

GAS CHROMATOGRAPHY/MULTIPHOTON IONIZATION/TIME-OF-FLIGHT MASS SPECTROMETRY FOR APPLICATION TO CRUDE OIL

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Introduction

There have been many accidental oil spills, and the effects to the environment become serious problems.¹ Last year, the Deepwater Horizon oil drilling platform located in the Gulf of Mexico, owned and managed by Transocean for British Petroleum (BP), caught fire on April 20 and sank. The oil leak resulted in an environmental disaster for the Gulf region. The U.S. Coast Guard (USCG) and BP undertook operations to collect and burn the surface oil as one means of limiting its environmental impact.² In situ burning of oil spills has the benefit of minimizing contamination of coastal marine environments with relatively lower cost than other crude oil treatment. However, emissions of polychlorinated dibenzodioxins and polychlorinated dibenzofurans (PCDD/Fs) from the oil burns are of interest due to their health effects including immunotoxicity, carcinogenicity, and teratogenicity.³ The potential for PCDD/Fs emissions from the in situ burns exists due to the apparent presence of the following conditions for formation: incomplete combustion, the presence of trace metals as catalysts, and availability of chloride in the seawater. Few measurements of PCDD/Fs have been made from oil fires from an at-sea burns.³ Results from them at sea level were reported as indistinguishable from background levels.^{4,5} However, it is important to measure the concentration of PCDD/Fs around the sea environment with various conditions for the risk monitoring.

Since PCDD/Fs exist in ultratrace levels in the environment, detection of them requires a sensitive analytical method. High-resolution gas chromatography combined with high-resolution mass spectrometry (HRGC/HRMS) is required in the protocol (K0311) provided by the Japanese Industrial Standards (JIS). However, numerous organic compounds such as aliphatic and aromatic hydrocarbons can be present in a sample and can act as interference and be simultaneously ionized by the electron beam (EI) employed in HRGC/HRMS. Therefore, it is difficult to determine PCDD/Fs using a single mass chromatogram, and several mass chromatograms measured at different mass/charge ratios (m/z). They must be carefully checked to identify the peaks arising from PCDD/Fs congeners and to avoid interference from contaminants. Thus, a new technique for ionization is desirable in order to reduce the background interference and to improve the reliability of quantitative analysis of PCDD/Fs.

In our former study,⁶ performance of gas chromatography/multiphoton ionization/time-of-flight mass spectrometry (GC/MPI/TOF-MS) was evaluated by measuring a standard mixture solutions of PCDD/Fs. All the criteria in the protocol of JIS K0311, such as detection limits and relative standard deviations, were satisfied for all the congeners. Soil samples were measured using GC/MPI/TOF-MS and HRGC/HRMS, and the results were nearly the same, even when a curtailed pretreatment procedure was utilized in the laser ionization technique. Moreover, we measured PCDD/Fs in the certified reference material of soil. The results were in good agreement between GC/MPI/TOF-MS and HRGC/HRMS. The results suggest that GC/MPI/TOF-MS has equivalent, or even superior, performance in the determination of PCDD/Fs due to negligible levels of background from interference, and would be more practical than HRGC/HRMS for trace environmental analysis of PCDD/Fs.

When crude oils are analyzed, it is necessary to remove interferences in samples. Many studies have been focused on the methods to remove interference species, such as sulfuric acid treatment, liquid-liquid partitioning, gel permeation chromatography, and normal-phase liquid chromatography and so on. Those pretreatment procedures take times and troublesome handworks. Therefore, it is possible to simplify the process of pretreatment using a more selective analytical technique in the final step of instrumental analysis. The

GC/MPI/TOF-MS is one of the options for the analysis of PCDD/Fs in crude oils due to superior sensitivity and selectivity. In the present study, we study the possibility of using this GC/MPI/TOF-MS for screening PCDD/Fs in crude oils using a third harmonic emission (266 nm) of a femtosecond Ti:sapphire laser (800 nm).

