Improved NO$_x$ Monitor for Measurements in Tropospheric Clean Air Regions

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The sensitivity of the well known technique for the measurement of NO$_x$ in air by the chemiluminescence from the NO$_2$ produced in the reaction of NO with O$_3$ has been improved so that it is possible to measure routinely the sum of NO$_2$ and NO or NO at mixing ratios in the pptv range. Thus it will be possible to perform such measurements in rural continental and coastal maritime environments. The details of the instrumentation are discussed.

Field tests of the instrument were conducted at the station of the German Environmental Agency in Deuselbach (Hunsrück) and at the Loop Head peninsula at the west coast of Ireland.

KEY WORDS: NO$_x$-Monitor; measurement; clean air

INTRODUCTION

The well known chemiluminescence reaction of ozone with nitric oxide has been widely used for the detection of NO and NO$_x$ = NO + NO$_2$ in air, and several commerical NO$_x$ analysers based on this reaction are available. The reduction of NO$_2$ to NO, required to determine NO$_x$ is accomplished by means of catalytic converters. The lower limit of detection for these instruments usually lies in the range 1–5 ppbv. This is sufficient for measurements in urban air. In order to assess the extent of local pollution it will be necessary to determine background mixing ratios of NO$_x$ in unpolluted continental and maritime regions and here, the NO$_x$ mixing ratios are below the detection limit of commercial instruments. Efforts to improve the sensitivity of the chemiluminescence method have been under way for some time. Progress has been achieved mainly for NO

by increasing the sampling flow rate.[1] Large flow rates reduce the conversion efficiency of the convertors, however, by lowering the contact time, so that the detection limit for NO_2 has not been improved to the same extent. In this paper we describe an instrument of improved sensitivity for both NO_2 and NO. A moderate sampling flow rate at atmospheric pressure is used to achieve a sufficient contact time in the convertor. The chemiluminescence reaction is then carried out at greatly reduced pressures to minimize collisional quenching of the excited NO_2 formed and thereby maintain the chemiluminscence efficiency.

PRINCIPLE OF THE METHOD
AND OPERATING PARAMETERS

The reaction mechanism for the oxidation of nitric oxide by ozone involves the four reactions.[2]

1) $NO + O_3 \rightarrow NO_2 + O_2 \quad k_1$
2) $NO + O_3 \rightarrow NO_2^* + O_2 \quad k_2$
3) $NO_2^* \rightarrow NO_2 + h\nu \quad\quad k_3$
4) $NO_2^* + M \rightarrow NO_2 + M \quad k_4$

Consider a tubular, linear flow reactor into which the sample gas and oxygen containing ozone enter at one end, and the reactor contents are pumped off at the other end. Under conditions where $k_4[M] \gg k_3$, i.e. at reactor pressures greater than 1 mb, and when $m(O_3) \gg m(NO)$, one obtains the total flux of photons emitted from the reactor as

$$J = \frac{k_2 k_3}{k_1 + k_2} \frac{[NO]_0}{k_4 [M]} F[1 - \exp(-(k_1 + k_2)[O_3] V/F)]$$

$$= \frac{1013 \, k_2 k_3}{(k_1 + k_2) k_4} m^0(NO) \left(\frac{F_s^0}{p}\right) [1 - \exp(-E)] \quad \text{with}$$

$$E = \frac{(k_1 + k_2)}{1013} \frac{\alpha V m^0(O_3) F_{O_2}^0 p^2}{(F_{O_2}^0 + F_s^0)^2}$$

Here, we have the rate coefficients k_1, k_2 and k_4 given in units of $cm^3 \cdot$ molecule^{-1} s^{-1} and k_3 in s^{-1}; number densities are denoted by brackets; $F = F_{O_2} + F_s$ is the total flow rate in the reactor at pressure p in mbar; V is the reactor volume in cm^3; F_s^0 and $F_{O_2}^0$ are the sample and oxygen flow rates at atmospheric pressure, respectively, given in $cm^3 \cdot s^{-1}$; $m^0(NO)$ is the NO mixing ratio in the sample flow, $m^0(O_3)$ is the mixing ratio of

ozone in the oxygen flow, and $\alpha = 2.44 \times 10^{16}$ is a conversion factor to convert from number density to pressure, the latter being measured in mb.

