

FAST GAS CHROMATOGRAPHY WITH LUMINOL DETECTION FOR MEASUREMENT OF NITROGEN DIOXIDE AND PANs

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Abstract

Fast capillary gas chromatography has been coupled to a luminol-based chemiluminescence detection system for the rapid monitoring of nitrogen dioxide and peroxyacyl nitrates. A first-generation instrument was described recently (Gaffney et al., 1998). This system is capable of monitoring nitrogen dioxide and peroxyacyl nitrates (PANs; to and including the C4 species) with 1-min time resolution. This is an improvement by a factor of five over gas chromatography methods with electron capture detection. In addition, the luminol method is substantially less expensive than laser fluorescent detection or mass spectroscopic methods. Applications in aircraft-based research have been published electronically and will appear shortly in *Environmental Science and Technology* (Gaffney et al., 1999a). An improved version of the instrument that has been designed and built makes use of a Hamamatsu photon-counting system. Detection limits of this instrumentation are at the low tens of ppt. The range of the instrument can be adjusted by modifying sampling volumes and detection counting times. A review of past work and of recent application of the instrumentation to field measurements of nitrogen dioxide and PANs is presented. The data clearly indicate that the luminol approach can determine the target species with time resolution of less than 1 min. Examples of applications for estimation of peroxyacetyl radical concentrations and nitrate radical formation rates are also presented. This instrumentation can further be used for evaluation of surfaces for loss of nitrogen dioxide and PANs, phenomena of possible importance for sampling interfaces and chamber wall design. Our high-frequency field data clearly indicate that the "real world" is not well mixed and that turbulent mixing and plume-edge chemistries might play an important role in urban- and regional-scale interactions. Dynamic flow systems might be required to evaluate such effects in new-generation chamber studies.

Abriß

Schnelles kapillares Gas chromatography zu einem luminol chemiluminescent Entdeckung System für die schnelle Überwachung von Stickstoffdioxid und peroxyacyl nitrates verkoppelt worden hat basiert. Ein erstes Generation Werkzeug ODER Gerät ist kürzlich in der Literatur (Gaffney et al., 1998) vorhergehend beschrieben worden. Dieses

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System kann zu, Stickstoffdioxid und PFANNEN (zu und einschließli der C4 Spezies) mit 1min. Zeit Beschlußfassung überwachung. Dies ist eine Verbesserung eines Faktors von fünf über GC/ECD Methoden, und ist wesentlich weniger teuer als laser fluoreszierende Entdeckung oder Masse spectroscopic Methoden. Anwendungen in Flugzeug Forschung sind elektronisch herausgegeben worden werden und erscheinen bald in Umweltwissenschaft & Technologie (Gaffney et al., 1999a). Eine verbesserte Ausführung dieses Werkzeugs ODER Geräts ist entworfen worden gebaut ist worden und, der Gebrauch einen Hammamatsu photon macht, der System zählt. Entdeckung Grenzen dieser Meßgeräte sind an den niedrigen zehn von ppt. Bereich des Werkzeugs ODER Geräts kann durch Probieren von Bänden und Entdeckung Zählen Zeiten einstellt werden. Eine Nachprüfung der vergangenen Arbeit und der neuen Anwendungen dieser Meßgeräte zu Feld Messungen von Stickstoffdioxid und PFANNEN werden überreicht. Diese Daten anzeigen deutlich kann, daß diese Annäherung diese Spezies mit weniger als 1 min. Zeit Beschlußfassung bestimmen. Ebenso Beispiele für Anwendungen für Schätzung von peroxyacetyl radikale Konzentrationen und nitrate werden radikale Formung Raten überreicht. Diese Meßgeräte können auch für Abschätzung der Oberflächen für Verlust von Stickstoffdioxid und PFANNEN benutzt werden können, die wichtig für Probieren Schnittstellen und auch für Kammer Wand Entwurf sein. Merken Sie unseren fieldwork auch deutlich anzeigt wird können jener hohen Frequenz Daten Schau, daß das "alltägliche" nicht gut gemischt, und jene turbulent Mischung und Feder-Kante Chemie spielen eine wichtige Rolle in Städtische und regionale maßstabgetreue Wechselwirkungen. Dies kann erfordern zu, daß dynamischer Ablauf Systeme diese Arten Wirkungen in neuem Generation Kammer Studien bewerten.

