



Using collision-induced dissociation techniques to constrain sensitivities of ammonia chemical ionization mass spectrometry ($NH_4^+ - CIMS$) to oxygenated organic compounds in the gas and particle phases

Frank Keutsch (1,2,3), Alexander Zaytsev (1), Martin Breitenlechner (1), Abigail Koss (4), Christopher Lim (4), James Rowe (4), and Jesse Kroll (4)

(1) School of Engineering and Applied Sciences, Harvard University, Cambridge, United States, (2) Department of Chemistry & Chemical Biology, Harvard University, Cambridge, United States, (3) Department of Earth and Planetary Sciences, Harvard University, Cambridge, United States, (4) Department of Civil and Environmental Engineering, Massachusetts Institute of Technology, Cambridge, United States

Chemical ionization mass spectrometry (CIMS) has become an important analytical tool for measurements of organic molecules in the atmosphere. A variety of reagent ions can be used to detect different classes of volatile organic compounds (VOCs) and to analyze submicrometer particulate organic matter. However, detection efficiency and sensitivity of CIMS instruments depend critically on both the reagent ion and the measured sample molecule.

We have developed a new CIMS instrument that is equipped with three similar corona discharge ion sources and currently can be operated in two different modes: (1) ligand switching reactions from adduct ions $NH_4^+ \bullet (H_2O)_n$, ($n = 0, 1, 2$) ($NH_4^+ - CIMS$) and (2) proton transfer reactions with $H_3O^+ \bullet (H_2O)_n$, ($n = 0, 1$) ions ($PTR - MS$). We present a mass spectrometric voltage scanning procedure which is based on collision-induced dissociation that allows for the determination of the stability of detected ammonium-organic clusters. We observe a strong correlation of the binding energy of these clusters and the measured sensitivities for calibrated compounds, and thus we show a method to effectively constrain the sensitivity of the ammonia chemical ionization mass-spectrometer to a vast array of detected oxidized volatile organic compounds for which no calibration standards exist in a matter of minutes. We demonstrate the application of this procedure by quantifying the composition of gas-phase oxidation products and secondary organic aerosols formed in multiple generations of photooxidation of various precursors (1,2,4-trimethylbenzene, alpha-pinene, 3-methylcatechol) in a series of laboratory experiments.