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A Fast-Response Method for Determination of Atmospheric Isoprene Using Quadrupole Ion Trap Mass Spectrometry

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A fast-response detection system for measurement of atmospheric isoprene (2-methyl-1,3-butadiene) is described which involves a tubular silicone membrane sampling system interfaced to a quadrupole ion trap. This method can be adapted to determination of a variety of atmospherically important alkenes that have short atmospheric lifetimes and, thus, for which high-frequency measurements are desirable. In this paper, we describe the development of a novel multimembrane air-sampling system in conjunction with selective chemical ionization and tandem mass spectrometry for the rapid quantitative determination of isoprene and other alkenes. In this method, we use vinyl methyl ether as an alkene-selective CI reagent, with which isoprene undergoes a [2 + 4] cycloaddition reaction, followed by loss of methanol, to generate an adduct ion at *m/z* 94 $[M + 58 - 32]^{\cdot+}$. This adduct ion undergoes loss of a methyl radical upon collision-induced dissociation. Quantitation is based on measurement of this fragment ion (*m/z* = 79). In this method, isoprene and other volatile organic compounds are preconcentrated using a combination silicone membrane and cryogenic trap inlet system. A linear calibration curve was obtained for gas-phase isoprene concentrations between 0.5 and 10 ppb. The multimembrane sampling system was shown to be relatively insensitive to changes in sample humidity and to membrane temperature.

Biogenic volatile organic compounds (BVOCs) are emitted into the atmosphere at a total annual rate estimated at 1150 Tg/yr, 43% of which is emitted in the form of one highly reactive species, isoprene (2-methyl-1,3-butadiene).[1] These biogenic hydrocarbons play a significant role in the formation of tropospheric ozone (O_3). Ground-level ozone, which is a respiratory irritant that is regulated through the U.S. Clean Air Act, is produced via a photochemical chain oxidation process, catalyzed by OH radicals, which can be summarized by the reaction below:[2]

$$\text{VOCs} + NO_x + h\nu \rightarrow O_3 + \text{particulate matter} \quad (1)$$

where $NO_x = NO + NO_2$. Despite a good general understanding of this process, government regulations aimed at reducing tropospheric ozone through controls of anthropogenic precursor VOCs and NO_x have met with little success.[3] Part of this failure is related to the significant contribution from biogenic compounds, such as isoprene, to the total VOC reactivity in the ozone production chemistry.[4−6]

The most common method utilized for determination of atmospheric VOCs involves sampling into pressurized stainless steel canisters followed by cryogenic focusing and chromatographic analysis.[7−9] Recent evidence indicates that this technique is not very reproducible for lower volatility non-methane hydrocarbons (NMHCs) and more polar oxygenated VOCs, which adsorb to and react on the walls of the canisters,[9−11] or for light alkenes such as ethene that may be generated on the canister walls. Another technique for sampling biogenic compounds utilizes porous polymeric adsorbents followed by thermal desorption-GC or GC/MS. Problems that may arise with solid adsorbents include the potential for unwanted surface reactions between analyte and oxidizing species such as ozone.[12−14] The most significant limitations of the above two techniques is that they

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are quite tedious and the cycle time usually exceeds the time scale of the chemistry. For example, for a daytime maximum [OH] of 1×10^7 molecules/cm^3, the atmospheric lifetime of isoprene is 17 min, given the rate constant for its reaction with OH of 1.0×10^{-10} cm^3 molecule^{-1} s^{-1}.[15] Thus, chromatographic analytical detection schemes normally produce data sets that have insufficient time resolution to capture the temporal behavior of this and other reactive VOCs, such as terpenes.

The need for fast time response methods for VOCs has been recently addressed. Lewis et al.[16] introduced a programmed vaporization injector two-dimensional gas chromatographic method for the measurement of isoprene and other hydrocarbons at a sampling rate of 12 min/sample; however, their sampling system consisted of a charcoal-packed (solid adsorbent) preconcentration trap. In another study, Greenberg et al.[17] utilized a reduction gas detector (RGA) interfaced with a gas chromatograph for the determination of isoprene in a variety of environments. The analysis time from sample injection to detection was ~4 min; however, the air-sampling system was not automated. Instead, stainless steel canisters were utilized for collecting air samples, which is tedious and severely limits the effective long-term sample time resolution. In addition, RGA detectors are known to have shortened lifetimes in the presence of aromatic and halogenated compounds. In these traditional chromatography-based methods, the selectivity of the method is limited by the chromatographic resolving power, and the time resolution of sampling by the need for high peak capacity for the highly complex atmospheric samples at low concentrations.

