

Fast gas chromatography with luminol chemiluminescence detection for the simultaneous determination of nitrogen dioxide and peroxyacetyl nitrate in the atmosphere

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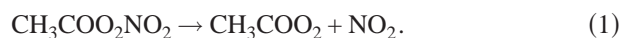
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An instrument has been designed and constructed for the simultaneous determination of nitrogen dioxide (NO₂) and peroxyacetyl nitrate (PAN) in atmospheric samples. The instrument's design is based on separation by fast gas chromatography (GC) with a 30 ft capillary column (DB-1) followed by detection by luminol chemiluminescence. The chemiluminescent reaction between NO₂ or PAN and luminol takes place at the gas-liquid interface on the surface of a solid support. The chemiluminescent emission at 425 nm is detected with a photon counting module. The instrument is controlled by a 1.8 GHz Notebook computer with a WINDOWS 2000 operating system and a custom software application programmed in LABVIEW. Detection limits are in the low parts per trillion (ppt) with a time resolution of 30 s to 1 min. The instrument was operated during the Mexico City Metropolitan Area/Mexico City Megacity 2003 collaborative air quality study. Results for NO₂ from this fast GC method were compared with results from a co-located differential optical absorption spectrometer (DOAS) and a tunable diode laser absorption spectrometer (TDLAS). The results support the application of the new luminol-based instrument for atmospheric measurements. © 2004 American Institute of Physics. [DOI: 10.1063/1.1805271]

I. INTRODUCTION

Nitrogen dioxide (NO₂) and peroxyacetyl nitrate (PAN) are important atmospheric trace gas species associated with photochemical air pollution. The photolysis of NO₂ leads to the formation of tropospheric ozone (O₃), while the oxidation of NO₂ by hydroxyl radical (OH) leads to the formation of nitric acid (HNO₃), an important aqueous aerosol species and a gaseous aerosol precursor via its reaction with gas-phase ammonia.¹ Peroxyacetyl nitrate (CH₃C=OO-O-NO₂) is formed by photochemical oxidation of nonmethane hydrocarbons in the presence of NO₂. One important property of PAN in the atmosphere is its thermal equilibrium with NO₂ and the peroxyacetyl radical (CH₃C=O-OO·):



This equilibrium is strongly temperature dependent such that PAN is more stable at colder temperatures. Consequently, PAN can be transported over long distances in the upper to middle troposphere before thermally decomposing in the warmer boundary layer.^{2,3} Thus, PAN acts as an important source of NO₂ in remote areas leading to the formation of O₃ and secondary aerosols on regional scales.

Nitrogen oxide (NO) and NO₂ are known collectively as NO_x. The instrument most commonly used for routine measurement of atmospheric NO_x species is based on the gas-phase chemiluminescent reaction of NO with O₃.¹ This instrument has detection limits of approximately 0.5 ppb (parts per billion) in most commercial instruments. However, NO₂ cannot be measured directly with this technique. Since NO is the reactive species, hot catalytic surfaces must be used to decompose NO₂ to NO prior to detection by O₃ chemiluminescence. The signal then represents a sum of NO+NO₂, or total NO_x.

The NO₂ can be determined quantitatively by subtraction of the NO signal observed prior to exposure of the sample to the hot catalyst. A difficulty with this approach is that other nitrogen-containing species (HNO₃, PAN, organic nitrates, etc.) are also decomposed to NO by exposure to the hot catalyst and are, therefore, measured along with NO₂.⁴ Subtraction of the NO signal from the total signal will then be representative of the combined concentrations of all nitrogen species decomposed to NO by the catalyst. A variation of this instrumentation developed for the specific detection of NO₂ utilizes a high-pressure xenon lamp with dielectric filters—in place of the hot catalyst—to selectively photolyze NO₂ to NO without decomposing other nitrogen-containing species.⁵ The only reported interferences with this photolytic technique are nitrous acid (HONO), nitrate radical (NO₃), and

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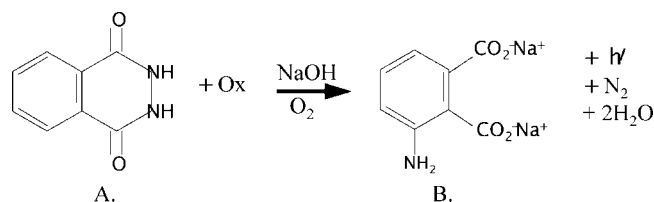


FIG. 1. Reaction of luminol (A) with an oxidizing agent in basic solution to yield nitrogen, sodium aminophthalate (B), and light at 425 nm.

peroxy nitric acid (HO₂NO₂), all of which are expected to be at very low concentrations during daytime hours.

The main problem with the use of O₃ chemiluminescence for NO_x detection lies in the inherent difficulty of detecting the chemiluminescent emission. The product of the reaction of O₃ with NO is electronically excited NO₂, which emits light over a broad wavelength region in the near infrared, beginning at approximately 660 nm and with a maximum at 1270 nm (1.27 μm). This emission maximum lies outside the spectral response of most commonly available photomultiplier tubes. To achieve adequate sensitivity, photodetection requires a red-sensitive photomultiplier tube with a photocathode that is more sensitive to longer wavelengths (typically 800–900 nm). The difficulty of obtaining a rugged, inexpensive detector with high radiant sensitivity at the emission maximum of the O₃ chemiluminescence is the ultimate limiting factor for this NO_x detection method.

Luminol is one of the most efficient and best known chemiluminescent compounds in the condensed phase. Light is produced when basic aqueous solutions of luminol (5-amino-2,3-dihydro-1,4-phthalazinedione) containing oxygen are treated with an oxidizing agent. The products of the reaction are nitrogen and sodium aminophthalate (Fig. 1). Oxidizing agents capable of initiating this reaction include NO₂ and PAN, as well as hydrogen peroxide, O₃, and other atmospheric oxidants.

The luminol chemiluminescence method for direct detection of NO₂ has a greater inherent sensitivity than the indirect O₃ chemiluminescence method, with reported detection limits of 30 ppt (parts per trillion).^{6,7} This detection system employs a gas–liquid surface reaction between an alkaline solution of luminol and NO₂ in air leading to a chemiluminescent emission with a maximum at approximately 425 nm. This emission, which coincides with the maximum sensitivity for many commercially available photomultiplier tubes, is responsible for the increased detection sensitivities of the method. The main difficulty with the luminol detection method for continuous direct measurement of NO₂ is that PAN and other peroxyacyl nitrates also react with luminol and therefore act as interferences, especially when very low detection limits of NO₂ are required.^{5,6}

Typically, PAN is measured by using a gas chromatograph (GC) with electron capture detection (ECD). This method has detection limits in the low parts per trillion and has made use of both packed and capillary columns to achieve separation and subsequent detection.^{2,8,9} Unfortunately, a number of other atmospheric gases, including oxygen, also have strong ECD signals and can act as interferences, limiting the speed of the analysis. Typically this

technique requires 15–30 min for the analysis to be completed, principally because a very large positive background signal from oxygen and a negative signal from water require sufficient time to allow for the separation of PAN and column recovery before the next analysis can be performed. At least 1 to 2 min is needed for the background levels from the oxygen peak to decrease enough to allow reasonable detection of the eluting PAN. In addition, the presence of water vapor affects the analysis and extends the delay required before the next sample can be injected to 10–15 min or more (depending on water vapor levels and sample injection size), until the baseline becomes stable. Thus, these large interferences determine the achievable detection limits and the analysis times for rapid detection of PAN by GC/ECD. Optimization of the GC/ECD method by combining two short megabore columns of different polarities has decreased the analysis time.^{10,11} The interfering peaks, including oxygen, are separated on a precolumn and vented prior to separation of PAN on the main column. With this approach, analysis times of 4 to 5 min have been achieved.

