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CHEMILUMINESCENT DETECTION OF ORGANIC AIR POLLUTANTS

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Abstract. Chemiluminescent reactions can be used for specific and highly sensitive detection of a number of air pollutants. Among these are chemiluminescent reactions of ozone with NO or organics and reactions of luminol with a variety of oxidants. Reported here are studies exploring (a) the use of the temperature dependence of the chemiluminescent reactions of ozone with organic pollutants as a means of differentiating types of hydrocarbon classes and (b) the use of luminol techniques to monitor atmospheric concentrations of nitrogen dioxide (NO_2) and organic oxidants, specifically peroxyacyl nitrates (PANs). Coupling gas chromatography to the chemiluminescent detectors allows the measurement of individual species at very low concentrations.

INTRODUCTION

Chemiluminescence techniques lend themselves readily to real-time monitoring of atmospheric species. These techniques are selective because of the relatively small number of compound classes that can produce a chemiluminescent signal upon reaction. These are also very sensitive methods, because they examine a signal above a dark cell background that is theoretically zero.

One of the chemiluminescent reactions most commonly used for atmospheric monitoring is the reaction of ozone with NO, which produces electronically excited NO_2. This excited species emits a broad band of light that begins at about 660 nm and peaks at 1.3 micron. The chemiluminescent emission can be monitored to determine either ozone or NO concentrations in the troposphere.

Another commonly used chemiluminescent reaction is the reaction of ozone with ethylene:

$$CH{=}CH_2 + O_3 \text{ ---> } H_2CO^* + OH^* \qquad (1)$$

The products, electronically excited formaldehyde and vibrationally excited OH, emit a luminescent signal at 380-550 nm and 550-800 nm, respectively. This reaction has been used to monitor ozone in the troposphere, but it could just as easily be used to monitor ethylene concentrations. Since many other olefins also react with ozone at room temperature, the reaction could be used to monitor reactive alkenes in the air.

Another useful group of chemiluminescent reactions is the oxidation of luminol (5-amino-2,3-dihydrophthalazine-1,4-dione) with a variety of oxidants (nitrogen dioxide, hydrogen peroxide, etc.) in basic aqueous solution. The resulting emission peaks at 425 nm. This system has been used to measure concentrations of NO_2 in environmental studies (1).

In the simplest terms, the intensity of a chemiluminescent signal is directly proportional to the concentration of the reacting species (2). The intensity of the signal, I, is equal to the rate of reaction, k, times the concentrations of the reactants, [A] and [B]:

$$I = k[A][B] \tag{2}$$

However, a number of experimental parameters control the signal in a gas-phase chemiluminescent analyzer. These parameters are chamber volume, reagent flow rate and mole fraction, sample flow rate, pump outflow, chamber pressure, and temperature (3). In addition, the rate constants for the production and destruction of emitting species will control the overall sensitivity.

In the reaction between ozone and organics, the more reactive hydrocarbons (olefins) will give a chemiluminescent signal at room temperature, while the less reactive hydrocarbons (alkenes) will react only at elevated temperatures. The studies reported here investigated the utility of controlling the temperature of the reaction chamber to determine the atmospheric reactivity of organic pollutants and thereby differentiate between types of hydrocarbon classes.

In an analogous study, the reaction of luminol with atmospheric oxidants was used to determine nitrogen dioxide (NO_2) and organic oxidants, specifically peroxyacyl nitrates (PANs). Coupling both chemiluminescent detectors to gas chromatographic columns allowed specific measurements of individual species at very low (less than parts per billion) levels.

REACTIVE HYDROCARBON MONITOR

The ozone chemiluminescent reaction system is shown in Figure 1. The cell

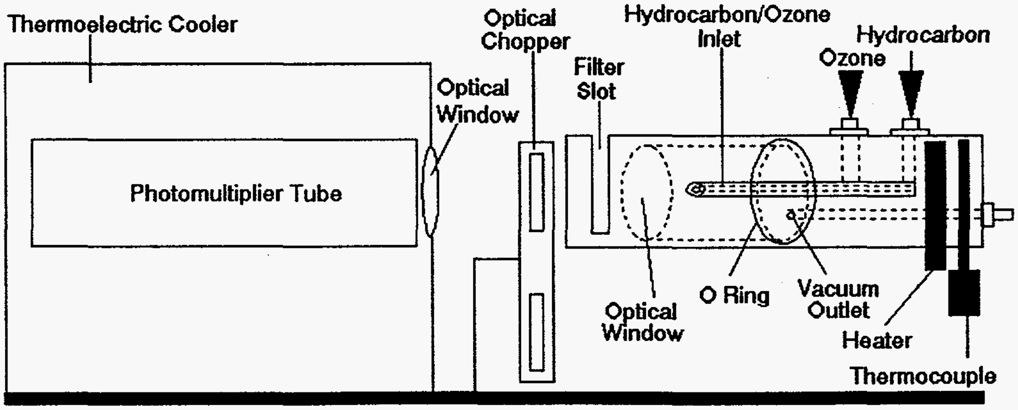

FIGURE 1. Diagram of the ozone chemiluminescent reaction chamber with optical chopper and photomultiplier.