Introduction

The interaction of hydrocarbons and oxides of nitrogen in sunlight to produce "photochemical smog" has been well studied over the years (Finlayson-Pitts and Pitts, 1986). Indeed, to assess this type of process under simulated atmospheric conditions, many studies have used smog chambers and or other very large reaction cells and bags to investigate the potential ozone-forming relationships between the various volatile hydrocarbons and nitrogen oxides. These studies were very productive in establishing a first-order knowledge of the complex chemistry involved in the formation of ozone and other oxidants. However, problems in past work typically limited studies in smog chambers to relatively high nitrogen oxide levels. Limiting factors included wall adsorption and desorption of nitrogen oxide species, analytical limitations, and difficulties in speciating the various nitrogen oxide compounds. In the past, the workhorse for the measurement of nitrogen dioxide and nitric oxide was the chemiluminescent reaction with ozone. This method has detection limits of approximately 0.5 ppb for most commercial instruments, but it cannot detect nitrogen dioxide directly, because the instrument detects NO and uses hot catalytic surfaces to decompose all other nitrogen oxides (including NO₂) to NO for detection (Finlayson-Pitts and Pitts, 1986). The main problem with this method is inherent difficulty in the detection of the emitting species (excited nitrogen dioxide). This species emits over a broad region

beginning at approximately 660 nm, with a maximum at 1270 nm, and requires a red-shifted photomultiplier for detection.

Use of luminol for direct detection of NO_2 was demonstrated to have greater inherent sensitivity than indirect ozone chemiluminescence detection (Wendel et al., 1983). Detection limits of 5 ppt have been demonstrated for the luminol method. The 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 this method for direct measurement of NO_2 has been interferences 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 $\text{RC}=\text{OO}-\text{O}-\text{NO}_2$. The most common PANs are peroxyacetyl nitrate (PAN; $\text{R}=\text{CH}_3-$), peroxypropionyl nitrate (PPN; $\text{R}=\text{CH}_3\text{CH}_2-$), and peroxybutyryl nitrate (PBN; $\text{R}=\text{CH}_3\text{CH}_2\text{CH}_2-$).

The PANs are in thermal equilibrium with the peroxyacetyl radical ($\text{RC}=\text{O}-\text{OO}\cdot$) and NO_2 (Gaffney et al., 1989). Because PANs are trapped peroxy radicals, they are an important indicator species of the photochemical age of an air parcel, as well as a vehicle for long-range transport of NO_2 leading to the formation of regional ozone and other oxidants. Typically, PANs are measured by using a gas chromatograph with electron capture detection (ECD). Once automated, this method has been shown to be reliable and quite sensitive, allowing levels of PANs to be measured in the troposphere at low parts per trillion (e.g., Gaffney et al., 1993). Unfortunately, a number of other atmospheric gases (e.g., O_2 , Freons, H_2O) also have strong ECD signals or act as interferences and limit the speed with which the analysis can be completed. Currently, the shortest ECD analysis time for PAN, the simplest peroxyacyl nitrate, is approximately 5 min (e.g., Williams et al., 1997).

Peroxyacetyl nitrate was shown to react with luminol by our group and by Stedman's research group in the late 1980s. Both research groups demonstrated that a simple packed column could separate the PAN signal from the NO_2 signal. Indeed, a method was demonstrated for measuring PAN and NO_2 by using a gas chromatograph coupled to a luminol detector (Burkhardt et al., 1988). This method is the basis for a commercial instrument (Scintrex, LMA-4) that has demonstrated the potential of the approach and has achieved detection of NO_2 and PAN with 5-min time resolution. We revisited this approach and applied fast capillary gas chromatography to accomplish the analysis for NO_2 , PAN, PPN, and PBN with an analysis time of less than 1 min (Gaffney et al., 1998). Recently, we used this approach for aircraft measurements of NO_2 and PAN (Gaffney et al., 1999a). Described here is a new design for a smaller instrument based on the application of a Hammamatsu photon-counting system. Examples of the type of information that can be accessed with this method are also presented and discussed.