Recently, negative ion chemical ionization mass spectrometry (NICI-MS) has been used for the ambient detection of PAN¹² and as a gas chromatographic detector for PAN, peroxypropionyl nitrate (PPN), and peroxyacetyl nitrate (MPAN).^{13,14} Because of PAN's very large electron capture cross section, the NICI-MS sensitivity for this species is quite high. The fragment ions have been identified as CH₃COO⁻, with a mass-to-charge ratio (*m/z*) of 59; NO₃⁻, with *m/z*=62; CH₃CO₃⁻, with *m/z*=75; and NO₂⁻, with *m/z*=46. Among the four fragment ions, NO₃⁻ gives the best signal-to-noise ratio, with a detection limit for PAN of 15 pptv and with an accuracy of 20%. However, these instruments have not seen widespread use as chromatographic detectors because of their high costs and the need for skilled operators.

The reaction of PAN with luminol was reported as an interference in the direct detection of NO₂ by this technique with a response equal to that for NO₂.⁸ Subsequently, a method was reported for measuring both PAN and NO₂ in atmospheric samples by using a packed-column GC coupled to a luminol detector.¹⁵ Since luminol detection of the peroxyacyl nitrates does not suffer from the oxygen interference that affects ECD, separation of NO₂ and the peroxyacyl nitrates can be accomplished in a much shorter analysis time. We recently revisited this approach and applied fast capillary GC to accomplish the simultaneous analysis of NO₂ and PAN, along with the PAN analogs PPN and peroxybutyryl nitrate (PBN), with an analysis time of less than 1 min.¹⁶ This first attempt made use of a commercially available luminol detector system designed for continuous NO₂ determination (Scintrex; Luminol LMA-3). We used this prototype for simultaneous fast-response measurements of NO₂ and PAN on an aircraft platform¹⁷ and in ground-based field studies.¹⁸ In addition, because this system allowed simultaneous measurement of NO₂ and PAN, we were able to estimate the atmospheric peroxyacetyl radical concentrations from temperature and pressure data, the gas-phase rate coefficients, Eq. (1), and the following relationship:^{17,18}

$$[\text{CH}_3\text{CO}_3] = k_2/k_1[\text{PAN}]/[\text{NO}_2]. \quad (2)$$

The commercial luminol detector system used in the prototype instrument presented several limitations for use as a GC detector. In order to improve the sensitivity of the method, a means of interfacing the capillary column to the reaction cell, which maximized contact of the column effluent with the luminol solution, was required. In addition, a new cell design, which minimized dead volume and provided a means of easily disposing of the carrier gas and luminol solution with minimal spillage, was necessary.¹⁹ By applying recent advances in miniaturized photon counting systems, a faster response and enhanced sensitivity could be achieved with a major reduction in the size and weight of the instrument.²⁰ In order to facilitate data collection, a system was also needed which would allow synchronous control of the sample injection and data acquisition from the detector as well as on line peak integration and concentration determination.

A new instrument has now been constructed for the simultaneous determination of NO₂ and PAN in the atmosphere, with a design based on capillary GC with luminol chemiluminescence detection (GC/LCD). The instrument is contained in a rack-mountable instrument case and weighs a total of 16.14 kg (35.5 lb), suitable for easy deployment on aircraft platforms. LABVIEW software is used for real-time data integration and synchronous operation of sample injection and data collection. Detection limits are in the low parts per trillion with a time resolution of 30 s to 1 min. The instrument was operated during the Mexico City Metropolitan Area (MCMA)/Mexico City Megacity 2003 collaborative air quality study in April 2003. Results obtained for NO₂ during this study were compared with results from a co-located differential optical absorption spectrometer (DOAS) and a tunable diode laser absorption spectrometer (TD-LAS). The results of this comparison support the applicability of this new instrument for rapid, selective measurements of NO₂ and PAN in the atmosphere.

II. INSTRUMENT DESIGN

A schematic representation of the general instrument design is in Fig. 2. A small external sample pump (Neptune Products, Inc., Dyna-Pump, Model 2) attached to the instrument exhaust is used to pull the air sample continuously from a Teflon sample manifold (not shown) and through a sample loop attached to a six-port, two-position valve (described in Sec. II A). The valve is used to inject the contents of the loop onto a 30 ft capillary column. Teflon tubing is used for all sample lines, both inside and outside the instrument case. Carrier gas is supplied to the column through the injection valve, either from a standard gas tank for long-term ground-based studies or from a 105-1 refillable cylinder (Matheson Mini Mat) for studies of short duration such as onboard aircraft, where size and weight may be an issue. Mass flow meters connected to needle valves are used to monitor and control the carrier (Omega Engineering, Inc., FMA 1808) and sample (Omega Engineering, Inc., FMA 1814) flow rates.

A small (7½ in. × 3½ in. × 3½ in.) dual-channel, variable-speed tubing pump (Cole Parmer, Masterflex C/L

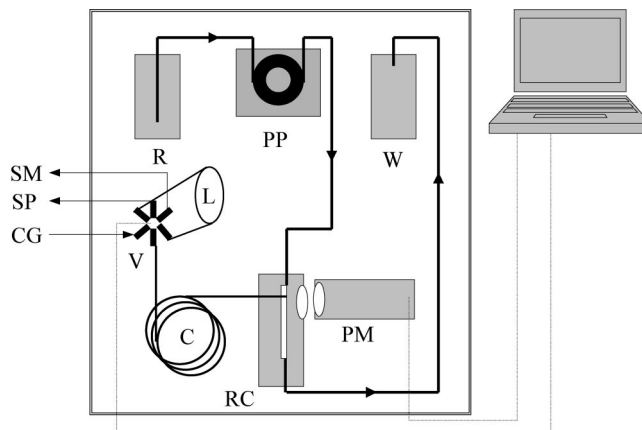


FIG. 2. Schematic diagram of the fast GC with luminol chemiluminescent detection (GC/LCD). R=luminol reservoir; W=luminol waste receptacle; PP=peristaltic pump; L=sample loop, V=six-port valve; SM=sample manifold; SP=sample pump; CG=carrier gas; C=capillary column; RC=reaction cell; PM=photon counting module.

Model 77120-52) directs the luminol solution flow from a 250 ml reservoir to the top of the reaction cell at a flow rate of about 0.01 ml/min. Luminol waste solution and carrier gas effluent are removed together from the bottom of the reaction cell and emptied into a 250 ml waste receptacle, where carrier flow is vented through the receptacle top. Detection of the chemiluminescence emission is accomplished with a photon counting module (described in Sec. II C). Injection of the sample onto the column and data acquisition are both controlled automatically by interfacing the RS-232 connections from the valve and the photon counting module to the USB ports of a laptop computer with a USB-serial converter. Synchronous control of sample injection, data acquisition, peak integration and data storage is accomplished with LABVIEW 6.1 graphical programming software operating in a WINDOWS 2000 environment.