design is similar to those used for the reaction of ozone with NO in commercial ly available NO monitors. The cell was modified for temperature control and to maximize the chemiluminescent signal. The signal was detected with a large-area, head-on, cooled photomultiplier tube (Hamamatsu R1332). The spectral response of this tube peaked at 400-450 nm at a sensitivity of 95 mA/W. Light detection was achieved by using optical chopping coupled to lock-in amplification of the signal (Oriel Merlin).

Three hydrocarbons of varying reactivity were chosen for preliminary studies of the chemiluminescent temperature dependence. The results are shown in Figure 2. The chemiluminescence signal from the most reactive hydrocarbon, propylene, showed little temperature dependence, while both toluene and hexane gave a chemiluminescent signal only at higher temperatures. These results demonstrated that varying the temperature of the reaction chamber allows organics with different reactivities to be detected. At room temperature, the reactive olefins can be detected; at an intermediate temperature (110°C) both olifins and aromatics can be determined; and at high temperatures (<140°C), all organics should react, and the detector response will be a measure of total non-methane hydrocarbons in the atmosphere.

The most commonly used detector for total hydrocarbons is the flame ionization detector (FID). Coupling the ozone chemiluminescent detector (OCD) to a gas chromatograph (Shimadzu Mini 2) equipped with a capillary column allowed the responses of the two detectors to be compared directly. Table 1 gives this comparison for 27 hydrocarbons representing a variety of reactivities. Sensitivities were determined from the slope of the analytical linear correlation between concentration and signal response for each detector. Detection limits were calculated from the equation

$$3(s_y/S) = \text{detection limit}, \qquad (3)$$

where s_y is the standard deviation of the intercept of the analytical linear correlation, and S is the sensitivity.

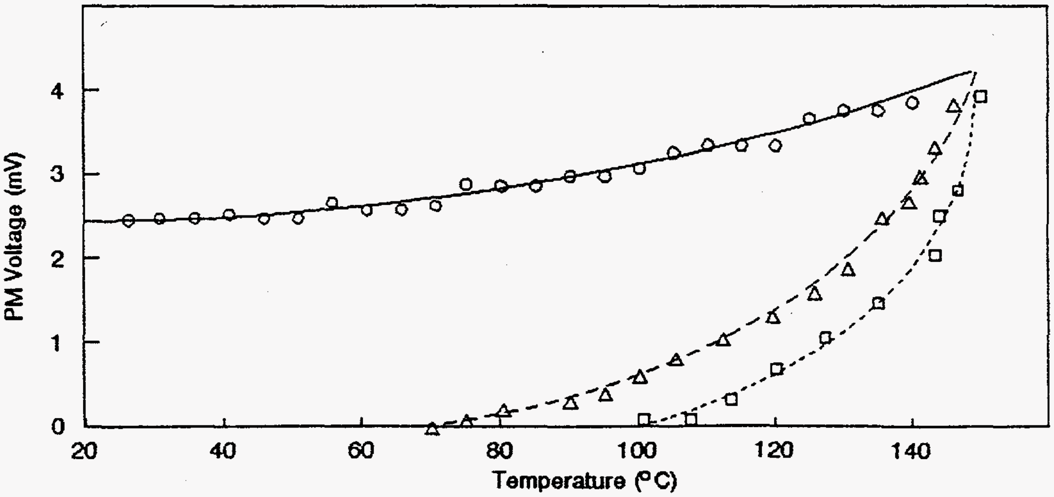

FIGURE 2. Chemiluminescent signal of propylene (○), toluene (△), and hexane (□) as a function of temperature.

TABLE 1. Sensitivity (counts/ug) and detection limits (ug) for the flame ionization detector (FID) and the ozone chemiluminescence detector (OCD) at 170 °C.

