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Field and laboratory emission cell automation and control system for investigating surface chemistry reactions

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A novel system [field and laboratory emission cell (FLEC) automation and control system] has been developed to deliver ozone to a surface utilizing the FLEC to simulate indoor surface chemistry. Ozone, humidity, and air flow rate to the surface were continuously monitored using an ultraviolet ozone monitor, humidity, and flow sensors. Data from these sensors were used as feedback for system control to maintain predetermined experimental parameters. The system was used to investigate the chemistry of ozone with α-terpineol on a vinyl surface over 72 h. Keeping all other experimental parameters the same, volatile organic compound emissions from the vinyl tile with α-terpineol were collected from both zero and 100 ppb (parts per 10^9) ozone exposures. System stability profiles collected from sensor data indicated experimental parameters were maintained to within a few percent of initial settings. Ozone data from eight experiments at 100 ppb (over 339 h) provided a pooled standard deviation of 1.65 ppb and a 95% tolerance of 3.3 ppb. Humidity data from 17 experiments at 50% relative humidity (over 664 h) provided a pooled standard deviation of 1.38% and a 95% tolerance of 2.77%. Data of the flow rate of air flowing through the FLEC from 14 experiments at 300 ml/min (over 548 h) provided a pooled standard deviation of 3.02 ml/min and a 95% tolerance range of 6.03 ml/min. Initial experimental results yielded long term emissions of ozone/α-terpineol reaction products, suggesting that surface chemistry could play an important role in indoor environments. © *2007 American Institute of Physics.* [DOI: 10.1063/1.2432243]

I. INTRODUCTION

In the past 20 years, an increased awareness of the importance of indoor air quality (IAQ) and its potential impact on human health has stimulated an interest in indoor air research.[1] As a result of such increased awareness, the National Occupational Research Agenda (NORA) created an Indoor Environment Team which identified three-types of health effects as priorities for increased research: (1) building-influenced respiratory infections, (2) building-related asthma and allergic disease, and (3) nonspecific building-related symptoms. Nonspecific building-related symptoms include the acute effects of indoor exposures or conditions, as well as so-called "sick-building syndrome."[2] There are many potential initiators of sick-building syndrome as a part of IAQ including particulates, carbon monoxide, carbon dioxide, ozone, environmental tobacco smoke, and volatile organic compounds (VOCs).[3] VOCs are of environmental interest because they could be responsible, even at low concentrations, for indoor air environment health effects.[4] Previous research conducted on VOCs in the indoor environment has mainly focused on the individual VOCs and their specific health effects.

A recent review of indoor environment chemistry by Weschler highlights several research areas important to the field.[5] Significant observations from this review article are that there are still several fundamental questions regarding the gas-phase and surface-phase chemistry of indoor environments, and that the indoor environment is chemically more complex than is previously thought. Experimental evidence has demonstrated that several initiator species such as ozone (O_3), hydroxyl radical (OH), and nitrate radical (NO_3) are likely to be present in indoor air and the indoor concentrations of VOCs are higher by a factor of 10 or more than typically found in outdoor environments.[5,6] These indoor species (OH, O_3, and NO_3) can react with VOCs to produce oxygenated organic compounds such as aldehydes, ketones, carboxylic acids, and dicarbonyls. Recently, Jarvis *et al.* associated chemicals with these carbonyl structures with an occupational asthma hazard, particularly when the functional group such as a carbonyl was present twice or more in the same molecule.[7]

VOCs in the indoor environment come from a number of sources, but a significant portion results from the use of cleaning products and air fresheners.[8] While these products are used to clean surfaces and improve or mask odors, additional chemistry influenced by surfaces is possible. Surfaces can remove chemicals from the environment by adsorption, act as long term emission sources, and/or function as chemical reaction sites as, for example, ozone interacts with chemicals in or on the surface material. Importantly, surfaces can do all these things at the same time. Unlike indoor environment gas-phase chemistry, indoor surface chemistry is not constrained by air exchange rates; reactants can be continually in contact with one another and kinetic and/or concen-

