

# Detection of Inorganic and Organic (RO<sub>2</sub>) Radicals with the Vocus Aim CI-TOF

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Volatile organic compounds (VOCs) can be rapidly oxidized in the atmosphere to form a suite of oxidized VOCs (OVOCs) comprising a broad range of chemical formulas and structures. Of specific interest to climate are OVOCs exhibiting low and/or extremely low vapor pressures, which play a key role in the formation of atmospheric aerosols by either condensing onto pre-existing aerosol particles or by forming new particles. A critical starting point in the formation and growth of particles is the generation of highly oxygenated organic molecules (HOMs) through autoxidation. The initiation step for rapid oxygen addition is the formation of peroxy (RO<sub>2</sub>) radicals, formed via the initial oxidation of a VOC. Intramolecular hydrogen shift reactions yields increasingly oxygenated RO<sub>2</sub> radicals leading to a variety of closed shell products depending on the fate of the RO<sub>2</sub> radicals. Radical chemistry not only controls the formation of OVOCs and ultimately the formation of new particles, but also impacts the production of secondary pollutants such as O<sub>3</sub> and NO<sub>2</sub>.

Providing an accurate concentration of radical species, formed from the oxidation of organic and inorganic species, remains analytically extremely challenging due to the high reactivity and trace concentrations of relevant radical species.

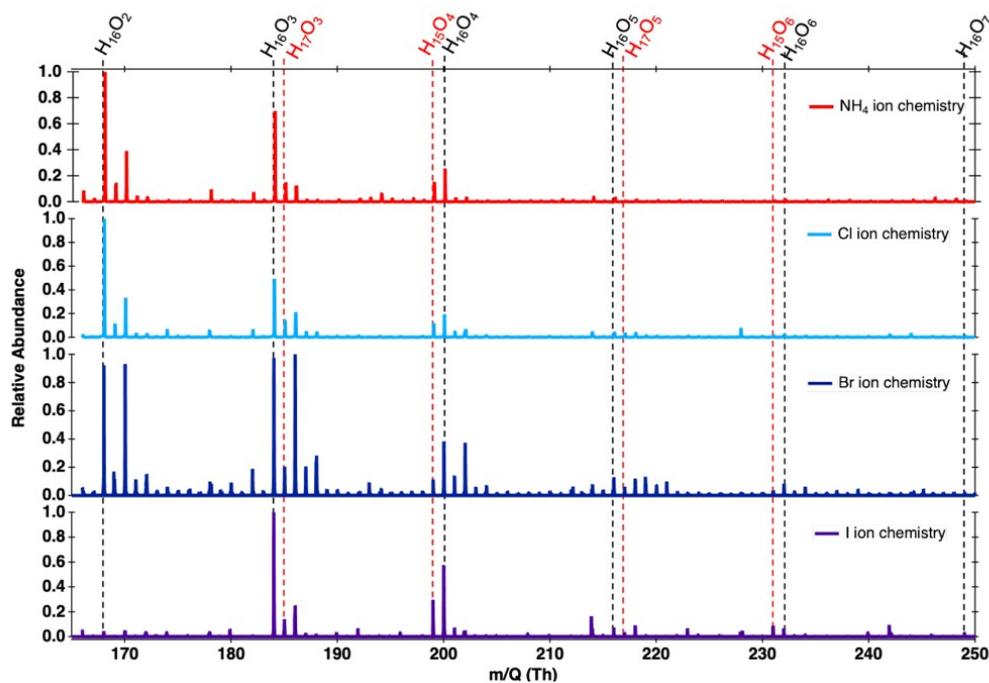
## Chemical Ionization as an Ideal Radical Detector

Chemical ionization mass spectrometry (CI-MS) is the most promising approach to detect trace radical species, due to its high sensitivity, selectivity, and ability to measure many species simultaneously. TOFWERK's Vocus Aim Reactor provides fragmentation-free chemical ionization and detection using field-free adduct-based chemical ionization and provides detection limits in the pptv-ppqv range. In addition, the geometry of the Aim Reactor is optimized for fast time response by minimizing the interaction between the reactor walls and the analytes. Here, we explore the suitability of the Vocus CI-TOF with an Aim Reactor (Vocus Aim CI-TOF) operated with a variety of reagent ion

chemistries of both positive and negative polarities for the detection of both organic and inorganic radicals. The flexibility of the Vocus Aim Reactor and its supported ion chemistries offer a unique platform to measure a suite of both inorganic and organic closed shell and radical species with a single instrument. The reagent ions used were ammonium ( $\text{NH}_4^+$ ), chlorine ( $\text{Cl}^-$ ), bromide ( $\text{Br}^-$ ), and iodide ( $\text{I}^-$ ). Radicals as well as closed-shell products were detected as adducts with the respective reagent ions with negligible fragmentation.