	FID		CLD	
	SENSITIVITY	DETECTION LIMITS	SENSITIVITY	DETECTION LIMITS
PENTANE	2.46×10^{4}	12.3	2.00×10^{5}	8.2
2-METHYLBUTANE	1.84×10^{4}	12.7	1.11×10^{5}	14.1
N-HEXANE	4.53×10^{4}	6.6	7.86×10^{5}	4.9
CYCLOHEXANE	4.96×10^{4}	5.9	3.73×10^{5}	2.6
HEPTANE	6.26×10^{4}	2.5	8.77×10^{5}	3.2
OCTANE	8.53×10^{4}	3.4	1.85×10^{6}	2.2
2,2,4-TRIMETHYLPENTANE	4.28×10^{4}	8.3	3.06×10^{5}	4.2
ETHYLENE	1.35×10^{4}	16.4	1.43×10^{6}	7.3
PENTENE	1.62×10^{4}	11.2	1.56×10^{6}	11.4
ISOPRENE	1.91×10^{4}	8.4	3.36×10^{6}	9.3
LIMONENE	4.04×10^{4}	0.24	3.21×10^{7}	0.27
a-PINENE	4.36×10^{4}	0.37	3.97×10^{7}	0.25
TERPINENE	9.45×10^{4}	0.11	8.66×10^{7}	0.10
BENZENE	5.38×10^{4}	3.6	1.03×10^{6}	3.4
TOLUENE	1.03×10^{5}	3.5	3.34×10^{6}	1.7
o-XYLENE	7.69×10^{5}	0.52	7.44×10^{6}	0.69
MESITYLENE	8.03×10^{4}	0.37	1.09×10^{7}	0.65
ACETALDEHYDE	1.32×10^{4}	19.9	1.28×10^{6}	5.2
PROPIONALDEHYDE	3.01×10^{4}	5.2	2.27×10^{6}	3.2
BENZALDEHYDE	1.12×10^{5}	0.72	4.13×10^{6}	1.6
ACETONE	2.16×10^{4}	12.4	1.56×10^{5}	12.4
METHYL ISOBUTYL KETONE	5.05×10^{4}	2.2	8.64×10^{5}	3.3
t-BUTYLMETHYL ETHER	3.54×10^{4}	5.1	5.24×10^{5}	5.2
METHANOL	1.54×10^{4}	2.2	2.03×10^{6}	2.5
ETHANOL	3.16×10^{4}	1.3	1.41×10^{6}	0.69
2-PROPANOL	2.61×10^{4}	1.1	1.04×10^{6}	0.73
BUTANOL	1.94×10^{5}	0.29	1.97×10^{6}	0.47

The responses of the OCD detection system, operated at 170°C, correlated linearly with the FID responses, but sensitivities were 10 to 100 times higher than those of the FID. Detection limits remain similar for both detectors, be cause in this study the photomultiplier was operated at room temperature. Cooling the tube should lead to an improvement of 10-100 fold in detection limits.

ORGANIC OXIDANT MONITOR

A Luminox chemiluminescent detection system (Scintrex LMA-3) was modified and coupled to a unheated capillary gas chromatographic column (3 m DB-1), an automated injection valve, and a 2 cc sample loop. This instrument makes use of a gas-liquid surface reaction cell that allows the effluent from the gas chromatograph to react with the luminol in basic aqueous solution. The chemiluminescent reaction was monitored by using an IP-128 side-on photomultiplier tube operated at of 800 volts. The DC signal from the photomultiplier tube was sent directly to a recording integrator (Hewlett-Packard Model 3395) and measured as a function of time as in standard gas chromatographic analysis practice. The instrument is sensitive to bboth NO_2 as well as peroxyacyl nitrates. Calibrations were made on NO_2 with a 100-ppbV certified gas standard (AGA), as well as on synthesized peroxyacetyl nitrate (PAN) samples by using diffusion tubes (4). Samples of peroxypropionyl nitrate (PPN) and peroxybutyrl nitrate (PBN) were synthesized by the appropriate modification of the synthetic procedure. These were used to optimize separation and analysis times and to determine relative retention times of the peroxyacyl nitrates and NO_2.

