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New Technologies for Use in Acid Deposition Networks

REFERENCE: Drummond, J. W., Castledine, C., Green, J., Denno, R., Mackay, G. I., and Schiff, H. I., **"New Technologies for Use in Acid Deposition Networks,"** *Monitoring Methods for Toxics in the Atmosphere, ASTM STP 1052*, W. L. Zielinski, Jr., and W. D. Dorko, Eds., American Society for Testing and Materials, Philadelphia, 1990, pp. 133–149.

ABSTRACT: Several new developments associated with the sensitive Luminox NO_2 monitor (the LMA-3) are presented: (1) A peroxyacetyl nitrate (PAN) converter has been developed for use with the LMA-3. It achieves a 3-sigma detection limit of 30 parts per trillion (ppt) with a time cycle of 5 min, which allows measurements in even clean background air. It is presently being commercialized with an integral Luminox detector. (2) A second converter, sequencer for NO_x (NO_x = NO_2 + NO) and NO_2 is described. It uses CrO_3 for the NO conversion and presents significant advantages over the competitive commercial NO_x detectors presently available, namely, sensitivity down to 10 ppt or less, and virtual freedom from interferences that now plague other methods. (3) An ozone scrubber has been developed that removes ozone (O_3) from the sample air without destroying more than 10% of the NO_2. This removes the major interference associated with the luminol method for NO_2 measurements. Finally, the nonlinearities outside of the 1 to 50 ppb range have been characterized. An algorithm is presented for making corrections to ambient measurements, not only for nonlinearities but for residual ozone and PAN interferences. Typical atmospheric measurements (PAN, NO_2, NO_x, and O_3) are given both for clean background air and for urban air in Long Beach, California.

KEY WORDS: toxics, nitrogen dioxide, nitrogen oxide, peroxyacetyl nitrate, measurements, ambient measurements, ozone scrubber, interference testing, ozone

In the past year, several new developments have taken place that extend the usefulness of the Luminox NO_2 detector [*1*]:

1. A converter has been developed to allow measurements of peroxyacetyl nitrate (PAN).
2. A second converter has been developed to measure NO_x (here NO_x = NO + NO_2).
3. The minor interferences associated with the highly sensitive Luminox technique have been characterized so that corrections to the data can be made for both ozone (O_3) and PAN.
4. An ozone scrubber has been developed which passes NO_2; it enables an interference-free measurement of NO_2 or NO_x in background tropospheric air.

The ambient measurement of NO_2 or NO_x by using Luminox technology offers significant advantages over other commercial instruments based on ozone chemiluminescence NO detectors with "NO_2 to NO" converters. First, the Luminox instruments are truly portable.

[1] Unisearch Associates, Inc., Concord, Ontario, Canada L4K 1B5.

They are considerably smaller and power efficient. The NO_2 detector can be operated on its internal battery for over 3 h. However, the strongest advantage of the Luminox NO_2 detector is its some thousandfold increase in sensitivity relative to other commercial instruments. Indeed, there are strong arguments, based upon the current state of knowledge of atmospheric chemistry, for insisting on the improved detection limits and relative freedom from interferences now available.

It can be argued that of all of the gaseous species that are released by human activity, NO_x (NO_x = NO + NO_2) makes the largest impact on atmospheric chemistry. A brief summary of its chemistry is given here. The NO_x is rapidly oxidized in the atmosphere to form HNO_3 and particulate nitrate [2,3], which contribute directly to the problems of acid rain and the excess nitrification of forests. Of perhaps even greater importance is the participation of NO_x in the formation of ozone [4]. The NO_x can act as catalysts in smog formation processes and, in contrast to most other atmospheric pollutants, they have more effect on chemistry at relatively low-mixing ratios (~1 ppb) than at the much higher levels typically found in urban air (20 to 1000 ppb). This effect is predicted by models and verified by measurements [4]: the rate of photochemical ozone production is shown to peak for NO_x near 1 ppb. This photochemical production of ozone is particularly worrisome since ozone has been increasing significantly at many ground-level monitoring stations, and ozone is increasingly blamed for crop damage and forest destruction.

The fate of NO_x and its effect on air chemistry is complex, but it can be outlined by a few reactions. One of the most important daytime oxidation reactions for NO_x is the reaction

$$NO_2 + OH \longrightarrow HNO_3 \qquad (R1)$$

This reaction acts as a sink for both NO_x and OH radicals, and for high concentrations of NO_2, it tends to inhibit photochemical activity.

At lower mixing ratios of NO_x, a catalytic generation of ozone proportional to NO_x becomes more important. As first steps in ozone formation, carbon monoxide or hydrocarbons are oxidized by OH and then O_2 to form HO_2 or one of the organic peroxy radicals (RO_2) as products. The next step (Reaction 2 or Reaction 3) is the key to ozone production:

$$NO + HO_2 \longrightarrow NO_2 + O_2 \qquad (R2)$$

$$NO + RO_2 \longrightarrow NO_2 + RO \qquad (R3)$$

The NO_2 produced in these reactions is subsequently photolyzed and ozone is produced:

$$NO_2 + h\nu \longrightarrow NO + O \qquad (R4)$$

$$O + O_2 + M \longrightarrow O_3 + M \qquad (R5)$$

where M is any molecule. Note, however, that the NO_2 produced by the reaction

$$NO + O_3 \longrightarrow NO_2 + O \qquad (R6)$$

serves to recycle all of the reactants but without producing ozone. Thus, Reactions 4 through 6 constitute the simple "photostationary state" that continually recycle the NO_x during daytime. Their time constant is on the order of 1 to 5 min, depending on availability of sunlight to photolize NO_2. The daytime ratio of NO_2/NO is normally 3:5 near ground level for nonurban air [5]. As a consequence of this high ratio, together with an often much larger

reservoir of other odd-nitrogen species, an interference-free measurement for NO_2 is mandatory for successful determination of the NO_x.

In summary, there are two major problems with competing commercial NO_x detectors that are alleviated by the instrumentation described here: (1) Although the NO_x chemical production of ozone becomes most significant at levels on the order of 1 ppb, this NO_x level is already below the detection limit of those instruments. Further, the frequency of ambient NO_x measurements of <1 ppb is surprisingly high. (2) It has been documented that the "NO_x" converters, such as the hot molybdenum or stainless steel converters also convert other nitrogen containing species (besides NO_2) into NO [6]. Initial test of the NO_x converter/sequencer described below has demonstrated far fewer interferences.

