

# On-line Analysis of Gas and Particulate Products in Air Using Electrospray/Atmospheric Sampling Glow Discharge Ionization

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**Introduction.** Atmospheric chemistry of nonmethane biogenic hydrocarbons has received a great deal of attention because of their natural occurrence, large emissions globally, and high reactivity. These biogenic hydrocarbons can be readily oxidized by ozone, OH radicals, and NO<sub>3</sub> radicals to form secondary organic aerosols (SOAs) and are precursors to particulate matter formation. Analysis of trace organics in air, including SOAs, is becoming increasingly important for several reasons. Airborne particulate matter and ozone affect air quality and have been linked to increased mortality and morbidity rates. Off-line techniques based on sample pre-concentration with denuder/filter systems, cryotrap, or cartridges followed by solvent extraction and GC-MS are time consuming and limit the possibility for field analysis. Techniques for real-time measurements include FTIR spectroscopy, which does not allow quantification of single components, and APCI ion trap mass spectrometry, which has only recently been introduced. This work shows a new on-line method utilizing Atmospheric Sampling Glow Discharge Ionization (ASGDI) coupled to a quadrupole ion trap mass spectrometer for gas and particulate oxidation product analysis. With ASGDI, no solvent extraction or derivatization is involved, allowing all products formed in the reaction chamber to directly enter the mass spectrometer for analysis.

**Methods.** Ozonation reactions were carried out in a 500 L Teflon bag surrounded by a black curtain to exclude light. After ozone was generated from medical air and pumped into the chamber to give an ozone concentration of 150 to 400 ppb, each biogenic hydrocarbon (617 ppb), including  $\alpha$ -pinene,  $\beta$ -pinene, d-limonene, and  $\Delta^3$ -carene, was injected separately and allowed to react with ozone. Formation of oxidation products was monitored via direct introduction of the chamber air into an air sampling glow discharge ionization (ASGDI) source, where ionization occurs. The discharge is sustained between two stainless steel plates in the first differential pumping region of the mass spectrometer, using a potential difference of ~350V (resulting in 4 mA current) and 5 L/hr flow of air as the discharge gas.<sup>1</sup> Standards for reaction products, including limononaldehyde, pinonaldehyde, pinic acid, pinonic acid, and norpinic acid, were prepared at 10 to 15 mM in acetone and analyzed by electrospray/atmospheric sampling glow discharge ionization (ES/ASGDI). Mass spectrometric analysis was performed on a customized Finnigan ITMS quadrupole ion trap.

**Results and Discussion.** On-line ASGDI mass spectra were obtained for gas and/or particulate oxidation products formed from the reaction of four biogenic compounds with ozone. The spectra for the  $\alpha$ -pinene reaction immediately after injection into the Teflon bag and after one hour of reaction with ozone are shown in Figures 1a and 1b, respectively. After injecting the hydrocarbon, a number of reaction products were clearly identified along with the parent hydrocarbon. After one hour of reaction, the intensity of the reaction products increased by two to three times, and the intensity of the ions with  $m/z$  lower than the parent hydrocarbon (in-source fragment ions) doubled, indicative of increased reaction product formation. Gas and particulate reaction products identified with on-line ASGDI analysis include dicarboxylic acid, keto-carboxylic acid, hydroxy-keto-carboxylic acid, and ketone products and are consistent with previous off-line techniques.

To determine optimum instrumental parameters and compound behavior in the glow discharge, standards of each biogenic compound and several reaction products were analyzed via electrospray/ASGDI. The mass spectrum for pinonaldehyde (PAHD), a representative reaction product, is shown in Figure 2a. In addition to the protonated molecule, the fragment ions specific to PAHD allow it to be distinguished from limononaldehyde (LAHD), a reaction product of d-limonene with the same molecular weight but different characteristic fragment ions. Collision induced dissociation was utilized for definitive identification of the