A. Fast gas chromatography

The choice of column media and the separation conditions are important considerations in instrument design. A nonpolar column is best for the separation of NO₂ and PAN as well as the PAN analogs, because the latter are not very water soluble but are readily soluble in nonpolar media.²¹ The column should be kept at room temperature, as PAN is quite thermally unstable and rapidly equilibrates to the peroxyacetyl radical and NO₂ at temperatures significantly above room temperature, per Eq. (1). Indeed, thermal decomposition and loss of PAN on the column can occur even at room temperature in the time required for analysis with conventional GC/ECD methods. In general, the longer the analysis time, the greater will be the destruction on the column and the lower the sensitivities that can be achieved. Thus, the advantages of luminol chemiluminescence over ECD as a chromatographic detector for PAN lies in the faster analysis achievable. The capillary column used to separate NO₂ and PAN for the GC/LCD is a 30-ft-long (J&W Scientific) megabore (0.53 mm i.d.) fused-silica column with a 3.00-µm-thick dimethylpolysiloxane film (DB-1). The column is operated at room temperature to minimize thermal

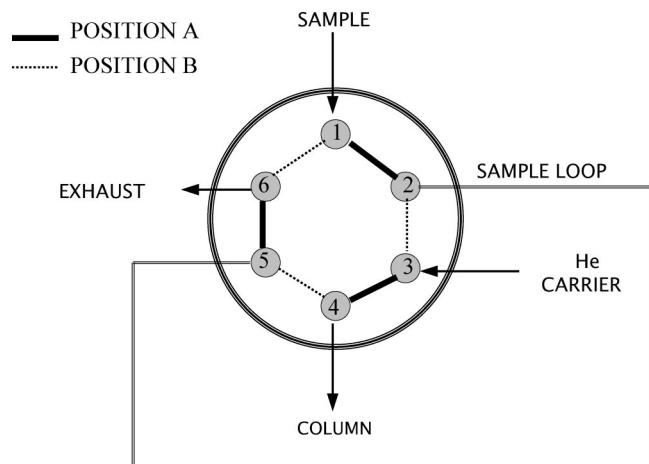


FIG. 3. Port connections (1–6) made to the valve used to inject the sample onto the capillary column. When the valve is in Position A, the sample flows through the external sample loop, and the carrier gas flows directly onto the column. When the valve is switched to Position B, the carrier gas flows first through the sample loop and then through the column, so that the sample in the loop is injected onto the column.

decomposition of PAN on the column. The ends of the fused-silica capillary are run through standard rubber syringe injector septa (Schimadzu GC-Mini-2) to make gas-tight connections at the injection valve and reaction cell. The septa are held in place by backing them up with a Teflon Swagelok fitting at the reaction cell and with a Cheminert fitting (VICI, Valco Instruments, Co.) at the valve.

The six-port, two-position injection valve (VICI, Valco Instruments, Co., Cheminert Model C22) is connected to the sample loop, carrier gas, and capillary column as shown in Fig. 3. Sample loop sizes of 1, 2, and 5 cm³ are used to achieve adequate sensitivity over a wide range of sample concentrations.¹⁵ The size of the loop used determines the amount of sample injected onto the column; larger volumes are required when low concentrations are anticipated, and smaller volumes are needed when levels are expected to be higher. Sample loops are cut from 1/8 in. (o.d.) Teflon tubing, and the selected loop is attached to the injection valve with Cheminert fittings. When the valve is in Position A of Fig. 3, sample flows through the external sample loop while the carrier gas flows directly to the column. When the valve is switched to Position B, the carrier gas first flows through the sample loop and then through the capillary column, forcing the sample onto the column. The valve is actuated with a two-position microelectric actuator (Model EH) with a built-in RS-232 serial port, which allows for software control of sample injection. A sample injection time (Position B) of 10 s, followed by an analysis time (Position A) of 1 min to 30 s, is adequate to achieve baseline separation of NO₂ and PAN with a carrier flow rate of 40–60 cm³/min (see Fig. 4). The peak eluting first in Fig. 4 is NO₂, at a retention time of approximately 12 s, and the peak eluting second is PAN, at a retention time of approximately 24 s. These conditions are also adequate to achieve separation of the higher analogs PPN and PBN with a 1 min analysis time.¹⁵

Nitrogen, helium, or air can be used as a carrier gas.^{15,16} The best separation is achieved with helium as the carrier.

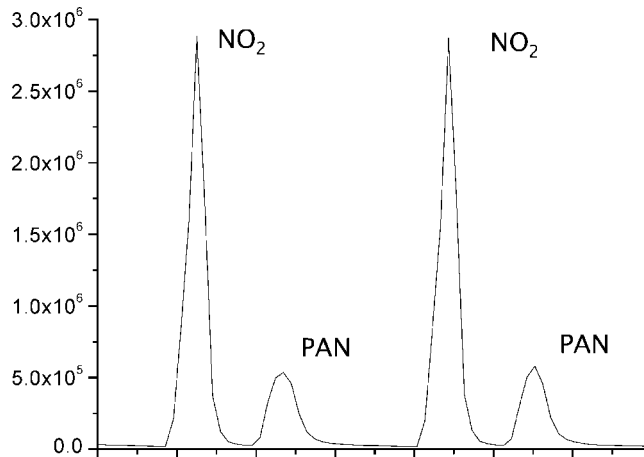


FIG. 4. Gas chromatogram of two consecutive injections of a standard containing NO₂ (10 ppb) and PAN (3 ppb) with a 5 cm³ sample loop.

However, when air was used in combination with small sample loops, a larger PAN response was observed than with helium. This increased response is caused by the excess oxygen in the air which forms an adduct with the aminophthalate ion, thereby increasing the chemiluminescent yield.²² To compensate for this loss in sensitivity and still achieve baseline separation in less than one minute, a carrier gas consisting of 5% oxygen in helium was proposed.²³ However, with the larger 5 cm³ sample loop, there is sufficient oxygen in the sample that the oxygen–helium mixture is not required to achieve the higher sensitivity and helium alone can be used as the carrier gas.

B. Reaction cell

Since the chemiluminescent reaction between luminol and NO₂ or PAN takes place between gas and liquid phases, reaction cells require a major departure from those used for chemiluminescence in the gas phase only. Early attempts at constructing a luminol reaction cell for the detection of NO₂ in air made use of a small pool of luminol solution with the sample gas flowing over the surface of the pool.⁷ Because luminol is oxidized in the reaction with NO₂, new solution must be continuously supplied to the pool. This cell design proved to be excessively sensitive to movement and positioning of the cell. In addition, although the reaction occurred primarily at the gas–liquid interface, the chemiluminescence emission signal was complicated by reactions occurring within the bulk liquid, resulting in memory effects. A new cell design was subsequently proposed, in which a solid support constructed of Whatman filter paper was continuously wetted by a flowing luminol solution.⁸ This design effectively eliminated the problems incurred by using a liquid pool of luminol solution and was subsequently modified for use in the commercial NO₂ monitor available from Unisearch Associates, Inc. (LUMINOx, LMA-3D).