The measurement of PAN (peroxyacetyl nitrate) in the atmosphere is important for several reasons. It is known to be the major irritant in urban smog [7], it is known to be harmful to plants and animals, and it has recently been shown to be a powerful mutagenic agent and is therefore implicated as a carcinogen [8]. In clean air, the PAN acts as an important reservoir of chemically active odd-nitrogen, and it participates significantly in long-range transport. In short, there is now a strong impetus for routine measurement of PAN in both clean air and urban air.

A highly sensitive instrument for ambient atmospheric PAN measurements is described below. It is based on the PAN detector that was developed at the University of Denver [9]. Their system consists of a self-contained gas chromatograph (GC) which uses a Luminox LMA-3 NO_2 monitor as a detector. We have now significantly improved on the already good sensitivity of their system and have solved the problems of nonlinearity and poor peak separation. According to our laboratory results, the detection limit (3 X baseline noise) for PAN in air is now 30 parts per trillion (ppt). Since an injection sequence is repeated every 5 min, the 3-sigma hourly average detection limit is better than 10 ppt.

Although the Luminox NO_2 monitor offers sufficient sensitivity to measure NO_2 anywhere in the background troposphere, it has been plagued by an ozone interference of approximately 1%. Therefore, unless ozone is corrected for as described in the next section, or chemically removed using the ozone scrubber, the usefulness of the LMA-3 NO_2 measurements is effectively limited to about 1 ppb, where the ozone interference becomes a significant portion of the total signal. Now, by placing the ozone scrubber in the LMA-3 sample line, measurements of NO_2 at less than 10 ppt are now possible.

Ambient measurements for PAN, NO_2, NO_x, and ozone, (all using Luminox techniques) were gathered at a site in Long Beach, California. Data are presented below for 15 November 1987.

The LMA-3 NO_2 Monitor

Instrumental Description

A detailed description of the Luminox instrument, its interference testing, and results of its intercomparison with a tunable diode laser absorption spectrometer (TDLAS) measurement of NO_2 in ambient air is given in Schiff et al., [10]. In this section we give only an abbreviated description of the LMA-3 itself and concentrate instead on the recently developed improvements within the LMA-3. A block diagram is shown in Fig. 1. The sample air is drawn through a small chamber which is viewed by a photomultiplier tube. The NO_2 in the sample air that contacts a wetted wick reacts with a specially formulated solution containing luminol, $NaSO_2$, NaOH, and alcohol. The signal is proportional to the strong chemiluminescence from luminol oxidation. The basic instrument responds principally to the concentration of NO_2; its interferences are discussed below. The detection limit (2 sigma) is 5 ppt, which corresponds to variations in the short-term noise as seen on either the front

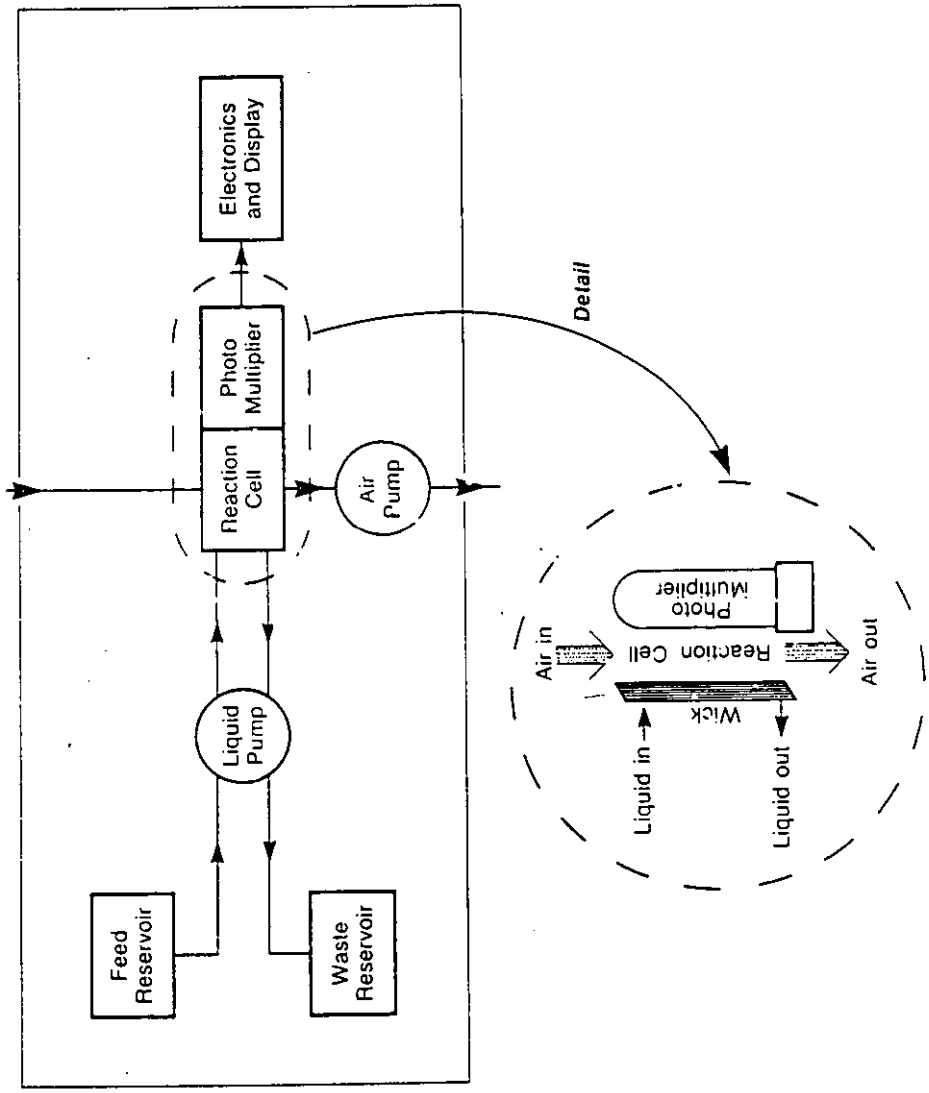


FIG. 1—*A block diagram of the Luminox NO_2 monitor.*

panel meter or a chart recorder. Even better detection limits are readily attainable by taking a zero every 10 min (see LNC-3, below) and averaging the signal electronically, for example, by using a data logger. For example, an integration time of 1 min results in a 2 sigma detection limit of less than 1 ppt. The time response (0 to 95%) for a step change of 10 ppb NO_2 is 1 s. The signal is electronically compensated for both the temperature dependence of the photomultiplier dark current and the negative temperature dependence (−2%/°C) of the NO_2/luminol reaction.

