WHITE PAPER

A Standalone Photolytic Converter for Chemiluminescence Analyzers to Measure Nitrogen Dioxide (NO_2) accurately

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INTRODUCTION

Nitrogen dioxide, NO_2, is a common trace air pollutant linked to negative health impacts on humans, ecosystem health, and ozone production in the troposphere. The ozone made is as toxic as NO_2 and have the environmental effects if not worse. Because of these known effects, NO_2 is regulated and classified as a criteria pollutant by the US-EPA under the Clean Air Act.[1-2] NO_2 is also central in the processing of nitrogen oxide species in the troposphere to form other highly oxidized species such as peroxyacetyl nitrates (PANs), multifunctional organic nitrates ($RONO_2$), nitric acid (HNO_3), and particulate nitrate (pNO^{3-}). All these species together with ozone production and/or destruction can deposit to ecosystems and can adversely affect acid sensitive ecosystems, smog formation, etc. The effects of NO_2 listed above is the underlying reason for the need for accurate quantification of this species to better understand its chemical processing in ambient air and how to control it. Recent studies published clearly show that heated Molybdenum NO_2 converters inside chemiluminescent NO_X analyzers overestimate NO_2.[3-4] This challenge can be solved using an alternative 'true' NO_2 converter which can selectively convert NO_2 to NO as published in literature.[5] The photolysis product, NO, is then reacted with ozone in the chemiluminiscence chamber and quantified. There are commercial photolysis based NO_x analyzers available which have been approved as a federal equivalent method (FEM) for 'true' NO_2 measurement by the US-EPA, but the question of what happens to the plethora of existing heated catalyst based NO_X analyzers in use today remains. In this presentation, it is shown that a photolytic NO_2 converter can be used as a simple add-on to existing chemiluminescence analyzers to provide indirect but 'true' NO_2 measurement. It has been proven through laboratory and field trials, and was tested as a direct replacement, or retrofit, of a heated Molybdenum NO_2 converter. Experiments were conducted at reduced pressure (200 mmHg), and over a wide linear dynamic range (tested from 0.03 to 37.30 ppm) with a converter efficiency greater than 96%, which show results that have surpassed the performance of any known photolytic converters. A case study of device implementation in an ambient application side by side with an analyzer using a heated metal catalyst is presented and discussed.

EXPERIMENTAL METHODS

The prototype PhoNO has been tested both under laboratory and field conditions. In the Laboratory, the experiment was set-up to test the photolytic converter's efficiency with two

different LED modules (different suppliers and technologies). Two prototype PhoNO converters were each integrated with a Thermo Scientific 42C or 42i NO-NO_2-NO_x chemiluminescence analyzer. The sample tubing to/from the molybdenum converter was disconnected, and the photolytic converter was connected in its place to convert NO_2 into NO prior to detection by NO-O_3 chemiluminiscence. The two Thermo analyzers received sample gas from an API calibrator, which was set-up to dilute 37.3 ppm (±1%) NO_2 with Zero Air or using gas phase NO-O_3 titration to generate required NO_2 in-situ. Both gases used in the dilution calibrator were drawn from certified compressed gas cylinder(s) from Praxair. See Fig. 1 for flow schematic of the set-up.

Fig. 1: Schematic of NO_2 experimental set-up

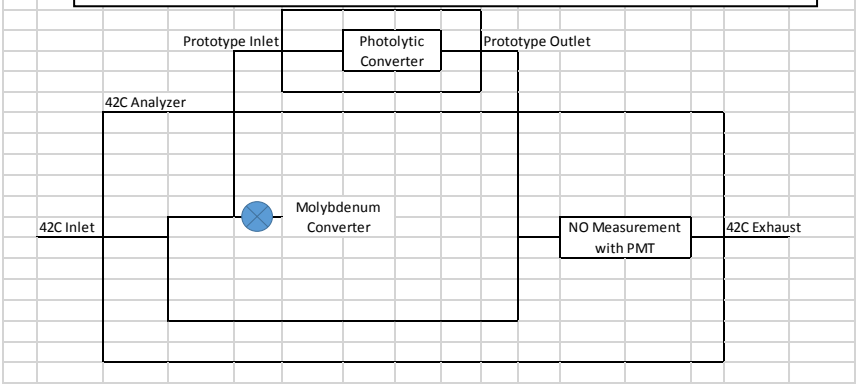

Fig. 1: Schematic of the sample flow through the 42C/42i analyzer and the PhoNO system

