

ANALYSIS OF BURNED CRUDE OIL BY GAS CHROMATOGRAPHY/ MULTIPHOTON IONIZATION/TIME-OF-FLIGHT MASS SPECTROMETRY

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Introduction

Many accidental oil spills have occurred, and the damages to environments were serious problems.¹ One of the largest oil spills was took place in 2010, the oil drilling platform located in the Gulf of Mexico, owned and managed by Transocean for British Petroleum (BP), caught fire and sank. The oil leak resulted in an environmental disaster for the Gulf region. In this case, the U.S. Coast Guard (USCG) and BP collected and burned the surface oil as one way of limiting its environmental impact.² However, emissions of polychlorinated dibenzodioxins, polychlorinated dibenzofurans (PCDD/Fs) and polychlorinated biphenyls (PCBs) from the oil burns are of interest due to their health effects including carcinogenicity, immunotoxicity, and teratogenicity.³ Few measurements of PCDD/Fs and PCBs 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 takes time to measure the concentration of PCDD/Fs and PCBs around the sea environment with various conditions. Consequently, there are demands for appropriate analytical techniques.

The disaster of earthquake followed by tsunami and fire has resulted in serious environmental problems in Japan last year. The earthquake on March 11th (EQ3.11) caused huge tsunami and fires in the northeastern region (Tohoku and Kanto regions) of Japan. Because of the tsunami, large amounts of sea water came up not only to the coast area but also to the inland areas. Oil tanks near the coast area got damages from the earthquake and tsunami. The ruptured oil tanks leaked black liquid around, and burned for long time. Moreover, houses and fields were fired. The contamination of oils in these areas are serious problems. There are demands for fast and simultaneous analysis using appropriate analytical techniques.^{6,7}

When crude oils and their extracts are analyzed, it is necessary to remove interferences in samples with time consuming and troublesome handworks. However, it is possible to simplify the process of pretreatment using a more selective analytical technique in the final step of instrumental analysis. The gas chromatography/multiphoton ionization/time-of-flight mass spectrometry (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 former study, we reported that the GC/MPI/TOF-MS based on ultraviolet femtosecond laser ionization has a potential as a powerful tool for use in screening for not only PCDD/Fs but also other environmental pollutants, such as polycyclic aromatic hydrocarbons and polychlorinated biphenyls in crude oils.⁸ Therefore, we applied the method for sea sands and soils. 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) and also applied the methods to the soils burned with crude oils to screening the chemical pollutants such as PCDD/Fs, PCBs and other polycyclic aromatic hydrocarbons.

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. Crude oil, sodium chloride were burned with soils collected from general field. 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 ^{13}C -labeled isotopes were purchased from Wellington laboratories, Guelph, ON, Canada. The reagents and solvents were of the highest grade for chemical analysis. The schematic diagram of the experimental apparatus used in this study is shown in elsewhere.⁸ The third harmonic emission of a Ti:Sapphire laser (266 nm, 100 fs, 1 kHz, 150 μJ , 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). Samples were separated by 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 and other conditions were written in our previous paper.⁹ 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. The detection limits for the instrument, relative response factors, and calibration curves were estimated. The shapes of mass spectrum for native and labeled tetra to octa PCDD/Fs were clearly observed, and make it easy to determine the isomers of each PCDD/Fs from tetraCDD to octaCDF.

After pretreatment, the residues and vapor fractions of burned oils were prepared. The PCDD/Fs standards were added to the vapor and residue samples and analyzed. When the data were shown in a two-dimensional display obtained by GC/MPI/TOF-MS, the peaks for mass spectra and chromatograms of PCDD/Fs were clearly observed. For example, figure 1 shows the mass spectra of tetraCDF in the vapor of burned crude oil sample. The results suggest that for the analysis of PCDD/Fs in residue and burned crude oils, it is possible to apply the curtailed pretreatment which is different from Japanese standard method (JIS). For this study, the curtailed pretreatments were employed and shorten times and handworks. Therefore, using GC/MPI/TOF-MS is one of the suitable ways 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. It was suitably separated the molecular ion of PCDD/Fs and the fragment ion arising from samples, since the initial velocity was not compensated for in the TOF-MS, which was in contrast to a reflectron-type TOF-MS, as we mentioned before.⁸

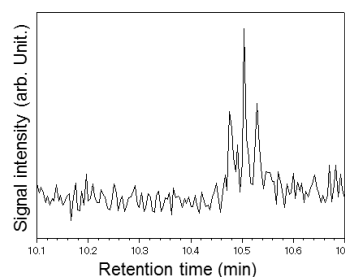


Figure 1. Mass spectra of the data for the tetraCDF in vapor of burned crude oil sample by GC/MPI/TOF-MS.

Three kinds of soil were burned with crude oil and sodium chloride. After extracted and clean-up the samples, they were analyzed using this GC/MPI/TOF-MS. Two of them contained no toxic dioxins, however, one of them contained little toxic dioxins and also other polychlorinated aromatic hydrocarbons. Figure 2 shows the results of the third sample. As shown in this figure, octaCDD/F and heptaCDD/Fs were detected from the data obtained using GC/MPI/TOF-MS and the elution order reported in a reference.¹⁰ Moreover, other polychlorinated aromatic hydrocarbons were observed, though, the figure is too small to identify each peak for that area. The area which is surrounded by yellow lines in figure 2 was magnified.

