Characterization and application of an externally mounted catalytic converter for aircraft measurements of NO$_y$

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A novel design for an airborne NO$_y$ converter was implemented, characterized in the laboratory, and used extensively for *in situ* tropospheric and stratospheric measurements of total reactive nitrogen (NO$_y$). During field deployments, the converter is mounted outside the aircraft fuselage, avoiding the need for an inlet line. In flight, the converter can be calibrated by the addition of standard gases close to the sample inlet, compensating for any changes in the instrument sensitivity caused by changing operating conditions. The system has been used successfully during several Stratosphere Troposphere Experiments by Aircraft Measurements campaigns in the lowermost stratosphere and upper troposphere for the measurement of total reactive nitrogen. The detection limit of the system is approximately 100 pptv for 10 s integrated data (2σ). The precision, deduced from the reproducibility of the in-flight calibrations, is 7% and the accuracy is about 30%. Laboratory studies demonstrate that interference from HCN, NH$_3$, and CH$_3$CN is negligible for background conditions. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1488680]

I. INTRODUCTION

A solid knowledge of the chemical reservoirs of reactive nitrogen species is crucial for the assessment of their influence on the photochemistry of the atmosphere. In the upper troposphere and the lower stratosphere, determination of all relevant individual reactive nitrogen species with high accuracy is difficult because of instrumental and platform (aircraft) constraints. The development of the concept of a family of reactive nitrogen species[1,2] led to simplifications in the instrumental requirements.[3,4] From a modeling point of view, the grouping of total reactive nitrogen into one parameter, NO$_y$, led to simplifications in the numerical treatment of the data and reductions in computing time.[3–5] Crosley[5] defines NO$_y$ as all reactive nitrogen oxides, where the oxidation state of N is $+2$ or greater: NO, NO$_2$, HONO, HNO$_3$, ClONO$_2$, PAN, 2*N$_2$O$_5$, HNO$_4$, NO$_3$, organic nitrates, and particulate nitrate. Other nitrogen containing compounds, like N$_2$, N$_2$O, NH$_3$, HCN or CH$_3$CN, if detected, are treated as interfering species. The widely used measurement technique for NO$_y$ utilizes heated catalytic converters to reduce the constituent species to NO, which is subsequently detected.[6] Although different catalysts have been used (see Ref. 5 for a review of NO$_y$ instruments), most techniques rely on an approach similar to the one described by Fahey *et al.*,[3] using a heated Au surface as the catalyst, and either CO or H$_2$ as the reducing agent. In order to achieve an accurate and precise measurement of NO$_y$ in the atmosphere, one has to guarantee that ambient air can be faithfully delivered to the instrument. The use of an inlet line as a duct from the atmosphere to the converter is a potential source of error. In particular, the quantitative detection of nitric acid, the dominant NO$_y$ species in the lower stratosphere, requires a careful design of the inlet system to avoid losses and memory effects in the sampling line.[7–9] The most promising way to overcome sampling artifacts is an inlet line of zero length, enabling the detector to measure directly in the atmosphere. We have therefore developed a novel converter design for airborne measurements of upper tropospheric and lowermost stratospheric NO$_y$. The design is based on a heated gold tube with CO as the reducing agent and with the converter itself mounted outside the aircraft fuselage, avoiding the need for a separate inlet line. A similar approach has been used for ground based measurements.[10] The critical species (such as HNO$_3$) thus encounter the converter for reduction to NO immediately after entering the system. Transport of the product NO from
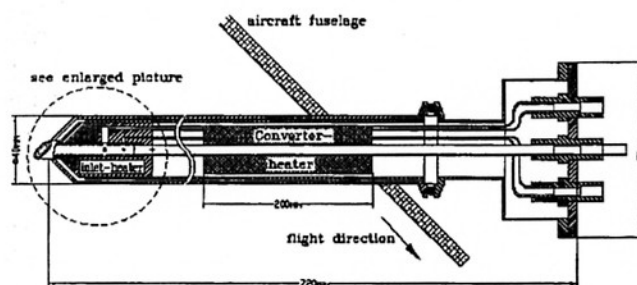

FIG. 1. Drawing of the converter system.