Experimental Approach

The experimental approach for the original configuration of our instrument has been described in detail (Gaffney et al., 1998). Figure 1 is a photograph of the second-generation instrument that we are currently developing for aircraft and ground-based measurements.

The major improvements in the second-generation system are the replacement of the LMA-3 (Scintrex) luminol detection system with photon counting. This gives us direct access to the photomultiplier tube via computer control for both PMT voltage and digital signal processing. We are currently using a simple basic program for data acquisition and processing of the signal. An electronic sampling valve with a timer is used to collect an air sample and inject it onto the gas chromatographic column for analysis. The sample volume injected is typically 1-5 cm³, depending upon the sensitivity required for the measurement. Current detection limits of this system with a 5-cm³ sample are approximately 20 ppt for NO₂ and PAN. A 5% O₂/He carrier gas mixture is used at a flow rate of 40 cm³ min⁻¹. The capillary column used, 3 m long with a DB-1 coating, allows for sufficient separation of NO₂ from PANs. Calibration standards for PANs were prepared by using a strong acid nitration of the corresponding peracid and extraction into n-tridecane (Gaffney *et al.*, 1984).

Results and Discussion

Figure 2 shows raw data for three samples taken at random in a recent study in Vineland, New Jersey, as part of the collaboration of the U.S. Department of Energy's Atmospheric Chemistry Program in the Northeast Oxidant and Particulate Studies (NEOPS), based in Philadelphia, Pennsylvania, in July-August of 1999. The first peak monitored, NO₂, is followed by PAN. A 2-cm³ sample loop was used for these measurements. The data correspond to PAN levels of approximately 0.5 ppb and NO₂ levels of approximately 2 ppb. The results were obtained by taking the photon-counting data at 1-sec intervals. We are currently examining signal-to-noise levels at faster counting times as part of our instrument development work. The second-generation system successfully acquired data in automated operation for approximately two weeks during this study.

Our first-generation instrument, which coupled a fast gas capillary column to a commercial LMA-3 detection system with a Hewlett Packard integrator and a laptop computer with Peak 96 software (Hewlett Packard) for data processing was used in our previous studies (Gaffney et al., 1998, 1999a, 1999b). One advantage of the luminol detection method is that it can collect data for both NO₂ and PAN at the same time. This advantage can allow the estimation of the peroxyacetyl radical if pressure and temperature data are obtained simultaneously. We have done this in previous aircraft-based work and have measured PAN/NO₂ ratios that are consistent with the anticipated thermal properties of PAN (Gaffney et al., 1989, 1999a, 1999b). During summer 1998, we made ground-based measurements over a period of approximately one month at a site in the foothills east of Phoenix, Arizona. We will be reporting results from this study at

the upcoming annual meeting of the American Meteorological Society (Gaffney et al., in press).

In the Phoenix study, we noted that rapid, specific measurement of NO_2 with our first-generation instrument and concurrent measurement of ozone allowed us to determine the production rate of nitrate radical. Data obtained in this field study clearly showed that NO_2 was being produced at night by the titration of ozone with locally generated NO . These plumes then were transported in the nighttime boundary layer winds into and past our site at Usery Pass. Calculations clearly indicate that nitrate radical production rates will be very high on the edges of the plumes. This is, of course, where the ozone from background air and the high NO_2 in the plume mix to form NO_3 . Future chamber studies will have to address such mixing issues. Rapid measurement techniques like this method, which we believe can be improved to reduce the analysis time for NO_2 and PAN to approximately 30 sec (see Figure 2), and other methods based on fluorescence spectroscopy or negative ion mass spectroscopy will be useful for evaluating such effects, because they will have the time resolution to determine the effects of spatial inhomogeneities and turbulent mixing on the chemistry.