The luminol reaction cell constructed for use in the GC/LCD also has a solid support for the luminol solution. The cell is constructed in two halves from $\frac{3}{4}$ in black Delrin. To ensure that the reaction takes place at the gas–liquid interface, the luminol solution is supported by a twill tape, $1\frac{3}{4}$ in. by $\frac{1}{4}$ in., that sits in a shallow channel on the back of the cell

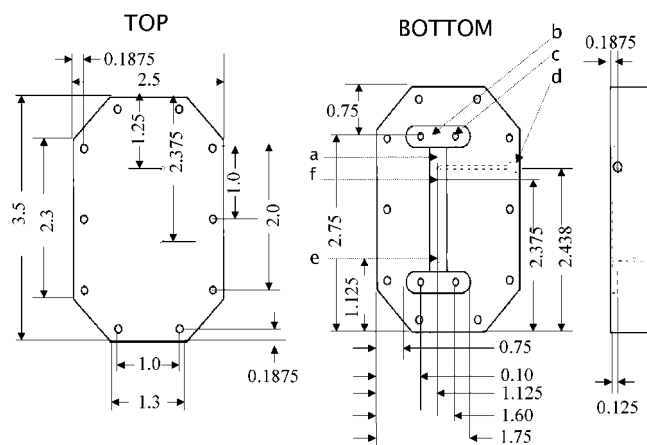


FIG. 5. Construction diagram for the back half of the reaction cell, showing the tape position in channel (a) (milled 5/16 in. wide, 0.015 in. deep). The tape is secured by two plastic clips that sit in channel (b) (milled 5/16 in., 0.125 in. deep) and are held in place by screws in holes (c) (4 each, 6–32 ths, 3/8 in. deep). The luminol solution enters through hole (d) (1/16 in. diam, 3/16 in. deep) from the side of the reaction cell (1/8 in. diam, 1/4 in. deep) and is removed, along with the carrier gas, through hole (e) (1/16 in. diam). The capillary column enters the reaction cell through hole (f) (1/16 in. diam).

[Fig. 5(a)]. The tape is secured to the back of the cell by two plastic clips [Fig. 5(b)] held in place by plastic screws [Fig. 5(c)]. Luminol solution is continuously supplied through a small hole in the back of the cell near the top of the tape [Fig. 5(d)] keeping the tape wet with solution. The solution flows down the length of the tape, and excess solution at the bottom is pumped out of the cell, along with the carrier gas, through a hole near the bottom of the tape [Fig. 5(e)]. The end of the fused-silica capillary column enters the reaction cell from the back and extends through the tape to the front side [Fig. 5(f)]. The chemiluminescent reaction takes place where the column effluent makes contact with the wet tape surface.

The chemiluminescence emission is detected by the photomultiplier tube (PMT) through a viewing port in the front of the cell. This port is an elongated slot aligned with the tape, exposing only the luminol-soaked surface to the viewing area of the PMT [Fig. 6(a)]. To prevent peak broadening and assure maximum contact of column effluent with the luminol solution, the dead volume within the reaction cell must be reduced. This was accomplished by using a thin neoprene gasket cut to fit tightly between the two cell blocks leaving only the tape channel exposed.

The luminol solution used in these initial studies was purchased from Unisearch Associates (Luminol II solution). The chemiluminescence intensity, and therefore, the sensitivity of the method, is strongly dependent on the concentrations and components making up the luminol solution. This necessitates recalibration of the instrument with each new luminol lot. Luminol can be purchased dry as 5-amino-2,3-dihydro-1,4-phthalazinedione or 3-aminophthalhydrazide. Solutions are commonly made with a luminol concentration of 1×10^{-4} to 1×10^{-3} M (molecular weight = 177.17) and a sodium hydroxide concentration of 0.05 M. This combination has been shown to yield maximum chemiluminescence emission intensity that is independent of luminol concentra-

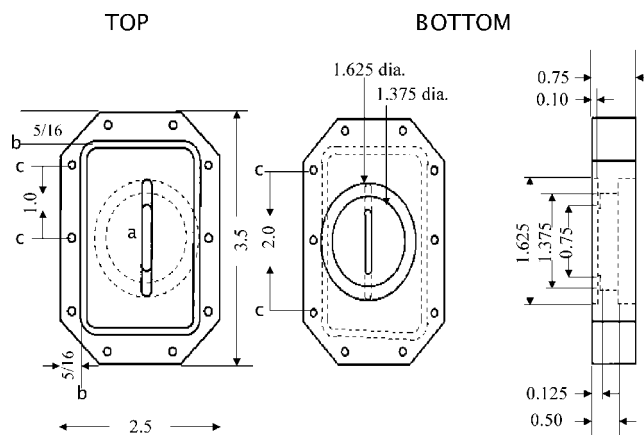


FIG. 6. Construction diagram for the front half of the reaction cell, showing the photo detector view port (a) (slot 3/16 in. wide). The cell is sealed by an “O” ring that sits in groove (b) (0.125 in. wide, 0.080 in. deep), and the front is held to the back of the reaction cell by bolts through holes *c* (10 ea, 1/8 in. diam, with 6–32 ths inserts) at the perimeter of each side.

tion within this concentration range.^{7,8} However, O₃ will also react with luminol under these conditions to give a chemiluminescence signal. This is undesirable for instruments intended for continuous measurements of NO₂ and PAN in ambient air where background O₃ levels are 30 ppb or higher. Sodium sulfite (Na₂SO₃) at concentrations of 0.01–0.1 M is routinely added to the luminol solution to effectively remove this interference.⁸ In addition, the addition of an alcohol, either methanol⁸ or *t*-butyl alcohol,¹⁵ at concentrations of 0.05% has been used to enhance the sensitivity of the luminol solution to NO₂. Surfactants such as Triton X-100 have also been used to enhance the luminol response to NO₂.²⁴

Past studies of optimizing the luminol solution have concentrated on increasing the chemiluminescence intensity from NO₂ while decreasing the intensity from other species, including PAN. Recent work has indicated that the solution conditions can be manipulated to increase the sensitivity to PAN and its analogs by factors approaching 55 times the response to NO₂.²⁴ However, under most conditions, the response to O₃ is also increased and, if these solutions were to be used for GC/LCD, care should be taken to optimize the chromatographic conditions to assure the separation of NO₂ and O₃ prior to detection.

C. Photodetector

The chemiluminescent emission is detected with a photon counting module (Hamamatsu, HC135-01). The module utilizes a 1 in., low profile, R1924A bi-alkali photomultiplier tube (PMT). The HC135-01 is a high speed PMT with an inherent pulse rise time of less than 2 ns. The PMT can be operated at voltages up to 1200 V, supplied by an internal Cockcroft-Walton-type high-voltage supply, used to limit current consumption and prevent unwanted temperature rise of the assembly. An embedded microcontroller (Motorola 68HC11, 8-bit) and an RS-232-C interface allow for computer control of the module and transmission of data to the host computer. The PMT has peak spectral sensitivity (4.5×10^5 cps/picowatt) and peak counting efficiency (30%) at

400 nm ($\sim 350\text{--}450$ nm), with a linear range of 0 to 2×10^7 counts per second (cps). This peak sensitivity coincides exactly with the luminol chemiluminescence emission maximum of 425 nm.

