3.1 IMPROVED INSTRUMENTATION FOR NEAR-REAL-TIME MEASUREMENT OF REACTIVE HYDROCARBONS, NO₂, AND PEROXYACYL NITRATES

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1. INTRODUCTION

The measurement of reactive hydrocarbons and associated nitrogen oxides, NO₂, and peroxyacetyl nitrates (PANs) is of key importance to unraveling the complex chemistries involved in daytime photochemical oxidant formation and nighttime chemistry driven by the nitrate radical. Recent work has demonstrated that chemiluminescent reactions of ozone with hydrocarbons (and the temperature dependence of the reactions) can be used as a means of detecting a wide variety of organic compounds in the gas phase with sensitivity comparable to or better than that of the conventional flame ionization detection method (Marley and Gaffney, 1998).

We have implemented a new design and built a new instrument to evaluate this approach for the monitoring of alkenes. This instrument makes use of a computer-controlled photon-counting system with a reaction chamber operated at room temperature. Signals are compared to those for an ethene standard to estimate relative reactivity. The instrument is described in detail here, along with a new version of a luminol-based chemiluminescence detection system with fast gas chromatography for measurement of NO₂ and PANs.

The photon-counting system, the reaction chamber, and the luminol detection system have been combined on one instrument rack for field use on both ground-based and aircraft platforms. Data presented show the response times of the instruments and indicate applications for examining reactive hydrocarbon emissions from both vegetation and anthropogenic sources. In addition, the luminol chemiluminescence instrument was field tested, and the data obtained are compared with data from a commercial NOₓ analyzer. Preliminary results demonstrating the potential use of this instrumentation for rapid measurement of key tropospheric trace species are presented and discussed.

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2. EXPERIMENTAL METHODS

2.1. The Real-Time Hydrocarbon Monitor

The reaction rate of ozone and a hydrocarbon depends on the temperature and the class of hydrocarbon. Alkenes react readily at low temperatures, oxygenated hydrocarbons require higher temperatures, and alkanes require temperatures of over 150°C for chemiluminescent reaction with ozone (Marley and Gaffney, 1998). A system has been designed and constructed that uses the temperature dependence of the chemiluminescent hydrocarbon-ozone reaction specifically for field measurements. The initial studies presented here focused on the rapid measurement of alkenes (olefins) by operating the instrument at near ambient temperature.

Air was drawn into the system and flow was controlled by a Cole Parmer 32708-26 mass flow controller. Sample air was introduced into the stainless steel reaction cell. Here it was mixed into a flow of oxygen and ozone in front of a quartz window, and the chemiluminescent reaction took place. The ozone generator used for this system was a Matheson OZ-Gen1. The oxygen flow was maintained at 430 cm³/min by using a mass flow controller. The ozone concentration of 6% was determined by calorimetric analysis with a Beckman UV-visible spectrometer.

The light from the ozone reaction was collected by a Hamamatsu HC135 photomultiplier tube (PMT) placed on the other side of the quartz window. To ensure that only the light from the chemiluminescent reaction was measured, the reaction cell and PMT were connected in a light-tight enclosure, and the entire system was housed in a steel junction box 14 in. x 12 in. x 6 in. The HC135 PMT RS232 output was collected by a personal computer (PC) with the EVAL40.BAS program supplied by Hamamatsu. The HC135 PMT uses photon counting and does not require cooling below room temperature. The HC135 can operate with up to 1,200 V on the tube.

To vary the temperature in the reaction cell, an Omegalux rope heater can be attached to the inlet tubing, and a Chromalox cartridge heater can be placed in the reaction cell. Such heaters are controlled by an Omega CN5000A temperature controller. For this study, the heaters were not required, because only alkenes were analyzed, and...
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high temperatures could have led to interference from other hydrocarbons. All tubing and the reaction cell were constructed of stainless steel to avoid corrosion by ozone. A KNF Neuberger NC35 two-stage pump provided the vacuum for the reaction cell. A vacuum gauge and a valve in the outlet line allowed the pressure in the reaction cell to be varied between 5 and 25 in. of mercury.