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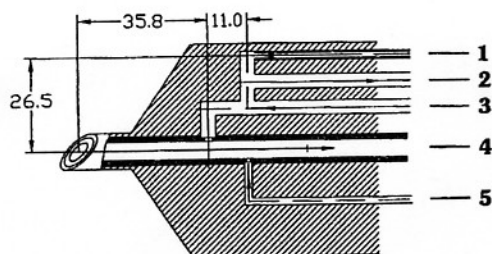
FIG. 2. Detailed drawing of the inlet of the system. (1) NO_2 inlet, (2) vacuum flow, (3) NO calibration gas and synthetic air, (4) sample inlet, and (5) CO inlet.

the converter to a chemiluminescence detector is via PFA tubing, which has been demonstrated during laboratory tests to be free of sampling artifacts for NO. In order to monitor the sensitivity of the instrument, regular in-flight calibrations can be performed by the addition of trace gas standards close to the inlet tip of the converter. The instrument has been mounted on a Cessna *Citation II* jet aircraft and successfully used for upper tropospheric and lower stratospheric measurements of NO_y during several Stratosphere Troposphere Experiments by Aircraft Measurements (STREAM) campaigns at high and middle northern latitudes.[11–13]

II. TECHNICAL DESCRIPTION OF THE NO_y MEASUREMENT SYSTEM

Figures 1 and 2 show detailed drawings of the converter system, and Fig. 3 shows the experimental setup and the gas flow system for the airborne NO_y instrument described herein. The innovative feature of the converter is its use as an inlet system. For this purpose, the gold tube reaches to the tip of the converter inlet, thus avoiding any contact between the sampled air and surfaces other than heated gold. This minimizes potential sampling artifacts. The thermal converter consists of a 72 cm long, 5 mm inner diameter gold tube heated to 300 °C over a 20 cm section near the tube center. The converter is mounted outside the *Citation* fuselage by use of a modified escape hatch carrying several gas inlet systems. It is contained in a stainless-steel housing and po-
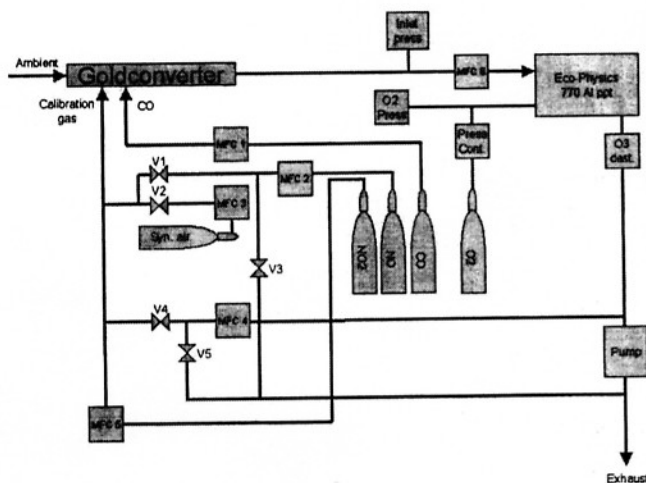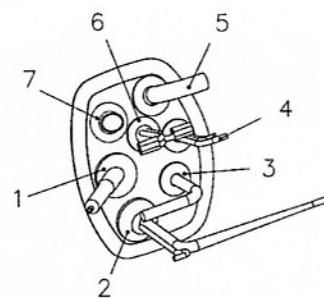

FIG. 4. Schematic of the inlet system used for the Cessna *Citation*. The illustration shows the escape hatch which was replaced. The inlets are (1) NO_y converter, (2) isokinetic aerosol inlet, (3) and (6) backward facing gas inlet, (4) forward facing gas inlet, (5) inlet for mass spectrometer, and (7) exhaust.

sitioned at an angle of 135° relative to the flight direction (Fig. 4 shows the inlet systems). The tip of the converter itself is cut at 45°, so that air is sampled against the flight direction. The intake is located approximately 20 cm away from the fuselage.

