

# ANALYSIS OF HIGHLY CHLORINATED DIBENZOFURANS USING GAS CHROMATOGRAPHY/MULTIPHOTON IONIZATION/TIME-OF-FLIGHT MASS SPECTROMETRY

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## Abstract

The advantage of ultraviolet femtosecond ionization was applied to the determination of highly chlorinated dibenzofurans, having short singlet-excited-state lifetimes. The detection limits of hexachlorinated dibenzofurans, were less than 0.2 pg, and the fluctuation of the relative response factors were less than 10%, which were prescribed in the standard method in the Japanese Industrial Standards. This is the first time to detect highly chlorinated dibenzofurans using multiphoton ionization/time-of-flight mass spectrometry with femtosecond laser.

## Introduction

Polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs) are well known as toxic substances in the environment. Their toxicities are quite different depending on the positions and numbers of the chlorine atoms substituted in the benzene rings in dioxins and dibenzofurans. Since a trace quantity of PCDD/Fs exists in the environment, a highly sensitive and selective analytical method is required. High-resolution gas chromatography combined with high-resolution mass spectrometry (HRGC/HRMS) is used for the protocols provided by the Japanese Industrial Standards (JIS).<sup>1</sup> However, interference species such as aliphatic and aromatic compounds existing in the samples are simultaneously ionized by an electron beam (EI) employed in HRGC/HRMS. Therefore, a new ionization technique is desirable for the improvement of selectivity in the analysis of PCDD/Fs.

Multiphoton ionization/time-of-flight mass spectrometry (MPI/TOF-MS) is a selective, as well as sensitive analytical technique. Moreover a femtosecond laser has the apparent advantage in the efficient ionization of PCDD/Fs compared to a nanosecond laser.<sup>2</sup> In this study, the third harmonic emission of a femtosecond Ti:Sapphire laser emitting at 261 nm was used for efficient one-color two-photon ionization, and to get further improvement in the selectivity, this technique (MPI/TOF-MS) was combined with gas chromatography (GC) for separation. The performance of the GC/MPI/TOF-MS was confirmed by quantification of pentachlorinated dibenzofurans (pentaCDFs) standards.<sup>3</sup> The results satisfied the criteria which prescribed in standard methods such as JIS.<sup>1</sup> Consequently, in this study other highly chlorinated dibenzofurans, such as hexachlorinated dibenzofurans (hexaCDFs), heptachlorinated dibenzofurans (heptaCDFs), and octachlorinated dibenzofurans (octaCDFs), including tetrachlorinated dibenzofurans (tetraCDFs) and pentaCDFs were analyzed by the GC/MPI/TOF-MS for the first time.

## Materials and Methods

Standard solutions which contain 23 different PCDD/Fs isomers and their  $^{13}\text{C}$ -labeled isotopes were purchased from Wellington laboratories, Guelph, ON, Canada. The reagents and solvents were of the highest grade available. The schematic diagram of the experimental apparatus used in this study is shown in Figure 1. The third harmonic emission of a Ti:Sapphire laser (Thales, Concerto, 261 nm, 200 fs, 1 kHz) was used as the excitation/ionization source. The laser was focused on a TOF-MS using a fused-silica planoconvex lens with a focal length of 300 mm. One microliter of a sample was injected into a GC (6890GC, Agilent Technologies, Santa Clara, CA, USA) by an automatic sampler (6890N, Agilent Technologies). Separation was achieved using a GC column (HP-5, i.d. 0.25 mm, 30 m, Agilent Technologies) with helium as a carrier gas. The GC oven temperature used for the column was programmed from 130 °C to 300 °C at a rate of 15 °C/min and then held for 15 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 (MCP, F4655-11, Hamamatsu Photonics K.K., Shizuoka, Japan). The mass spectrum and chromatogram were recorded using a digitizer (AP240, Agilent Technologies), and the data processing was performed by a personal computer.

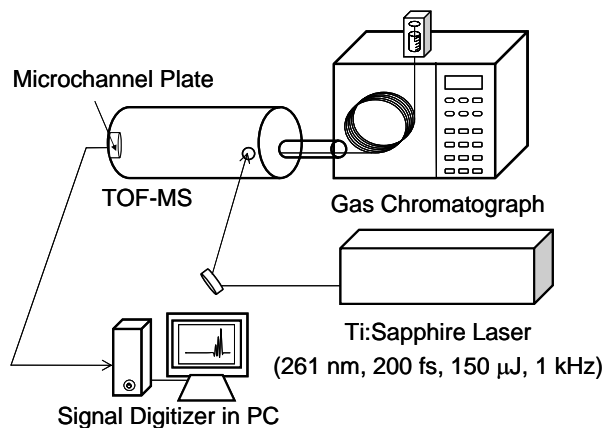


Figure 1 Schematic diagram of the apparatus used for GC/MPI/TOF-MS.

