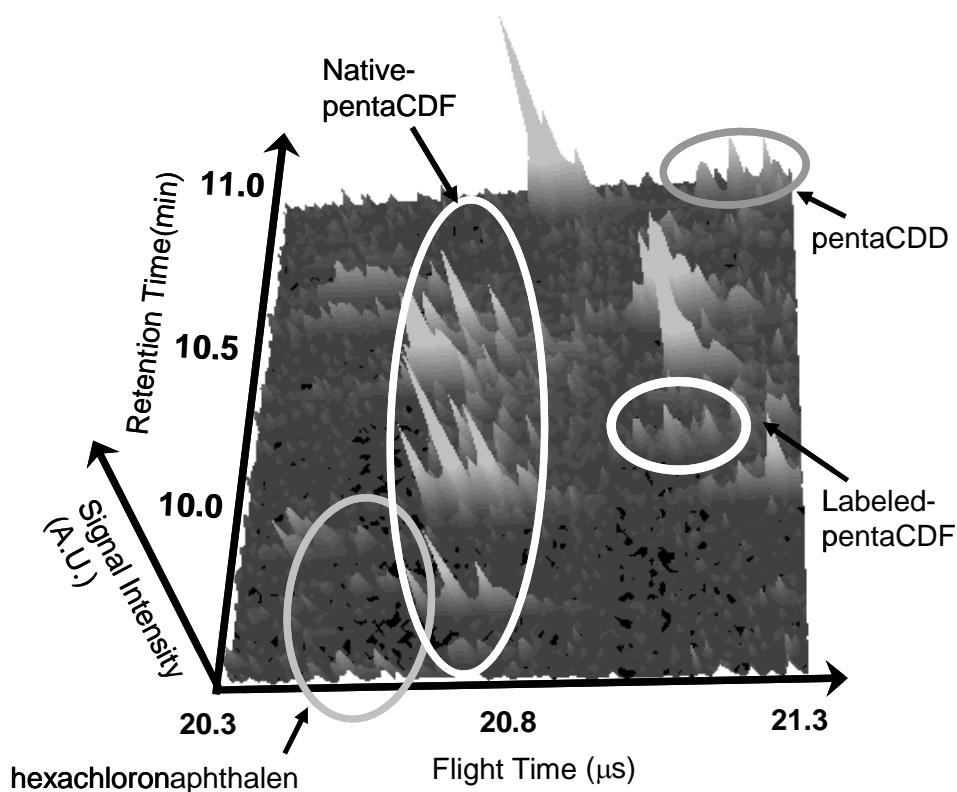
Figure 4. Two-dimensional display of the data obtained by GC/MPI/TOF-MS from the soil sample.

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