As an attractive alternative, mass spectrometric methods involving chemical ionization (CI) in conjunction with tandem mass spectrometry (MS/MS), employing collision-induced dissociation (CID), have been utilized to solve a variety of analytically challenging problems.[18−22] Although there has recently been a great deal of activity in applications of CI-MS/MS to studies of compounds of biological importance, this powerful technique can also be successfully applied to smaller molecules important to environmental and atmospheric chemistry. With the combined selectivity of CI and MS/MS, analysis of complex environmental mixtures may be possible without chromatographic separation, enabling the development of fast time response techniques. For example, in a recent study, Dearth et al.[23] developed a fast time response method that used nitric oxide CI with CID for the nonchromatographic analysis of automotive exhaust gases in a quadrupole ion trap equipped with a special Townsend glow discharge external source. However, a potential concern for the direct inlet used may be the effect of ambient (highly variable) water vapor on sensitivity. Ambient humidity levels in the sample can cause unwanted ion−molecule reactions in the high-pressure source resulting in lower and variable sensitivity for both polar and nonpolar VOCs.[24] This compromise of the CI chemistry makes effective removal of water vapor from air-sampling systems essential.

The utility of membrane inlet mass spectrometry (MIMS) for the effective reduction of water from the sample stream has been well documented.[25−31] Although MIMS can provide good sensitivity for aqueous samples, relatively few studies have shown detection limits that are adequate for measurement of reactive atmospheric VOCs.[31,32] To attain sufficient limits of detection, preconcentration is often required for the determination of many atmospheric analytes that are present in the atmosphere at concentrations reaching to the very low ppt levels. In this study, we have developed a novel membrane sampling cryogenic focusing system for the determination of isoprene in a quadrupole ion trap utilizing vinyl methyl ether (VME) as a CI reagent coupled with CID.

EXPERIMENTAL SECTION

All experiments were carried out using a Varian Saturn 2000 gas chromatograph/ion trap mass spectrometer. Our intention was to identify and employ a CI reagent that would be selective to atmospheric alkenes, e.g., isoprene (C_5H_8) and the terpenes ($C_{10}H_{16}$). For the experiments described here, we used vinyl methyl ether (Matheson), which was introduced into the vacuum chamber via a Varian leak valve and was allowed to react with the analyte for a period of 100 ms. To achieve low detection limits, preconcentration of the sample components was conducted by drawing the sample air through a 30-in. Silcosteel (Alltech) sample tube containing a smaller diameter tubular silicone membrane that was continuously purged with helium at 30 cm^3/min. A concentric tube MIMS configuration was used previously for water samples.[33] The analytes were then transferred to a cryogenic sample preconcentration trap (SPT) packed with glass beads that ballistically heated and injected the analytes into a 30-m (0.25-mm-i.d,) Supelco DB-1 column held isothermally at 150 °C. At this temperature, there is very little analyte retention, and the column thus acts largely as a heated sample-transfer line. CID of selected mass ions was performed at q_z-values of 0.4 and a resonance excitation voltage of 600 mV for a period of 20 ms. Helium served as the carrier, bath, and collision gas.

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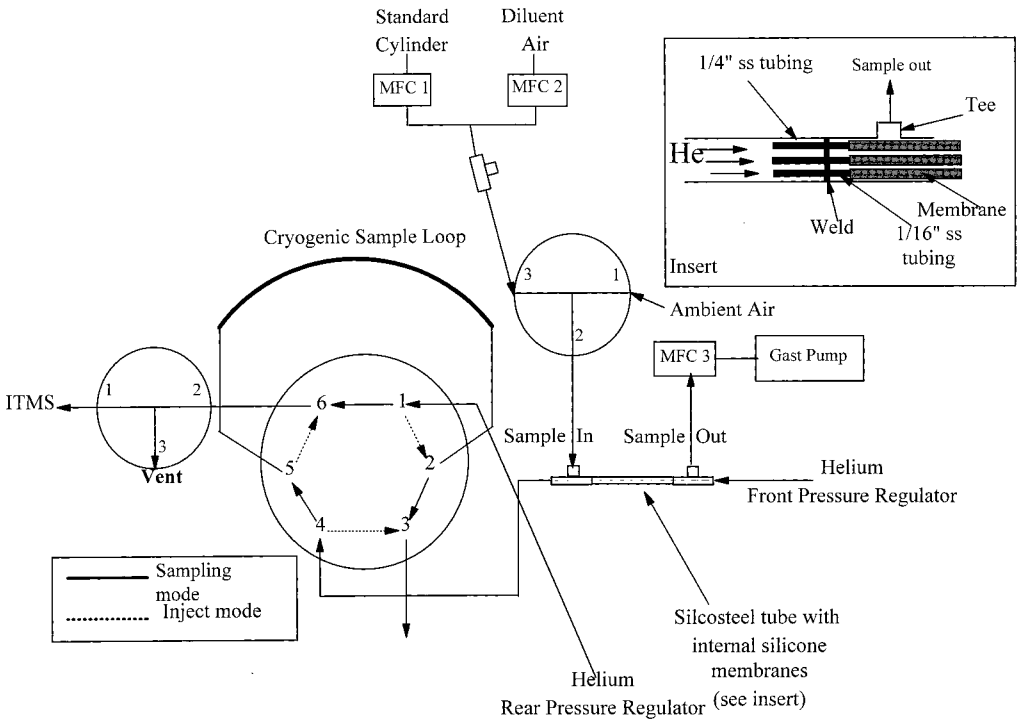