Materials and methods

Crude oils (Idemitsu Kosan Co., Ltd.) were burned with sodium chloride and sea sand (Wako pure chemical Industries, Ltd) supposing the coast environment . The residues and vapor fractions of burning oils were collected. 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.

Standard solutions which contain 23 different PCDD/Fs isomers and their ¹³C-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 (266 nm, 100 fs, 1 kHz, 150μJ, Libra, Coherent Inc., CA) 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 temperature of the GC oven was programmed from 120 °C (1 min hold) to 180 °C at a rate of 50 °C/min, then to 280 °C at a rate of 3 °C/min, where it was 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.

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, and calibration curves were estimated. The shapes of mass spectrum for native and labeled tetra to octa PCDFs and tetra to hexa PCDDs were clearly observed, and make it easy to determine the isomers of each PCDD/Fs.^{7,8}

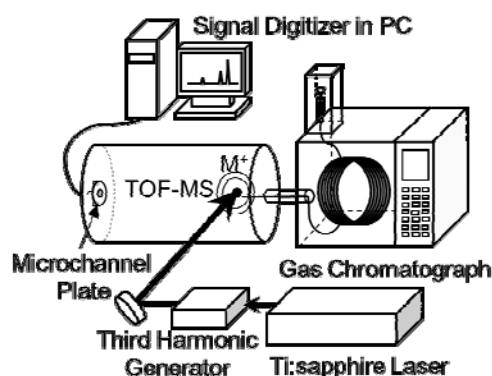


Figure 1. Schematic diagram of the apparatus used for GC/MPI/TOF-MS.

First of all, to check the effects of interferences for the analysis of PCDD/Fs, a crude oil was diluted with *n*-hexane for a thousand times, and directly measured by GC/MPI/TOF-MS. The result was shown in Figure 2. Major components of a crude oil are hydrocarbon compounds, and peaks for aromatic hydrocarbon compounds can be seen in Fig. 2. The observed peaks were grouped into categories specified from A to C in Fig. 2. The peaks for A were crossed over with the peaks for toxic PCDD/Fs, and B, C would be crossed over with the peaks for other aromatic hydrocarbons. Thus, the area for PCDD/Fs is interfered by major components of the crude oil. Though, peaks for the direct measurements of crude oil might be less than electron ionization method compare to GC/MPI/TOF-MS, since GC/MPI/TOF-MS is a soft ionization mass spectrometry. As a result, it is difficult to measure trace amounts of PCDD/Fs in diluted crude oil directly. Also, we measured mineral oils used as insulating and heat-transfer oils and noticed that they contain numerous aromatic hydrocarbons and disturb the analysis of PCDD/Fs even when using GC/MPI/TOF-MS. Therefore, a process for removing undesirable interference is necessary for the determination of PCDD/Fs, and the analytes can be concentrated in a pretreatment process. Then this method enables the identification of numerous signal peaks arising from PCDD/Fs and the avoidance of interference from contaminants based on a two-dimensional display, which is an advantage of TOF-MS.⁶ In addition, selectivity in the process of ionization is strongly enhanced by spectral matching of the laser wavelength and by the absorption spectrum of the analyte. For example, nontoxic aliphatic hydrocarbons in the sample are not efficiently ionized, and their signals are significantly suppressed.

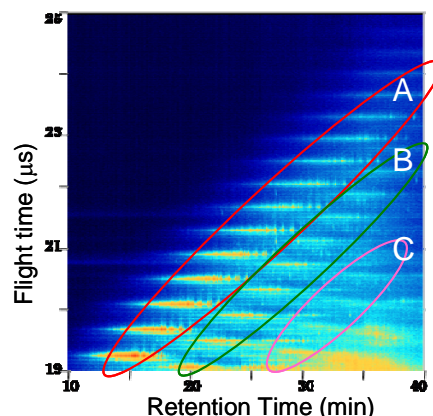


Figure 2. Two-dimensional display of the data for the diluted crude oil sample by GC/MPI/TOF-MS.

