Measurements of fast varying emission factors of atmospheric pollutants

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http://www.comp.tmu.ac.jp/jm-strategy/index-j.html

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 placed at the center of 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 with OH and NO3 radicals were focused. As a result, fast varying emission factors of aromatic hydrocarbons (benzene, toluene, o-, m-, p-xylenes, phenol, and o-, m-, p-cresols) were successfully captured with the temporal intervals of 1-s for an idling motorcycle, a mode-driving diesel automobile on a chassis-dynamometer, a metal plate just after painted, and environmental tobacco smoke. As a whole, high correlations were observed among 1-s data of highly-volatile compounds (benzene, toluene, xylenes) but the variation of phenol was quite different. It was suggested that the variations of VOCs were dominated by different processes among these groups: for example, VOC formation during combustion, and VOC evaporation from the fuels or paint solvent, and vaporization of VOC adsorbed on the surface of catalyst only when the gas temperature was sufficiently high. It was experimentally found that emission factors of highly volatile VOCs as benzene and toluene were significant just after painted. Fast-response analyzers like REMPI-MS are promising to capture such fast and short-term phenomena. Impacts of emission sources on the atmospheric chemistry are to be reported in view of OH and NO3 radical reactivity, and ozone formation potential, as follows: (1) In exhaust gases from an idling motorcycle and a driving diesel truck, toluene and m-xylene were the most critical for OH reactivity and ozone formation. For NO3 reactivity, phenol was dominant; (2) In exhaust gas from a diesel vehicle, phenol emitted during high-speed driving (60km/h and more) was quite significant for all of OH reactivity, ozone formation, and NO3 reactivity; (3) Benzene and toluene were critical just after painting. Meanwhile, importance of xylenes and phenol became greater with the painted liquid getting dryer.

This study was conducted with grateful cooperation of Tokyo Institute of Technology for their REMPI-MS instrument and National Traffic Safety and Environment Laboratory for their chassis-dynamometer.