Figure 1. Schematic diagram of membrane preconcentration sample inlet.

The automated sampling system (Figure 1) consisted of three silicone membranes (Konigsberg Instruments, Inc., i.d. = 1.47 mm, o.d. = 1.96 mm, length 45 cm) arranged within a 1/4-in.-diameter Silcosteel tube (See inset in Figure 1). The sample (standard or ambient air) was pumped through the Silcosteel tube using a Gast diaphragm pump controlled by a mass flow controller (MKS instruments) at a rate of 300 cm^3/min. Compounds that permeate through the membrane were carried by helium into the cryogenic sample loop via a heated six-port valve (Valco Instruments Co. Inc. (VICI), Houston, TX). After a 5-min sampling period, the six-port valve switched to the injection mode. The sample loop was purged with helium at 300 cm^3/min for 12 s to remove air and vented to the atmosphere through a three-port switching valve (VICI). After purging, the three-port switching valve reverted back to injection mode as the SPT was ballistically heated to 250 °C. The helium from the rear pressure regulator delivered the sample plug to the ion trap for analysis. All valves were controlled by external events available in the GC electronics and Varian Saturn software which made automation possible.

Gas-phase cylinder standards for system testing were generated in-house. A glass vacuum manifold was pumped down to $\sim 10^{-4}$ Torr using a diffusion pump. Attached to the manifold was a gas-transfer cylinder (GTC) of accurately determined volume (V = 311 cm^3), which was also evacuated, via its high-pressure shut-off valves. To achieve the desired concentration, the analyte was introduced into the manifold and the analyte pressure within the GTC was measured using a Baratron pressure gauge (MKS Instruments; accuracy ±0.12%). The GTC was then placed between the source (N_2) and target cylinders via high-pressure Swagelok fittings. The target cylinder was an evacuated specially treated Accu-Life cylinder (Scott gases) and the source cylinder was a high-pressure (1000−2500 psi) zero-grade nitrogen cylinder (BOC gases) utilized to transfer the components in the GTC. The total quantity of diluent N_2 added was determined from the weight change upon filling, using an Ohaus balance, accurate to ±0.005 kg. The total mass increase of the cylinder upon filling is typically 2 kg. Final analyte concentrations in the Accu-Life cylinders were usually in the 5−10 ppm (m/m) range. The uncertainty of the calculated cylinder concentration was typically ±0.5%. Multiple-component mixtures in N_2 were prepared by transferring each component individually from the GTC, using a portion of the total amount of diluent N_2. The gas-phase standard cylinder was placed on-line in the sampling system (Figure 1). Standard gas-phase samples in the 0.1−10 ppb concentration range were prepared by dynamic dilution of the standard cylinder contents using calibrated mass flow controllers and zero air, as shown in Figure 1. All analytes were purchased from Sigma and utilized without prior purification.

Experiments designed to examine the dependence of the system on sample humidity were performed by passing the diluent air through an impinger bottle filled with distilled water. A series of valves controlled the extent of flow through the bubbler in order to obtain the desired relative humidity values, as measured by a hygrometer (Cole Parmer).

As a test of system performance under ambient conditions, measurements of isoprene emission from velvet bean leaves (Glendale Enterprises, Defuniak Springs, FL) were performed at the Purdue University greenhouse over a period of 3 days (March 16−18, 1998). Approximately 100 1-L pots of velvet bean (*mucuna sp.*) plants were grown in a 13-m^2 room. Sun lamps (500−1000 W) were placed in the room to assist in plant growth and stimulate isoprene emission. Temperatures in the room ranged from 30 to 35 °C while relative humidities varied from 20 to 60%.

