1.6 NEW IMPROVED FAST GC-LUMINOL INSTRUMENT FOR PAN AND NITROGEN DIOXIDE MEASUREMENTS

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1. INTRODUCTION

The interaction of hydrocarbons and oxides of nitrogen in sunlight to produce "photochemical smog" has been well studied over the years. In the past, the workhorse for the measurement of NO_2 and NO was the chemiluminescent reaction with ozone (Finlayson-Pitts and Pitts 2000). This method has detection limits of approximately 0.5 ppb for most commercial instruments, but it cannot detect NO_2 directly. The instrument detects NO and uses hot catalytic surfaces to decompose all other nitrogen oxides (including NO_2) to NO for detection. Thus, nitrogen-containing species such as nitric acid and peroxyacetyl nitrate are also detected. A variation of this instrumentation has been developed for the specific detection of NO_2 by using a high-pressure xenon lamp coupled with dielectric filters to selectively photolyze NO_2 without decomposing other nitrogen-containing species (Fehsenfeld et al. 1990). The only reported interferences with the photolytic technique are nitrous acid (HONO), nitrate radical (NO_3) and peroxy nitric acid (HO_2NO_2), all of which are expected to be at very low concentrations during daytime hours.

The main problem with this method is inherent difficulty in detecting the emitting species (excited NO_2). This species emits over a broad region beginning at approximately 660 nm, with a maximum at 1,270 nm; thus, a red-shifted photomultiplier is required for detection.

The use of luminol for direct chemiluminescent detection of NO_2 was demonstrated to have greater inherent sensitivity than the indirect ozone chemiluminescence detection, with reported detection limits of 30 ppt (Wendel et al. 1983). The luminol detection system uses a gas-liquid reaction leading to light emission with a maximum at approximately 425 nm. This emission, at the maximum sensitivity for most photomultiplier tubes, is responsible for the increased detection sensitivities. The biggest problem with the luminol method for direct measurement of NO_2 has been interference from other soluble oxidants, particularly peroxyacyl nitrates (PANs).

Along with NO_2, PANs are important trace gas species associated with photochemical air pollution. The PANs are a class of organic oxidants having the general chemical structure RC=OO-O-NO_2. Peroxyacetyl nitrate (PAN) is the primary peroxyacyl nitrate produced during the oxidation of hydrocarbons in the presence of NO and NO_2. PAN is in thermal equilibrium with the peroxyacetyl radical (RC=O-OO·) and NO_2 (Gaffney et al. 1989). Because PAN is a trapped peroxy radical, it is an important indicator species of the photochemical age of an air parcel, as well as a means for long-range transport of NO_2 leading to the regional formation of ozone and other oxidants. Typically, PAN is measured by using a gas chromatograph (GC) with electron capture detection (ECD). Once automated, this method has been shown to be reliable and quite sensitive, allowing PAN to be measured in the troposphere at levels of low parts per trillion. Unfortunately, a number of other atmospheric gases (e.g., O_2, Freons, H_2O) also have strong ECD signals or act as inferences and limit the speed with which the analysis can be completed. Typically measurements are obtained at 15- to 30-min resolution. Currently, the shortest ECD analysis time for PAN is approximately 5 min (Williams et al. 2000).

The reaction of PAN with luminol, demonstrated in the late 1980s, is the basis for a commercial instrument (Scintrex, LMA-4) that has demonstrated the potential of the technique and has achieved detection of NO_2 and PAN with 5-min time resolution. Indeed, a method was reported for measuring PAN and NO_2 by using a packed-column GC coupled to a luminol detector (Blanchard et al. 1990). We recently revisited this approach and applied fast capillary gas chromatography to accomplish the analysis of NO_2 and PAN, along with

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the analogues peroxy propionyl nitrate (PPN) and peroxybutyryl nitrate (PBN), with an analysis time of less than 1 min (Gaffney et al. 1998). We have also used this approach for aircraft-based measurements of NO_2 and PAN (Gaffney et al. 1999).

The simultaneous measurement of NO_2 and PAN enables determination of levels of the peroxyacetyl radical in the air, as PAN is in thermal equilibrium with the peroxyacetyl radical and NO_2 (Gaffney et al. 2002). Past measurements of PAN and NO_2 with this method were made in Centerton, New Jersey; Deer Park, Texas; and Phoenix, Arizona. We redesigned our previous instrument to make it smaller and lighter for easy deployment on aircraft platforms and modified the software to allow real-time data integration and synchronous operation of sample injection and data collection. In this work, we review the method and highlight the modifications made to the instrument, including a new cell design that enables easy monitoring of luminol detection with a Hamamatsu HC-135 photon counting system. We present data taken onboard the National Oceanic and Atmospheric Administration (NOAA) Twin Otter in the recent Bay Region Atmospheric Chemistry Experiment (BRACE) in Tampa, Florida, in May 2002. The NO_2 concentrations measured by the fast GC-luminol technique are compared with simultaneous onboard measurements made by photolytic conversion of NO_2 to NO followed by ozone chemiluminescence.