Because the inlet of the converter is opposite to the flight direction, ambient particles above a certain size will be prevented from entering the instrument due to inertial separation.[14] The cutoff of the sampling with respect to the particle size is not known. Since particulate nitrate belongs to the NO_y family, this will probably lead to an underestimation of total NO_y in particular situations were particulate nitrate is associated with rather large particles. However, Feigl *et al.*[14] demonstrate that in the upper troposphere and lower stratosphere, particulate nitrate is a rather small contributor to NO_y outside cirrus or polar stratospheric clouds (PSC). On the other hand, the rearward inlet avoids a strong enrichment of particulate nitrate due to subisokinetic sampling of large particles. Subisokinetic sampling via a forward facing inlet has been used in the past to detect particulate nitrate associated with circus particles or PSC.[14,15]

A supplementary heater maintains a temperature of ~120 °C at the tip of the converter. Four cm behind the tip, two vacuum-soldered connections to the gold tube (see Fig. 1) enable the addition of calibration gas standards or zero gas and the addition of the reducing agent, which consists of pure CO (99.997%, Messer–Griesheim) at a flow rate of 5 $cm^3 min^{-1}$, yielding a concentration of 0.6% CO at 0.8 $l min^{-1}$ sample flow. Mass flow controllers mounted inside the aircraft provide stable flows of zero gas, calibration gas standards, and CO (Fig. 3 and Table I). A system of five solenoid valves enables the control of the measurement status (see Table II). 15 cm behind the inlet tip, the converter is heated to a temperature of 300 °C over a 20 cm long section (see Fig. 5). At 0.8 s l m and ground level pressure, the residence time in the >300 °C regions is ~300 ms, similar to other converter designs.[16] At maximum cruise altitude, the residence time is reduced to ~60 ms, which may in part

FIG. 3. Gas flow scheme for the NO_y system. MFC 1–6: Mass flow controller; $V1–V5$: solenoid valves.

TABLE I. Mass flow controllers (MFC) flow ($cm^3 min^{-1}$).

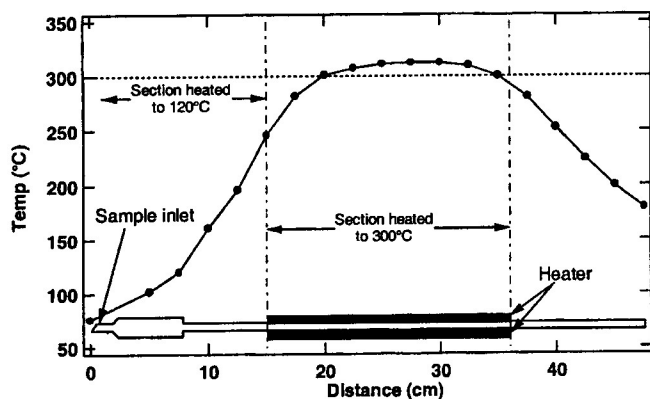| MFC:	MFC1	MFC2	MFC3	MFC4	MFC5	MFC6
Flow:	5	5–10	2000	100	10	800

FIG. 5. The temperature inside the converter. In the laboratory, the supplementary heater at the tip is turned off. During field operation, the tip is heated to 120 °C.

account for reduced conversion efficiency discussed next. The temperature is maintained at the setpoint to an accuracy of ± 0.1 °C using thermosensors and an electronic control loop. The heater itself consists of a 500 W ohmic heater operated at 28 V, which is powerful enough to maintain the setpoint temperature of 300 °C even under stratospheric conditions. The gold tube is connected to a 1/4 in. Swagelok fitting at the flange inside the aircraft. From this point, a 1/4 in. perfluoroalkoxy (PFA) tube of 6 m length leads to the chemiluminescence detector (CLD) mounted in the rear of the aircraft for NO measurement. The instrument, an Eco-Physics 770 Al ppt, has been modified for airborne operation to guarantee a pressure and mass flow independent signal. The detection of the product NO relies on the reaction between ozone and NO to form NO_2, which is partially in an excited state (NO_2^*), which subsequently decays to the ground state, either by quenching or by emission of a photon with a wavelength between 600 and 3600 nm. The photons are detected with a photomultiplier tube (PMT), sensitive from 600–1200 nm. A silent discharge produces the required ozone at concentrations of a few percent from high-purity oxygen. To eliminate signal contributions from interfering species (e.g., hydrocarbons) and to determine the noise level of the PMT, the instrument switches between two different modes of operation. In the measurement mode, ozone is added to the sample air in the main reaction chamber, where photon emissions from the excited NO_2^* and from any interfering reactions are detected by the photomultiplier. In the prechamber mode, the sample gas and ozone flows are directed through a prereaction chamber, thus delaying the sample flow before it enters the main chamber. During the delay, the excited NO_2^* deactivates completely ($>99\%$), while the slower interfering reactions of hydrocarbons still