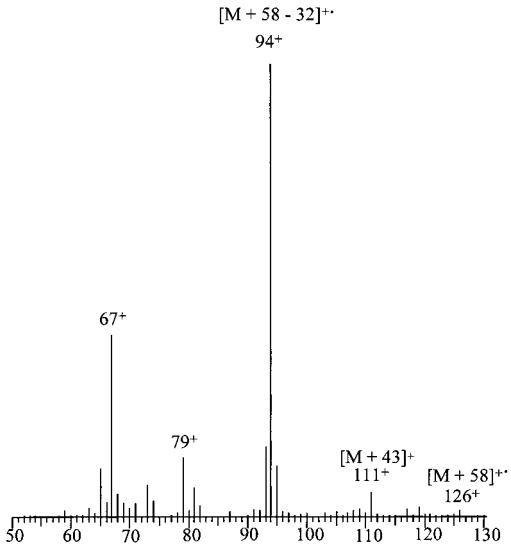

Figure 2. Vinyl methyl ether chemical ionization mass spectrum of isoprene.

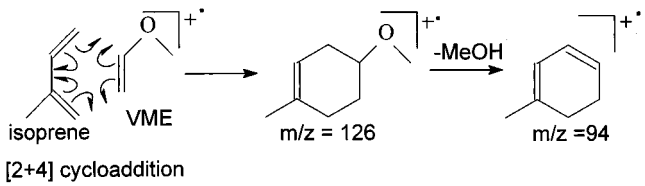

Figure 3. Proposed reaction mechanism for the formation of the $[M + VME - MeOH]^{\bullet+}$ adduct ion.

RESULTS AND DISCUSSION

VME/Isoprene CI Chemistry. The utility of VME as a selective reagent for olefinic functional groups has been well documented.[34−37] Compounds ranging from simple low-molecular-weight alkenes to much larger systems have been thoroughly examined. When VME is introduced into the quadrupole ion trap, the most abundant ions present are the acetyl cation ($m/z = 43$) and the VME molecular ion ($m/z = 58$). The acetyl cation has also been shown to react selectively with alkenes, via cycloaddition at the double bond.[38,39] The VME CI spectrum of isoprene is dominated by an adduct ion corresponding to $[M + VME - MeOH]^{\bullet+}$ at $m/z = 94$, as shown in Figure 2. As discussed by Van Doorn et al.,[35] ionized VME most likely reacts with dienes via a [2 + 4] Diels−Alder cycloaddition process that forms a highly unstable methoxycyclohexene radical cation which further fragments to lose methanol, as shown in Figure 3. Other ions generated with VME CI of isoprene were a hydride exchange product at $m/z = 67$, i.e., $[M - H]^+$, the acetyl cation adduct at $m/z = 111$, and a small abundance of the VME/isoprene adduct ion at $m/z = 126$. To conduct quantitative isoprene measurements without chromatographic separation may likely require additional specificity beyond the CI chemistry, as there are several species

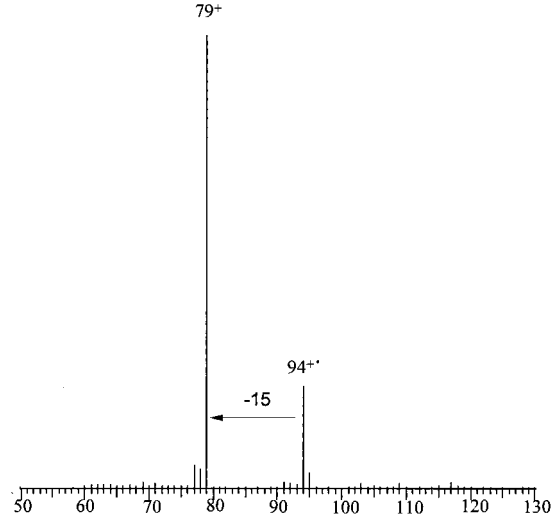

Figure 4. Collision-induced dissociation product spectrum of the $m/z = 94$ adduct ion.