For constant conditions, the photon flux is always proportional to the NO mixing ratio in the air sample. If one wishes to optimize the signal, conditions must be found which maximise E so that the value inside the brackets approaches unity. The signal increases linearly with the sample flow rate, but since E decreases at the same time, F_s cannot be increased too much. Also, the conversion of NO$_x$ to NO requires a minimum of catalytic contact time, and, in addition, the flow is limited by the pump capacity. Still, the function E can be optimized by a suitable choice of the mixing ratio of ozone and the volume of the reactor. In the instrument described below, an ozonizer is used which provides $m^0(O_3) \approx 0.04$ in pure oxygen, and the reactor volume is about 1500 cm^3. The flow rates of oxygen and the air sample are $F_{O_2}^0 \approx 0.8$ and $F_s^0 \approx 8$ cm$^3 \cdot$ s^{-1}, respectively. The pressure in the reactor is kept fairly low, about 5 mb, so that the quenching of light-emitting NO$_2$ molecules by reaction (4) is reduced as much as possible. With these parameters we obtain $E = 6.38$ and a value of 0.998 for the expression within the brackets, which means that the extent of the reaction within the reactor is close to completion. The conversion of NO$_x$ to NO is done at atmospheric pressure; the reduction of pressure to reactor conditions occurs after the sample has passed the convertor. This positioning of the convertor assures sufficient contact time. At reactor pressures the flow rates are increased by about two orders of magnitude and the contact time would be correspondingly shorter. In principle, the system can detect all nitrogen-containing species which can be converted to NO. Our interest is centred mainly on NO$_2$. Molybdenum at temperatures of about 350°C is used in several commercial instruments (for example Thermo Electron or Monitor Labs). This catalyst is reported to convert to NO both NO$_2$ and some other gaseous nitrogen compounds which may be present in the atmosphere. Hence, we have used as a second convertor crystalline FeSO$_4$. This material has been shown to have a high conversion efficiency for NO$_2$ at room temperature.

DESCRIPTION OF THE INSTRUMENT

A schematic diagram of the flow system and the individual components of the instrument is shown in Figure 1. A brass cylinder with an internal diameter of 4.4 cm and a length of 98 cm is used as the reactor. The length is actually greater than needed. The internal walls are gold-plated and polished for reflectance and to obtain an inert surface. An infrared-sensitive photomultiplier (RCA Type 8853) views the reaction chamber end-on through a 590 nm cut-off filter. The photomultiplier housing is
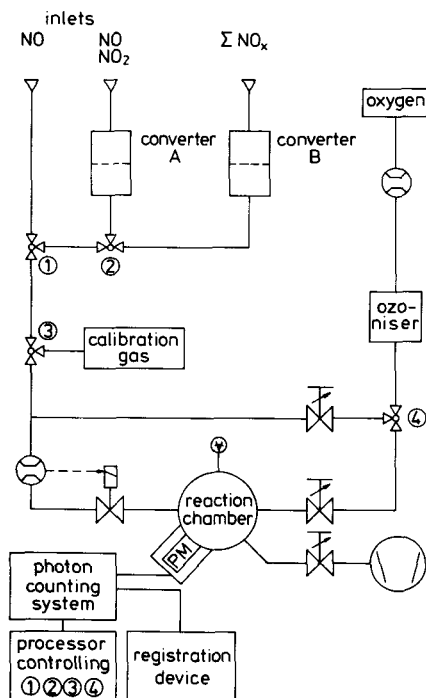
FIGURE 1   Schematic diagram of the flow system and the individual components.

held at a temperature of about $-20°C$ by refrigeration to keep the dark current low. Oxygen, taken from a steel cylinder, is passed through the ozonizer and then enters the reactor near the window. A needle valve at a fixed setting controls the flow. The sample enters the reactor near the ozone injection point. The sample flow is controlled by means of a regulating valve which keeps the total flow constant. A portable rotary vacuum pump is used to maintain the flow through the reactor. A molecular sieve trap between reactor and pump keeps the oil vapours from entering the reaction chamber, and an additional filling with silver wool destroys excess ozone for the protection of the pump.

