

Application of REMPI-TOFMS technique to molecular-selective and real-time analysis of atmospheric VOCs

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Volatile organic compounds (VOCs) play important roles as precursors of secondary products of photochemical reactions (eg. ozone, aerosols). To clarify photochemical processes in the atmosphere, it is essential to capture the detailed characteristics of emissions of VOCs from the sources. VOCs emitted from anthropogenic sources can vary rapidly and exhaust gases are usually the mixtures of traces of various VOCs. Sensitivity, molecular-selectivity, and real-time response are simultaneously required for analyzing VOCs at the sources. In this study, the resonant enhanced multiphoton ionization / mass spectroscopy (REMPI/MS) was examined for analyzing VOCs in real exhaust gases. For example, benzene and its derivatives in the exhaust gas were explored. Especially, differences of atmospheric reactivity of VOC isomers were focused. As a result of calibration, the typical limit of detection (LOD) was acquired as 1 ppbv for benzene ($S/N = 3$, 1 sec). Next, exhaust gas of a motorbike was analyzed. Rapid variations of VOC concentrations in the exhaust gases were successfully observed on the second time scale. Concentrations of VOCs varied in response to the operation of the motorbike. As for molecular-selectivity, xylene isomers ($m/z = 106$) were individually monitored by adopting their specific wavelengths of the excitation laser: 268.0 nm (o-xylene), 270.6 nm (m-xylene), 272.2 nm (p-xylene). As a result of analyzing xylenes in the exhaust gas, it was found that the contribution of m-xylene to ozone production was largest among xylene isomers. In addition, simultaneous measurements of multiple VOCs by the REMPI-MS were also examined. Emission properties of VOCs were investigated by correlation analyses. It was suggested that VOCs in the exhaust gas could be categorized into two groups: (a) compounds originating from vaporization of unburned fuels and/or oils (eg. benzene, toluene, xylenes); (b) compounds emitted as combustion products (eg. phenol, biphenyl). It was presented that the REMPI-MS technique is useful to study VOC emission. As a next step, these results on VOCs emission can be combined with photochemical processes in the atmosphere in order to clarify how significant the contributions of these VOCs are.