produce photons in the main chamber, thus allowing a measurement of the interference signal and the noise level of the PMT. Subtraction of the two signals provides the NO_2^* signal exclusively due to the NO in the sample gas. During field deployment, a "quasicontinuous" measurement mode was used. Ambient air was sampled for 5 s, then the prechamber signal was determined for 2 s. After switching the modes of operation, a delay time of 1 s was introduced to account for pressure fluctuations. This procedure yielded a 9 s duty cycle with five data points and minimized long data gaps which is especially important during aircraft ascents and descents if the structure of the atmospheric layers is to be recorded. Since the ambient and background signal are not measured simultaneously, a systematic error can be introduced by this procedure, if the concentration of the interfering hydrocarbons vary rapidly. Observations during the field mission nevertheless indicate that the prechamber signal changes only slowly [the standard deviation (σ) of the prechamber signal is below 18 counts per 9 s duty cycle, which corresponds to a concentration of 8 ppt], indicating that the background concentration of interfering species is rather constant on short-time scales of the order of a few seconds. In general, the variability of the prechamber signal, as well as the main chamber signal, is dominated by photon-count statistics of the PMT.

The photon yield from the $NO+O_3$ reaction is a function of the NO concentration in the sample gas, the chamber pressure, and the mass flow through the chamber. In the present setup, therefore, pressure and flow are held constant using a constant pressure loop and a mass flow-controller upstream of the CLD. Absolute calibration of the CLD is achieved by NO standard addition to the converter inlet on a regular basis during measurement flights. Besides in-flight calibrations with NO to account for changes in the CLD sensitivity, the conversion efficiency for NO_2 is determined regularly by in-flight calibrations with a NO_2 standard gas mixture. Additionally, regular background measurements using zero air are made to determine the detection limit of the instrument and to account for memory effects of the converter. All calibration gases, as well as the zero gas, are added to the converter close to the inlet tip. A permanent NO_2 flow to the converter tip is maintained to guarantee that the NO_2 calibration line is always preconditioned and to minimize switching times between ambient and calibration measurements. During ambient measurements, the NO_2 calibration gas is dumped into an exhaust line. Closing the dump by switching valve No. 4 to "closed" and valve No. 5 to "open" provides a surplus of NO_2 calibration gas to the converter tip, added either to the ambient air flow or to zero air from a tank (synthetic air hydrocarbon free, grade 5.0,

TABLE II. Valve status during the possible modes of operation.

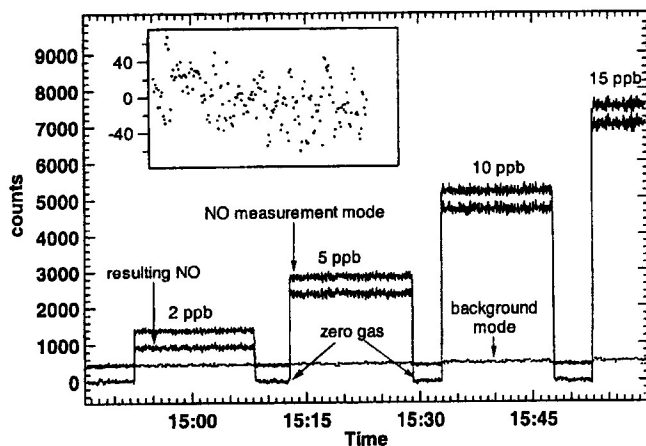| Mode	Valve 1	Valve 2	Valve 3	Valve 4	Valve 5
Sample	closed	closed	open	open	closed
NO calibration	open	open	closed	open	closed
NO_2 on synthetic air	closed	open	open	closed	open
NO_2 on ambient air	closed	closed	open	closed	open
Flush synthetic air	closed	open	open	open	closed

FIG. 6. Results of the addition of calibration gases with increasing NO mixing ratio on zero air (laboratory data). The gray line shows the results of the "measurement mode" and the dotted line the background measurement (prechamber mode of the CLD). The resulting NO curve is shown in black. The inset shows the enlarged scatter of zero air measurement. Each point represents the average of one 9 s duty cycle.

FIG. 7. Linearity of the response to variable NO calibration gas input.

delivered from Linde AG). Table II gives an overview of the valve settings for ambient, zero, and calibration mode.