The sample line has three intakes. One admits air directly for the determination of NO. The second intake passes the air through the $FeSO_4$ convertor, while the third intake passes the air through the molybdenum convertor. Under laboratory conditions, both convertors give the same signal. In the field, the signals are rarely the same, however. The inlet lines to the convertors are kept short to avoid losses of NO_x by adsorption to the walls of the tubing. The convertors are mounted together on one head

which can be exposed to the atmosphere at a desirable distance from the ground. The magnetic valves 1 and 2 connect the three intakes to a common suction line. The valves are actuated in sequence. Each intake is operated for a fixed time, so that the sequence is completed within a period of 1 h. These valve settings provide three measurement modes. Additional modes are used for the purpose of calibrating the instrument. Switching the magnetic valve 3 provides a calibration point from a standard sample of NO contained in compressed nitrogen. Switching the valve 4 redirects the oxygen flow to the sample inlet at the reactor, so that the NO contained in the sample is oxidized to NO$_2$ before entering the reaction chamber. The photomultiplier signal should then be the same as in the absence of NO in the sample. This signal is used as zero value. This zero reading is still higher than the dark current of the photomultiplier due to a weak chemiluminescence arising from ozone even in the absence of NO.

The pulses arriving at the photomultiplier anode are processed by means of a photon counting system consisting of a pre-amplifier, and a discriminator followed by both a counter and a rate meter. The latter unit is connected to a strip chart recorder to provide a continuous record of the signal. A typical recording for sequences of the three measurements modes is given in Figure 2 showing the log of the count rates versus time.
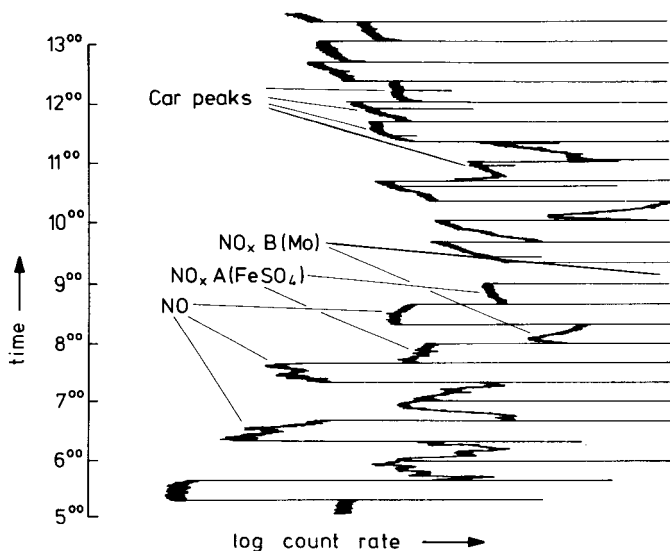

FIGURE 2   Typical recording showing the different modes in sequence with log count rates vs. time.

The different steps show the measurement without convertor, i.e. NO; with the $FeSO_4$ convertor, i.e. $NO + NO_2$; and with the molybdenum convertor, i.e. the sum of convertible compounds and NO. The former unit integrates the number of pulses for a time period of 100 sec and registers the results on a printer. Simultaneously, the results are stored in a small computer for later averaging. During each measurement mode, integrated counts are obtained ten times before the mode is changed. Results from the first two integration periods after switching to a new mode are discarded to allow the suction line to adjust to the new conditions. The remaining eight integrated count numbers are averaged and the result including the standard deviation is printed out. From these data and the calibration points obtained once or twice during a day, the mixing ratios of NO and NO_x are computed.

SENSITIVITY AND CALIBRATION

The instrument was subjected to a variety of laboratory tests to show that it meets the requirments of linearity and sensitivity in the pptv region of NO_x mixing ratios. For this purpose, mixtures of NO in nitrogen and NO_2 in air were prepared by dynamic dilution methods. To reach the pptv region, we started with test gases having NO_x mixing ratios in the ppmv range and diluted them further. The test gases were checked periodically for stability and were found generally stable. Figure 3 shows that the signal above the background increases linearly with the mixing ratios of both NO and NO_2. The gases used as diluents were not free from either NO or NO_2 themselves, and this contamination is in part the cause of the observed background signal. The data were obtained during a period when the final version of the instrument was still being developed and the reactors used for the measurements show in Figures 3a and 3b were different. The main purpose of presenting the data is to demonstrate linearity of signal with mixing ratios for both NO and NO_2 in the pptv range.