### Organic and Inorganic Radical Detection

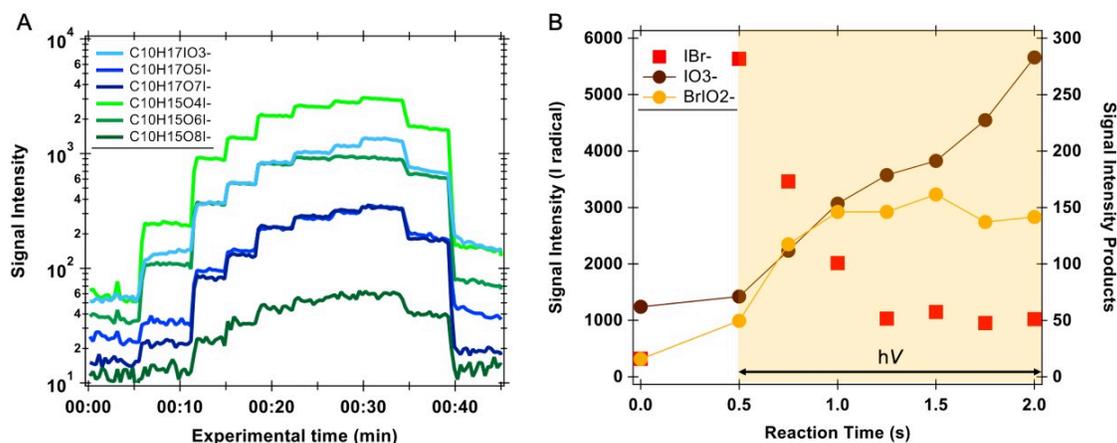
Experiments were performed in a flow reactor, designed to measure organic (i.e.,  $\text{RO}_2$ ) and inorganic radicals. Ozonolysis and OH radical-initiated oxidation of  $\alpha$ -pinene ( $\text{C}_{10}\text{H}_{16}$ ) or photolysis of iodine ( $\text{I}_2$ ) were performed under dry conditions at room temperature and atmospheric pressure. It is important to note that the reaction time was extremely short (0–2 seconds). As the result, the amount of reacted  $\alpha$ -pinene and  $\text{I}_2$  was very low, explaining the relatively low abundance of radicals and associated oxidation products



**Figure 1.** Mass spectra of closed-shell products and peroxy radicals formed from the combined ozonolysis and OH radical reaction of  $\alpha$ -pinene measured with the Vocus Aim CI-TOF. Ammonium ( $\text{NH}_4^+$ ), chlorine ( $\text{Cl}^-$ ), bromide ( $\text{Br}^-$ ), and iodide ( $\text{I}^-$ ) served as reagent ions. Selectivity of the reagent ions is organized from least selective (top) to most selective (bottom).

To highlight a key feature of the Vocus Aim CI-TOF, we focused our attention on the analysis of products from the ozonolysis of  $\alpha$ -pinene with different reagent ions. OVOCs and peroxy radicals were detected as clusters with  $\text{NH}_4^+$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$  ions as shown in Figure 1.  $\text{RO}_2$  radicals formed from  $\alpha$ -pinene ozonolysis/OH radical-initiated oxidation, including  $\text{C}_{10}\text{H}_{15}\text{O}_{4,6,8}$  and  $\text{C}_{10}\text{H}_{17}\text{O}_{3,5,7}$  were detected with all reagent ions employed. While the mass spectra are generally similar between the different reagent ion chemistries, iodide ions are by far the most selective of the reagent ions we tested, while  $\text{Cl}^-$  and  $\text{NH}_4^+$  ions are the least selective. The selective nature of ion chemistry is highlighted in Figure 1, where iodide ions exhibit a smaller ion signal intensity for chemical species containing less than three oxygen atoms (e.g.,  $\text{C}_{10}\text{H}_{16}\text{O}_2$ ).

As depicted in Figure 2A, the formation of  $\text{RO}_2$  radicals produced from the combined ozonolysis and OH radical reaction of  $\alpha$ -pinene can be characterized in a straightforward way with the Vocus Aim CI-TOF. Using different reagent ions (i.e.,  $\text{NH}_4^+$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$ ), the main  $\text{RO}_2$  radicals from  $\alpha$ -pinene oxidation,  $\text{C}_{10}\text{H}_{17}\text{O}_x$  ( $x = 3, 5, 7$ ) and  $\text{C}_{10}\text{H}_{15}\text{O}_x$  ( $x = 4, 6, 8$ ) were detected even at the shortest reaction time. While the sensitivity towards less oxidized compounds is limited to the less selective reagent ions (i.e.,  $\text{NH}_4^+$ ,  $\text{Cl}^-$ ), more selective reagent ions, such as iodide, can unambiguously measure highly oxidized species. The selectivity of the reagent ion plays a pivotal role in limiting the backgrounds and potential interferences that might hamper the detection of the compounds of interest.



**Figure 2.** (A) Evolution of peroxy radicals formed from the combined ozonolysis and OH radical reaction of  $\alpha$ -pinene as a function of experimental time, measured with the Vocus Aim CI-TOF using iodide reagent ion. (B) Evolution of I radicals produced from the photolysis of  $\text{I}_2$  and formation of iodic acid ( $\text{HIO}_3$ ) and  $\text{IO}_2$  in the presence of  $\text{O}_3$  as a function of reaction time measured with the Vocus Aim CI-TOF using  $\text{Br}^-$  ion chemistry

Hence, even the highest oxidized RO<sub>2</sub> radicals, i.e., C<sub>10</sub>H<sub>17</sub>O<sub>7</sub> and C<sub>10</sub>H<sub>15</sub>O<sub>8</sub>, can be identified, highlighting the very high sensitivity of the Vocus Aim.

In a similar type of experiments, inorganic radicals can also be characterized, as shown in Figure 2B. Iodine radicals were produced from I<sub>2</sub> photolysis and measured using Br<sup>-</sup> ion chemistry. Meanwhile O<sub>3</sub> was introduced in the flow reactor at different positions to vary the reaction time between the I radicals and O<sub>3</sub>. Hence, the reactivity of inorganic species can be studied under atmospheric relevant conditions with the same instrument.

This study demonstrates the capabilities of the Vocus Aim CI-TOF to characterize a challenging set of molecules and reactions with fast, highly sensitive inorganic and organic radical detection.

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