Figure 3 shows the chemiluminescent signal observed for calibration standards for NO_2 and PAN. The calibration factors for PAN were determined by using a conventional ozone chemiluminescence detection system for oxides of nitrogen

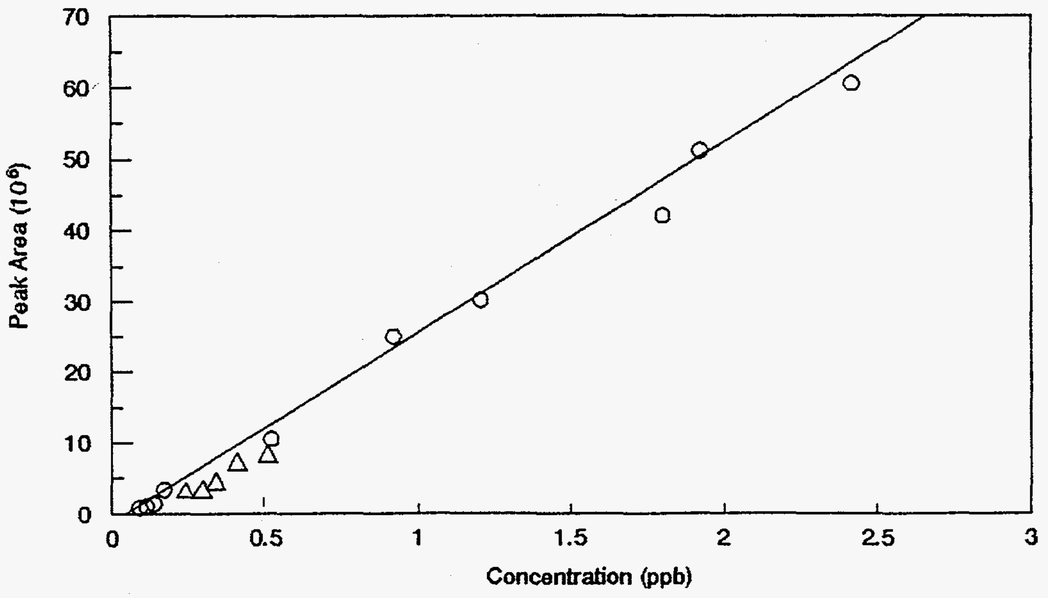

FIGURE 3. Chemiluminescent detection of NO_2 (○) and PAN (△).

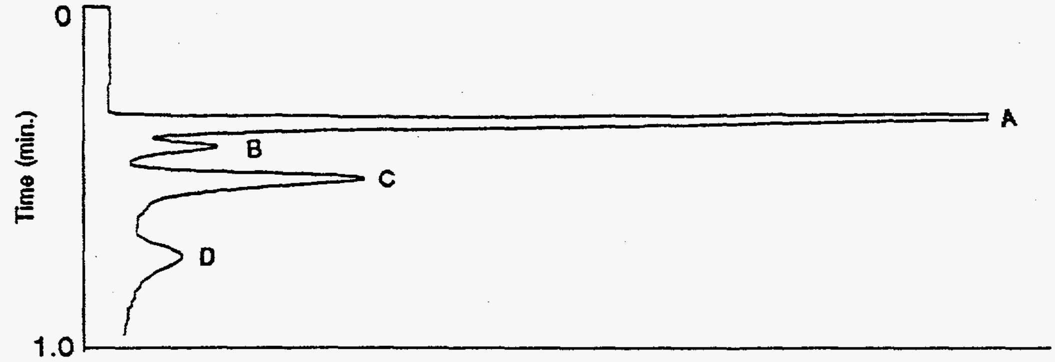

FIGURE 4. Chemiluminescent signal of NO_2 (A), PAN (B), PPN (C) and PBN (D).

to compare the PAN levels from the diffusion tube directly with the NO_2 gas standard. The chemiluminescence signals for PAN and NO_2 in the ozone chemiluminescence analyzer for nitrogen oxides are known to be the same. Gas dilu tion was used to obtain measurements at lower concentration, levels by assuming a linear dilution with diluent gas. Sensitivities calculated from the data in Figure 3 were found to be 2.7×10^7 and 1.8×10^7 counts/ppb for NO_2 and PAN, respectively. Detection limits calculated with equation (3) were determined to be 0.17 ppb and 0.10 ppb for NO_2 and PAN, respectively.

Figure 4 shows a typical chromatogram for NO_2 and three peroxyacyl nitrate derivatives. All can be separated from an atmospheric sample in less than one minute with detection limits in the parts-per-trillion range. This capability provides a near real-time-method of analysis for these atmospheric oxidants.

CONCLUSIONS

Chemiluminescent methods provide a rapid, sensitive method of detection for organics in the atmosphere. The reactive hydrocarbon monitor based on the temperature dependence of the ozone chemiluminescent reaction provides useful information regarding the atmospheric reactivities of organic pollutants in a real-time framework. This capability can be used to characterize gaseous emissions from mobile and stationary sources. Use of the temperature dependence to separate reactive classes of compounds provides more information than does FID alone without the time and expense required for the more complicated methodology.

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