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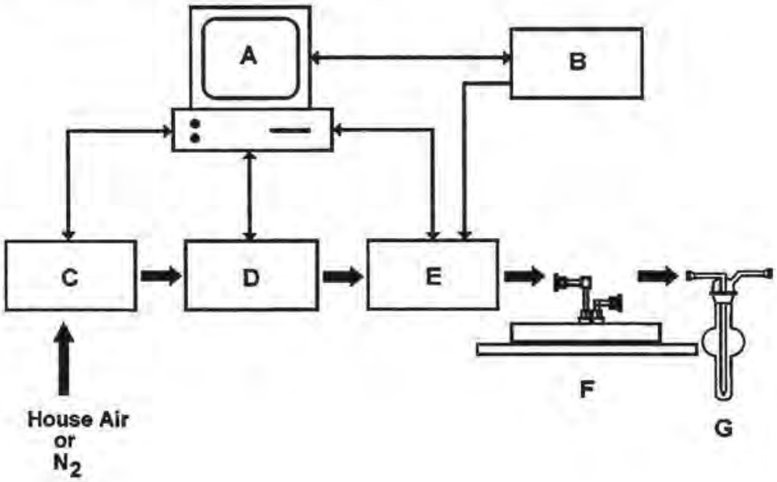

FIG. 1. Diagram of the FACS components: (A) computer, (B) reaction injection (OH, O_3, or NO_3), (C) air purification stage, (D) air humidification stage, (E) sample delivery stage, (F) FLEC, and (G) impinger for sample collection

tration limitations can be overcome. The need to accurately assess building product emissions in both composition and rate has led to the development of new measurement devices such as the field and laboratory emission cell (FLEC).[9,10]

The FLEC was developed to satisfy the need for a portable, easy to use, and reliable climate chamber for nondestructive emission sampling of building materials.[11] Since its inception, the FLEC has been incorporated into a number of international standards with goals of regulating building material emissions.[12–17] Advantages of this device include easy cleaning, negligible sink effects, quick thermal equilibrium times, and minimal invasiveness.[11] However, the air control unit that is supplied with the FLEC lacks some capabilities that would be advantageous for investigating long term surface chemistry reactions. System improvements might include a controlled feedback system, a convenient reactant (OH, O_3, and NO_3) delivery system, automated humidity control, and a data or sensor recording function.

To obtain these capabilities, a novel system has been developed to investigate how VOC-covered surfaces can influence the chemistry in the indoor environment. The FLEC automation and control system (FACS) is designed to provide a well-regulated, steady supply of consistent quality air to the FLEC for use in various experiments. The system utilizes several mass flow controllers in order to mix and regulate the air to the desired humidity and flow rates. All of these conditions are monitored and controlled by a computer with a user-friendly interface.

The FACS is similar to previous designs which required well-regulated air to be delivered to samples for analysis.[18,19] Umstead *et al.* developed an ozone delivery system for *in vitro* exposure of proteins.[18] This system used a series of mass flow controllers, humidification jars, and pressure gauges to provide well-regulated air to protein samples at a rate of 15 l/min. However, this system was not computer controlled and required manual setting and adjustment of all parameters. Allen further refined the design for an ozone delivery system for exposure of cultured cells.[19] In this design, a computer controlled the delivery of ozone to samples. A feedback design using an ozone analyzer was able to make adjustments of mass flow controllers within the system as needed. Additionally, the air flow through the instrument was reduced to 5 l/min. In both systems, a primary concern was to maintain a high humidity in order to prevent cell cultures from drying and to do so at human body temperatures; therefore neither system can provide variable humidity air flow. In addition to a stable ozone profile, the FACS is designed to provide a stable humidity between 10%RH (relative humidity) and 90%RH at experiment flow rates between 100 and 600 ml/min.

The system presented here has been used to monitor the surface chemistry reactions of α-terpineol ((R)-2-(4-methyl-3-cyclohexenyl)isopropanol), a major constituent of pine oil, on a vinyl composition tile with both clean house air and air mixed with 100 ppb (parts per 10^9) ozone (O_3).

II. INSTRUMENT

A. Overview

The FACS (Fig. 1) can be considered to be composed of three stages: the air purification stage, the air humidification stage, and the reactant injection and delivery stage. The air purification stage (C) regulates, cleans, and dries the air for delivery to the rest of the system. The air humidification stage (D) mixes both dry and humid air to create and deliver the desired humidity for the duration of the experiment. The reactant ejection and delivery stage (B and E) introduces the reactant, at the desired concentration, into the air stream and delivers the air to the FLEC for the experiment.

The entire system is controlled by a standard desktop computer which houses an analog output card, a multifunction data acquisition card, and a multiport serial card. The control program is a C/C++ windows application that was written in-house and utilizes libraries provided by National Instruments.

