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Measurement of Gas- and Particle-phase Organic Species in Diesel Exhaust Using Vacuum Ultraviolet Single Photon Ionization Time-of-flight Mass Spectrometry

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Organic compounds present in diesel exhaust were measured using vacuum ultraviolet single photon ionization time-of-flight mass spectrometry while heating the inlet line at high and low temperatures. Increases in signal intensities were observed when the inlet was heated at 623 K because of enhanced volatilization of the organic fraction emitted in the particle phase.

Diesel exhaust particles (DEPs) are major contributors to suspended particulate matter (SPM). SPM is known to have adverse environmental and human health effects in urban environments.[1] In Japanese megacities, SPM pollution occurs frequently, resulting in prolonged periods of SPM concentrations that exceed the ambient air quality standards in Japan.[1] DEPs mainly consist of highly agglomerated, solid carbonaceous material and ash, along with volatile organic and sulfur compounds. Kittelson indicated that several types of particles were possible; including solid carbonaceous particles with adsorbed hydrocarbon/sulfate layers, sulfuric acid particles, and hydrocarbon/sulfate particles.[2] The volatile organic fractions (VOFs) and soluble organic fractions (SOFs) consist of species adsorbed to carbonaceous particles.[3] Unburned fuel and lubricant oil escaping oxidation are the main contributors to the VOFs and SOFs.

To better understand the organic fraction composition, numerous studies have been performed using filter-based sampling and gas chromatography/mass spectrometry (GC/MS) to identify and quantify emissions from specific sources.[4,5] Although GC/MS, after solvent extraction, is a powerful method for the identification of organic compounds in particles, filter sampling can be very time consuming.

To overcome the disadvantages of filter sampling, online aerosol mass spectrometers have been developed for the characterization of ambient aerosols.[6–10] In aerosol mass spectrometry, airborne particles are vaporized and ionized, with the ions produced analyzed using a mass spectrometer. Widely used aerosol mass spectrometers can be categorized on the basis of their vaporization technique.[6] The first category is laser desorption[7,8] and the second is thermal desorption.[9,10] Both vaporization techniques require high energy to convert particles to gases. The high energies cause organic species to be fragmented during the vaporization and ionization processes.

Ionization technique is an important parameter in a mass spectrometer. To avoid fragmentation of organic compounds, a soft ionization method must be used to encourage the identification and quantification of individual species. A single photon ionization time-of-flight mass spectrometer (SPI-TOFMS) using 118 nm vacuum ultraviolet (VUV) light has been widely used for the detection of volatile organic compounds.[11–14]

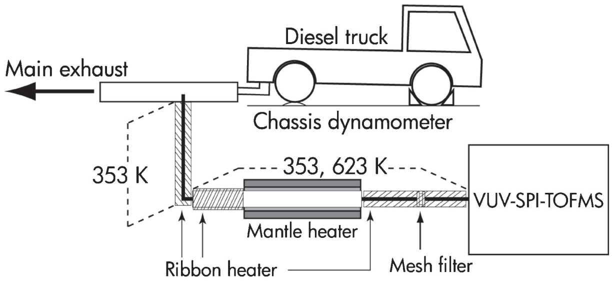

Figure 1. Schematic diagram of the diesel exhaust measurement experimental setup.

Focusing on the volatile organics of DEPs, we developed an online mass spectrometer with a heated inlet line, where low volatility compounds were vaporized, mixed with the gaseous fraction, and delivered to the mass spectrometer. In this letter, we report the application of VUV-SPI-TOFMS to DEPs and the characterization of organic compounds present in diesel exhaust. Additionally, the volatile and semi-volatile organic fractions (VOF and SVOF) of DEPs were estimated by comparing the mass spectra of specific compounds when the inlet line was heated at 623 and 353 K.

A schematic diagram of the experimental setup is presented in Figure 1. The exhaust from a diesel truck was directly introduced into the heated inlet through a 2 m long tube. The heated inlet was a 45 cm long, 9.4 mm inner diameter, stainless steel tube covered with a heating mantle (30 cm long) and a ribbon heater (15 cm long). Other tubes and a mesh filter were covered with a ribbon heater featuring thermocouples to control the temperature. The tube temperatures were kept higher than 353 K to prevent particles sticking to the wall. Particles ≥0.5 µm in diameter were trapped on a mesh filter made of a sintered element (SS-4FWS-05, Swagelok). Heating at 623 K was not only to prevent particle sticking but also to vaporize the VOF and part of the SVOF of DEPs. The inlet temperature was set at 623 K to ensure the stability of the inlet line temperature and to keep in accordance with the specifications of the heating apparatus.