Interferences and Linearity of the LMA-3

The only significant interferences are ozone (about 1% or less, see below) and PAN (25%), where the interference is expressed as the observed signal as compared to an equivalent mixing ratio of NO_2. A partial list of species that produce no measurable interferences at their normal range of atmospheric concentrations includes NO, HNO_3, HONO, NO_3, SO_2, H_2O_2, HCHO, CO, and CO_2. Because ozone and PAN could contribute substantially to the NO_2 signal under clean "background air" conditions, we have developed techniques to eliminate these interferences. Nevertheless, the interferences have been characterized well enough to justify retroactive corrections for measurements already made.

An algorithm to generate an excellent estimate for ambient NO_2 mixing ratios from the LMA-3 signal obtained under adverse monitoring conditions has been developed. It consists of two major parts, a correction for nonlinearities, if any, followed by a correction for ozone and PAN interferences. It should be noted that whenever NO_2 mixing ratios are between 1 and 50 ppb, the LMA-3 signal obtained during most rural ambient air measurements typically requires very little, if any, correction. First, the response of the LMA-3 (with the standard "Luminol II" solution) is linear within 5% between 1 to 50 ppb. Second, as argued below, the ozone and PAN corrections are typically less than 5% whenever NO_2 is in this range.

The LMA-3 signal correction algorithm is based primarily on empirical laboratory data, but it is also consistent with the predictions of our reaction-kinetics computer model of the NO_2/luminol chemiluminescence (to be described elsewhere). The procedure is to first correct the signal, S, for nonlinearity, and then, if available, for the concurrently measured O_3 and PAN mixing ratios. The correction for nonlinearities can be expressed as a polynomial in S with coefficients given by Table 1.

$$NO_2(\mathrm{LIN}) = a + b^*S^{1/2} + c^*S + d^*S^2 + e^*S^3 \quad (1)$$

The value of the coefficients (a to e) depend on the range of S. Since these may vary a few percent from instrument to instrument, the coefficients and their break points have been rounded off. Figures 2 and 3 give the calibration curves for >50 ppb and <1 ppb, respectively,

TABLE 1—*Coefficients for Eq 1, above.*

	Range of S, ppb			
Coefficient	0 to 1	1 to 50	50 to 200	>200
a	0.0	0.4	23.0	−2067
b	0.63	0.0	0.0	0.0
c	0.77	1.0	0.312	27.45
d	0.0	0.0	0.006 763	−0.111 6
e	0.0	0.0	0.0	0.001 747

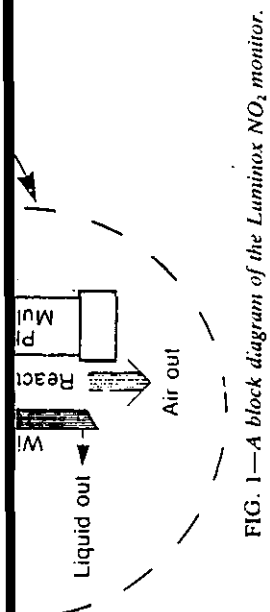


FIG. 1—*A block diagram of the Luminox NO_2 monitor.*

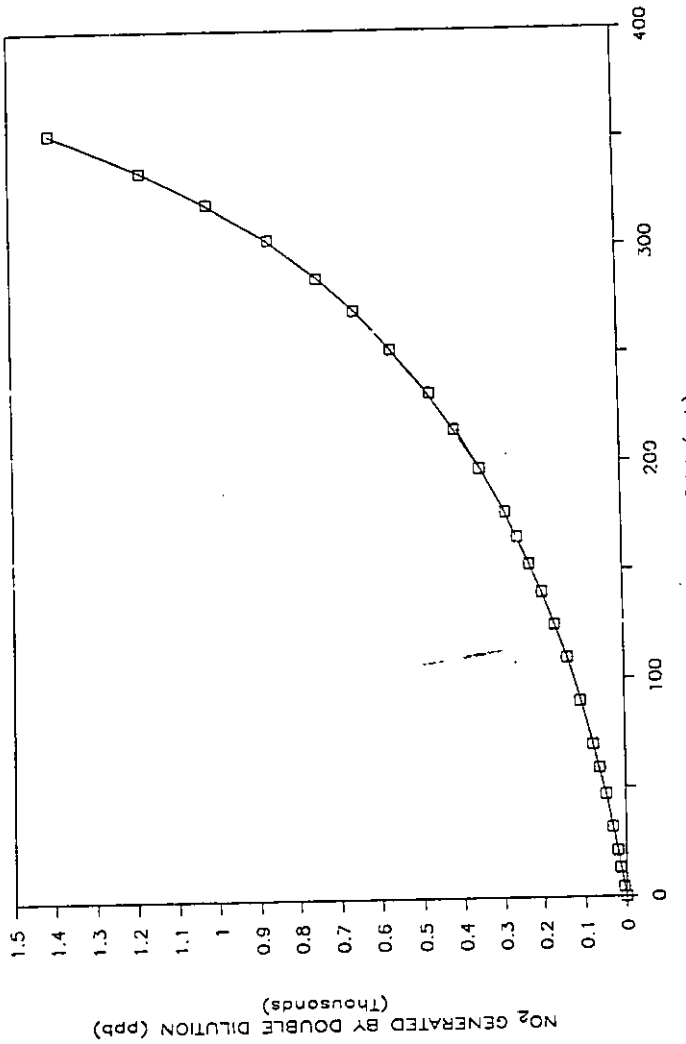


FIG. 2—*Results of double-dilution calibration (squares) for NO_2 mixing ratios greater than 1 ppb. In order to show the signal correction algorithm, given by the curve, the LMA 3 signal is plotted on the abscissa.*