B. Design and assembly

The air purification stage begins with the compressed air available in the laboratories throughout the NIOSH facility. This air is supplied at 90 psi (nominal) with a varying relative humidity of 2%–7%. The first element is a regulator set to 20 psi to ensure a constant pressure and air flow to the system. After the regulator, the air encounters the first control element which is a normally closed solenoid valve (Omega Engineering, Stamford, CT). This valve allows the control computer to enable or disable air flow to the system without disturbing any of the prior connections or the facility compressed air valve. Also, it allows the system to automatically disable the air flow in the event of a problem.

The air then passes through an oil vapor filter (Wilkerson, Richland, MI) to remove any hydrocarbons that may be present in the compressed air line. After this, the air encounters two Drierite (W. A. Hammond Drierite Co. Ltd., Xenia, OH) columns. The first column contains indicating Drierite only (p/n 26840), while the second column is the gas purifier which contains both indicating Drierite and molecular sieves (p/n 27068). Two columns are used for ease of Drierite replacement. Since multiple 72 h duration experiments will deplete the desiccant, it is easier and faster to change the column if it only contains indicating Drierite.

After the second column, an optional three-way stainless steel ball valve has been inserted. One position allows the air to continue onto the remainder of the system. The other position allows the connection of an ultrahigh purity nitrogen tank, or other gases, to the system. The air purification stage ends with the air flowing past a pressure sensor (Omega Engineering, Stamford, CT), which the system uses as a verification of the air availability.

The air humidification stage begins with the air being split into two paths, a dry path and a humid path. The dry path air passes through a mass flow controller followed by an in-line temperature and humidity sensor and then goes to the air mixing chamber. The humid path air also begins by passing through a mass flow controller. The air then flows into a humidifying tank, where the air encounters warm water and leaves the tank nearly saturated. The humid air flows through an in-line temperature and humidity sensor and then proceeds to the air mixing chamber. The mixing chamber is a Kontes (Vineland, NJ) gas bubbler (p/n 652250) which has been modified to accept $\frac{1}{4}$ in. Ultra-Torr® (Swagelok, Solon, OH) fittings. The dry air and humid air enter via separate ports at the top chamber and mix. The air then flows into the bottom chamber and exits. The mixed air passes through another in-line temperature and humidity sensor and is delivered to the reactant injection chamber. The dry air and humid air sensor units are used by the system for verification purposes, while this final temperature and humidity sensor serves as a feedback to control the relative humidity of the experiment air. Since 99% of the total system air flows through this sensor, there is no need for additional sensors downstream that may be contaminated or compromised by the reactants.

The final step in the process is to inject the reactant. To date, only ozone has been used. High concentration ozone (45–50 ppm) is prepared in advance by placing a UV lamp (Jelight ozone generator, Model 600, Irvine, CA) in a 70 l Teflon chamber filled with clean dry air. The ozone/air mixture is then pumped from the chamber and delivered to a mass flow controller. Typical flow rates through the mass flow controller are between 2 and 11 ml/min. Since the pump has a higher delivery rate (around 80 ml/min) than is required to deliver the ozone, excess ozone is returned to the Teflon chamber. Ozone from the mass flow controller is mixed with the humidified air in a 2 l, three-necked Woulff bottle. Air leaving this final stage is now ready for delivery to the FLEC.

The experiment air is split and delivered to two mass flow controllers. One of these mass flow controllers supplies experiment air to an ozone monitor [Thermo Electron 49C (Waltham, MA)]. Feedback from this device is used to adjust the flow of high-concentration ozone from the chamber through its corresponding mass flow controller. The mass flow controller on the other side of the split delivers the experiment air to the FLEC at the specified flow rate.

C. Control

As stated previously, the system is controlled by a desktop computer with additional cards installed. In this case, the computer is a Dell (Round Rock, TX) Optiplex GX400, but any computer with three unused peripheral component interconnect (PCI)-bus slots should be suitable. The additional cards consist of one NI PCI-6040E multifunction input/output data acquisition (DAQ) board, one NI PCI-6713 analog output board, and one Sealevel Systems (Liberty, SC) Comm+8.LPCI eight-port serial board.

The computer runs an application that was written using Microsoft VISUAL C/C++ 6.0. The application allows the researcher to define the parameters of the experiment such as flow rate through the FLEC, relative humidity of the experiment air, ozone concentration, duration of the experiment, and the recording interval for data collection.