The hydrocarbons were introduced into the system in two ways: a pulse mode and a continuous sampling mode. In pulse mode, a syringe was used to inject a known volume of the alkene of interest into the inlet air line. For alkenes that are liquid at room temperature, the sample was taken from the headspace of a sealed beaker containing the alkene, and the vapor pressure was used to calculate the response per microgram. The continuous method used a 10.0-ppm ethylene standard obtained from Matheson gas products. Dilution air was mixed with the ethylene standard, and both flows were monitored by Alicat Scientific flow meters.

2.2. The Luminol Instrument

The chemiluminescent reaction between luminol and NO$_2$ has been used as the basis for many instruments, both for ground-based measurements (Wendel et al., 1983) and in aircraft operations (Kelly et al., 1990). Most of these instruments suffered from the sensitivity of the luminol reaction to both NO$_2$ and PANs. In a first-generation instrument, we demonstrated in the laboratory that combining fast capillary column gas chromatography with luminol detection could achieve specific, relatively fast (less than 1 min) analyses of NO$_2$ and PANs up and including the C-4 species (Gaffney et al., 1998). We recently reported using this reaction in conjunction with a gas chromatography column to determine NO$_2$ and PAN rapidly in an aircraft study (Gaffney et al., 1999). Experience in that study showed that the weight and size of the first-generation fast gas chromatography-luminol system needed to be reduced to allow the system to be mounted more readily in an aircraft or transported to a ground study site.

In our improved system, outside air was brought into the 2-cm$^3$ sample loop by using an Ametek MG-5P air sampler that weighs only 28 oz and has a battery pack to sustain operation for up to 8 hr if main power is lost. The inlet air flow was maintained at 100 cm$^3$/min by a Cole-Parmer 32708-26 mass flow controller. The sample air was injected once a minute, for 10 sec, into a 3-m-long DB1 gas chromatography column. Between injections, the column was flushed with 5% O$_2$ in He, flowing at 30 cm$^3$/min. The switching was performed by a Valco Instruments Co., Inc. (VICI), six-port valve controlled by a VICI digital valve sequencer programmer and a VICI two-position actuator control module. The oxygen in the carrier gas maintains the luminol chemistry at maximal sensitivity for the species of interest (Gaffney et al., 1998, 1999).

Beyond the gas chromatography column, the air sample passed through a modified Unisearch LMA3 reaction cell. The cell was modified in the second-generation system by filling the dead spaces with epoxy resin to reduce the dead volume, and the gas capillary column was coupled to the system by drilling a small hole at the top of the cell and inserting the capillary column. A Hamamatsu HC135 PMT was mounted to the window of the LMA3 reaction cell with a completely light tight connection. The Hamamatsu HC135 RS232 interface was connected to a PC, and data were obtained by using a modification of the EVAL40.BAS software supplied by Hamamatsu. Luminol solution, obtained from Scintrix, was pumped into and out of the cell with a Masterflex 77120-52 peristaltic pump that weighs 2 lb (0.91 kg), significantly less than the Rabbit peristaltic used pump previously.

The whole luminol system was mounted on two aluminum shelves measuring 10.5 in. by 19 in. The two shelves were mounted in a rack constructed of high-strength aluminum extrusions supplied by AMCO. The luminol chemiluminescence instrument was calibrated for NO$_2$ with a standard obtained from AGA Gas. A PAN standard was made by wet chemical synthesis and stored in n-tridecane (Gaffney et al., 1984).

3. RESULTS AND DISCUSSION

The sensitivity of the hydrocarbon monitor to pressure, ozone flow rate, and PMT voltage was examined as follows:

- The PMT voltage was set to 850 V to avoid dark currents at high PMT voltages.
- The ratio of the oxygen flow to sample air was kept at 1.0 to ensure that ozone would always be in excess.
- The pressure in the cell was maintained at a vacuum of 25 in. of mercury.

To verify that only alkenes could be detected, acetaldehyde, acetone, pentane, and toluene were injected with the reaction cell at room temperature. The output of all these runs showed no discernible difference from the background readings.

The eight alkenes tested with the pulse method were 1-butene, 2-butene, ethylene, isoprene, limonene, α-pinene, propene, and terpinene. The response curves are shown in Figure 1. The relative sensitivities show two trends. First, the response of the instrument decreased as the number of carbon atoms in the straight chain increased. The response of 2-butene was much higher than would otherwise be expected from this rule, because the double
Figure 1. Relative sensitivities of alkenes, defined as the ratio of the response of the alkene divided by the ethylene response.