A modified version (LICAMS-400, TOYAMA Co., Ltd.) of our homemade VUV-SPI-TOFMS[15] was used in this study. A detailed description of the VUV-SPI-TOFMS design was reported previously.[15] Briefly, the VUV-SPI-TOFMS consisted of a sample inlet system connected to a time-of-flight mass spectrometer. The mass spectrometer was operated as a reflectron-type TOFMS.[16] Single photon ionization by VUV light was used. A coherent VUV laser at 10.5 eV (118 nm), generated by frequency tripling of the third harmonic (355 nm)

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of a Nd:YAG laser, was chosen because of its high intensity, tight collimation, and ease of generation. The 355 and 118 nm beams were directed 5 mm apart from the center of the MgF_2 lens which disperses the different wavelengths and only 118 nm light was introduced into the ionization region. The ionization energy of 10.5 eV was not enough to ionize main atmospheric components like nitrogen, oxygen, carbon dioxide, and water. Since the ionization energies of many volatile organic compounds present in diesel exhaust are at or below 10 eV,[17,18] VUV light at 10.5 eV ionized most of the volatile organic compounds and minimized the possibility of producing fragment ions. A part of exhaust gases were introduced into the ionization region to maintain the ionization and time-of-flight chambers at low pressure. Our VUV-SPI-TOFMS achieved a detection limit of 11 ppbv for toluene at a signal to noise ratio of 2.[15]

A diesel vehicle, featuring an oxidation catalyst system, was used as the test vehicle. A 4.8 L engine, with a common rail injection system, was loaded and the vehicle was acceptable under the emission regulations of 2003 in Japan. The vehicle was driven on a chassis dynamometer according to the JE05 cycle (Japanese approval test cycle for heavy-duty vehicles).

The VUV light intensity was calibrated by using toluene signals from a standard sample generated via a standard gas generation system that included a diffusion tube (Permeater PD-1B-2, GASTEC). This calibration was performed before and after every exhaust measurement. The normalized signals were converted into concentration profiles using premixed standard gas. The standard gas was a mixture of 58 hydrocarbons with N_2 (TERRA gas PAMS 58, Takachiho Chemical Industrial).

Figure 2 presents the time series contour maps of the diesel exhaust mass spectra from the JE05 driving cycle for the range of m/z 50–150. The x axis presents the measurement time and the y axis presents the m/z. Figure 2a presents the results when the inlet was kept at a temperature of 353 K and Figure 2b presents the results obtained when both the tubes and the mesh filter were heated at 623 K. Signals at mass numbers indicating alkanes, alkenes, and dienes appear bright in Figure 2 (alkanes: $m/z = 14n + 2$, alkenes: $m/z = 14n$, dienes: $m/z = 14n - 2$ for $n = 4, 5, \ldots, 10$). With heating at 623 K, these signals were greater than those with heating at 353 K. Differences between the signals with the inlet temperatures at 623 and 353 K were more evident in the m/z range of 80–130. When the inlet was kept at 353 K, signals were only strong when the vehicle was idling. When the inlet was heated at 623 K, strong signals were also observed when the vehicle was fully running (the idle state is presented in Figure 3).

Figure 3 presents concentration time series of benzene, toluene, and styrene. Gray lines in the plots indicate the idle state in the JE05 cycle. Peaks in the signals of benzene were often observed in the idle state. Sharper signals in the idle state were observed when the inlet temperature was 353 K. On the other hand, broad time variations in the benzene signal at 623 K were observed from 6 min until the end of the measurement (Figure 3a). Differences in the signals between the different inlet temperatures were apparent, especially during the running time. High temperature heating at 623 K likely leads to an enhancement of vaporization of the organic species, especially benzene, in DEPs, resulting in increased baselines for low m/z species during the running time. To determine that the inlet line heating causes only the vaporization or both the vaporization and the pyrolysis, a more detailed study, such as operating at different inlet line temperatures and/or using glass lined tubes, is needed.

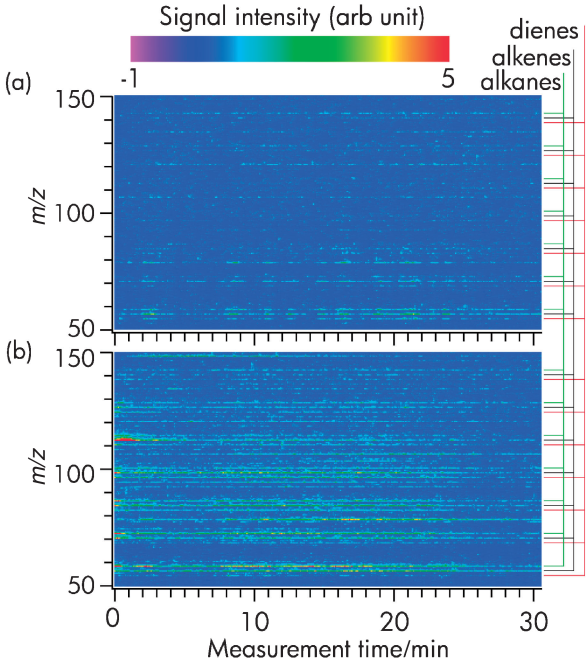

Figure 2. Contour maps of signals (a) with lower temperature heating and (b) with higher temperature heating (at 623 K) in the range of m/z 50–150. The mass numbers representing alkanes, alkenes, and dienes are pointed out.