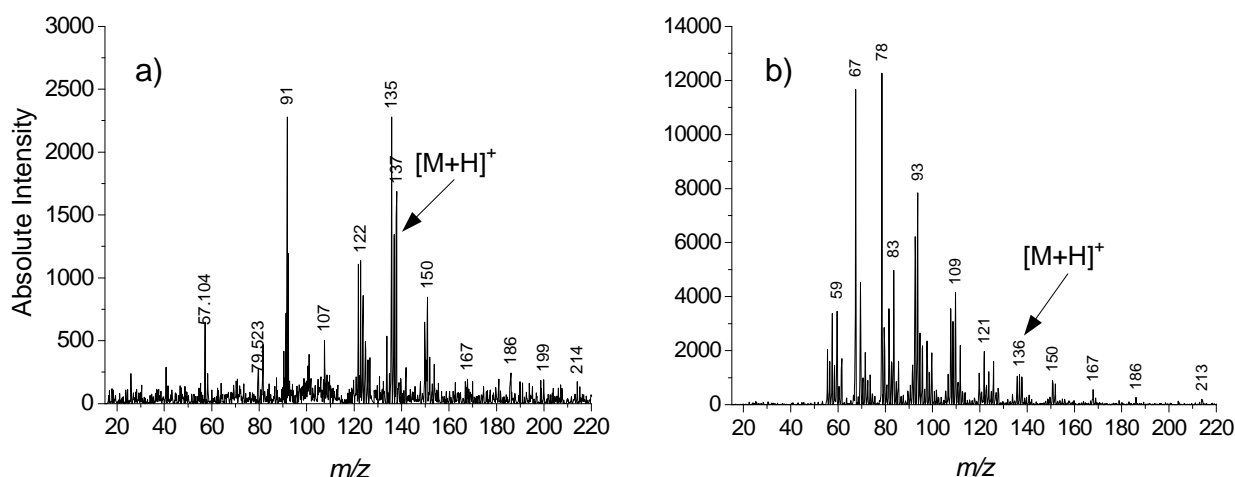
reaction products and to elucidate fragmentation pathways. The MS/MS spectra for pinonaldehyde and pinic acid are shown in Figures 2b and 2c, respectively. Characteristic fragment ions were identified in the spectra from the chamber studies for each reaction product, allowing positive identification of the reaction products.

**Conclusions.** This study demonstrates real-time monitoring of gas and particulate reaction products through a new on-line method using ASGDI on a quadrupole ion trap. Chamber studies show that unambiguous mass spectra are obtained when ppb levels of biogenic hydrocarbons and ozone are used to initiate the oxidation reaction. ES/ASGDI analysis along with CID of standards of reaction products was used to elucidate structural information of the reaction products, which are consistent with published techniques.

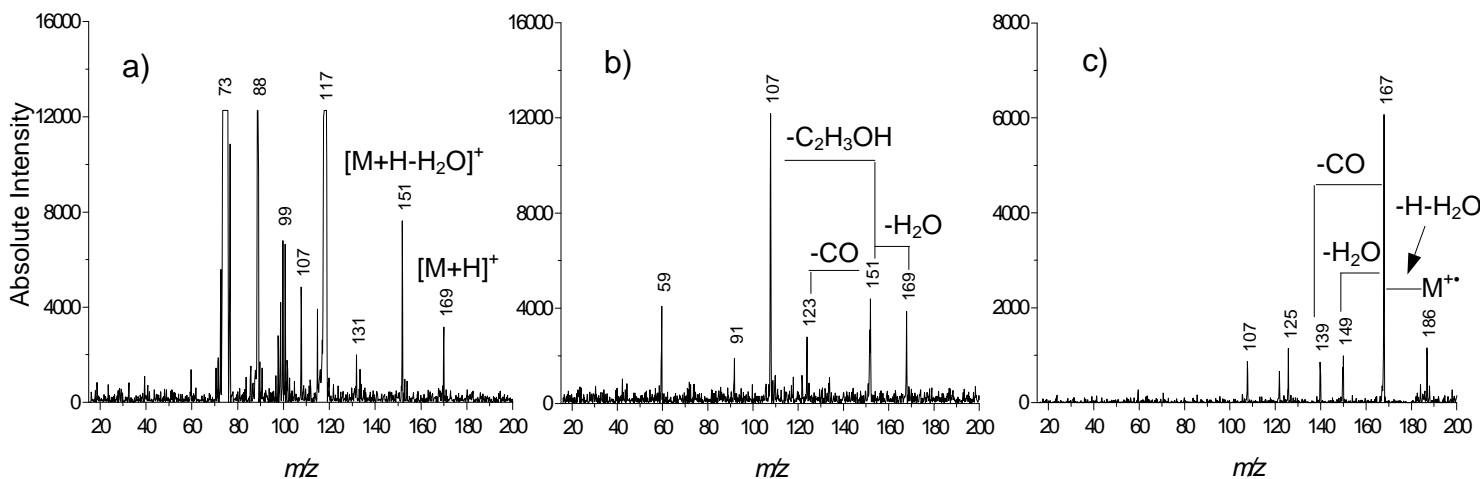
#### References.

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**Figure 1.** Results from chamber study of reaction of  $\alpha$ -pinene with ozone. a) spectrum immediately after injection of  $\alpha$ -pinene; b) spectrum 1 hour after injection of  $\alpha$ -pinene.



**Figure 2.** a) ES/ASGDI spectrum of a representative reaction product, pinonaldehyde; b) MS/MS spectrum of pinonaldehyde; c) MS/MS spectrum of pinic acid.