All of the devices in this system require either standard 120 V ac, 60 Hz power, or 12 V dc power, which is supplied by a single 12 V, 17 A linear power supply.

This system uses Aalborg (Orangeburg, NY) mass flow controllers, which vary in maximum flow rate from 100 ml/s to 2 l/s depending on the application. They are all remotely settable, meaning the flow rate is controlled by applying a 0–5 V dc signal to the set point pins. The flow rates from each controller are read for control, verification, error checking, and data recording purposes.

An in-line temperature and humidity sensor was developed to meet control and feedback requirements. The base temperature sensor is a National Semiconductor (Santa Clara, CA) LM335. The base humidity sensor is a Honeywell (Freeport, IL) HIH-3602-L-CP. This sensor has been discontinued and its replacement is the HIH-4602-L-CP. While this sensor has similar characteristics to its predecessor, it has not been tested in the system. Each sensor is individually sealed into a tee fitting so that air may pass freely over it. One of each type of sensor is used to create the in-line unit. The analog signals from the sensors are collected by a Microchip (Chandler, AZ) PIC 16F876A microcontroller, where the firmware transforms the raw analog data into temperature and relative humidity information and transmits those readings to the control application via an RS-232 serial line. This approach was chosen for two reasons. First, the cable length for the single-ended analog data is less than 6 in. long and therefore less susceptible to electronic noise. Secondly, the temperature and humidity sensor unit is usable as a stand-alone device, and the serial data stream can be captured by a wide variety of programs and data loggers.

The ozone monitor is capable of remote operation and of providing data via a serial port. The ozone concentration data received from this monitor are used to adjust the flow rate through the mass flow controller attached to the ozone chamber.

Introducing ozone into the air stream presented a challenge for this system. The ozone monitor uses a 1.4 l/min pump to draw air into the internal cells used for ozone detection. When combined with a desired variable FLEC air flow rate of 100–600 ml/min, this generated a required total air flow of 1.5 –2.0 l/min. As stated previously, typical flow rates through the ozone delivery mechanism range from 2 –11 ml/min. The challenge was to quickly adjust the flow through the ozone mass flow controller for large differences between the measured and the desired concentrations while making minor adjustments when those differences were small.

Also, the ozone monitor can only perform a measurement and produce a reading every 10 s. In addition, the system uses an ozone concentration decision threshold of ±5 ppb, meaning if the difference between the measured and desired ozone concentrations is within 5 ppb, then the system does not attempt to adjust the ozone flow rate. Finally, because of the slow system dynamics due to dead time and lag, the control program only attempts to adjust the system every 30 s.

Initially, a simple set of conditional logic statements was used to adjust the ozone flow rate. As the system design matured, the number of conditional statements grew in an attempt to properly adjust the ozone flow rate. Eventually, the decision tree grew too large to be comfortably maintained, and it was replaced with a control algorithm.

An analysis of the decision tree, along with some testing of the coefficients, produced the following third-order equation:

Ozone flow rate $\text{adjustment} = -0.000\,02x^3 - 0.015x$, where $x = \text{actual ozone concentration} - \text{desired}$.

When x is small, the cubed term effectively drops out due to the small coefficient and allows for minute adjustments in the ozone delivery. Conversely, when x is large, the cube term dominates the equation and allows for large adjustments to the ozone mass flow controller. The results of the equation are bounded to prevent adjustments that are beyond the capabilities of the system or that would otherwise overwhelm it.

This equation only deals with the current ozone reading without regard to previous readings or the rate of change. Therefore, the system uses a variation of a basic proportional control algorithm. As the system design changes to incorporate more features and encompass additional reactants, the control equation above may be replaced by a more traditional proportional-integral-derivative (PID) control algorithm, provided it can produce marked control improvements due to the slow ozone measurement times and generally slow system dynamics.

Prior to performing an experiment, the system incorporates a 30 min warmup period. This allows the electronics, sensors, and mass flow controllers to thermally equilibrate and stabilize and allows the ozone concentration to be properly adjusted. During this warmup period, the FLEC air flow is shunted to the exhaust instead of allowed to flow through the FLEC device. When the experiment begins, the air flow is routed directly to the FLEC at the preset flow rate and conditions.