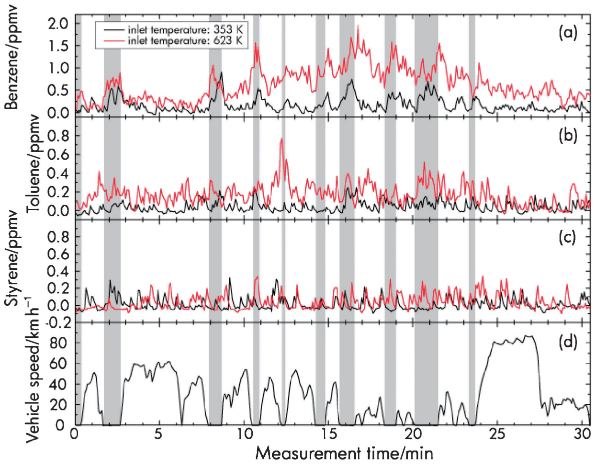

Figure 3. Time series of signals for (a) benzene ($m/z = 78$), (b) toluene ($m/z = 92$), and (c) styrene ($m/z = 104$) while (d) shows the vehicle speed.

We define the integrated signals for each m/z thoughout the JE05 cycle at an inlet temperature of 353 and 623 K as I_l and I_h, respectively. Figure 4 presents signal ratios, I_h/I_l, for an m/z range of 58 to 184 in intervals of 14 m/z to represent the alkanes (C_nH_{2n+2}, $4 \leq n \leq 13$). I_h indicates the sum of the gas-phase organics and vaporized particle-phase organics through additional heating. On the other hand, I_l indicates the gas-phase organics. If the additional heating was sufficient to completely vaporize any VOF of DEPs, the signal ratio for those

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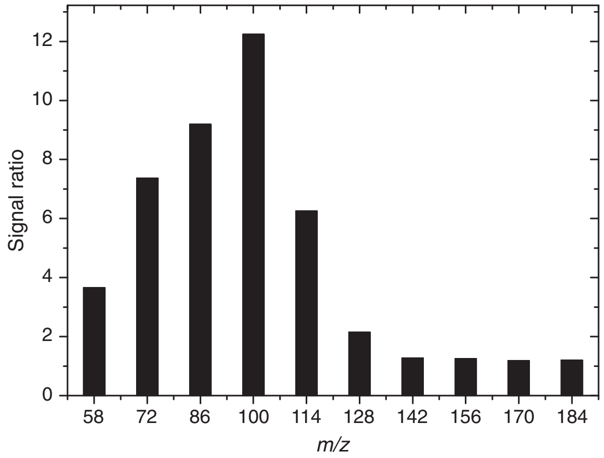

Figure 4. Ratio of signals obtained with heating to signals obtained without heating for an m/z range of 58–184. The intervals of 14 m/z represented alkanes from C4 to C13.

compounds would provide an indication of how much of that compound was in the particle phase. In Figure 4, the signal ratio at $m/z = 100$ (reflecting C_7H_{16} alkanes) was the highest, while the signal ratios at m/z higher than $m/z = 142$ (reflecting $C_{10}H_{22}$ alkanes) were almost unity. In a thermal desorption/pyrolysis study for urban particulate matter,[19] the pyrolytic processes of larger species start to take place around 613 K. In the present study, the inlet heating was done under an aerobic atmosphere with metallic inlet and filter surfaces, thus the signal ratio in the m/z range of 58–114 might be very large because of the pyrolysis of larger materials. The unity signal ratio at higher than $m/z = 142$ might be due to the sensitivity of this VUV-SPI-TOFMS and the concentration of these species in the gas phase. Based on current results, additional studies are needed to define the range of appropriate inlet line temperatures and to determine the correlation between these temperatures and signal intensity. The results presented here, however, satisfactorily show the effectiveness of the heating process on improving real time observations of particle-phase organics.

In summary, we have established a new technique to identify volatile organic species in DEPs using a heated inlet line attached to a VUV-SPI-TOFMS. Signals assigned to gas-phase organic compounds including alkanes, alkenes, dienes, and aromatics at low m/z were increased because of the enhancement of the volatilization of particle-phase organic compounds by high temperature heating. Taking advantage of the heating system, which can be set between the exhaust manifold and the analyzer, we demonstrated the real-time measurement of the VOF of DEPs. The system can vary the inlet temperature and be used for online analysis, making it possible to study the organic fraction composition of DEPs under different engine operating conditions.

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