- Bond is not located on the end of the carbon chain.
- Second, increasing the number of double bonds in the molecule increases the relative sensitivity of the detector. Isoprene is the exception to this rule, probably because isoprene is a substituted 1,3-butadiene and is conjugated. These results are consistent with the reactivities of ozone with these olefins. For example, 1-olefins are known to react at similar rates with ozone at room temperature because the reaction is primarily addition. 2-Butenes are more reactive to addition and are known to have a much higher reaction rate with ozone than do the 1-olefins. 1,3-Butadiene and isoprene are known to react more slowly with ozone than do other dienes because of conjugation effects that stabilize these two compounds toward ozone attack.

The hydrocarbon monitor was also run in continuous mode. The response to an increase in the concentration of ethylene was a linear increase in the number of photons detected by the PMT, as shown in Figure 2. The slope of the line is 275 counts/ppm, with the limit of detection at 0.25 ppm.

Figure 2. Continuous-mode operation of the hydrocarbon monitor. The instrument has a linear response to an increase in alkene concentration in the sample gas. Data shown are raw data, uncorrected for baseline signal before injection.

The hydrocarbon monitor was rack mounted beneath the luminol instrument. However, the lack of a portable ozone generator made a field test impractical at this time. We plan to field test this instrument at Argonne during the next year and are using an integrating sphere approach to design a new reaction cell allowing better light collection.

The second-generation instrument combining fast capillary gas chromatography with luminol chemiluminescence was run for two weeks in August 1999 in Elmer, New Jersey, as part of the Northeast Corridor Oxidant Study (NEOPS). As mentioned above this instrument will measure NO2 and PAN in less than 1 min. The field site was located at the Arthur P. Schalick High School in Elmer, New Jersey, 40 miles southeast of Philadelphia. The luminol instrument was located inside a fifth-wheel trailer parked next to an athletic field adjacent to a large cornfield. Air was sampled at the site from an inlet line attached to a tripod that also served as the mount for a UV-B monitor on the top of the trailer. This sampling line was 5 m above the ground. All sampling inlet lines were Teflon®.

A Columbia Scientific Instruments Corporation (CSI) series 1600 Mark III oxides of nitrogen analyzer was also run at the same site. This part of New Jersey is rural, but it is surrounded by many major metropolitan centers. Figure 3 shows data from the two instruments for the morning of August 10, 1999. The luminol instrument was running with 1-remin spacing between injections into the gas chromatography column. The output from the CSI instrument was collected by a computer every 10 sec and then minute averaged. Figure 3 shows the level of NO2 detected by each instrument. The two instruments agreed very well and showed the same behavior over the 12-hr run time. Just after midnight the levels fluctuated, probably because of the onset of the nocturnal boundary layer and

Instrument Comparison

Figure 3. Comparison of the CSI and luminol instruments during the NEOPS study. The luminol instrument is also sensitive to PAN, which appears as a second peak after the NO2.
associated jets. The increase in NO\textsubscript{2} in the early morning could reflect NO emission from the surrounding fields, followed by reaction with boundary layer ozone:

\[ \text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2 \]  

[1]

The study coincided with a severe drought in the region. After dawn the levels of NO\textsubscript{2} decreased dramatically as the photochemical production of ozone began and as the boundary layer height rose rapidly.

Figure 4 shows PAN values over the same time period on August 10, 1999. The PAN level behaves like the NO\textsubscript{2} level shown in Figure 3, with a large variation just after midnight and a slight increase and then a rapid decrease after dawn.

![PAN measured at Elmer, NJ 8/10/99](image)

Figure 4. PAN measured at Elmer, New Jersey, on the morning of August 10, 1999.

Clearly, rapid changes in the atmospheric concentrations of PAN and NO\textsubscript{X} species are associated with the establishment and breakup of the boundary layer, and the details of these changes would be lost without fast-response instruments. The coupling of NO\textsubscript{X} and hydrocarbon data with a knowledge of the underlying chemistry allows demonstration of the diurnal photochemical cycles, as well as inflows of pollutants from surrounding regions.

We obtained these data while wind fields were being determined at the site with SODAR and radio acoustic sounding system instruments operated by Argonne National Laboratory's boundary layer meteorology group, led by Dr. Richard Coulter. We are currently examining the results and will be attempting to model the data to determine NO fluxes during the evening at the site.

4. ACKNOWLEDGMENTS

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5. REFERENCES