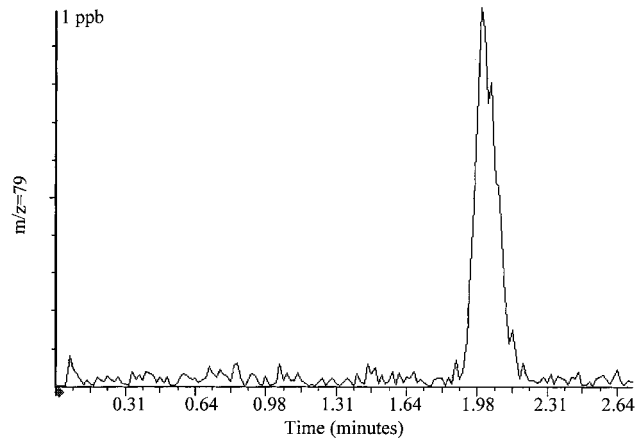

Figure 5. Selected reaction monitoring chronogram of $m/z = 79$ fragment ion, for a 1 ppb isoprene/air mixture.

that may react with VME to yield a $m/z = 94$ ion (e.g., any C_7H_{10}). CID of the 94^+ adduct ion (using an optimum ac resonance excitation voltage of 600 mV) results in the loss of a methyl radical, as shown in Figure 4. The $m/z = 79$ fragment ion can then be used for quantitation. MS/MS experiments show a 70% fragmentation efficiency, as defined by the magnitude of the $m/z = 79$ signal with application of ac resonance excitation divided by the magnitude of the $m/z = 94$ signal during isolation without the application of ac resonance excitation. Experiments also demonstrate the CID reaction efficiency is unaffected by small (i.e., ×2) changes in helium pressure. This results from the fact that as the He pressure increases the $m/z = 79$ fragmentation efficiency increases, while the fraction of $m/z = 94$ ions that dissociate decreases. A sample-selected ion chronogram (so-called since there was no chromatography occurring) for a 1 ppb isoprene/air sample is shown in Figure 5. A calibration curve obtained from the integrated area for the $m/z = 79$ peak, for gas-phase isoprene samples in the 0.5−10 ppb (mole/mole) range is shown in Figure 6. As shown in the figure, the membrane inlet/VME-CI/CID system responds linearly, and with good precision (the error bars for individual points represent the 95% confidence interval for replicate injections), over the concentration range we

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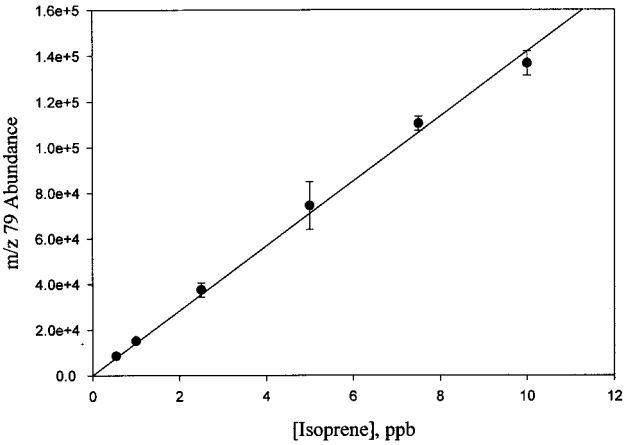

Figure 6. VME CI/CID calibration curve for isoprene in air.

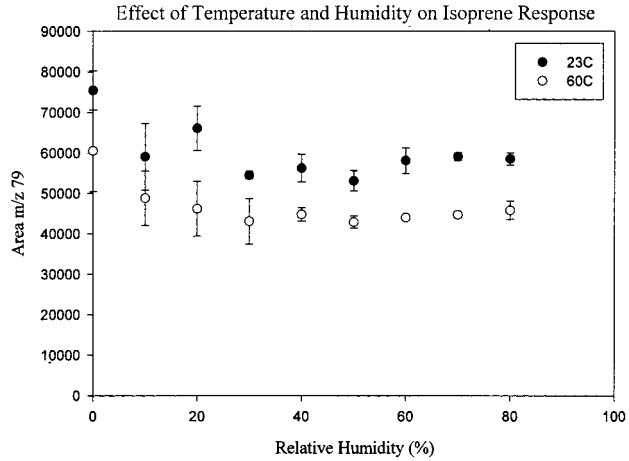

Figure 7. Effect of temperature and humidity on isoprene response.

examined (which is a typical range of ambient isoprene concentrations for deciduous forest environments).[40]