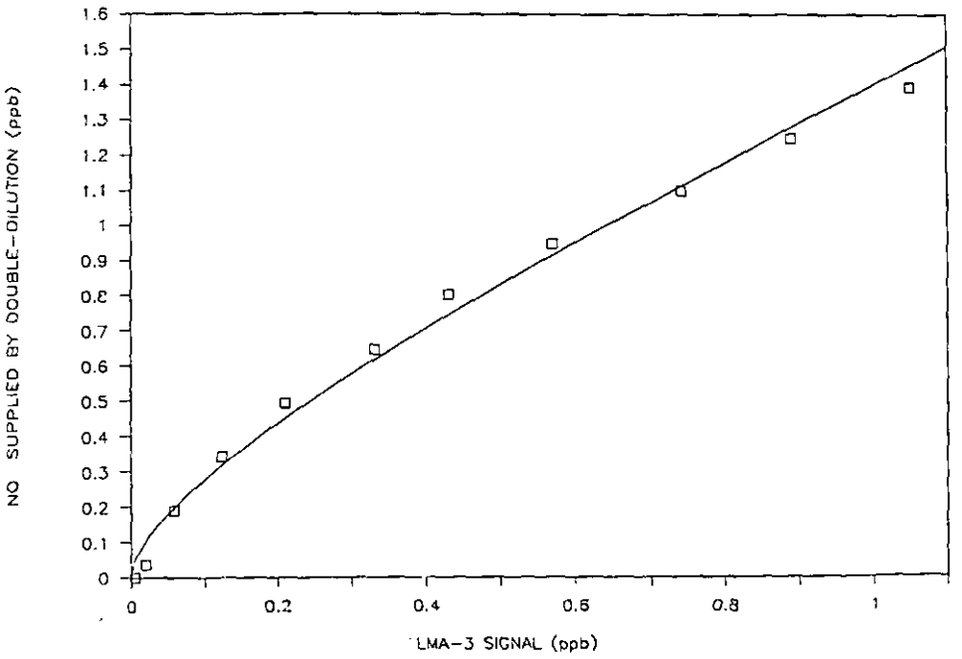


FIG. 3—*Comparison of double-dilution calibrations (squares) with the steady state predictions of our kinetic model (curve) for mixing ratios less than 1.5 ppb.*

using the standard Luminol II solution. (Note that if the measurements are consistently above 50 ppb, a "special" solution formulation is recommended). The individual points were obtained by using a double-dilution calibration system, and the curves represent the fit of polynomial Eq 1.

Note that in the linear range (1 to 50 ppb), the intercept with the NO_2 axis (coefficient a) is 0.4. This is a direct consequence of the nonlinearity observed for a signal below 1 ppb. It arises from forcing the slope of the calibration curve (in the linear range) to be 1.0 while using the observed zero of the instrument (see Fig. 3). Therefore, while in the 1 to 50 ppb linear range, this 0.4 ppb must always be taken into account during both calibrations and measurements by adding it to the signal ($NO_2 = S + 0.4$ ppb).

At lower mixing ratios, the kinetics of the NO_2/luminol solution reaction become second order, and less signal is obtained for an equivalent concentration of NO_2. In fact, two molecules of NO_2 are required to produce every chemiluminescence.[2] The polynomial, Eq 1, was fit to the steady state predictions of our model. This function of the square root of the signal is also shown in Fig. 3.

It is stressed that the nonlinearities should be calculated before corrections are made for O_3 since it should behave chemically similar to NO_2 (although with reduced response). The nonlinearity effects of PAN are not yet known, but PAN should probably be corrected in the same order as for ozone. The correction algorithm for the interferences is

$$NO_2 = NO_2(LIN) - (15 - S)/15^*.01^*O_3 - 0.25^*PAN \quad (2)$$

[2] Delany, A., personal communication. National Center for Atmospheric Research, 1987.

FIG. 2—*Results of double-dilution calibration (squares) for NO_2 mixing ratios greater than 1 ppb. In order to show the signal correction algorithm, given by the curve, the LMA-3 signal is plotted on the abscissa.*
LMA-3 SIGNAL (ppb)

The second term on the right gives the correction for ozone. It is empirically derived from laboratory tests for ozone, NO_2, and synthetic air mixtures (0 to 200 ppb O_3 and 0 to 40 ppb NO_2). Presumably, the interference by ozone is complicated by the fact that the ozone reacts with the alcohol in the solution to produce products that tend to inhibit the NO_2 response. At approximately 15 ppb of NO_2, the loss of response balances the direct positive signal due to ozone, and no correction is required. Above 15 ppb of NO_2, the ozone correction term remains negligible (<5%) for ambient air measurements, since O_3 rarely exceeds 200 ppb. The square symbols in Fig. 4 represent the laboratory double-dilution calibrations with 40 ppb of ozone added. The "+" symbols were calculated by shifting the linearity curve from Eq 1 according to the ozone correction algorithm Eq 2.

The last term describes the effect of PAN on the LMA-3 signal. Two sets of laboratory experiments were carried out to determine the PAN response. In the first test, PAN was generated by photolyzing a flowing mixture of Cl_2, acedaldehyde, and NO_2 under blacklight for durations of up to 10 min. The primary product under these conditions is predicted to be PAN, although other products, including NO_2, would also be present. The effluent was then diluted by zero air at a flow rate of 6.0 l/min (STP) and fed simultaneously to an LMA-3 and two ancillary instruments, described below. First, the LMA-3 was checked for sensitivity to Cl_2 and acedaldehyde; there was no change in response to step changes of either for constant NO_2 over 0.0 to 13.0 ppb. A given experiment was run for several (~20) *different PAN and NO_2 mixtures (0.0 to 6.9 and 0.1 to 13.0 ppb, respectively).* The actual PAN concentration was determined by use of a gas chromatograph calibrated for PAN [*11,12*], and the residual NO_2 was unequivocally determined by means of a tunable diode laser absorption spectrometer (TDLAS) built by Unisearch [*10*]. In order to separate out the effects on the LMA-3 signal due to PAN and NO_2 in the mixtures, a multivariate linear regression was carried out using PAN and a "predicted" LMA-3 signal as variables. This predicted signal was calculated from the actual NO_2 (as measured by the TDLAS) by using the inverse of the first three terms of Eq 1. The resulting PAN response, using the standard Luminol II solution, was 26 ± 3% (R^2 = 0.99; n = 19). The interference is expressed as the percentage of PAN response compared to the equivalent mixing ratio of NO_2. One of the experiments was carried out for a solution without alcohol; its response to PAN was several times larger than for the standard solution, and it was in agreement with the results of Wendel et al [*13*].