The entire system is powered by 28 V dc. Instrument control and data acquisition are provided by a built-in personal computer. In addition to the concentration values, a number of housekeeping data, e.g., several temperatures (instrument, converter, PMT, and aircraft cabin), pressures (sample inlet and reaction chamber), valve status, flows (sample and calibration gases), and instrument status (zero/ambient mode) are checked and logged on a 1 s time basis.

III. CHARACTERIZATION OF THE SYSTEM

A. Sensitivity and linearity

The sensitivity of the CLD converter system is defined by its response (in counts) to a NO signal and thus given in counts/ppb NO. To record a calibration curve, we employed two trace gas standards. As an in-field working standard, we used a 10 ppmv $\pm 5\%$ NO standard from Linde AG. This secondary NO standard was calibrated against a primary National Institute of Standards and Technology (NIST) 5 ppmv $\pm 5\%$ standard reference material (SRM 2627a). The standards agreed within $<0.3\%$. Linearity checks of the ECO-Physics 770 Al ppt were performed by the dilution of the reference material to variable concentrations with zero air. Zero air was taken from a Headline filters zero air generator in combination with charcoal and purafil cartridges. The response of the instrument to such a step-wise addition of NO is shown in Fig. 6. Here, between the NO calibration gas additions, zero gas was flowing to the inlet. Figure 6 shows the prechamber and main chamber signals of the instrument as well as the difference between the two. The resulting calibration curve can be established from the mean values of the individual measurements and is shown in Fig. 7. From the slope of this curve, the sensitivity was deduced to be 443 counts/ppb NO.
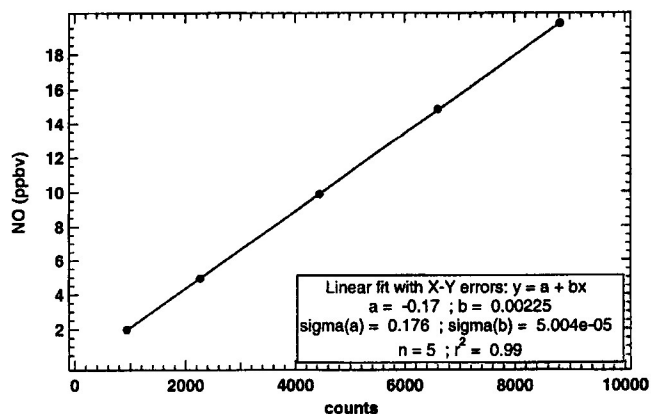
B. Conversion efficiency

Due to space and weight restrictions associated with airborne operation, in-flight calibrations are limited to NO and NO_2, for which gas tanks can be used. NO_2 calibration helps to account for any changes in the conversion efficiency. This approach is justified by laboratory investigations showing that the HNO_3 conversion efficiency is generally within a few percent of that for NO_2 and the fact that losses of sticky molecules are low due to the inlet design. In-flight calibrations of HNO_3 would require the airborne operation of a permeation device, which is technically difficult to achieve, due to the strong pressure and temperature dependency of these devices. Extensive tests of the conversion efficiency for NO_2 and HNO_3 were performed in the laboratory. Here, we used three different sources for NO_2: A NIST traceable 10 ppmv $\pm 5\%$ standard gas mixture of NO_2, delivered by Messer–Griesheim, a permeation device (VICI Metronics Inc., USA, 109 ng min^{-1} $\pm 2\%$ at 40 °C) and a gas phase titration system (GPT) (Ansyco Model SYCOS K-GPT).

The NO_2 flow from a 10 ppmv standard gas cylinder was diluted with zero air to different ambient concentrations in the range 2–20 ppbv to determine the conversion efficiency of the converter for NO_2 as 98.8$\pm 2\%$ at ambient pressure. The permeation device was housed in a pyrex cell and kept at a temperature of 40 °C ± 0.05 °C. A constant flow (40 cm^{-3} min^{-1}) of zero air through the permeation holder generated a calibration gas with a NO_2 mixing ratio of 1.4 ppmv. Dilution with variable amounts of zero air to generate ppbv levels of NO_2 showed a conversion efficiency of the converter of 98.5% $\pm 1\%$ at ambient pressure. The GPT system is the Environmental Protection Agency (EPA) recommended calibration system for NO_2 converters.[17] For the actual gas phase titration, the NO reference material was partially converted to NO_2 by reaction with ozone. The conversion back to NO is monitored and thus, the conversion efficiency can be determined. This procedure resulted in a determination of the conversion efficiency as 97% $\pm 3\%$.