Since the detector uses photon counting, the light signal from the PMT takes the form of high-speed current pulses that are amplified and converted directly to digital pulses by embedded high-speed amplifier/discriminator, prescaler, and counting circuitry. This results in very accurate A-to-D conversion. The main limitation in the use of photon counting for the measurement of larger light levels is the speed of the associated amplifiers, discriminators, and counting circuits. When a single photon is detected, a pulse is produced with a width of 5–10 ns. During this time the system cannot respond to a new photon. As the light level increases, the chance of pulse overlap increases, and the system dead time is reflected in a loss of linear response between input light and count rate. However, if the dead time of the system is known, the measurement error can be predicted as

$$S = S_m / (1 - S_m DT). \quad (3)$$

Here S_m is the measured signal in cps, S is the actual signal in cps, and DT is the system dead time.²⁵ Since all of the necessary components of the system are included in the module, the dead time can easily be measured. This dead time value is measured at the time of manufacture and is programmed into permanent memory in the embedded microcontroller. The data are, therefore, corrected automatically for pulse overlap. This increases the linear range of the module over that of most photon counting systems and makes it ideal for chemiluminescence applications.

The voltage of the PMT can be adjusted continuously from 0 to 1200 V by software command. However, the measured count rate becomes relatively insensitive to increases in voltage above approximately 950 V. In addition, at the highest voltages (>1100 V) the dark current count rate begins to increase. Because of this, an optimum operating point, determined as the point on the plateau curve where the slope is less than 10% of the count rate per 100 V increase, is also programmed into permanent memory as the default voltage for each module. Operation at or near this point substantially improves the overall stability of light measurement.

Since the detector module uses photon counting, its signal-to-noise ratio (S/N) is based on Poisson statistics and can be calculated as

$$S/N = (N_s^2 T / (N_s + 2N_{dk}))^{1/2}. \quad (4)$$

Here N_s is the signal intensity in cps, N_{dk} is the dark signal intensity in cps, and T is the integration time. The typical dark count is 100–200 cps at room temperature. The integration time is adjustable from 10 ms to 1 s in intervals of 10 ms. Longer integration times will enhance S/N . Therefore, an integration time of 1 s is recommended as optimum for most measurements. In addition, care must be taken to keep the detector at room temperature, because the dark count increases sharply at higher temperatures. The module is constructed to operate at room temperature with a baseline stability of 11% / °C.

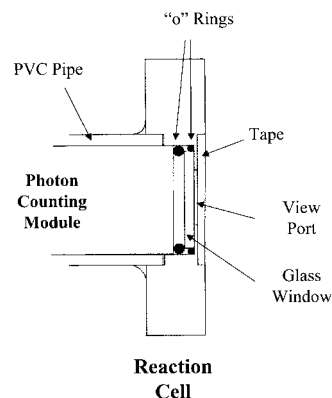


FIG. 7. Interface between the reaction cell and the photon counting module, showing the head of the photon counting module fitted to the face of the reaction cell by means of a PVC pipe and silicone seal.

The dark count rate roughly doubles with every increase of 4–6 °C, thus limiting both the accuracy of the measurement and the minimum detectable signal. In this regard, a small fan is used to circulate air within the instrument case and limit heat buildup near the detector module.

The entire photon counting module is 4.75 in. long with a 1.375 in. diameter and is very light in weight (approximately 180 g). The module head has an active area of 0.827 in.² and is interfaced to the reaction cell as shown in Fig. 7. The circular head of the module sits inside a 1.5 in. polyvinyl chloride (PVC) pipe that has been slotted for flexibility. The pipe is sealed to the front of the reaction cell with silicone sealer. The head of the detector module is locked in place by a hose clamp on the outside of the PVC tube. A 1.25 in glass window is placed on the outside of the reaction cell view port and held in place by two “o” rings to isolate the reaction area from the detector module and prevent the basic luminol solution from contacting the face of the PMT.

D. Layout

The instrument is contained in a case 8.7 in. high by 17 in. wide by 20 in. deep (Buckeye Enclosures, RP Series), with ear mounts designed to fit in a standard 19 in. instrument rack. The physical layout of the bottom plate, face, and rear panel of the instrument case is shown in Fig. 8. A DC fan (60 mm \times 25 mm; Comair Rotron Flight II 60) is mounted on the rear panel to circulate air within the case and reduce heat buildup, which would limit sensitivity by promoting the decomposition of PAN on the column and increasing the dark current of the detector. A small DC power supply (Astec; LPT42) supplies +5 V to the photon counting module and +12 V to the fan, tubing pump, and mass flow meters. A 24 V power adapter supplies power for the valve actuator.

A window in the front panel, 3 in. \times $\frac{1}{4}$ in., allows for visual monitoring of the luminol solution level in the waste reservoir and promotes air circulation in the instrument case. The 3 $\frac{1}{2}$ in. digital liquid crystal display for each mass flow meter is removable and can be remotely located and mounted on the front panel with a remote cable assembly (Omega Engineering, FMA18RC). Two needle valves mounted on the front panel are used to control the sample and carrier gas

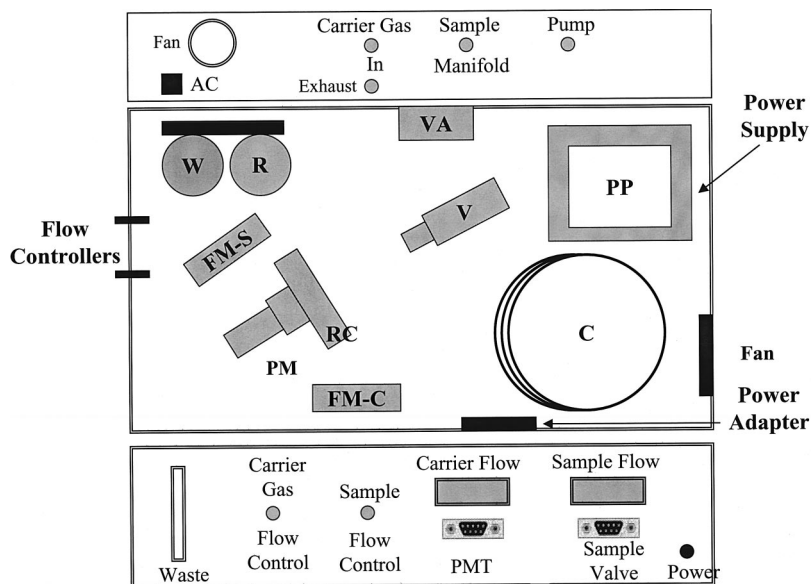


FIG. 8. The layout of the bottom plate (center), front panel (lower), and rear panel (upper) of the fast GC/LCD instrument case. *R*=luminol reservoir; *W*=luminol waste receptacle; *PP*=peristaltic pump; *V*=six-port valve; *VA*=valve actuator, *C*=capillary column; *RC*=reaction cell; *PM*=photon counting module, *FM-S*=mass flow meter for the sample, *FM-C*=mass flow meter for the carrier gas.

flows. The serial connections to both the detector assembly and injection valve are also mounted on the front panel. All gas line connections are made with $\frac{1}{4}$ in. stainless steel Swagelok fittings mounted on the rear panel of the instrument case. Carrier gas, sample manifold, and sample pump inlets are connected internally to the injection valve. The exhaust outlet is connected to the top of the luminol waste reservoir and acts to remove the carrier gas overpressure from the gas/solution waste exiting the reaction cell.

