Direct Sampling Mass Spectrometry in Atmospheric Chemistry

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Global emissions of biogenic volatile organic compounds (BVOC) are estimated at 1150 Tg/yr. These biogenic hydrocarbons play a significant role in tropospheric ozone production and chemistry. The reactivity of these compounds is dominated by OH radical oxidation, with lifetimes often on the order of hours to minutes. Current methods of analysis are quite often lengthy, tedious, and usually exceed the time scale of the chemistry; thus, important information may be lost. Fast-response detection methods are highly desirable in cases where relatively short-lived species are to be examined, e.g., isoprene. Mass spectrometry is a leading candidate to become a standard instrument in real-time atmospheric analysis.

Canister sampling followed by GC/MS analysis in the laboratory is a common sampling technique among atmospheric scientists. There are inherent issues with remote sampling, among these are: analyte wall loss, reactions in the canisters, long times before data availability, and the inability to analyze data at the field site. In the last 10 years there has been a concerted effort in the atmospheric chemistry community to development on-line sampling and detection methods. The on-line systems alleviate the issues of canister sampling and provide approximately real-time data. Unlike remote sampling this provides the flexibility to alter the scientific plan during the course of the field study.

In the Shepson group we have designed and built transportable auto-samplers fitted to GC/MS instruments that were deployed in remote forested sites as well as lab sites near the North Pole. In this paper we will review progress in this area, focusing on methods based on the use of Tenax® absorbant trap for GC/MS, cryo-focusing for QIT/GC, and gas phase membrane introduction mass spectrometry (MIMS) sampling coupled with selective CI MS/MS methods, as well as ideas for the future.