Pyrolysis-Gas Chromatography/Multiphoton Ionization/Time-of-Flight Mass Spectrometry for the Rapid and Selective Analysis of Polycyclic Aromatic Hydrocarbons in Aerosol Particulate Matter

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Gas chromatography/multiphoton ionization/time-of-flight mass spectrometry (GC/MPI/TOFMS) coupled with a Curie-point pyrolyzer as a sample introduction technique was applied for the rapid and selective analysis of the polycyclic aromatic hydrocarbons (PAHs) that are a part of aerosol particulate matter. Increasing the operating temperature of the pyrolyzer also increased the number of observed peaks, but the peak areas of a few PAHs decreased due to thermal decomposition. In the present study, more than 100 peaks were confirmed using 0.3 mg of an aerosol particulate matter, and further sensitive detection would be achievable. The advantages of MPI/TOFMS, such as optical selectivity and simultaneous determination properties, allowed the trace analysis of highly complicated particulate matter—even in the absence of pretreatment. Therefore, this method would help elucidate the origin of particulate matter when sampling from different points for short periods of time.

Keywords Suspended particulate matter, polycyclic aromatic hydrocarbons, pyrolyzer, gas chromatography, multiphoton ionization, time-of-flight mass spectrometry

(Received April 12, 2014; Accepted July 11, 2014; Published September 10, 2014)
(ACE), 4. fluorene (FLU), 5. phenanthrene (PHE), 6. anthracene (ANT), 7. fluoranthene (FLT), 8. pyrene (PYR), 9. benzo[a]anthracene (BaA), 10. chrysene (CHR), 11 benzo[g,h,i]fluoranthene (BbF), 12. benzo[k]fluoranthene (BkF), 13. benzo[a]pyrene (BaP), 14. indeno[1,2,3-cd]pyrene (IND), 15. dibenzo[a,h]anthracene (DBA), and 16. benzo[g,h,i]perylene (BPY)), was accumulated using a digitizer (AP240, 1 GHz, 1 GS/s, Acqiris/Agilent Technologies).

The data were processed using a homemade program written in LabVIEW (National Instruments). In the present study, a second-order Butterworth lowpass filter with a cutoff frequency of 0.1 was applied. The limits of detection (LOD) for the 16 PAHs, as obtained by conventional GC/MPI/TOFMS introduced by an autosampler, are listed in Table S1 (Supporting Information). The values were approximately two orders of magnitude worse than those in our previous report, which was due to the difference in the repetition rate of an ionization laser (1 kHz in Ref. 26), and to the insufficient optimization of the analytical instrument in the present study.

Results and Discussion

Py-GC/MPI/TOFMS

Two-dimensional displays of the data for an aerosol particulate matter were measured by Py-GC/MPI/TOFMS and are shown in Figs. 2(a) - 2(d). For comparison, a display of the extracts introduced by an autosampler is shown in Fig. 2(e). Expanded views of Figs. 2(d) and 2(e) are shown in Figs. S1 and S2 (Supporting Information).

As shown in Fig. 2, the number of observed peaks was increased with an increase in the operating temperature of a pyrolyzer; more than 100 peaks were found at an operating temperature of 590°C. Several nitrogen-containing compounds have not been confirmed in the isotope peak pattern. In the present study, compounds with higher masses have been measurable at higher temperatures—BPY can be found at a temperature of 445°C or higher. This tendency is reasonable from the point of view of a boiling point, and, therefore, the operating temperature of a pyrolyzer should be increased when PAHs containing a
larger number of aromatic rings must be detected. Table 1 shows the signal-to-noise ratio (S/N) for 16 PAHs in aerosol particulate matter at an operating temperature of 500°C. The minimum amount of the particulate matter that can be detected for each PAH is also shown in the table, providing an S/N of 3, when the mentioned amount of an aerosol particulate matter is used.

| Compound | m/z   | S/N  | Minimum amount/μg |
|----------|-------|------|--------------------|
| NAP      | 128   | 140  | 6.4                |
| ACY      | 152   | n.d. |                    |
| ACE      | 154   | 6.8  | 130                |
| FLU      | 166   | 120  | 7.5                |
| PHE      | 178   | 240  | 3.8                |
| ANT      | 178   | 4.8  | 190                |
| FLT      | 202   | 6.1  | 150                |
| PYR      | 202   | 120  | 7.5                |
| BaA      | 228   | 14   | 64                 |
| CHR      | 228   | 36   | 25                 |
| BbF      | 252   | 7.9  | 110                |
| BkF      | 256   | 6.6  | 140                |
| BaP      | 252   | 3.0  | 300                |
| IND      | 276   | n.d. |                    |
| DBA      | 278   | n.d. |                    |
| BPY      | 276   | 3.6  | 250                |

a. Average of two measurements.
b. The minimum amount means that the peak for each PAH can be detected, providing an S/N of 3, when the mentioned amount of an aerosol particulate matter is used.

In the present study, the pyrolyzer was immediately removed from the GC after 5 s of heating, which allowed no sample introduction for an extended period of time. The peaks from a few compounds with lower masses were substantially broadened with regard to retention time. For example, a peak at m/z = 92 (the candidate was toluene), which is denoted as A in Fig. 2, was observed for approximately 80 s at a temperature of 445°C or higher. A conceivable reason could be the progression of thermal decomposition after the introduction of the gas sample into the GC at higher temperatures, even when the temperature of the injection port was maintained at 300°C. In future studies, by confirming the difference between the peak areas and the shapes of such compounds as toluene, which exist as SPM or is generated from thermal decomposition, such peaks might be used as an index of thermal decomposition.