The conversion efficiencies of the two convertors were established in a similar way by comparing signals due to known mixing ratios of NO and NO_2. Table I indicates conversion efficiencies of close to 100 % for both types of convertors. Long integration times were used in these experiments to obtain the required precision. Also of interest in conjunction with convertor efficiencies are losses of NO due to wall effects in the suction line connecting the convertors with the instrument. No measurable losses occurred in teflon or stainless steel tubing of 6 mm I.D., even if the line was 50 m long. Copper tubing, by contrast, not only showed losses but
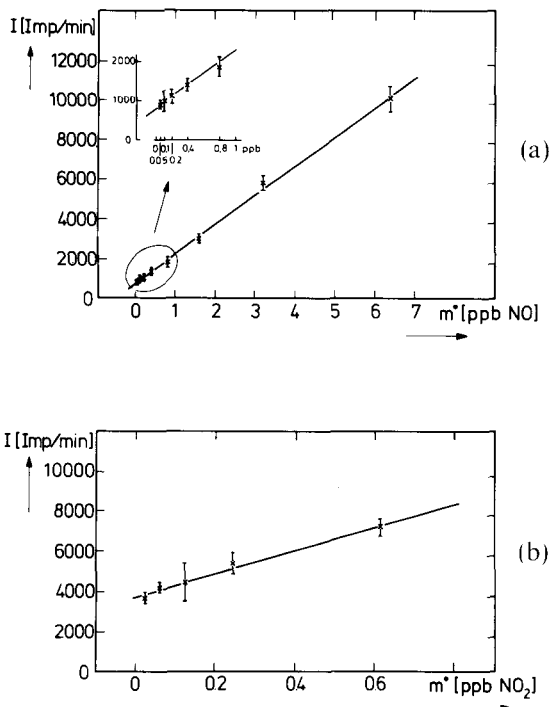
FIGURE 3 Chemiluminescence signal as a function of the mixing ratio of (a) NO and (b) NO$_2$.

TABLE I

Comparison of the conversion efficiency of molybdenum at 350°C and FeSO$_4 \times 7H_2O$

| Given mixing ratio NO$_2$ in synth. air (ppbv) | Measured mixing ratio as NO | | | |
| | Mo | | FeSO$_4$. 7 H$_2$O | |
	ppbv	%	ppbv	%
1.85	1.835	99.2	1.840	99.5
0.923	0.920	99.7	0.925	100.2
0.615	0.616	100.2	0.600	97.6
0.123	0.110	89.4	0.120	97.6
0.062	0.063	101.6	0.060	96.8
0.025	0.023	92.0	0.024	96.0
0.012	0.013	108.3	0.011	91.7

behaved also irreproducibly due to the liberation of NO from the walls by thermal desorption.

The sensitivity of the NO_x measuring device clearly depends on the type of photomultiplier used. With extended red multi-alkali photocathodes we have realized a sensitivity of 80 counts per 100 sec and pptv of NO in our field monitor. This sensitivity is much better than that implied by the slopes in Figure 3. The detection limit depends on the background signal which in turn is subject to variation with atmospheric conditions. If we define the detection limit as the signal due to NO of a magnitude of three standard deviations of the background noise divided by the measurement sensitivity, we find from the field measurements a detection limit of 5 pptv, on the average.