2. INSTRUMENTAL DESIGN

The first-generation fast GC-luminol detection system for NO_2 and PAN was described in detail previously (Gaffney et al. 1998). The second-generation instrument is shown in Figure 1.

Figure 1. Fast GC-luminol instrument for the simultaneous detection of NO_2 and PAN.

We modified the first instrument by replacing the Unisearch (Scintrex) LMA-3 luminol detection system with a newly designed reaction cell and a Hamamatsu photon-counting detection module (HC-135). The reaction cell has a wick design similar to that of the commercial cell (Unisearch). However, our cell has been reconstructed to reduce dead volume and to deliver the effluent of the capillary column directly to the face of the wick. This increases sensitivity and reduces peak width, enabling shorter analysis times. An electronic sampling valve is used to collect a 5-cm^3 air sample and inject it onto a 30-ft-long DB-1 capillary GC column for separation of NO_2 and PAN. Synchronous control of the sample injection and data collection is accomplished with Labview 6.0 graphical programming software (National Instruments) operating in a Windows 2000 environment. This software package also allows for real-time integration of the chromatographic peaks and final storage of both the raw data and integrated values in spreadsheet format.

We added a smaller peristaltic pump and mass flow controllers to maintain flow rates in the system. Pure He is used as a carrier gas at flow rates of 60-80 cm^3 min^{-1}; with a 5-cm^3 sample loop, sufficient oxygen is present in the sample so that the He-O_2 mixture used previously is not required to achieve higher sensitivity. The second-generation instrument is now capable of 30-sec time resolution for NO_2 and PAN.

The instrument is contained in a 19-in. instrument case designed to fit in a standard instrument rack and weighs a total of 35.5 lb. Carrier gas is provided by a Matheson Mini Mat refillable gas cylinder attached to the back of the rack. The cylinder weighs less than 2 lb and measures 2.3 in. in diameter and 12.25 in. in length. It holds a total of 105 L of carrier gas, sufficient for approximately 20 hr of analysis time.

3. CALIBRATION

Figure 2 shows the results of a typical calibration of the fast GC-luminol instrument with a commercial NO_2 standard for 1-sec, 0.5-sec, and 0.25-sec integration times. The sensitivities obtained were 0.98×10^6, 1.0×10^6, and 1.0×10^6 for 1-, 0.5-, and 0.25-sec integrations, respectively. Similarly, correlations (r^2) were 0.99, 0.98, and 0.95, corresponding to detection limits of 15-20 ppt.

Calibration standards for PAN were made by using diffusion tubes containing PAN synthesized by the wet chemical method (Gaffney et al. 1984). Relative sensitivities were obtained by thermally decomposing PAN samples delivered by a diffusion tube and measuring the resulting NO_2. Figure 3 gives the results for thermal conversion of PAN to NO_2, followed by reformation of PAN as the sample was reheated. The ratio of peak areas for PAN:NO_2 arising

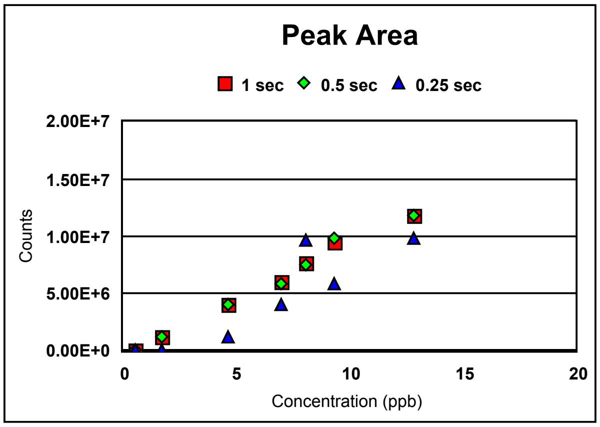

Figure 2. Calibration of the fast GC-luminol instrument for NO_2 at 1-sec, 0.5-sec, and 0.25-sec integration times.