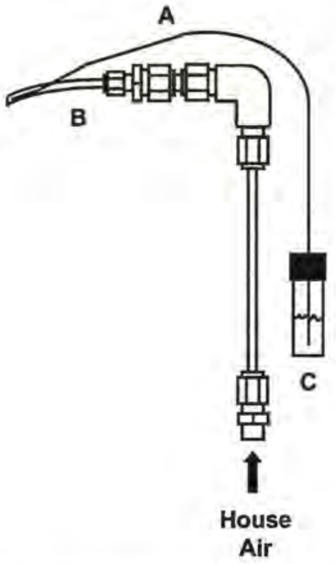

FIG. 2. Diagram of the aerosol spray device: (A) 0.53 mm i.d. fused silica capillary, (B) 1/8 in. o.d. Teflon tubing, and (C) 4 ml Amber glass vial containing α-terpineol solution

III. EXPERIMENTS

A. Chemicals and sample preparation

α-terpineol (90% Tech grade), O-(2,3,4,5,6-pentafluorbenzyl)hydroxylamine hydrochloride (PFBHA) (98+%), and acetonitrile (ACN) (≥99.93%) were purchased from Sigma Aldrich (St. Louis, MO). Methanol high performance liquid chromatography (HPLC grade) was purchased from Fisher Scientific (Pittsburgh, PA). Vinyl floor tiles that are currently used in the NIOSH facility (Morgantown, WV) were purchased from a local building supply center.

α-terpineol solutions (50 μl in 3 ml of methanol) were made in 4 ml amber glass vials and then sprayed on vinyl floor tiles (urethane finish side up) for each of the experiments below. Solutions were sprayed using a custom aerosol spray device (Fig. 2). Facility air was passed through two Drierite columns, one containing only eight mesh Drierite, the other containing both Drierite and molecular sieves. The air then flowed through a 5 in. long, $\frac{1}{4}$ in. outside dimeter (o.d.) stainless steel tube with $\frac{1}{4}$ in. Swagelok tube fittings. The output of the spray device consists of a 2 in. long, $\frac{1}{8}$ m. o.d. Teflon tube in which a 0.53 mm inside dimeter (i.d.) Siltek deactivated guard column has been threaded and is positioned approximately 0.5 cm from the end. The other end of the column is connected through a septum to a 4 ml amber glass vial which contains the α-terpineol solution to be sprayed on the tile. The solution can be sprayed on the tile in a fine mist based on the Bernoulli principle.[20]

Before application of the α-terpineol solution, the vinyl tiles were aerated to remove any gaseous emissions. New vinyl tiles were placed in a 10 l Teflon chamber filled with ultrahigh purity nitrogen (UHP N_2) and left overnight. The Teflon chamber was then emptied and allowed to refill and vent using UHP N_2 at 600 ml/min for approximately 6 h. After 6 h, the chamber was pressurized again with UHP N_2 and left overnight for experiments the next day. Before beginning an experiment, the chamber was again filled and vented at 600 ml/min for 45 min. This "ventilated" tile was then subjected to several background experiments where air only was flowing through the FLEC. These experiments showed that no emission products were observed after ventilation, compared to new "nonventilated" tiles where air only was present. Immediately following the ventilation step, the tile was sprayed and placed under the FLEC.

B. α-terpineol+air on vinyl flooring tile

For the α-terpineol/air experiment, the FACS was initialized using the following parameters: the reactant concentration (i.e., O_3) was set to zero, the relative humidity was set to 50%, and the flow rate through FLEC was set to 300 ml/min. After the 30 min warmup period, the α-terpineol sprayed tile was placed under the FLEC to start sample collection.

C. α-terpineol+O_3 on vinyl flooring tile

In this experiment, the FACS was initialized using similar parameters as above, except for the reactant concentration (O_3) which was set to 100 ppb. Again, ozone was generated in a Teflon chamber to a concentration of 45–50 ppm. The ozone/air mix was then regulated to 100 ppb for the air flow through the FLEC, as stated above.

D. Sample and data collection

Emissions from α-terpineol reactions were collected in a 50 ml glass impinger (p/n 652650-2440, Kontes, Vineland, NJ) connected to the output of the FLEC using $\frac{1}{4}$ in. o.d. Teflon tubing. To the impinger, 36 ml of HPLC grade methanol was added. Output air from the FLEC at 300 ml/min was bubbled through the impinger for 12 h with no effort to prevent methanol evaporation during sample collection. At the end of the 12 h, another impinger base filled with 36 ml of methanol was quickly inserted so as to minimize the interruption to flow in the system. This process was repeated until 72 h of total sampling was obtained for a total of six samples.