After pretreatment, the residues and vapor fractions of burning oils were measured. Figure 3 shows a two-dimensional display of the data obtained by GC/MPI/TOF-MS for the residue after burning of crude oils. As shown in Fig.3, the number of peaks observed were decreased compared to the unpretreatment crude oil (Fig. 2). The area which peaks were not observed was the area for PCDD/Fs. From the mass chromatogram for this sample, concentrations for PCDFs and tetra to hexaCDDs were lower than the detection limits which we detected before.⁶ These results support the results obtained by others.^{4,5} In Japanese standard method (JIS), pretreatment procedures for PCDD/Fs analysis are decided, which are complicated and take times and troublesome handworks. For this study, the curtailed pretreatments were employed and shorten times and handworks. For details, in JIS method more than 16 hours were taken for a Soxhlet extraction and more than several days for clean-up procedures, such as column chromatographys. On the other hand, our pretreatment procedures took less than one hour for extraction using ASE, and several hours for the clean-up procedure using automatic sample preparation device. The concentration of PCDD/Fs in crude oils could be analyzed within a day. Therefore, using GC/MPI/TOF-MS is one of the suitable way for screening PCDD/Fs in crude oils. Moreover, the advantage of this GC/MPI/TOF-MS for screening PCDD/Fs in crude oils are because the linear-type TOF-MS was used in the present study, which was suitably differentiated the molecular ion of PCDD/Fs and the fragment ion arising from them, since the initial velocity was not compensated for in the TOF-MS, which was in contrast to a reflectron-type TOF-MS.

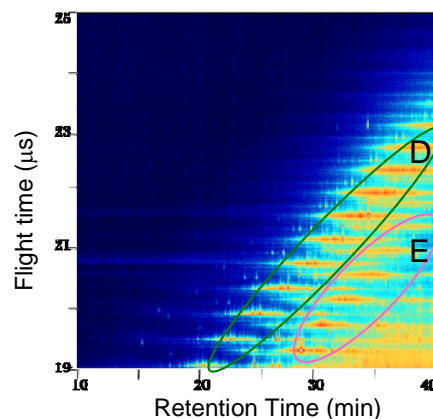


Figure 3. Two-dimensional display of the data for the residue after burning of crude oil with sodium chloride and the sea sands sample by GC/MPI/TOF-MS.

Figure 4 shows a two-dimensional display of the data obtained by GC/MPI/TOF-MS for the vapor fraction after burning of crude oil. The observed peaks are grouped into categories specified from G, H, and I which were similar with the unpretreatment crude oil. It seemed that the volatile crude oils were detected. The peaks for G were crossed over with the peaks for toxic PCDD/Fs, however, the interferences were lower than the direct crude oil measurement. Consequently, the mass chromatogram data could be analyzed. As a result, concentrations for PCDD/Fs in this sample were lower than the detection limits which we detected before for PCDFs and tetra to hexaCDDs.⁶ These results also support the results obtained by others.^{4,5}

Thus, GC/MPI/TOF-MS based on ultraviolet femtosecond laser ionization has a potential as a powerful tool for use in screening of not only PCDD/Fs but also other environmental pollutants, such as polycyclic aromatic hydrocarbons and polychlorinated biphenyls in crude oils.

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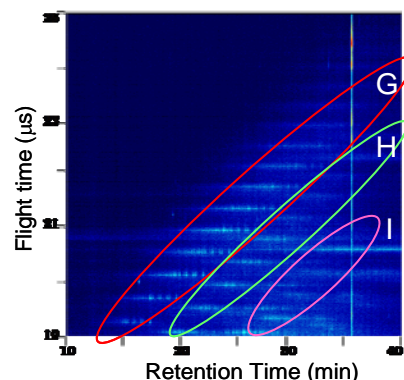


Figure 4. Two-dimensional display of the data for the vapor after burning of crude oil with sodium chloride and the sea sands sample by GC/MPI/TOF-MS.