Analysis of replicate blank samples led to a 95% confidence interval for the blank that corresponds to a detection limit of 80 ppt isoprene, for the operating conditions used to obtain the data in Figure 6. A determining factor in the detection limit for the current method is the flux of isoprene molecules across the membrane. From independent calibrations obtained by direct cryogenic sampling (i.e., bypassing the membrane), we determined the absolute sensitivity to isoprene, e.g., in counts per nanomole injected into the trap. This information was then used to determine the absolute quantity (N_i) of isoprene that permeates through the membrane for a sample time, t, and gas-phase isoprene concentration, N_i' (molecules/cm^3). From this measurement, we determined that ~10% of the isoprene was transported through the membrane, for the air sample flow rate and membrane configuration used. This number depends on the available membrane surface area, membrane composition and thickness, temperature, and nature of the analyte (solute). Since improvements in detection limit and time response may come from changes in membrane composition, dimension, operating conditions, etc., it would be useful to have a more direct means for comparison of membrane performance for other conditions, analytes, etc. We therefore define a new quantity, the mass-transfer velocity, γ_i, as defined in eq 1, where γ has units of

$$F_i = \gamma_i N_i' \qquad (1)$$

centimeter per second and F_i is the flux of isoprene across the membrane (in molecules/cm^2·s), which was determined from measurement of the isoprene collected per unit sample time, and given knowledge of the membrane surface area. This quantity is then independent of the membrane surface area. From our measured F_i, we obtain $\gamma_i = 6.03 \times 10^{-3}$ cm/s for the silicone membrane, at 298 K. We note that the mass-transfer velocity expression $\gamma_i = F_i/N_i'$ is identical in form to the expression for the definition of membrane "permeance"[41] (Π_i), i.e., $\Pi_i = F_i/P_i$, where P_i is the partial pressure of species *i* in pascals, which leads to units for the permeance[41] of mol/m^2·s·Pa. However, if the flux F_i is expressed in molecules/cm^2·s, and the partial pressure is multiplied by 10^{-6}(m^3/cm^3)/kT, the units for permeance become internally consistent, and those of a velocity, i.e., cm/s.

The actual flux of analyte across the membrane is inversely dependent on the membrane thickness. As described by Overney and Enke,[42] the rate of transport of molecules (N_i/t) across a tubular membrane is given by eq 2, where L is the tubing length

$$N_i/t = 2\pi L D_i K_i N_i'/\ln(d_o/d_i) \qquad (2)$$

(45 cm), D is the diffusion coefficient in the membrane, K is the partition coefficient for isoprene adsorption to the membrane, and d_o and d_i are the inner and outer membrane diameters, respectively. From our data for isoprene, we can thus calculate the product $D_iK_i = 1.68 \times 10^{-4}$ cm^2/s. According to eq 2, the flux of molecules increases in near-direct proportion to the change in membrane thickness, for the tubing dimensions used in this study (e.g., a factor of 11.3 increase in flux would occur if we decrease the thickness from 0.49 to 0.049 mm).

A related issue is that of the time response of the membrane inlet, given the fact that atmospheric species concentrations can change rapidly on minute time scales due to advection of chemically independent air masses. We conducted experiments to test this by switching between zero air and isoprene/air mixtures. Because of the sample flow rate, and the internal volume of the membrane and upstream connections, the residence time of analytes in the sample system is very short, and thus switching is effectively instantaneous. For these measurements, we find a 10−90% rise time of 120 s. However, the time between switching and a 10% increase above the baseline was quite significant, i.e., ~45 s. We interpret this in part to the time scale for transport across the relatively thick membrane used. We plan to investigate the dependence of sensitivity and response time on membrane thickness soon.

Temperature and Humidity Dependence of System Sensitivity. In MIMS, increasing the temperature of the membrane has been shown to increase the sensitivity of the analytical method, for aqueous samples, due to increased permeation of the analyte through the membrane.[34] This results from the negative temperature dependence of the Henry's law coefficient for the

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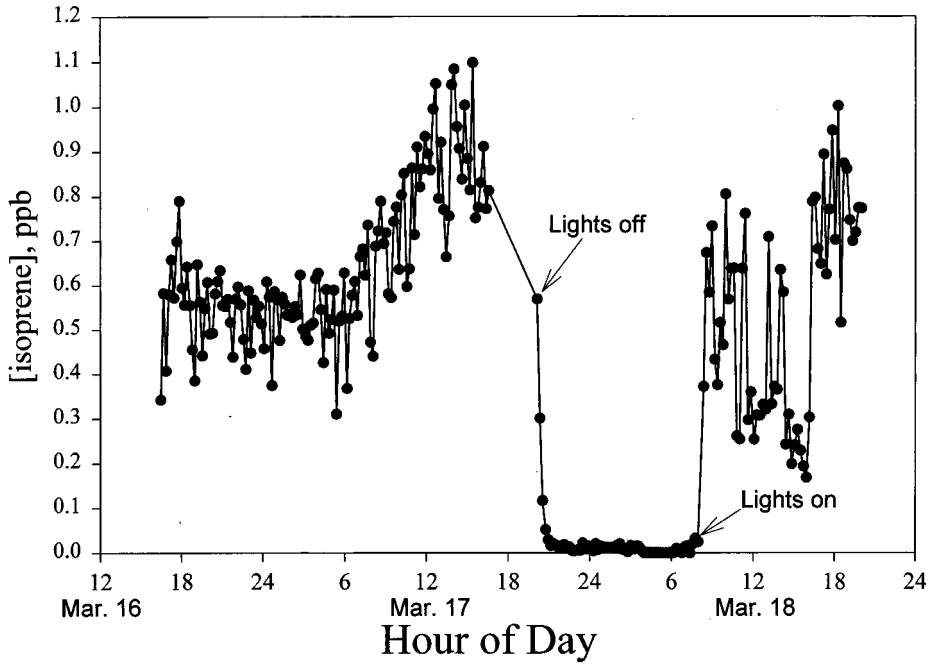