We have also used the rapid luminol detection method to examine losses of NO_2 and PAN on a variety of different surfaces including Teflon, aluminum, copper, and carbonaceous soots. The method could be useful for selecting appropriate materials for chambers used in studies of NO_2 and PANs. Along this line, we have set up a simple flow system with this detector and tested various tubing sections to determine loss of material. Examples of results with this type of approach have been reported (Gaffney et al., 1998). In comparisons to more conventional ECD measurement techniques in both laboratory and field studies, the rapid luminol detection approach has been found to agree quite well, with comparable detection sensitivities for PANs in the low tens of ppt. Calibration for PANs can be accomplished by the thermal decomposition of PANs to form NO_2 and subsequent monitoring of the resulting increase in NO_2 signal during chromatographic analysis. Nitrogen dioxide calibration gas standards (traceable to the National Institute of Standards and Technology) are used to calibrate the NO_2 and PAN signals by comparison of the ambient and thermally decomposed PAN standard chromatograms (Gaffney et al., 1998). Use of a chromate converter permits use of this method for NO measurements.

If we are to expand chamber studies to investigate the influence of very low nitrogen oxide levels on the production of oxidants and ozone, very low detection sensitivities will be required to measure and characterize nitrogen oxide species. Fast gas chromatography with luminol detection has real promise in this area. We are continuing detector development, with future attention to be given to minimizing dead volumes and optimizing signal processing aspects of the photon-counting system. An update on our results for this system and on our work on a real-time hydrocarbon detection system will be reported at the American Meteorological Society meeting (Drayton et al., in press).

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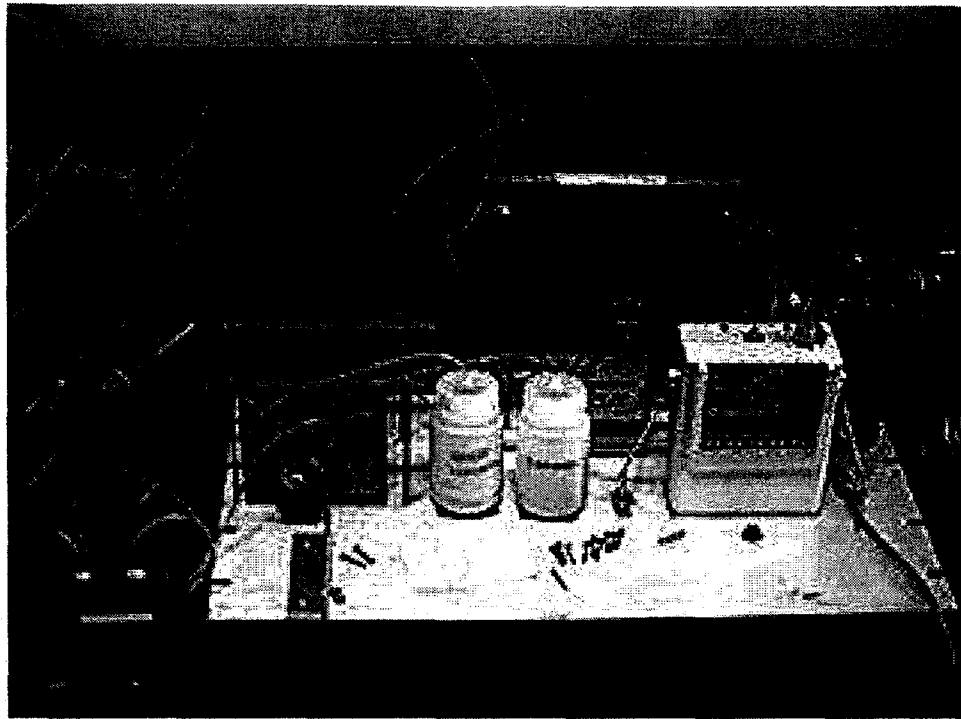


Figure 1. Luminol instrument with luminol cell and photon-counting system dismantled to show the various parts of the instrument, peristaltic pump, luminol reservoirs, air sampling pump, mass flow controller, and gas chromatographic column. An external automated sampling valve is used to sample the air pulled through a sampling loop at 1-min intervals.

Figure 2. Raw Data from Vineland, NJ, 7/30/99, 11:39 to 11:41 am EDT.