Additional tests were made to study the dependency of the NO_2 conversion efficiency on the ambient pressure. During airborne operation, the pressure inside the converter, which is not actively regulated, varies with ambient conditions between 1000 hPa at ground level and approximately 200 hPa at the highest flight levels (12.5 km altitude), while
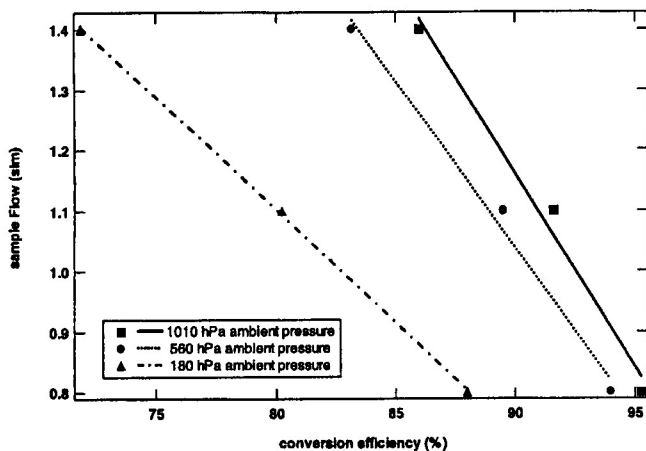
FIG. 8. Conversion efficiencies at different flows and different pressure in the converter.

the mass flow through the converter is held constant. These rapidly changing pressure conditions in the converter were simulated in the laboratory using the GPT system as a source for NO$_2$. The highest conversion efficiency was found at sea-level pressure and at flow rates of 0.81 min^{-1} (Fig. 8). The conversion efficiency was fairly constant down to 300 hPa then dropped by approximately 5%–6% at the lowest pressures simulated (Fig. 9, black curve, see also case study). Most probably, the shorter residence time of the sample air in the converter is the reason for this behavior. The mass flow is kept constant, but due to lower ambient pressure, the contact time with the catalytic surface decreases.

The reproducibility of the in-flight NO$_2$ calibrations can be used to estimate the precision of the NO$_y$ measurements. During individual flights, three to six calibrations are performed with a reproducibility of typically ±7%.

HNO$_3$ is a main contributor to NO$_y$, especially in the stratosphere. Thus, the conversion efficiency of HNO$_3$ to NO in the converter is of critical importance for the measurement. For laboratory calibration purposes, we used a permeation device (VICI Metronics, Inc., 68% HNO$_3$, 258 ng min^{-1} ± 2% at 70 °C). The characterization of the permeation tube involved monthly gravimetric and photometric calibrations. For the photometric calibration, the effluent of the permeation tube was collected over 24 h in an impinger containing 20 ml deionized water. The PFA tubing (50 cm
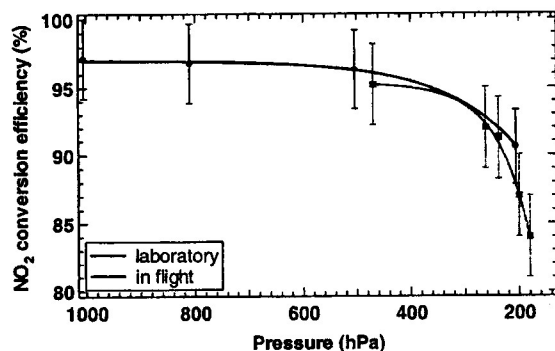
and 1/8 in.), necessary to transfer the calibration gas from the permeation tube to the impinger, was continuously flushed with the output of the calibration source to obtain the maximum transmission efficiency. The HNO$_3$ concentration was determined by photometric measurement employing the absorbance of the nitrate ion at 220 nm. For calibration of the photometric measurements, a commercially available nitrate standard (Merck AG) was used. The results showed an average permeation rate of 262± 15 ng min^{-1}, in agreement with the nominal value of the permeation rate, given by the manufacturer as 258± 5 ng min^{-1} at 70 °C.