Figure 8. Greenhouse measurements of isoprene from velvet beans by VME CI ion trap MS/MS.

analyte in water. Conversely, sensitivity decreases for air samples with increasing temperatures. This is due to a decreased solubility of the analyte in the membrane surface (i.e., ΔH_{sol} is negative). Sampling air at ambient temperatures, however, may be deleterious due to the possible accumulation of water and other, low-volatility, atmospheric species on the membrane limiting analyte permeation and creating significant memory effects. Heating, therefore, is a highly attractive option for keeping the membrane continuously cleansed. It should also be noted that the membrane performance is likely to be dependent on the sample humidity, which for ambient samples can vary between 0 and 4% (m/m). It is therefore important to characterize the membrane performance as a function of both humidity and temperature, information that is relatively scarce to date.

Figure 7 shows the effect of temperature and humidity on the rate of isoprene permeation through the membrane, measured as the $m/z = 79$ signal for a 5-min integrated sample. This experiment was conducted for a 5 ppb gas-phase isoprene/air mixture with varying added humidity. For both 25 and 60 °C, the isoprene response is highest under dry conditions (0% relative humidity). As the humidity increases from 0 to 20%, the response to isoprene decreases by ~20%. As shown in Figure 7, although the sensitivity is slightly less at 60 °C, the magnitude of the humidity effect is essentially the same for both temperatures. This reduction in response may be caused by several factors including a change in the permeability of the membrane by water adsorption, Coulombic repulsion in the quadrupole ion trap, and protonation of the VME molecular ion due to permeation of water through the membrane. This phenomenon has also been observed by Ketola et al.,[43] who showed that raising the humidity of the sample stream can decrease analyte response through a membrane from 10 to 30%, for toluene. Hygrometer measurements conducted here for humidified samples indicated that the silastic membrane used in this study allows a significant amount of humidity through the membrane. This and the fact that, as shown in Figure 7, the magnitude of the humidity effect is the same for both temperatures studied, indicates that the decrease in response is likely related to a change in the mass spectrometry, rather than a membrane permeance effect. Further investigation of this phenomenon will be performed in the future. However, we note that the signal is humidity independent for both membrane temperatures, for relative humidities of >20%. This result indicates that calibration can be done at humidities of >20%, and the resulting determined sensitivity will apply for most ambient measurement conditions.

Effect of Coeluting Compounds on Quantitation. As shown in Figure 5, in the method configuration described here, there is little chromatographic retention, and many compounds will coelute. A concern in performing a nonchromatographic separation is the ability to effectively quantify an analyte embedded in a sample plug containing a multitude of compounds. In a series of experiments aimed at testing the impact of large concentrations of coeluting compounds, we prepared compressed gas cylinder standards containing mixtures of isoprene, 1,1,1,2-tetrafluoroethane, methyl vinyl ketone, and methacrolein (the latter two are oxidation products of isoprene).[6] Because of its inertness, the hydrofluorocarbon was added to the cylinders to test the component stabilities (by measuring analyte signals over time relative to that for the fluorocarbon), i.e., to ensure that the analytes had not adsorbed to the walls of the cylinder over time. We find that VME CI/quadrupole ion trap MS/MS is well suited to mixture analysis. For example, any compound coeluting with isoprene can be removed effectively through application of wave forms on the end caps while selectively accumulating the isoprene adduct ion. From our multicomponent cylinder standards, we found no significant difference in $m/z = 79$ ion counts for isoprene only (15,105 ± 501 counts/ppb) and for isoprene in the four-component mixture cylinders (17 110 ± 1200 counts/ppb).