At the end of each 12 h sampling, the solution left in the impinger (~3 ml) was placed into 4 ml amber vials. To identify reaction products (i.e., aldehydes, ketones, and dicarbonyls), 200 μl of PFBHA (20 mM in ACN) was added to each of the six vials. PFBHA derivatizes products with these carbonyl substructures to oxime compounds to facilitate detection by gas chromatography/mass spectrometry.[21,22] All PFBHA vials were left overnight to allow for reaction to go to completion.

The following day, the six vials were blown down to complete dryness using ultrahigh purity nitrogen then reconstituted in 100 μl of methanol. All samples were then analyzed using a Varian (Palo Alto, CA) 3800/Saturn 2000 gas chromatography/mass spectrometry (GC/MS) system operated in the electron impact (EI) mode. Compound separation was achieved by a J&W Scientific (Folsom, CA) DB-5MS (0.32 mm i.d., 30 m leugth, 1 μm film thickness) column and the following GC oven parameters: 60 °C for 1 min, then 20 °C $\min^{-1}$ to 170 °C, then 3 °C $\min^{-1}$ to 280 °C and held for 5 min. 1 μl of each sample was injected in the splitless mode, and the GC injector was returned to the split mode 1 min after sample injection, with the following injector temperature parameters: 60 °C for 1 min. then 180 °C $\min^{-1}$ to 250 °C and held to the end of the chromatographic run. The Saturn 2000 ion trap mass spectrometer was tuned using perfluorotributylamine (FC-43). Full-scan EI ionization spectra were collected from m/z 40-650.

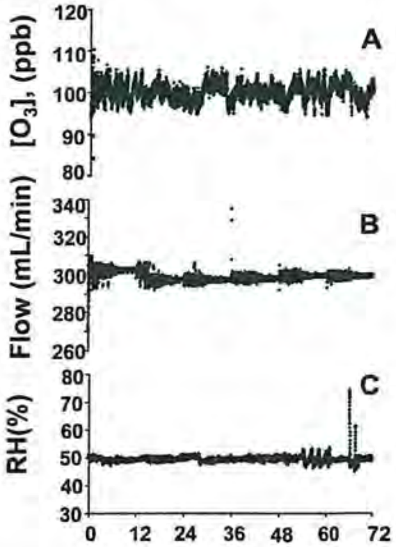

FIG. 3. Stability profiles for the α-terpineol+O_3 experiment over 72 h: (A) ozone concentration, (B) flow rate through FLEC device, and (C) relative humidity flowing through FLEC. Variations in B are due to switching sampling impinger at 12 h intervals. Variations in C are likely due to condensed droplet formation on the final humidity sensor.

IV. RESULTS AND DISCUSSION

A. Stability of FACS

One of the key features of the FACS is the ability to record all data from temperature/humidity sensors, mass flow controllers, and ozone monitor at intervals up to once every 10 s for the lifetime of the experiment. This allows for observation of any fluctuations that may have occurred and the ability to assess the source. Figure 3 shows the stability profiles obtained for the α-terpineol/O_3 experiment. The stability profile for the ozone concentration through the FLEC over 72 h is shown in Fig. 3(a). Ozone concentration was observed to be stable at 100 ppb over the 72 h sampling period.

Figure 3(b) shows the flow rate of the air/O_3 mixture flowing through the FLEC at 300 ml/min. The flow rate is very stable, except for the oscillations that begin and repeat every 12 h. This is due to changing of the impingers during sampling. There is a large spike observed at 36 h which is due to one of these changes. However, the system recognized this fluctuation and restabilized with 15 min.

Figure 3(c) shows the relative humidity of the air/O_3 mixture before entering the FLEC. The relative humidity is set at 50% and is shown to be stable throughout the experiment. However, at approximately 66 h it was noticed that the humidity spiked to 75%, and again at 68 h to 60%. It is believed that a condensed droplet that formed in the mixing chamber flowed through the air line and collided with the final humidity sensor, creating what the system interpreted as a sharp increase in humidity. Based on this fluctuation, the system adjusted and restabilized within 7.5 min. In order to prevent this from occurring in future experiments, a condensation trap (p/n 8762-20, Ace Glass Inc., Vineland, NJ) has been added between the humidity tank and the humid air temperature and humidity sensor unit.