The second experiment was somewhat more direct. It consisted of using the gas chromatographic (GC) part of the PAN converter, described below, to generate a pure source of PAN (without NO_2) during the time frame of a chromatographic peak. The PAN converter effluent was monitored by an LMA-3. The relative sensitivity of the LMA-3 to PAN could be determined by pyrolyzing the effluent at temperatures between 60 to 120°C. If one assumes that the pyrolysis of one molecule of PAN generates one molecule of NO_2, then the ratios in response before and after pyrolysis would be a direct measure of the relative response of the LMA-3 to PAN. The experiment yielded a 20.8 ± 8% response toward PAN. A best estimate of the PAN interference using the Luminol II solution is 25%.

The NO_x Converter, LNC-3

The conversion of NO to NO_2 by use of CrO_3 has been studied by Levaggi et al. [*14*] and developed by Wendel et al. [*13*] for a luminol-based NO_2 detector. Approximately 3 cm^3 of CrO_3 on a substrate of Chromosorb-A is used to convert NO to NO_2 quantitatively. A diagram of an LNC-3 is shown in Fig. 5. The sample air is first dried by means of a Nafion shell dryer (Permapur, Inc.) that removes excess humidity from the sample air without detectable loss of NO_2. An outlet valve array routes the dried (5 to 60% relative humidity)

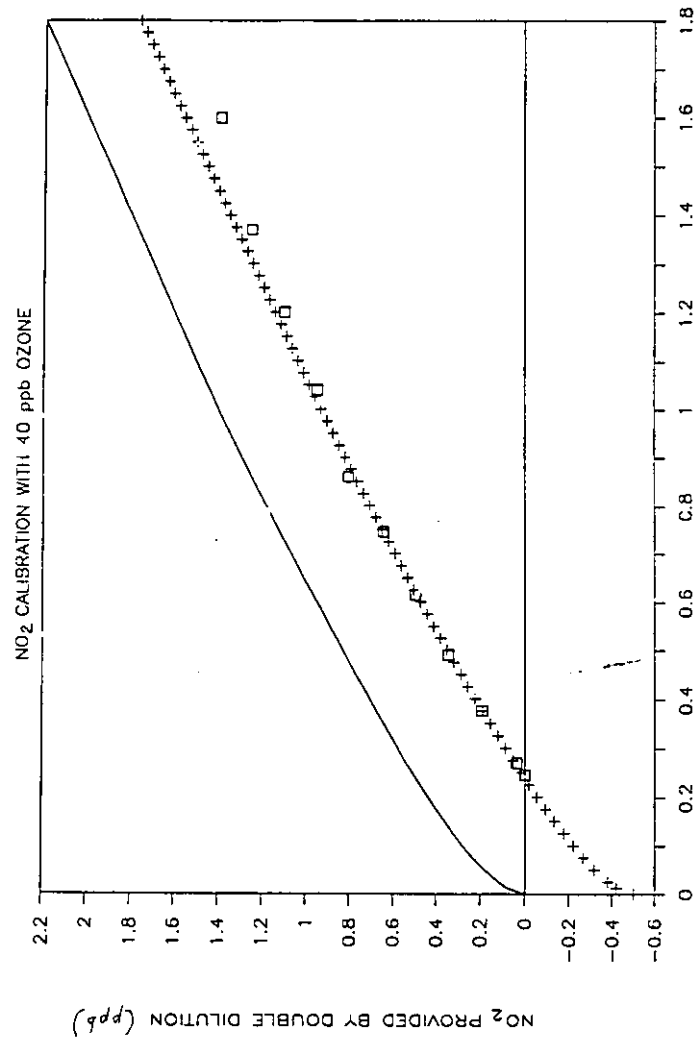


FIG. 4—*The square symbols represent the LMA-3 signal as a function of NO_2 mixing ratios provided by double-dilution in the presence of 40 ppb of ozone. The curve is taken from Fig. 3. The "+" symbols show the displacement of the curve by subtracting the ozone correction term of Eq 2. The "+" symbols show the same functional dependence as the squares, showing that the signal correction algorithm should be carried out in the order described in the text.*

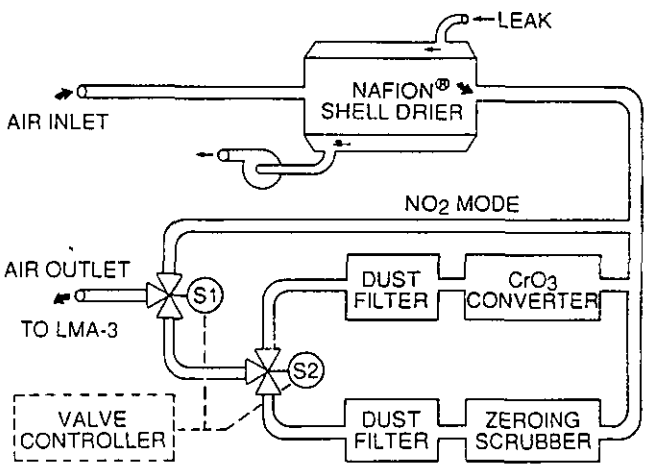


FIG. 5—*A block diagram of the LNC-3 NO_x converter/sequencer. The inlet air is dried in a Nafion shell dryer. It maintains a gradient for water vapor diffusion by means of pumping on the shell to 0.5 atm, thereby reducing its specific humidity. There are three modes: (1) The path without functional blocks constitutes the normal NO_2 mode. (2) The second path contains a CrO_3 NO to NO_2 converter. The LMA-3 thus reports the sum of NO and NO_2. (3) A scrubber removes NO_2 and O_3 to provide a zero signal. See text for PAN interference. Note that the ozone scrubber described below could be used for removing the ozone interference for ambient measurements with less than 1 ppb of NO_2.*

sample stream through one of three paths. The first path goes straight through and constitutes the normal NO_2 mode. The second path contains the CrO_3 converter. A dust filter inhibits migration of the CrO_3 to the LMA-3 detector. The third path is via a zero trap (proprietary) where NO_2 and O_3 are removed. A built-in sequencer cycles between the three modes according to the step time set by the operator. A status output is available for use with data loggers, and it supplies a different voltage for each mode. The valves may be remotely controlled via an optically isolated interface.

