



AccuTOF-GCv Series

Analyzing Polycyclic Aromatic Hydrocarbons in Diesel Particulate Matter using GCxGC-HRTOFMS

Introduction

Polycyclic aromatic hydrocarbons (PAHs) refer to aromatic hydrocarbons that have at least 2 benzene rings, such as naphthalene and anthracene which feature 2 and 3 benzene rings, respectively. PAHs are found in crude oil and are often released into the environment (water, atmosphere, etc.) when crude oil and oil products such as heating oil and light gas oil are burned. As it turns out most PAHs are carcinogenic with some of them identified as highly carcinogenic. Therefore, it is critical to determine the levels of PAHs present in the environment. In this work, we analyzed PAHs in diesel particulate matter using GCxGC-HRTOFMS, a technique that combines a JMS-T100GCV with comprehensive 2DGC (GCxGC).

Experimental

A commercial sample (2975 Diesel Particulate Matter, NIST) was mixed with chloroform (weight ratio 1:10) and heated at 100°C for 5 hours to accomplish solvent extraction. The extract was then centrifugally separated from the particulate material, and the resulting supernatant liquid was concentrated for measurement. Table 1 shows the instrument measurement conditions used for the analysis.

| | |
|------------------------|--|
| Instrument | JMS-T100GCV (JEOL Ltd.) KT2004 (Zoex Corporation) |
| Injection mode | Split 20:1 |
| Injection temp. | 300°C |
| Oven temp. program | 50°C (1min) → 5°C/min → 280°C (13min) |
| Injection volume | 0.2µL |
| Column | 1st: DB-1ms, 30m × 0.25mm, 0.25µm 2nd: DB-17, 2m × 0.1mm, 0.1µm |
| Carrier gas | He, 2.0 mL/min, Constant flow |
| Modulation | Perbd: 6sec, Releasing: 0.3sec |
| Ionization mode | EF, 70eV, 300µA |
| Ion source temp. | 280°C |
| m/z range | m/z 29–800 |
| Data acquisition speed | 0.04 sec (25 Hz) |

Table 1. GCxGCHRTOF-MS measurement conditions

Results and Discussion

Figure 1 shows the GCxGC TIC chromatogram acquired from the sample. The X axis represents analyte separation by the 1st column, DB-1ms, in which the components

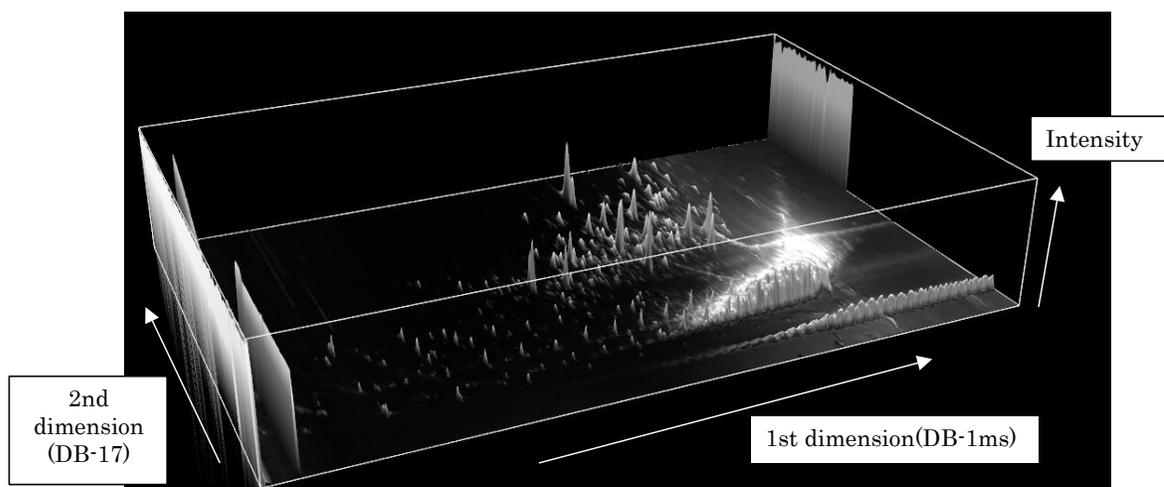
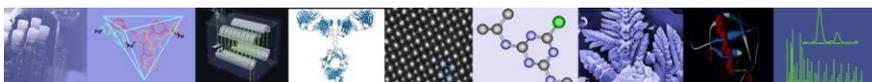


Figure 1. GCxGC TIC chromatogram (3D)



were separated according to their boiling points. The Y axis represents the separation in the 2nd column, DB-17, in which the components were separated according to their polarities. The Z axis represents the peak intensity of the ions in the TIC. Although the sample preparation consisted of a simple solvent extraction of the commercial sample, a wide variety of components were observed in the TIC (Figure 1).