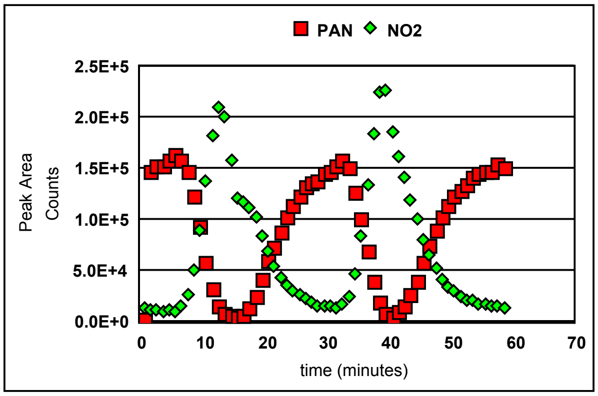

Figure 3. Thermal decomposition of PAN samples to NO_2, followed by reformation of PAN, as measured by the fast GC-luminol instrument.

from the same sample concentrations resulted in a relative sensitivity of 1.4 for NO_2 to PAN with the current instrument configuration. However, recent studies have indicated that this sensitivity ratio can be altered by modifying the luminol solution (Mikuska and Vecera 2000). Increased sensitivities for PAN of 50:1 might be possible with this approach.

4. AIRCRAFT MEASUREMENTS

Measurements of PAN and NO_2 in Tampa, Florida, were taken onboard the NOAA Twin Otter during BRACE in May 2002. Figure 4 shows results for a typical flight over the Tampa area. Concentrations of PAN there were found to be mostly below 100 ppt, with occasional higher values of 200-300 ppt.

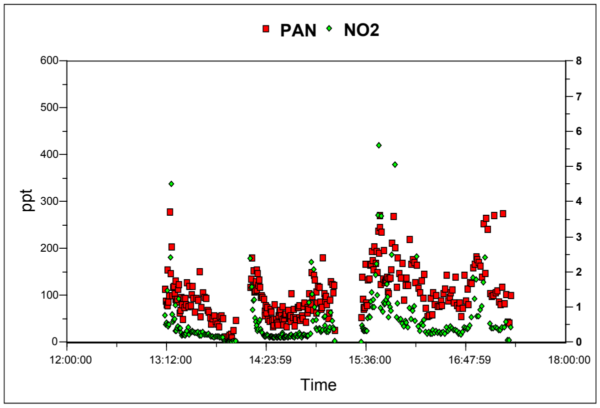

Figure 4. Typical NO_2 and PAN profiles obtained over the Tampa area (May 3, 2002).

Figure 5 shows the relative instrument responses for the two NO_2 measurement techniques available onboard the Twin Otter: fast GC-luminol (in peak area) and photolytic (in voltage). Also shown is the readout for NO_Y from a typical NO_X chemiluminescence detector. As expected, the NO_X detector gives higher values than the photolytic technique because of interferences from other nitrogen-containing species. However, the luminol and photolytic responses match well during the flight, even though the response times were not equal. A comparison of the two instruments for this flight (luminol/photolytic) gave a slope of 7.7×10^5 with a correlation (r^2) of 0.7. The high slope demonstrates the higher sensitivities obtained with GC-luminol detection.

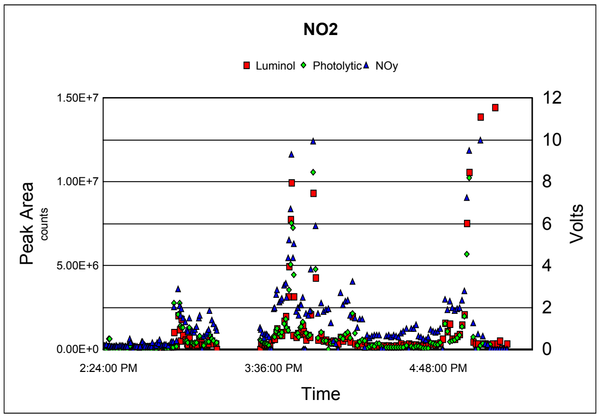

Figure 5. Comparison of instrument responses from the fast GC-luminol, photolytic, and conventional NO_X techniques for NO_2 detection on May 3, 2002, over the Tampa area.

5. CONCLUSIONS

This work demonstrated the use of the second-generation fast GC-luminol detection system for monitoring NO_2 and PAN from an aircraft platform. The instrument is lightweight (approximately 37 lb with carrier cylinder) and is housed in a standard 19-in. instrument case. The new cell design and data collection system allow for 30-sec time resolution of NO_2 and PAN with detection limits of 15-20 ppt. Instrument response agreed well with that of a photolytic NO_2 instrument.

6. ACKNOWLEDGMENTS

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