The raw data stream generated by the LNC3 LMA-3 pair is shown in Fig. 6. These measurements were of air drawn from outside our laboratory in Concord, Ontario. The signals consist of NO_2, the sum of the ambient NO and the NO_2, and a zero. The NO, the difference between the NO_x and the NO_2, did not reach zero during this night. Ozone, measured concurrently, never exceeded 5 ppb, inhibiting the normal titration of NO that occurs during windy conditions.

Interferences

Some measure of PAN rejection is provided by the LNC-3, since the installed zero scrubber passes PAN while removing ozone and NO_2. Therefore, if the zero is subtracted from the NO_2 measurements during the subsequent data analysis, the interference due to PAN is also removed. This removal of the PAN interference can be a very significant correction to the total signal during photochemical smog events. The NO_x mode of the LNC-3 has been tested for several potential interferences. Ozone results in a slight negative response: 80 ppb of ozone decreased the response of 22.0 ppb of both NO and NO_2 by 5%. The response due to PAN is marginally enhanced by the CrO_3 converter: a mixing ratio of 2.5 ppb PAN (as measured by our PAN converter, below) resulted in an interference relative to NO_2 of 30%.

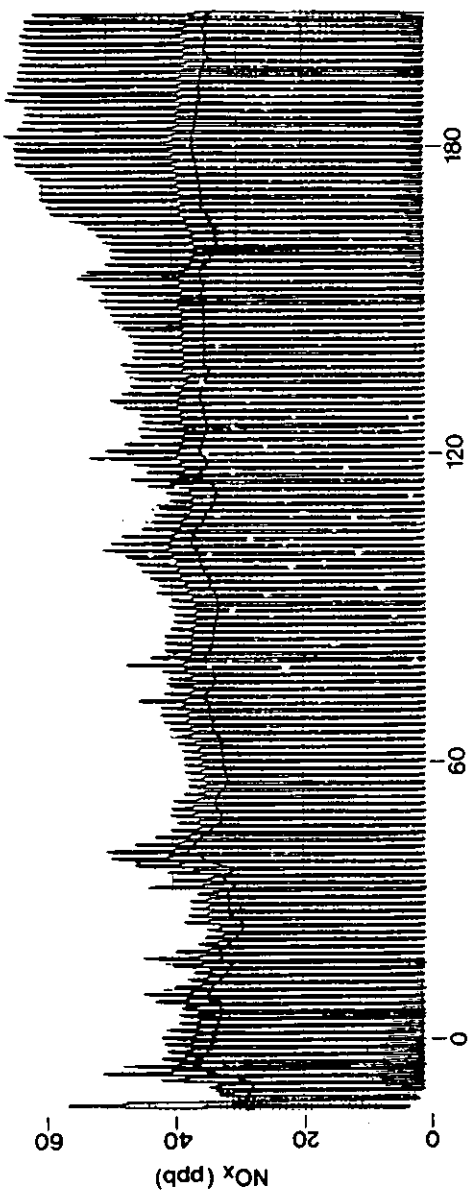


FIG. 6—*The signal stream (commutated) generated by the inlet sequencer/LMA-3 pair for relatively stagnant air taken from outside our lab in Concord, Ontario, between the times of 0130 and 0500 on 27 May 1987. The continuous trace represents the simultaneous NO_2 measurements using a second LMA-3; for clarity its zero and time were offset by 5 ppb and 2 min, respectively. The NO_x is shown by the largest signal. NO was always >3 ppb during the night. This would be compatible with the simultaneous O_3 measurements of <5 ppb throughout the night.*

Pan Converter, (LPC-3)

Instrumentation

A block diagram of the current configuration of our prototype LPC-3 PAN converter is shown in Fig. 6. The two major parts of the instrument are the GC and the Luminox detector. The carrier gas for the GC is generated from sample air within the instrument by scrubbing the air for NO_2 and PAN. (The contents of the various scrubbers and converters are proprietary information at this time). Every 5 min, 60 mL of ambient sample air is injected via an NO_2 scrubber onto the column. The column consists of a 25-cm long, 6-mm outside diameter Teflon tube filled with Chromosorb G coated with 10% Carbowax 400. The retention time for PAN is 1.5 min. The effluent of the column is passed through a converter to remove one NO_2 from each PAN molecule. The effluent flows to the Luminox Chemiluminescent NO_2 detector via a "linearity" module to insure that the detector remains in its linear range. Without the NO_2 scrubber, a peak due to NO_2 would appear with a retention time of 15 s. However, it was found that the NO_2 peak area was a strong function of relative humidity. Therefore, the NO_2 is removed from the sample in order to simplify the chromatogram and improve the resolution of the PAN peak.

During our field measurements, a CBM 4032 computer outfitted with a Unisearch data acquisition system was used to determine the areas under the PAN peaks. The LMA-3 data were averaged for 3 s and stored in an array versus time. The peak areas were calculated immediately following the subsequent injection using the following algorithm: The baseline was determined by fitting two straight lines to the data before and after the peak. The PAN peak area was calculated by summing the rectangles defined by the time, the stored signals, and the fitted baseline. The PAN mixing ratio was calculated by dividing this area by the measured injection time.

Calibration

Perhaps the major advantage of the Luminox PAN instrument is that calibration is accomplished by using known mixing ratios of NO_2 in zero air. The calibration bypass valve (shown in Fig. 7) is set to mimic the flow characteristics of the column, thus enabling the

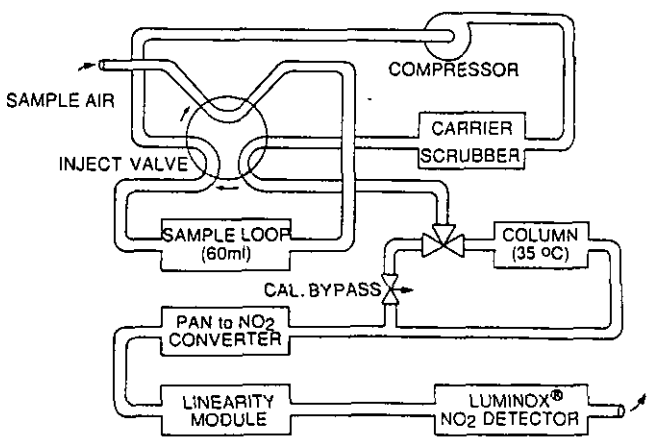


FIG. 7—*Block diagram of the PAN converter together with the LMA-3. The instrument is presently being commercialized as one unit.*

NO_2 detector to be calibrated. In this mode, 60 mL batches of NO_2 calibration gas can then be "injected" into the NO_2 detector. Since the flow rate is about 200 cm^3/min, calibration streams of about 20 s duration appear above a baseline, and the response of the detector can be properly adjusted. In our measurements, this calibration was carried out daily. Every month, a series of tests to quantify the losses and the PAN conversion to NO_2 (~100%) was carried out. A full description of these tests will appear elsewhere.