E. Software

The instrument is controlled by a 1.8 GHz Notebook computer (Gateway 400) with a WINDOWS 2000 operating system. A custom software application is programmed in LABVIEW version 6.1 (National Instruments; LABVIEW Professional Development Systems). LABVIEW, an acronym for Laboratory Virtual Instrument Engineering Workbench, is an object oriented, graphic programming language used primarily for building data acquisition and instrument control systems. It can construct a "virtual instrument," or VI, by using icons instead of lines of text to create applications.

The LABVIEW VI consists of a user interface or front panel and a graphic block diagram that contains the source code. The front panel imitates the operation of a physical instrument in both appearance and operation and serves as a user interface to the program, which allows for interactive control of the instrument.

The front panel of the GC/LCD VI imitates the operation of a traditional chromatograph (Fig. 9). This front panel is visible on the computer screen at all times and can be operated from the computer mouse and keyboard. From this screen, manual adjustments can be made for the high voltage applied to the PMT, the integration time for each data point, the time between sample injections, and the time for injection of the sample onto the column. The high voltage to the PMT can be turned on or off from a virtual push button to the right of the voltage control. The signal output is displayed on the screen in real time as a virtual chromatogram, along with the current run number (or injection number) since analysis

began and the absolute time of the last sample injection. The instrument runs continuously until one of the stop buttons on the front screen is activated. This stops data collection from the detector module, sample injection on the column, and the continuous display, either immediately or after the next sample is injected.

Two data files are created in spreadsheet format, one containing the raw signal in counts directly from the photomultiplier module and a second containing the peak integration values. File names are created from the name specified on the screen followed by an extension (i.e., "raw" or "pks") appended to identify each file. Each file contains a header with the date and time the instrument started taking data, followed by the elapsed time in seconds since the start time. The file containing the peak integration also contains the time of day the sample was taken, in Julian Day format; the number of peaks found in each sample; and peak height and peak area for the first two (NO₂ and PAN) peaks. The program requires an estimate of the approximate peak width of the NO₂ (first) peak, in seconds, in order to determine the peak separation and integration limits for the PAN peak. This estimate can be obtained from a trial run and entered on the front panel. A copy of the customized LABVIEW program can be obtained from the authors on request.

III. CALIBRATION

A. Nitrogen dioxide

Calibration of the GC/LCD for NO₂ was accomplished by dilution of a 2.8 ppm NO₂ tank standard in air with a gas calibrator (Dasibi; Model 1009-CP). The final concentrations were monitored with a NO_x chemiluminescence analyzer (Columbia Scientific Industries; Model 1600 NO_x Analyzer). The responses of the GC/LCD for NO₂ standards at detector integration times of 1.0, 0.5, and 0.25 s are shown in Fig. 10. Determination of the area of the NO₂ standard peaks resulted in a similar response for all three integration times. The sensitivity, as determined by the slope of the analytical curve shown in Fig. 10, is 1.23×10^6 counts/ppb, with a correla-

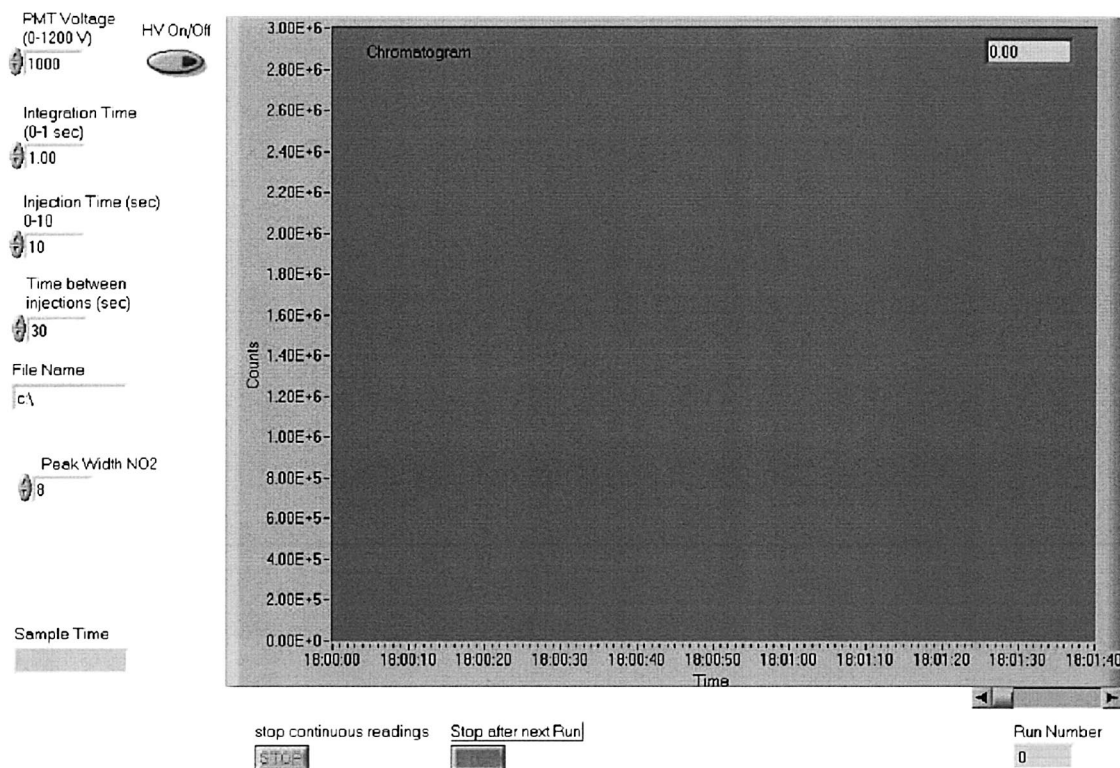


FIG. 9. The front panel of the LABVIEW virtual instrument used to operate the fast GC/LCD.

tion coefficient (R^2) of 0.995. The detection limit, as calculated from three times the standard deviation of the peak areas of a low-concentration standard (0.6 ppb), is 15 ppt.

The height of the NO_2 standard peaks varied with detector integration time, with the highest response occurring for the longest integration time. The resulting sensitivities, according to peak height determinations, were 2.13×10^5 counts/ppb for a 1.0 s integration, 1.18×10^5 counts/ppb for a 0.5 s integration, and 5.74×10^4 counts/ppb for a 0.25 s integration, with R^2 values of 0.999, 0.920, and 0.965, respectively. Peak width also varied with detector integration time, with the smallest width at half maximum for the longest integration time, thus giving similar peak areas for all times.