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 (MCP, F4655-11, Hamamatsu Photonics K.K., Shizuoka, Japan). The mass spectrum and chromatogram were recorded using a digitizer (AP240, Agilent Technologies), and the data processing was performed by a personal computer.

## Results and Discussion

The performance of the GC/MPI/TOF-MS was confirmed by quantification of PCDD/Fs standards. One micro liter of calibration standard solution was injected into the system several times, and the instrumental detection limits, relative response factors (RRFs), and calibration curves were estimated.

Figure 2 shows a mass spectrum for native and labeled polychlorinated dibenzofurans (PCDFs), respectively. Shapes of both native and labeled PCDFs were clearly observed, and make it easy to determine the isomers of each PCDF. Incidentally, the gate of the mass chromatogram was adjusted to the largest isotope peak whose abundance ratio was the highest among the isotope peaks: for example,  $\text{C}_{12}\text{H}_2\text{O}^{35}\text{Cl}_5^{37}\text{Cl}$ ,  $m/z = 374$  for native hexaCDF and  $^{13}\text{C}_{12}\text{H}_2\text{O}^{35}\text{Cl}_5^{37}\text{Cl}$ ,  $m/z = 386$  for labeled hexaCDF.

Figure 3 shows a two-dimensional display of the data obtained by GC/MPI/TOF-MS. The sample was a standard mixture solution, which contained 50 pg for native-tetraCDD/Fs, and native-pentaCDD/Fs, 100pg for native-hexaCDD/Fs, and native-heptaCDD/Fs, 250pg for native-OCDD/Fs, and 10pg for  $^{13}\text{C}$ -labeled-

tetra, penta, hexa, and heptaCDD/Fs, and 20pg for octaCDD/Fs. As shown in figure 3, isotope peaks of PCDD/Fs in the solution were detected, and can easily be assigned from the number of the peaks of isomers. For example, 4 native-hexaCDFs were completely separated by the HP-5 column and also isotopes of each hexaCDF can be seen clearly. Moreover, the detection limits ( $S/N = 3$ ) for 2,3,7,8-tetraCDF, 1,2,3,7,8-pentaCDF, and 1,2,3,7,8,9-hexaCDF were 0.1pg, 0.1pg, and 0.2pg, respectively. Those values satisfied the performance which required for dioxin analysis by JIS.<sup>1</sup> Since the HP-5 column was heated up to 300 °C to separate PCDD/Fs, the constituents of the stationary phase were partly decomposed and released into a mobile phase. These bleeding compounds were introduced as interference into the MS and could be ionized by the UV laser. The stationary phase of the HP-5 column consisted of (5%-phenyl)-methyl polysiloxane.<sup>4</sup> The heptaCDD/Fs peaks which should appear at  $m/z = 408$ , 420 and 424 were superimposed with these interference species, since they had the same mass to charge ratio ( $m/z$ ). Because of these interferences, we

could not obtain the values of the detection limits for heptaCDD/Fs. Therefore, to solve this problem, the wavelength of the UV laser should be converted into the near-UV region (300 nm),<sup>5</sup> or use other low bleed capillary columns. Then the undesirable peaks arising from the interference will disappear, and heptaCDD/Fs peaks will be detected completely. Furthermore, the detection limit ( $S/N = 3$ ) for octaCDF was 0.8pg. It was because the octaCDF peaks were partially superimposed with the octaCDD peaks. The separation by GC seemed to be insufficient. Consequently, using other capillary columns and also a suitable temperature program for GC will improve the separation, and could solve the problem. Additionally, further improvement in sensitivity would be possible by use of our recent developed novel data processing technique for use in GC/MPI/TOF-MS.<sup>6</sup>

In the relative calibration method, a linearity was observed in the relation between the signal response and the amount injected for every PCDFs except heptaCDFs, in the range investigated (from 0.5 to 250 pg per microliter). The determination coefficients ( $r^2$ ) were 0.99, 1.0, 1.0, and 0.99 for 2,3,7,8-tetraCDF, 1,2,3,7,8-pentaCDF, 1,2,3,7,8,9-hexaCDF and octaCDF, respectively. The RRF was calculated by dividing the ratio