Interferences

Since the Luminox PAN instrument uses the excellent selectivity offered by a GC, the likelihood of interferences are greatly minimized. We have tested the detector for interferences against several gases; no interferences could be observed during the time window of the PAN peak. For example, ozone at the 200 ppb level was sampled. Before installing the NO_2 scrubber (which also removes ozone), a peak due to ozone appeared during the retention time of the NO_2, although with a magnitude of only 0.1% of NO_2. Since then, no effect could be observed for ozone mixtures with either zero air or ambient air from outside. Further, methyl nitrate is likely present in our PAN source. It should produce a peak somewhat earlier than PAN, but such a peak has not been observed, even with a GC column twice as long. PPN (peroxy-propanyl nitrate) has been observed in the chromatogram in laboratory calibrations. It has a longer retention time than PAN (2.9 and 2.1 min, respectively), but its peak is not fully resolved.

Measurements

Figure 8 [*15*] shows the ambient measurements gathered over one 24-h period in Long Beach, California. Measurements are presented for NO_2, NO_x, PAN, and Luminox O_3 (see figure caption). It can be seen that the input of NO during the morning rush hour appears to inhibit the generation of the ozone and PAN peaks until later in the morning. Notice that the O_3 and the NO tend to titrate each other throughout the day; in the evening, the ozone quickly disappears, while PAN decays more slowly. Presumably, the spike at 1400 in PAN and O_3 is due to the transport of air from suburban locations.

Ozone Destruction Trap

As already discussed above, ozone does not always present a significant interference to the ambient NO_2 measurements obtained by the LMA-3. Urban and rural air often contain enough NO_2 such that the ozone interference constitutes less than 5% of the total signal. However, in very clean background air, this interference can become very large with respect to the NO_2 signal. Under these circumstances, the LMA-3 requires the use of an ozone trap to realize the full capabilities of the instrument. We have developed a trap that destroys O_3 while passing NO_2 at the ~90% level. The contents of the trap are proprietary. The trap has been tested extensively in the field under conditions of both polluted and very clean background air. As an example, Fig. 9 shows raw data from typical ambient air measurements taken at Niwot Ridge, Colorado, during July 1987, under westward wind conditions. Two LMA-3 NO_2 detectors were operated in parallel. One was equipped with a modified LNC-3 NO_x converter that contained an ozone scrubber in an extra fourth mode. It can be seen that the NO_2 mode (including the ozone interference) of the second instrument tracked the first to a high degree of accuracy. The ozone scrubbed mode gave a raw signal of approximately 40 ppt (~100 ppt after linearization). The difference (650 − 100 = 450 ppt) rep-

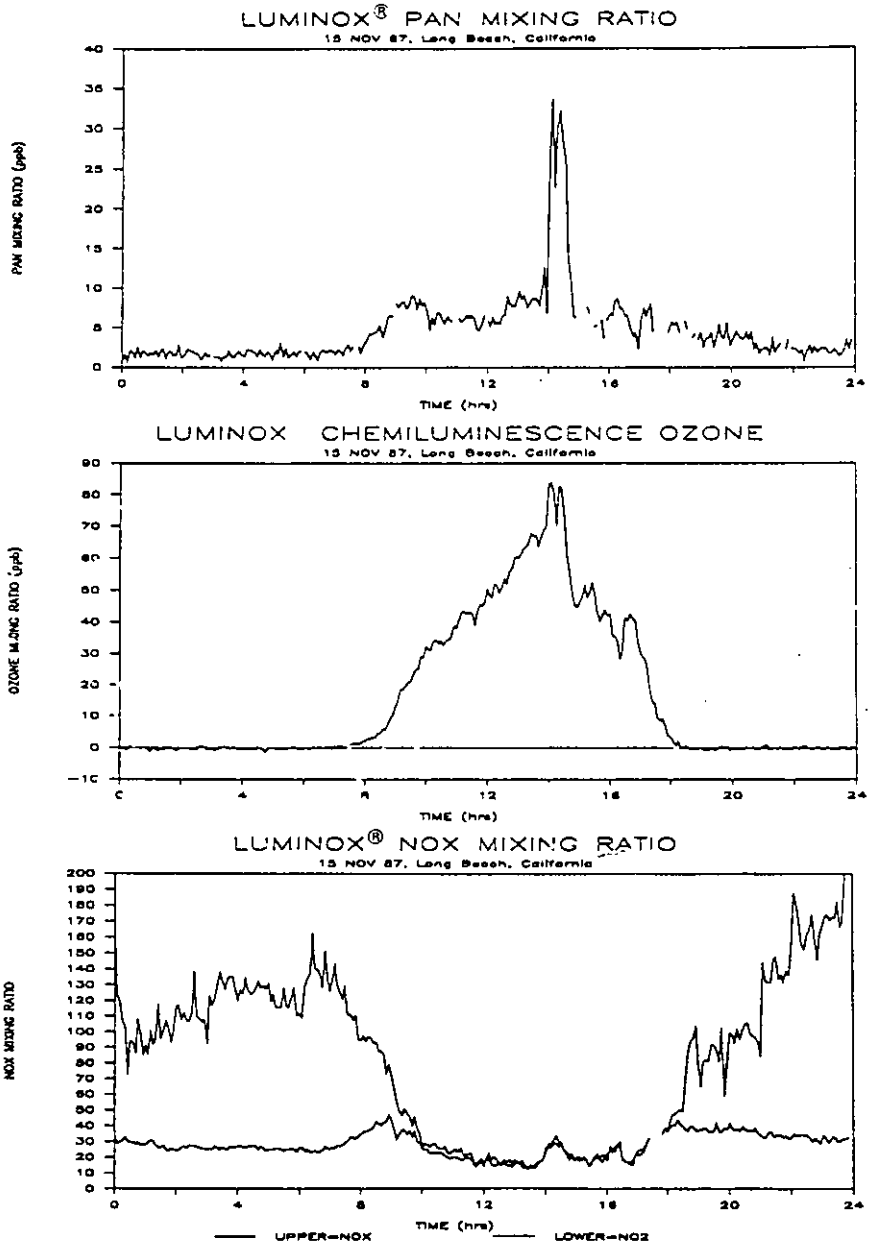
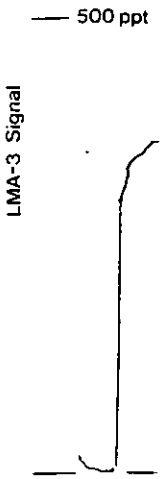