In at least one report, ambient urban aerosol samples (PM$_{2.5}$) were measured by thermal desorption/pyrolysis coupled with laser ionization/TOFMS, where the wavelength of a laser was 118 or 275 nm. In that report, the holding time for the desorption/pyrolysis was more than 500 s at temperatures of 120, 250, and 340°C, and volatile compounds such as phenol (m/z = 94) and indole (m/z = 117) were predominately observed at higher temperatures. In the present study, the peaks of the corresponding m/z (denoted as B and C in Fig. 2) were also prominent, where the lowest operating temperature was 386°C, and the holding time was 5 s. A preliminary experiment was not performed at lower temperatures, because lower operating temperatures are considered to be impractical due to a lack of sensitivity in the present system. Fushimi et al. has also used a furnace-type pyrolyzer. In the Fushimi report, the optimal thermal desorption conditions involved a ramped desorption from 50 to 450°C at 50°C/min, then holding for 2 min. In the present study, many compounds were clearly detectable at a holding time of 5 s. The observed retention times were almost identical to those obtained by measuring a PAH mixture solution introduced by an autosampler, and, therefore, the data obtained by the present system were easy to compare with that obtained by a conventional GC-MS using an autosampler.

Comparison between a Py-GC/MPI/TOFMS and a conventional GC/MPI/TOFMS

As a control experiment, extracts from aerosol particulate matter were measured using a conventional GC/MPI/TOFMS, as shown in Fig. 2(e) via two-dimensional display. As the figure shows, more than 20 peaks were confirmed. The number of peaks detected was fewer compared with that detected using the present system. Further improvement in sensitivity is achievable, Fushimi report, the optimal thermal desorption conditions involved a ramped desorption from 50 to 450°C at 50°C/min, then holding for 2 min. In the present study, many compounds were clearly detectable at a holding time of 5 s. The observed retention times were almost identical to those obtained by measuring a PAH mixture solution introduced by an autosampler, and, therefore, the data obtained by the present system were easy to compare with that obtained by a conventional GC-MS using an autosampler.
Py-GC/MPI/TOFMS, as shown in Figs. 2(a) – 2(d). The sample amount for one injection was calculated at 0.05 mg-SPM (≈ 100 mg x 1 μL/2000 μL), which was lower than that for Py-GC/MPI/TOFMS (0.3 mg). Conventional GC/MPI/TOFMS might be preferable for quantitative analysis, because the effect of thermal decomposition is not a consideration, as shown in Fig. S3 (Supporting Information), and the peaks observed for a higher mass were relatively strengthened compared with those obtained using a pyrolyzer. However, dilution and pretreatment should be normally performed, and not all the extracted solution could be introduced in one injection. On the other hand, Py-GC/MPI/TOFMS has the merit for detection using a small amount of SPM since all samples can be used in one injection without pretreatment. Unfortunately, the recovery of PAHs in SPM by Py-GC/MPI/TOFMS was not measured in the present study. Fushimi et al. has reported the recovery of PAHs determined using a thermal desorption GC/MS whereby recovery from the nanoparticles in diesel exhaust and the atmosphere decreased with an increase in the amount of the sample.\(^5\) In future studies, the relationship between the recovery and the amount of the sample should be measured using Py-GC/MPI/TOFMS.

**Advantages**

Py-GC/MPI/TOFMS offers several advantages when measuring SPM samples. As mentioned, the sensitivity of the present system was about 2 orders of magnitude lower than our previous report. That is to say, a sensitivity improvement of 2 orders of magnitude is available compared with the present experimental condition. Therefore, similar results shown in the present study, i.e., two-dimensional data indicating more than 100 peaks, are achievable using 3-μg of the sample, rather than the 0.3 mg used in the present study. An ionization laser that can be operated at several tens of kHz is now available,\(^9\) and, therefore, a small amount of sample is sufficient for the selective and sensitive detection of PAHs in SPM. Other work on the development of an ionization source and better sample introduction methods have been reported to improve the sensitivity of analysis.\(^{40,41}\) Py-GC/MPI/TOFMS offers the ability to detect the PAHs in SPM in a short period of time for collection, which is useful for establishing the time course of a peak pattern of PAHs at each sampling point, allowing elucidation of the origin of the sample.

Moreover, all data shown in the present study were obtained without pretreatment. Complicated peak patterns due to unknown contaminants have an adverse influence on the identification of each compound in a real environmental sample. However, the properties of spectroscopic selectivity and soft ionization make laser ionization well suited to the direct measurement of PAHs in an aerosol particulate matter. The number of peaks increased with increases in the temperature of the pyrolyzer. Many strong peaks could be obtained even using a small amount of SPM, which is preferable when measuring a real sample collected over a short period of time. In future studies, we will apply this system to gain rapid, sensitive and selective measurement of SPM, or even of an SPM-collected filter, which are sampled from different points/times, in order to elucidate the origin of each SPM based on the analysis of peak patterns and their kinetics.

**Conclusions**

In the present study, Py-GC/MPI/TOFMS was applied to the direct measurement of PAHs in an aerosol particulate matter. This research was supported by a Grant-in-Aid for Scientific Research from the Japan Society for the Promotion of Science (JSPS). We are indebted to M. Yoshikawa and A. Fukushima of the Fukui Prefectural Institute of Public Health and Environmental Science for their valuable advice during this study. We also express our gratitude to the Japan Analytical Industry for providing us with the opportunity to use a Curie-point injector.

**Supporting Information**

The LOD of the 16 PAHs as obtained by conventional GC/MPI/TOFMS introduced by an autosampler, expanded views of Figs. 2(d) and 2(e), peak areas of 16 PAHs in SPM obtained using Py-GC/MPI/TOFMS and from extracts measured via GC/MPI/TOFMS. This material is available free of charge on the Web at http://www.jsac.or.jp/analsci/.

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