By dilution of the outflow of the permeation device to mixing ratios of 0.5–2 ppbv, close to ambient HNO$_3$ levels, we obtained a realistic simulation of atmospheric conditions. The conversion efficiencies for HNO$_3$ and NO$_2$ were shown to agree within the errors of the measurement. The pressure dependence of the conversion efficiency for HNO$_3$ and NO$_2$ are expected to be similar, although due to the practical limitations referred to earlier, an in-flight test of the HNO$_3$ efficiency could not be carried out. This may introduce a small additional uncertainty in the high altitude NO$_y$ data.

C. Detection limit

The noise level and the detection limit of the NO$_y$ system were determined from zero air, free of reactive nitrogen. In the laboratory, a Headline Filters CAP 60 pure air generator was used in connection with Purafil and charcoal cartridges to generate zero air. The inset in Fig. 6 shows, on an expanded scale, the zero air measurements taken in between the NO calibrations. Each point shows the mean of one 9 s duty cycle (five data points). The standard deviation of these measurements is 25 counts, thus the detection limit at the 2σ level is equivalent to ~113 pptv.

During field deployments of the instrument, a degradation of the detection limit was observed, which is most probably due to unavoidable power interruptions (for safety reasons, the power in the aircraft has to be shut down during the night). This results in a generally higher background signal, which degrades the detection limit significantly. A further degradation of the detection limit has been observed during individual flights due to memory effects caused by aerosols or interfering species picked up from the boundary layer in the vicinity of the airport. These species and particulate have a high potential to poison or contaminate the converter, giving rise to memory effects and decreased conversion efficiency. Therefore, during operation on the airfield, the converter is flushed with onboard synthetic air until after take off and this is repeated while in the vicinity of the airfield during landing. In flight, the synthetic air is used for regular determinations of the instrument background, a measure for the in-flight detection limit. In general, the zero air from the tank used for in flight background measurements gives higher offset signals than those obtained from the zero air generator in the laboratory, indicating a certain level of reactive nitrogen contamination. For the zero gas used (Linde AG), this contamination level was of the order of 200 counts. The detection limit (2σ of the noise) during flight operation is typically ~150 pptv.

FIG. 9. Conversion efficiency for NO$_2$ vs ambient pressure. Shown are the results for laboratory experiments (black line and markers) and in-flight calibrations during STREAM Flight 6 (gray line and markers).
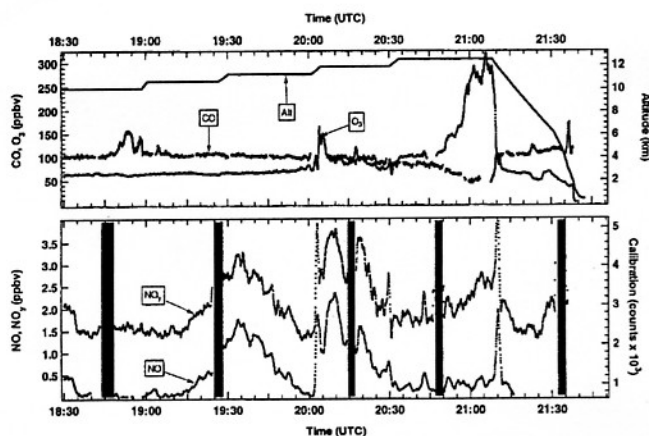
FIG. 10. Measured time series for STREAM Flight 6 from 12 July 1998. Shown are (upper panel) flight altitude, O_3, CO, and (lower panel) NO and NO_y. The gray boxes indicate the times of NO_y calibration (right-hand side axis).

D. Response time

The response time of the system is defined by the time needed to achieve a reading of 95% of the final value following a step-wise increase in sample concentration. In the *Citation* configuration, the sample line between the converter and the CLD in the aircraft setup has a length of 6 m, which significantly increases the response time of the system. Therefore, a similar setup was used in the laboratory for testing. The residence time of the sample in the 6 m, 1/4 in. PFA tubing at a flow rate of 0.8 l min^{-1} is 5.5 s at standard pressure. By switching from zero air to a 10 ppbv NO_2 calibration gas, the time elapsed before the signal reaches 95% of the final value was below 7 s. The response can be seen in Figs. 6 and 10 (see case study). Coming from a higher concentration plateau to a lower concentration takes approximately 8–9 s. Most probably, the difference is due to the time needed to empty dead volumes associated with the calibration gas delivery system.