B. Peroxyacetyl nitrate

Peroxyacetyl nitrate was synthesized by strong acid nitration of peroxyacetic acid, which was obtained by the reaction of 50% hydrogen peroxide (Fisher Scientific) with acetic anhydride (Aldrich Chemical Company). The PAN was separated from the resulting mixture by extraction into *n*-tridecane.²⁶ Since PAN has a vapor pressure at room temperature of about 30 Torr and that of *n*-tridecane is a few millitorr, PAN can be distilled from the solution as a standard of very high purity, with minimal contamination from the solvent. For easy instrument calibrations, the liquid solutions of PAN and *n*-tridecane can be placed in an open diffusion tube dropped vertically into a glass U tube capped with Teflon screw caps. The U tube is then placed in an ice bath to slow the diffusion of PAN from the solution. Ultra-zero air

passing through the U tube at different rates allows for dilution of the PAN leaving the solution to various concentrations.²¹

One problem with the direct calibration of the GC/LCD with PAN diffusion standards is the difficulty in obtaining an independent measurement of PAN concentrations in the ppt range. The NO_x chemiluminescence monitor is not reliable at concentrations below 1 ppb, and PAN standards are not stable at higher diffusion rates. However, since PAN is in thermal equilibrium with NO_2 , per Eq. (1), the relative responses of the GC/LCD to NO_2 and PAN can easily be determined by thermally decomposing a PAN standard and measuring the resulting NO_2 . This is accomplished by passing the PAN through heated tubing before injection into the GC/LCD.¹⁶ The sample delivery lines are long enough, and sample flows are low enough, so that the gas temperature at the sample loop is near ambient. However, the peroxy acetyl radical is lost to the tubing walls preventing the reformation of PAN as the gasses cool. Figure 11 gives the GC/LCD results for the thermal conversion of a 190 ppt PAN standard to NO_2 , followed by reformation of PAN as the sample cools. The ratio of peak area for NO_2 to peak area for PAN for the same sample concentrations indicated a relative sensitivity of 1.4 (NO_2/PAN) with the current instrument configuration and luminol solution. This results in a PAN sensitivity of 8.3×10^5 counts/ppb.

IV. AMBIENT MEASUREMENTS

In April of 2003, we used the fast GC/LCD to obtain measurements of NO_2 and PAN as part of the MCMA 2003 air quality study. The main field site in this study was on the

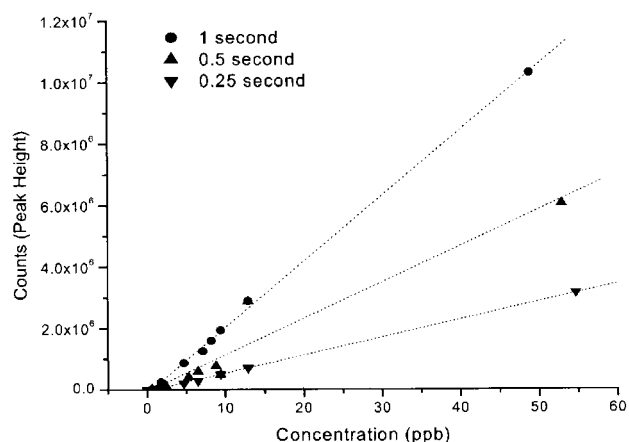
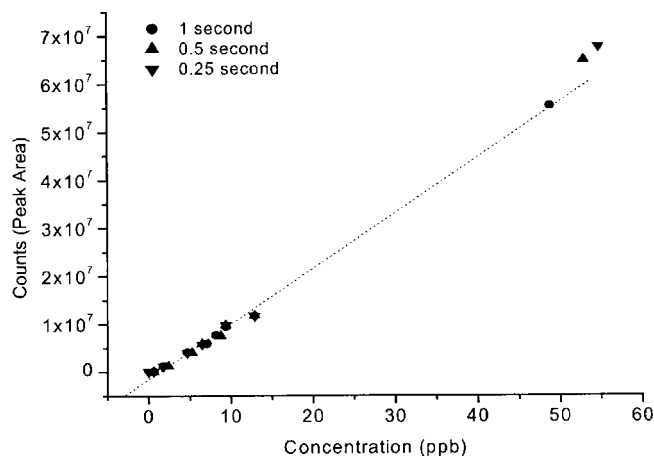


FIG. 10. Responses of the fast GC/LCD for NO₂ standards at detector integration times of 1.0, 0.5, and 0.25 s. For peak area, slope= 1.23×10^6 and $R^2=0.995$ for all times. For peak height, slope= 2.13×10^5 , 1.18×10^5 , 5.74×10^4 , and $R^2=0.999$, 0.920, 0.965, for 1.0, 0.5, and 1.0 s, respectively.

rooftop of the National Center for Environmental Research and Training (Centro Nacional de Investigación y Capacitación Ambiental, or CENICA), on the Iztapalapa campus of Universidad Autónoma Metropolitana at 19° 21.541' N, 99° 04.425' W, southwest of the Mexico City center. The overall goal of the effort was to contribute to the understanding of air quality problems in megacities. Field measurements were obtained at the CENICA “super-site” by a wide variety of state-of-the-art instrumentation contributed by many teams from the United States and Europe. The study was conducted from late March to early May. This time period was chosen to include the height of the annual photochemical season just prior to the onset of the rainy season and to include measurements taken before, during, and after Holy Week (April 14–20, 2003), when vehicular traffic is historically reduced as residents leave the city for the holiday.

The MCMA air quality study included a mobile laboratory designed and developed by Aerodyne Research, Inc. (ARI), which was used to determine vehicle emissions and to map background concentrations of a variety of pollutants in selected MCMA industrial, commercial, and residential districts.²⁷ Real-time measurements of selected trace gases were provided by ARI’s tunable diode laser absorption spec-

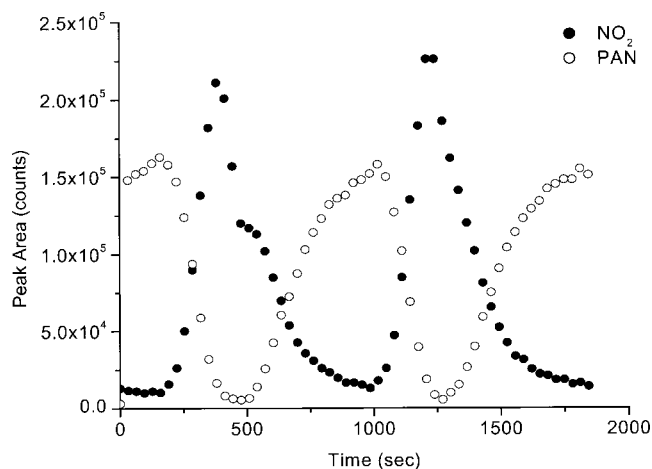


FIG. 11. Thermal decomposition of a 190 ppt PAN standard to NO₂, followed by reformation of PAN, as measured by the fast GC/LCD.

trometer (TDLAS). In addition, fine aerosol size distributions and nonrefractory chemical compositions were measured with a fast-response aerosol mass spectrometer (AMS) designed and built at ARI. Commercial air quality monitors (e.g., NO–NO₂, CO, and O₃) were also included.