In the field, the sensitivity of the instrument was determined with a test gas containing about 1 ppbv of NO in nitrogen. The NO mixing ratio of the test gas must be determined in the laboratory by comparison with mixtures prepared by dynamic dilution techniques. The stability of the test gas is checked periodically, at least once before and once after the field measurements. Additional confidence concerning the calibration procedures applied was obtained in the course of an inter-laboratory field comparison of various measurement techniques for nitrogen dioxide[3] conducted in April 1979 at the station of the German Environmental Agency in Deuselbach. The various techniques employed during these measurements were a modified Jacobs-Hochheiser wet chemical method,[3a] long-distance optical absorption,[3b] cryogenic sampling followed by electron spin resonance detection,[3c] in addition to our chemiluminescence technique. The results of the intercomparison field measurements are
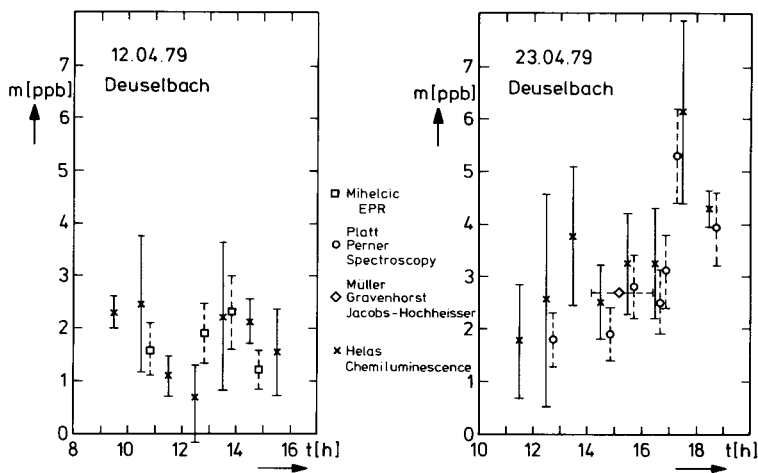

FIGURE 4 Inter-laboratory field comparison of various measurement techniques for NO_2.

shown in Figure 4. The agreement of the results is remarkably good in view of the widely different measurement techniques. Each method uses its own calibration and sampling procedures giving rise to individual systematic errors in addition to the statistical variations. The range of NO$_2$ mixing ratios observed in Deuselbach (1–10 ppbv) seems particularly well suited for such inter-laboratory comparison field tests.

FIELD MEASUREMENTS

To demonstrate the range of field conditions which the instrument is capable of handling, we show in Figures 5 and 7 examples for results
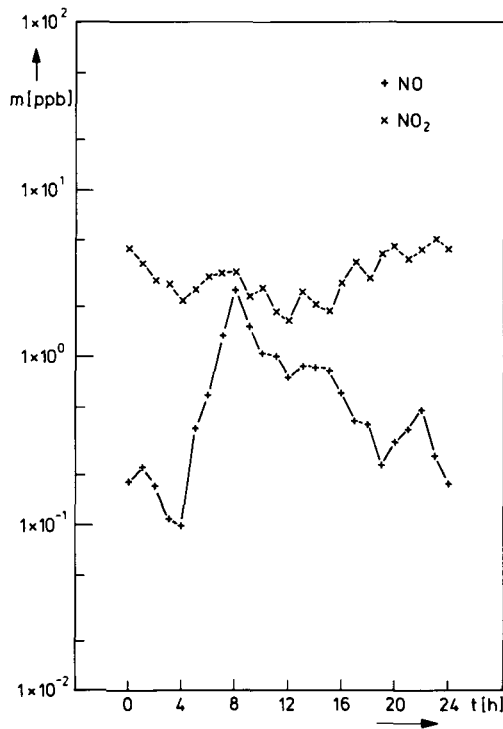
FIGURE 5   Diurnal variation of NO and NO$_2$ in Deuselbach from an average of 11 days.

obtained in Deuselbach and at Loop Head at the Irish west coast. The station at Deuselbach is located on a hill-top in an area of predominantly rural character. In Ireland we used the facilities of the Loop Head lighthouse situated on a cliff about 70 m above sea level north of Shannon bay.
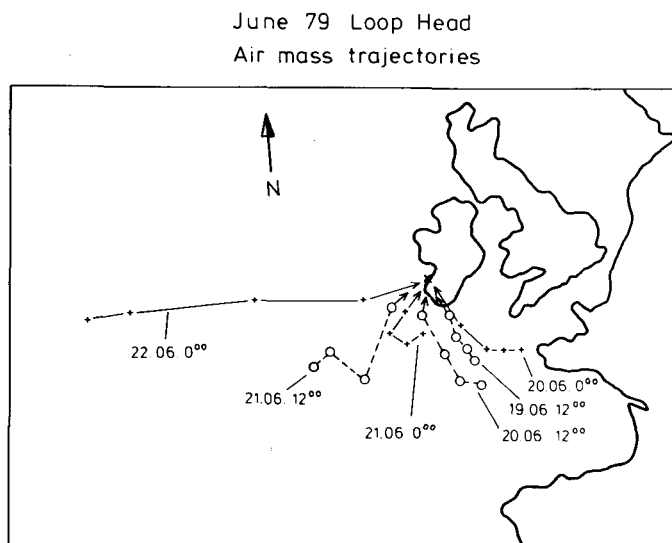
June 79 Loop Head
Air mass trajectories