E. Interferences

During a previous measurement campaign [Pacific Exploratory Mission West A], an intercomparison of two different NO_y systems was carried out. The results from the two systems significantly differed from each other.[18,19] As a possible explanation for this disagreement, among others, different conversion efficiencies of the converters for non-NO_y species such as HCN, CH_3CN, and NH_3 were discussed. To take these interferences into account, we tested the converter for its efficiency in converting these species to NO. The conversion efficiency of NH_3 was determined by using a 10

ppmv standard gas mixture (Linde AG). With a dilution system, the mixing ratios were varied up to mixing ratios well above ambient concentrations (above 10 ppbv) to obtain a signal strong enough to be detected above background noise. Under laboratory conditions, the conversion efficiency was found to be $1.4\% \pm 0.3\%$.

HCN was also delivered from Linde AG as a standard gas mixture with a mixing ratio of 10 ppmv. After dilution, the conversion efficiency was shown to be below 4.8% $\pm 0.4\%$. As a calibration standard for CH_3CN, a permeation source (VICI Metronics, Inc.) was used. Diluted with zero air to mixing ratios above ambient, we found a conversion efficiency of $0.9\% \pm 0.1\%$. The results as compiled in Table III show that, with the conversion efficiencies measured for these species, there is no significant interference in the background atmosphere, given the much higher mixing ratios of NO_y and even the lowest NO_2 (NO_y) conversion efficiencies measured during flights or in the laboratory. Further details about the chemical behavior of NH_3 HCN, and CH_3CN can be found in Refs. 20–22. Although the interferences in our converter are small, they have to be taken into account when highly polluted air masses are encountered, as can be seen from Table III.

F. Performance during field deployment

During STREAM 98, eight flights were performed with a Cessna *Citation II* aircraft in the midlatitude upper troposphere and lower stratosphere over Canada. The aircraft was equipped with an instrument package suitable for aerosol and trace gas measurements, including measurements of NO, NO_y, O_3, and CO. For general results and an overview of the campaign, see Ref. 23. During Flight 6 on 12 July 1998, an investigation of a frontal system was performed. The tracer time series for this flight (Fig. 10) shows high mixing ratios of NO and NO_y in the upper troposphere. Note the sharp peaks in NO and the instantaneous response of NO_y around 2005 UTC and 2110 UTC (universal time coordinated, local time= UTC-5 h), which occurred within a few seconds. Before takeoff (data not shown here) and during the flight calibrations of the NO and NO_y instruments were performed (in the graph only shown for the NO_y system) to account for changes in the conversion efficiency and sensitivity of the instruments. The necessity of in-flight calibrations is demonstrated in the decreasing conversion efficiency at higher altitudes. In Fig. 9, the conversion efficiency is shown as a function of changing ambient pressure. Figure 9 shows data obtained in the laboratory and on five different flight levels during the case study (see Fig. 10, the fifth calibration was performed during the descent). Generally, the

TABLE III. Compilation of the conversion efficiencies and the potential impact of interferences. Background and peak data from Refs. 21 and 22.

Interfering compound	Conversion efficiency (%)	Background mixing ratio (pptv)	Maximum mixing ratio (pptv)	Potential impact Bg–max (pptv)
NH_3	1.4	10	5000	0.14–70
HCN	4.8	150	200	7.2–9.6
CH_3CN	0.9	50	300	0.45–2.7
Sum		210	1000	7.6–87

agreement between the two curves is good with an overlap of the error bars although in the field, conversion efficiencies are somewhat lower. This may be a further indirect consequence of the power interruptions during ground time of the aircraft mentioned herein. At the highest flight altitudes, a definite decrease in the conversion efficiency of ~10% was measured, illustrating the necessity for such in-flight calibrations to account for changing conversion efficiency. The tropopause (ozone ≥ 120 ppbv) was crossed at 2030 UTC and the flight re-entered the troposphere at 2110 UTC. The high abundance of NO observed in the upper free troposphere region suggests pollution updraft or *in situ* production by lightning. Aircraft emissions are characterized by peaks with a duration of only a few seconds[24] and, hence, can be excluded as being responsible for large-scale enhancements of this spatial extent. The absence of a significant enhancement of pollution tracers like CO suggests that *in situ* production by lightning is responsible for the enrichment in NO.

ACKNOWLEDGMENTS

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