Measurements of NO₂ and PAN were obtained continuously at the CENICA supersite by fast GC/LCD from April 3 (Julian Day 93) to April 30 (Julian Day 120) with 1 min time resolution. The sample inlet for the GC/LCD was located 22.5 m above ground level. Measurements of NO₂ and PAN were also obtained by fast GC/LCD onboard the Aerodyne Mobile Laboratory from April 3 (Julian Day 93) to April 21 (Julian Day 111).

A. Differential optical absorption spectroscopy

A research-grade long-path differential optical absorption spectroscopy (DOAS) system provided by the University of Heidelberg was deployed and operated by the Massachusetts Institute of Technology (MIT) at the CENICA supersite during the MCMA 2003 air quality study. The DOAS measures the concentrations of several trace gases in the atmosphere simultaneously by recording their differential absorptions in the ultraviolet-visible spectral range over an extended path length. As such, DOAS measurements will average out localized sources and give an integrated result over the entire path. The DOAS measured NO₂ concentrations over the path length of 860 m defined by the light source located at CENICA and the reflector placed at the TELCEL antenna tower approximately 430 m southeast of the CENICA site, at an average height of about 16 m above the ground. Typical time resolution was on the order of 30 s, and detection limits were on the order of 1 ppb, well below the minimum concentrations observed in Mexico City. The GC/LCD measurements obtained at a single sampling point were more influenced by local sources. Figure 12 compares the NO₂ results obtained with the GC/LCD and the DOAS instrument from April 24 (Julian Day 114) to April 30 (Julian Day 120). The results compare fairly well, considering the integrating nature of the DOAS technique and the greater

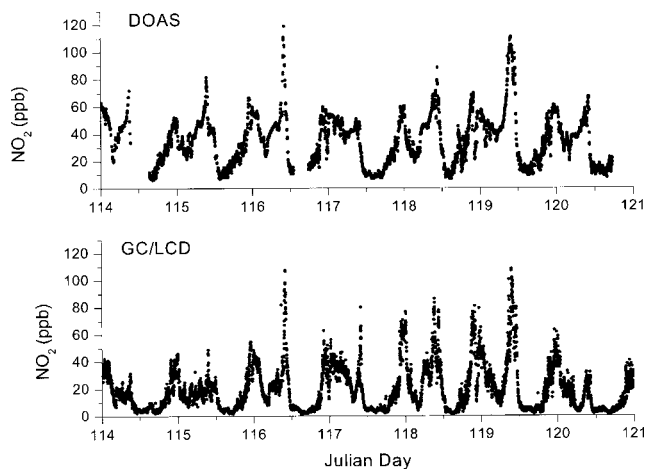


FIG. 12. Results for NO_2 from the fast GC/LCD and a co-located DOAS system at the CENICA supersite during the MCMA air quality study in Mexico City, from April 24, 2003 (Julian Day 114), to April 30, 2003 (Julian Day 120).

sensitivity of the GC/LCD single-point sampling to local sources.

B. Tunable diode laser absorption spectroscopy

A tunable diode laser absorption spectrometer (TDLAS) designed for continuous measurement of NO_2 ²⁸ was co-located with the GC/LCD on the Aerodyne Mobile Laboratory during the MCMA 2003 field campaign. The TDLAS is an absorption technique using lead salt diode infrared lasers as sources. The sample is drawn into a multipass cell that is used to increase the optical path length to 153.5 m, thereby increasing the sensitivity of detection. Reduced pressures are required inside the cell to minimize pressure broadening, reduce interferences, and maintain high sensitivity. Figure 13 shows a direct comparison of the NO_2 results obtained by the GC/LCD and the TDLAS system during a single run in the mobile laboratory on the night of April 12 to 13, 2003 (Julian Day 102 to 103). The TDLAS measurements, taken at a 1 s time resolution, were averaged to correspond to the 1 min time scale of the GC/LCD system.

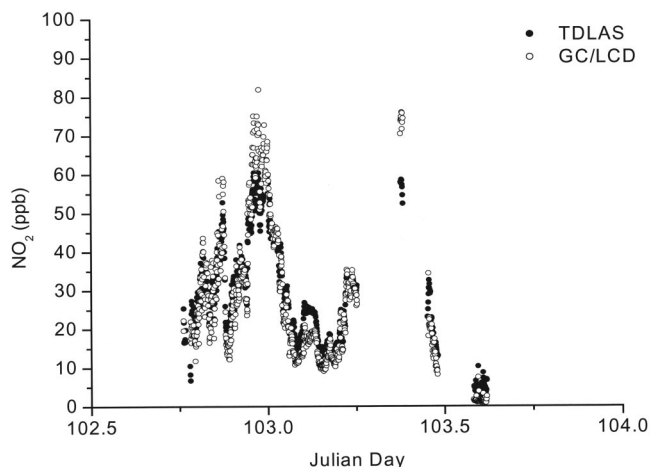


FIG. 13. Results for NO_2 from the fast GC/LCD and a TDLAS onboard the Aerodyne Mobile Laboratory during the MCMA air quality study in Mexico City, on the night of April 12 to 13, 2003 (Julian Day 102 to 103).

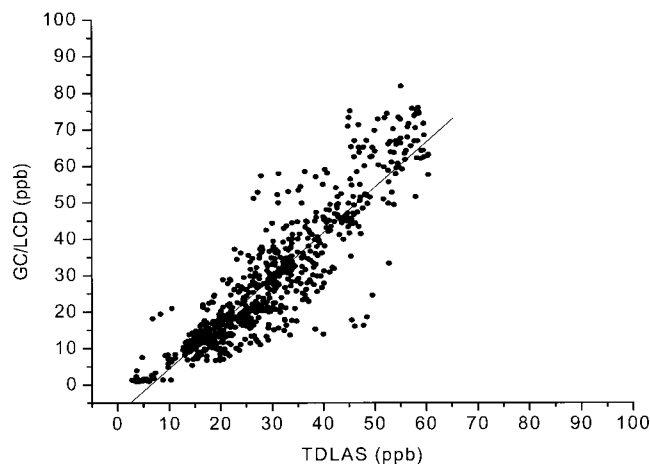


FIG. 14. Results for NO_2 from the fast GC/LCD plotted versus results from a TDLAS onboard the Aerodyne Mobile Laboratory during the MCMA field campaign in Mexico City, in April 2003.

A comparison of values taken by the two instruments simultaneously during the study is shown in Fig. 14. The correlation is a linear relationship with a slope of 1.24, an intercept of -8 ppb, and a correlation coefficient (R^2) of 0.83. However, if only concentrations below 50 ppb are considered, the slope of the comparison becomes 1.09 with an intercept of -4 ppb. There is some indication from this comparison that the GC/LCD may be giving high values for the higher concentrations. However, the sample inlets for the two instruments were not co-located, and the observed difference could indicate the sampling of different air parcels on the mobile vehicle. In addition, the TDLAS values represent 1 min averages of 60 readings, while the GC/LCD values are single samples taken every 60 s. This could result in significant differences when the mobile laboratory was in heavy traffic and NO_2 concentrations were highly variable over short time scales.

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