Figure 3 shows a magnified two-dimensional display of the figure 2. As shown in this figure, this sample was found to contain several types of polychlorinated aromatic hydrocarbons. Some of them could be assigned to ^{13}C -pentaCDFs, tetraCDDs, pentaCBs, tetraCB and pentachloronapthalenes (pentaCNs), as specified in the figure, as determined from the molecular weights and intensity distributions of the isotope peaks. Among the ^{13}C -pentaCDFs, peaks were assigned to ^{13}C -1,2,3,4,6-pentaCDF, and ^{13}C -1,2,3,7,8-pentaCDF from data obtained using GC/MPI/TOF-MS from the elution order reported in a reference.¹⁰ Also, among the tetraCDDs, peaks were assigned to nontoxic 1,3,6,8-tetraCDD, and 1,3,7,9-tetraCDD from data obtained using GC/MPI/TOF-MS from the elution order reported in a reference.¹⁰ For pentaCBs, the largest peak could be assigned to toxic 2,3',4,4',5-pentaCB(#118) and the other peak was attributed to toxic 2,3,3',4,4'-pentaCB(#105) from the elution order reported in a reference.¹¹ For tetraCB, the peak was attributed to toxic 3,3',4,4'-tetraCB(#77) from data obtained using GC/MPI/TOF-MS. For pentaCNs, the peak was attributed to 1,2,4,5,7-pentaCN, 1,2,3,6,7-pentaCN, 1,2,4,5,6-pentaCN, 1,2,4,7,8-pentaCN and 1,2,4,5,8-pentaCN from data obtained using GC/MPI/TOF-MS from the elution order reported in a reference.^{11,12} However, for pentaCN, it has been reported that 1,2,3,6,7-pentaCN is present at negligible levels in the commercial PCN mixture of Halowax. This isomer was, however, found in fly ash and flue gas from municipal solid-waste incinerators.¹³ Thus, the soil sample used in this study could have been contaminated with byproducts emitted from incinerators. The toxicity for this sample was 0.29pg-TEQ. From these results, crude oil can produce not only dioxins but also other chemical hazardous compounds. Although the concentration is very low, this fact suggests that we must pay attention to the production of chemical pollutants near the seashore, if it is contaminated by crude oils and sea water.

In this way, it is possible to analyze sample quantitatively and qualitatively for one measurement. Thus, GC/MPI/TOF-MS based on ultraviolet femtosecond laser ionization is proved to be useful in analyzing large

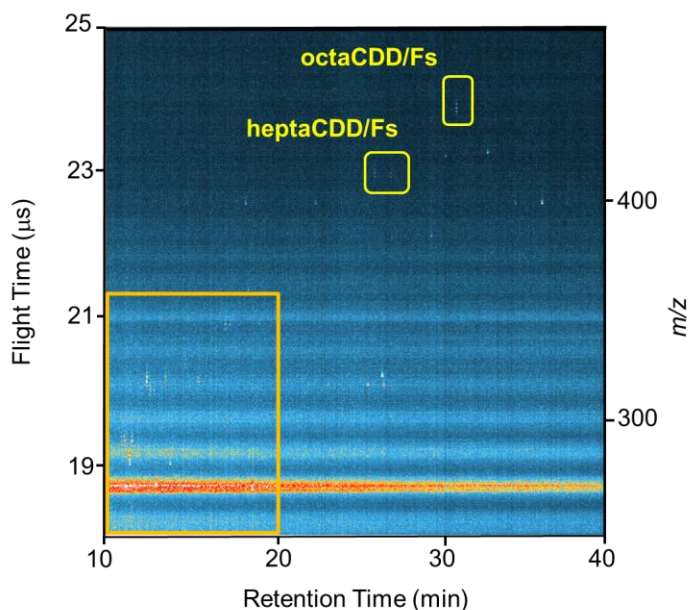


Figure 2. Two-dimensional display for the extracts from soil after burning with crude oil and sodium chloride by GC/MPI/TOF-MS.

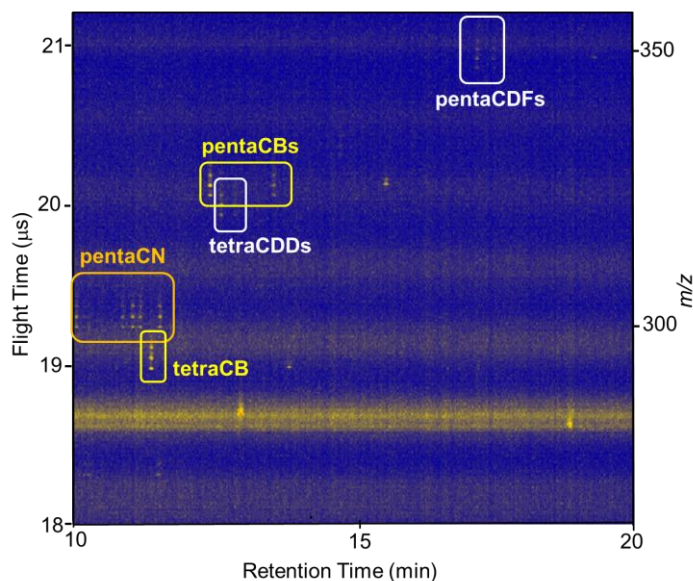


Figure 3. Two-dimensional display for extracts from a soil sample. The magnified two-dimensional data from figure 2.

number of samples in broad area such as the Great East Japan Earthquake, for screening not only dioxins but also other environmental pollutants, such as polycyclic aromatic hydrocarbons and polychloronaphthalenes.

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