

Development of new proton-transfer-reaction ionization sources for soft and selective ionization

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It is well known that volatile organic compounds (VOCs) are emitted from a variety of sources into the atmosphere, and play important roles in controlling air quality by acting as a fuel for gas-phase photochemistry, leading to the formation of ozone and secondary aerosols. However, there exist hundreds of VOCs, in particular, around urban area where VOC emissions from human and industrial activities are diverse and strong. It is also widely known that overwhelming amounts of VOCs are emitted from the biosphere including land ecosystems and the ocean into the atmosphere. Majorities of biogenically emitted VOCs are short-lived due to their high reactivity. For both anthropogenic and biogenic VOCs, unsaturated (alkene, diene), oxygenated (aldehyde, ketone, alcohol), and aromatic hydrocarbons are recently highlighted in several field studies. Owing to a variety of speciation and high reactivity, understanding of the behavior and the roles of these VOCs in the atmosphere is still limited by quantity and quality of the measurements, and requires advancement in measurement technologies.

Proton transfer reaction-mass spectrometry (PTR-MS) is a newly developed on-line method, having possibility to be complementary to the conventional GC technique. The PTR ionization is one of chemical ionization, which enables soft ionization of chemical species that have a proton affinity higher than that of the reagent species (i.e., water in many cases). The PTR from hydronium ions (H_3O^+) occur with many VOCs except low-molecular weight nonmethane hydrocarbons, and it produces predominantly protonated ions. However, fragment ions are sometimes observed. The PTR-MS technique provides only information on the mass-to-charge ratio, m/z , of ions. This sometimes complicates the assignment of the ion signals, and requires a careful identification of the chemical species involved. The fragmentation is caused mainly by the large kinetic energies for the protonation reactions, and in some cases by large excess energies of the protonation reactions. PTR-MS instruments are typically operated at field strength, E/N , of the ion drift tube of between 120 and 140 Td in order to minimize $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$ clusters.

In the present work, two types of ion sources based on hollow-cathode discharge were newly developed for soft and selective ionization of volatile organic compounds (VOCs) to couple with a proton transfer reaction time-of-flight mass spectrometer (PTR-TOFMS).

A discharge-based PTR ion source was operated using a mixture of H_2O and rare gases such as He, Ne, Ar, and Kr. In contrast to an H_2O -only discharge, which usually functions above a field strength (E/N) of 100 Td for a given drift tube, an H_2O -rare gas based discharge was successfully operated at the E/N value of only 40 Td. The intensity of H_3O^+ ions generated in the H_2O -rare gas discharge was comparable to that in the H_2O -only discharge. Although the detection sensitivities were decreased for isoprene, benzene, toluene, and *p*-xylene, they were improved for acetone and acetaldehyde. This is partly because of the extended PTR time at lower E/N values. Fragmentation in the drift tube was significantly suppressed for fragile species such as methyl nitrate.

Feasibility of a two-stage PTR ionization source was also examined to generate different reagent ions for a selective detection of VOCs. Reagent ions were selectively produced at the first stage by the PTR of H_3O^+ with a designated VOC. The second PTR ionization occurs only for VOCs in a sample, which have larger PAs than that of reagent VOC. Acetone and acetonitrile were found to be useful for the reagent VOCs since strong and approximately single peak of protonated molecule was obtained. We demonstrated the identification of isobaric VOCs such as ethyl acetate and 1,4-dioxane (mass 88) by using signals of protonated ions at m/z 89.