FIG. 8—*Ambient measurements for PAN, ozone, NO_x, and NO_2 taken in Long Beach, California. The PAN was measured with the LPC-3 PAN converter (see text). The ozone was measured using a modified LMA-3: its photomultiplier was replaced by a red-sensitive PMT, its solution was replaced by an Eosyn-Y laser dye solution (Ray et al. 1986), and it was outfitted with an automatic zeroing system. It was calibrated by using a stream of ozone in zero air, monitored also by a Dasibi 1003 AH. The NO_x and NO_2 were measured with the LNC-3. Calibrations were carried out at 1730 on the PAN and NO_x detectors.*



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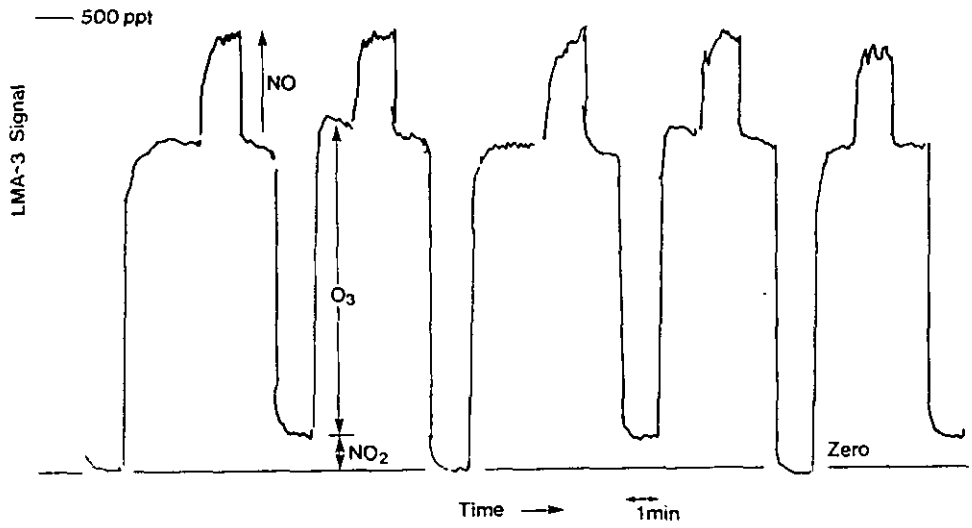

FIG. 9—*Raw data stream from a modified LNC-3 NO_x converter/sequencer obtained at Niwot Ridge (University of Colorado Mountain Research Station, Site C1). The data cover a time span of ~20 min during the afternoon with brisk winds from the west (i.e., clean background air). The four modes were represented by (1) the NO_x mode, (2) normal NO_2 measurement of the LMA-3 (50% duty cycle), (3) the ozone scrubbed mode, and (4) the zero mode. Since the signals are well below 1 ppb, they must be linearized according to Eq 1 (see text).*

resents the signal due to ozone interference. As described above; the difference between the NO_x and the NO_2 modes gives a measure for NO. It should be noted that since the ozone scrubber also passes NO, the operation of the NO_x mode would have also benefitted by using the scrubber in-line with the LNC-3.

Longevity tests of the ozone destruction trap are still in progress. The prototype scrubber used for the measurements shown in Fig. 8 consisted of a filter cartridge containing 54 cm^3 of the material and its substrate. It was used for 3.5 months (with a 12.5% duty cycle) in both clean and polluted atmospheres without losing its efficiency toward 40 ppb of O_3. Longevity tests are in progress for several production run scrubbers. Two scrubbers have sampled air from outside our laboratory (ozone mixing ratios average 10 to 50 ppb) with 100% duty cycle. One of the scrubbers has operated for over 3 months with no change in scrubbing efficiency for test streams of 40 ppb ozone. After this time, the throughput efficiency for NO_2 remains 92%. Finally, it is noted that the loss of NO_2 in the scrubber is a constant percentage of its mixing ratio; therefore, the LMA-3 NO_2 monitor can be calibrated together with its in-line scrubber.

Conclusions

Chemiluminescence with a luminol solution provides a direct and extremely sensitive method for measuring NO_2 in ambient air with no necessity to first convert the gas to NO, as required in other methods. Since, at ground level in nonurban air, the NO_2 already constitutes the major portion of NO_x, a good estimate for NO_x is immediately available.

No interferences were found for H_2O_2, NO, HNO_3, NH_3, NO_3, HONO, CO, CO_2, SO_2, or organic nitro compounds at concentrations normally found in air. The sensitivities to PAN and O_3 have been characterized, and corrections to the ambient measurements made

with the LMA-3 are possible whenever supporting measurements for PAN and ozone are available.

Several new developments have taken place that greatly expand the capabilities of the instrument. A NO_x converter, the LNC-3, which is inserted into the inlet line of the LMA-3, sequences between NO_2, NO_x, and zero measurements with any time step desired by the operator. Although the NO to NO_2 conversion technique is not new, it is ideal for use with the Luminox method for measurement of NO_2.

The PAN converter, LPC-3, consists of a gas chromatograph, followed by a PAN to NO_2 converter, so that the LMA-3 can be used as a sensitive detector. An injection sequence for PAN is repeated every 5 min, offering a 3-sigma detection limit of 30 ppt. The PAN converter is now being combined with the Luminox detector in a commercial PAN instrument. It will feature a microprocessor for on-board data reduction and instrument control.

Finally, an ozone scrubber has been developed for use in background tropospheric air measurements for NO_2. This scrubber allows the LMA-3 to make full use of its inherent sensitivity. Now, clean air measurements with NO_2 detection limits even better than relatively complex and expensive research instruments are possible.

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