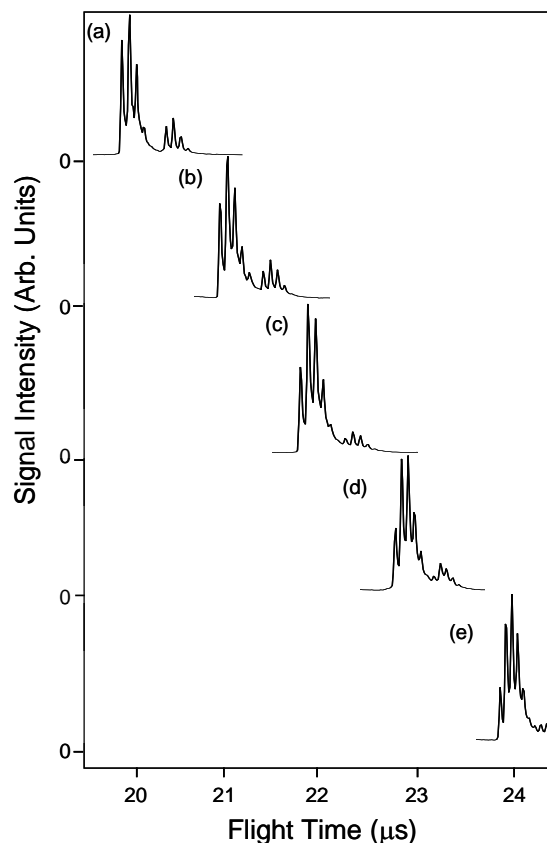


Figure 2 Mass spectra of (a)2,3,7,8-tetraCDF, (b)1,2,3,7,8-pentaCDF, (c)1,2,3,7,8,9-hexaCDF, (d)1,2,3,4,6,7,8-heptaCDF, (e)octaCDF.

of the signal response of one congener to that of the  $^{13}\text{C}$ -labeled congener by the ratio of the amount of the congener to that of the  $^{13}\text{C}$ -labeled congener. The relative standard deviations (RSDs) of the RRFs were 8.4, 9.5, 10, and 10% for 2,3,7,8-tetraCDF, 1,2,3,7,8-pentaCDF, 1,2,3,7,8,9-hexaCDF and octaCDF, respectively. Those values satisfied the performance which required for dioxin analysis by JIS.<sup>1</sup>

Until now, there is no report of analysis of highly chlorinated dibenzofurans using GC/MPI/TOF-MS based on ultraviolet femtosecond laser ionization. This is the first time of detecting, not only pentaCDFs but also other PCDFs by GC/MPI/TOF-MS. Therefore this instrument would be a powerful tool for use in PCDD/Fs analysis and could be easily determine the dioxins concentrations using two-dimensional displays.

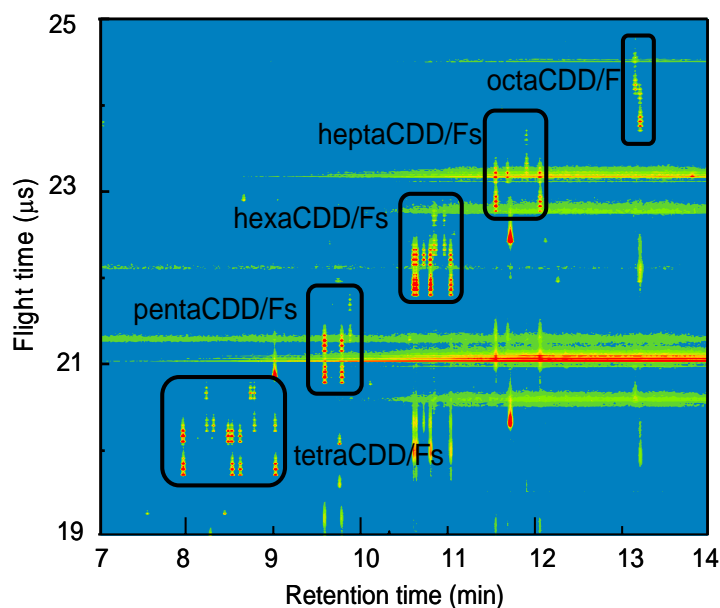


Figure 3 Two-dimensional display of the data obtained by GC/MPI/TOF-MS.

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