The experiment detailed above is one of several experiments that have been performed using this system. As stated previously, the system uses a decision threshold of ±5 ppb when determining if the ozone concentration is out of range. Data gathered from eight experiments at 100 pbb, with a combined elapsed time of approximately 339 h, provide a pooled standard deviation of 1.65 ppb and a 95% tolerance range of 3.3 ppb. The humidity decision threshold is ±3%. Data gathered from 17 experiments at 50% relative humidity, for a combined elapsed time of approximately 664 h, provide a pooled standard deviation of 1.38% relative humidity and a 95% tolerance range of 2.77%. The threshold for the flow rate through the FLEC is ±6 ml/min. Data gathered from 14 experiments at 300 ml/min, for a combined elapsed time of approximately 548 h, provide a pooled standard deviation of 3.02 ml/min and a 95% tolerance range of 6.03 ml/min.

Overall, these stability profiles indicate that the system is responsive to small fluctuations that occur. In most cases, the system recognizes and reestablishes system set points in less than 15 min. Over a 72 h sampling period, this readjustment time is 0.35% of the total sampling time. A nonfeedback system could possibly propagate a system parameter drift leading to erroneous results.

B. Reactions of α-terpineol with air or O_3 on vinyl tile

PFBHA-derivatized products of the reactions of α-terpineol with air only and an air/O_3 mixture on a vinyl flooring tile are shown in Fig. 4. The chromatograms show a segment of the total chromatograms obtained from these analyses.

α-terpineol/air only reactions show no or little formation of products formed in this section of the chromatogram as indicated by the absence of peaks. A number of chromatographic peaks were observed as products from the α-terpineol/O_3 reaction. From the chromatographic section seen in Fig. 4, peaks were observed at retention times of 20.0, 20.2, 21.2, 21.9, and 22.2 min. Derivatization of nonsymmetric carbonyls using PFBHA typically resulted in multiple chromatographic peaks due to geometric isomers of the oximes. Identification of multiple peaks of the same oxime compound is relatively simple since the mass spectra for each chromatographic peak of a particular oxime are almost identical. The PFBHA-oximes observed at the chromatographic retention times of 20.2 and 21.1 min are the same. Additionally, the peaks at the chromatographic retention times of 21.9 and 22.2 min are also the same. The identification of these reaction products is currently being determined and will be described in greater detail in a future publication.

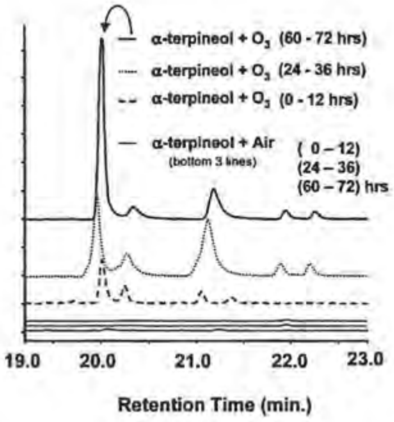

FIG. 4. Chromatograms for the α-terpineol+air (only) and α-terpineol $+O_3$ reactions for 0–12, 24–36, and 60–72 h and sampling intervals. All peaks are plotted on the same scale but are offset for clarity.

The peak at 20.0 min was observed to grow over time. Furthermore, it shows that these reactions keep occurring even after 72 h. Peaks at 20.2 and 21.2 min have an unusual emission profile in that at 36 h of sampling these peaks are produced by an emission spike and then decay. This indicates that the surface reaction chemistry that occurs is not a simple exponential decay, but a complex, dynamic process which requires further investigation.

In summary, this automated gas-phase reactant [ozone, hydroxyl radical (OH), or nitrate radical (NO_3)] delivery system provides exposure to surfaces in a highly controlled and reproducible manner. The system's ability to control and record reactant concentration, humidity, gas flow rate, and system performance data collection is important to investigate the complex chemistry of surfaces. Additionally, the integration of the field and laboratory emission cell (FLEC) allows for direct doping to a variety of "soiled" and "clean" surfaces such as vinyl, glass, linoleum, carpet, and dry wall board materials. Furthermore, the FLEC also affords the ability to collect emissions from reactions that occur at the surface for analysis and identification. The knowledge of surface chemistry gained by using this developed reactant delivery system will be useful in the fields of both materials science and indoor chemistry.

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