FIGURE 6   Air mass trajectories for Loop Head for the time from 19.06.79 12 h to 22.06.79 0 h.

The NO_2 mixing ratios in Deuselbach generally show a decrease during the day accompanied by a simultaneous increase of NO. The trend is reversed in the afternoon and in the evening. Such a behaviour is to be expected due to photodissociation of NO_2. At night, nitric oxide should be quickly scavenged by ozone. Although, as Figure 5, an average of eleven days, shows, NO steadily decreases at night, the decay is orders of magnitude slower than anticipated from the known rate of the reaction of NO with ozone.[4] At present, we have no basis for an interpretation of these data, and we must investigate this behaviour more closely.

The NO_2 and NO mixing ratios experienced in Ireland (Figure 7) were always at least an order of magnitude lower than those in Deuselbach even when the main wind direction was from the east with advection of continental air. But also for winds changing from southeast to west, shown by trajectory tracings (Figure 6) to advect pure marine air masses, NO_2 was detected with mixing ratios in the range of 25–100 pptv. Under such conditions, the mixing ratios of NO often were below the detection limit.

An important point to be discussed is the observation that generally, both in Deuselbach and at Loop Head, the signal produced by the molybdenum convertor exceeds that of the $FeSO_4$ convertor. We conclude
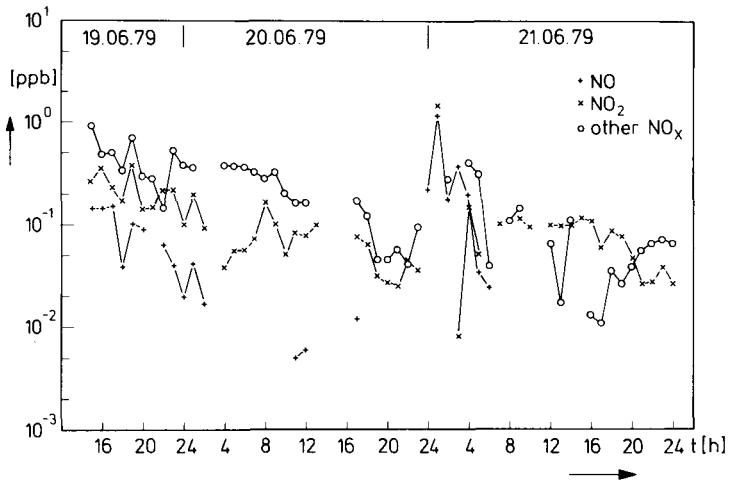
FIGURE 7   Variation of mixing ratios of NO, NO$_2$, and rest-NO$_x$ for the time 19.06.79
12 h to 22.06.79 0 h at Loop Head, Ireland.

that the molybdenum convertor produces NO also from nitrogen
compounds other than NO$_2$. Winer *et al.*[5] have come to similar results.
Spicer *et al.*[6] have pointed out that in Californian air, polluted by
photochemical smog, nitric acid occurs in significant amounts.
Peroxyacetyl nitrate (PAN) has also been reported to undergo
decomposition at high temperatures.[7] Our results show that these
compounds or perhaps additional nitrogen-containing compounds are
present in unpolluted background air (possibly due to natural emission
from the soil). We know that the conversion efficiency of ammonia is less
than 1 % in the molybdenum convertor at 350°C. To determine the exact
causes of the additional signal and to identify the chemical species
responsible for it will require further investigations.

Acknowledgements

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