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Velvet Bean/Greenhouse Isoprene Measurements. The VME CI-MS/MS system was evaluated in a series of experiments at the Purdue University greenhouse through measurements of isoprene in a greenhouse room filled with velvet bean plants. Velvet beans are known emitters of isoprene.[44] We conducted measurements in the greenhouse over a ~50-h period in March 1998. For the first ~24 h measurement period (beginning March 16, 16:28 EST and ending March 17, 16:35 EST), the sun lamps were on continuously, and thus isoprene emission occurred throughout this period. As shown in Figure 8, the measured isoprene concentrations varied from 0.4 to 1 ppb for the first 24-h period. During the first 12 h, the levels of isoprene remained constant. At ~0900 March 17, the levels of isoprene began to rise and plateau to 1 ppb in the afternoon. Isoprene emission is highly dependent on photon flux density and temperature.[1,44] Because sun lamps were used to provide a constant photon flux, the increase in temperature in the greenhouse room was most likely responsible for the rise of isoprene, since it is well documented that isoprene fluxes are an exponential function of temperature.[45] The variability of the data observed was most likely due to a combination of variability in the room air-exchange rate (estimated from measurements at 30 min) and variability of the emission fluxes, and not the reproducibility of the sampling system. Replicate measurements of 500 ppt isoprene standards indicate an rsd at this concentration level of ±4.9%, for quantitation using the $m/z = 79$ product ion.

In the second 24-h period, the sun lamps were turned off at 2010 (i.e., at approximate sunset) for a period of 12 h and then turned on for an additional 12 h. As shown in Figure 8, isoprene decays via first-order kinetics ($k = 0.0597$ min^{-1}) as the lamps were turned off. After 45 min, the levels of isoprene were essentially below the detection limit of 0.02 ppb. Within 30 min of turning the sun lamps on (0800, March 18), isoprene was detected at levels found the previous day. These data demonstrate that the conventional air sampling/analysis system would be inadequate in characterizing the temporal behavior of emission fluxes from the plants.

This set of experiments is also highly useful in demonstrating the likely lack of any interferences for isoprene determination. As the local vegetation was not foliated at this time, the only source of isoprene was from within the greenhouse. This is apparent from the rapid decay when the lights were switched off. Furthermore, it must be pointed out that the greenhouse air would be a highly complex mixture. Because of the fast exchange rate in the greenhouse, and its location in an urban environment, the isoprene emissions were adding to an already highly complex mixture in terms of VOC concentrations (at the subppb level). Furthermore, plants are well-known to emit a multitude of VOCs such as alcohols, saturated and unsaturated hydrocarbons, aromatic hydrocarbons, and amines to name a few.[46] Thus, the greenhouse air is likely to be even more complex than the surrounding urban VOC mix. The ambient anthropogenic VOC distribution would be unchanged with the lights switched off; therefore the observation that the signal dropped to below detection limits indicates no evidence for interference from these compounds, essentially all of which would have eluted with the isoprene peak. If there were any product at $m/z = 94$ generated during the chemical ionization period, tandem mass spectrometry provided the extra selectivity in discriminating the isoprene adduct ion from other compounds having the same nominal m/z.

CONCLUSIONS

A novel multimembrane sampling system is combined with a quadrupole ion trap for the determination of biogenic compounds utilizing the selectivity and specificity of chemical ionization and collision-induced dissociation. Work underway in our laboratories indicates that the VME CI chemistry can also be applied to other atmospheric biogenic compounds, such as methyl vinyl ketone, methacrolein, and terpenes. Currently, this automated system can make measurements every 10−12 min. The sampling frequency could be improved by using a thinner membrane, adding more membrane surface, or changing the nature of the membrane. It is also possible to conduct the analysis much faster, by sampling directly into the mass spectrometer, i.e., via the membrane but without cryofocusing. With direct sampling, a measurement frequency of at least 1 s^{-1} could be achieved, although this comes at the cost of sensitivity. However, with further improvement of the mass spectrometer sensitivity, ultrafast measurements should be possible. This is highly desirable, e.g., to enable flux measurements of biogenic VOCs using the eddy correlation technique.[47] The multimembrane sampling system described here was shown to be relatively insensitive to humidity and temperature changes, while allowing for reduction of ambient humidity and concentration of the sample, enabling ambient measurements at low detection limits. This automated and rugged system has also exhibited the ability to conduct isoprene measurements emitted from vegetation at concentrations well below those found in a typical diurnal cycle, under moderate to extreme conditions. Further work will focus on improvements to the sampling time resolution and application of this methodology to other atmospheric species, e.g., carbonyl compounds.

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