Next, several mass chromatograms for $C_{18}H_{12}$, which contains 4 fused benzene rings, were compared to examine the selective detection of PAHs. The wide m/z window GCxGC mass chromatogram in Figure 2 (a) shows a number of impurities in addition to the PAHs.

However, in the narrow m/z window GCxGC mass chromatogram in Figure 2 (b), only the PAHs were selectively detected. Figure 3 shows the mass spectrum for the PAHs detected in Figure 2. The mass spectrum shows that $C_{18}H_{12}$ (m/z 228.0930), a molecular ion of PAHs, was detected with high mass accuracy (0.3 mDa).

Conclusions

The results show that the GCxGC/HRTOFMS enhances the resolution of the GCxGC and the selectivity of HRTOFMS. Furthermore, combining these techniques is a powerful tool for analyzing complex samples that consist of many components and impurities.

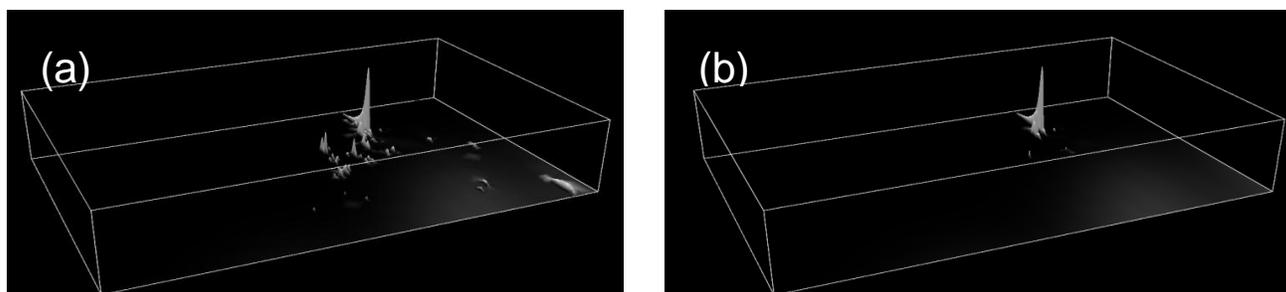


Figure 2. GCxGC chromatograms (3D)
(a) m/z 228 \pm 0.5 (b) 228.0930 \pm 0.01

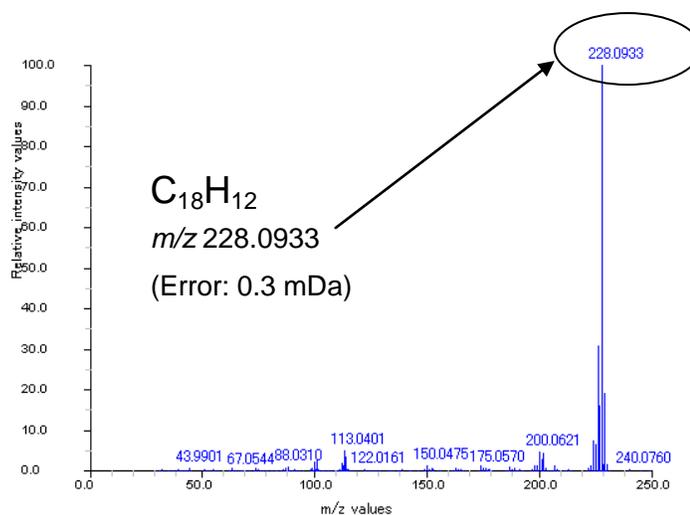


Figure 3. EI mass spectrum for $C_{18}H_{12}$ in Figure 2 (a) and (b)