The PhoNO has been deployed in two separate field studies. During each of the two separate ambient field deployments, the PhoNO device was operated for over a month. In the first, which is presented here, the field deployment occurred in Fort Saskachewan, Alberta, Canada. The PhoNO was deployed for 4 months from November 2016 to March 2017. The PhoNO was housed in an existing temperature controlled (~25 ^oC) ambient air monitoring shelter (Longitude 113^o 11'23.5" W, Latitude 53^o 41' 55.7988"N; Elevation 629 m a.g.l) operated by Fort Air Partnership (FAP). All the instruments listed above shared a common inlet and sampling manifold at a height of 5.2 m. All instrument were synched to the same time and data logged accordingly.

Table 1: Instruments and their operating principles used to evaluate the new photolytic device presented here

Instrument/Device	**Operating Principle**
Thermo Scientific 42i	Thermal conversion, gas-phase chemiluminiscence, FRM
Thermo Scientific 42C	Thermal conversion, gas-phase[1] chemiluminiscence, FRM
Thermo Scientific 17i	Thermal conversion, gas-phase chemiluminiscence, FRM
Direct NO_2 measurement	Cavity Ring-Down Spectroscopy (CRDS)
PhoNO	Standalone Photolytic converter*

[1]used for only laboratory testing

*integrated into either Thermo Scientific 42i or 42C as a replacement for heated Molybdenum converter

RESULTS AND DISCUSSION

Laboratory Evaluation

Extensive laboratory analyses and a summary of the highlights of the field deployment are presented. The flows and pressures of each analyzer deployed with PhoNO are consistent with manufacturer's specifications.

Calibration of the PhoNO device was done either using a diluted homogenous NO_2 concentration or gas phase titration of a known amount of excess NO with ozone (Fig. 2). Typical analyzer flow conditions are shown in the Table 2 below.

Fig. 2: Time series of CRDS NO_2 mixing ratio during conversion efficiency testing

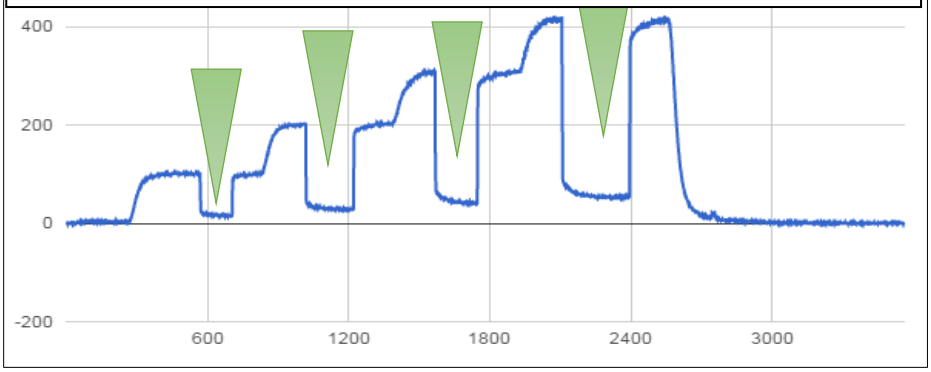

Fig. 2: Shows a time series calibration of a PhoNO-Thermo42i system with CRDS NO_2 measurement. The y-axis is in units of ppbv and x-axis is elapsed time (seconds). Green arrows show when the PhoNO device was turned on prior to NO_2 detection by the CRDS instrument.

Table 2: List of analyzer operating conditions after integration of PhoNO

Operational Parameter	Analyzer	
	Thermo 42C	Thermo 42i
Flow, lpm	0.40-0.70	0.40-0.70
Pressure, mmHg	~198	~210

Fig. 3: Comparason of NO_2 Measurements

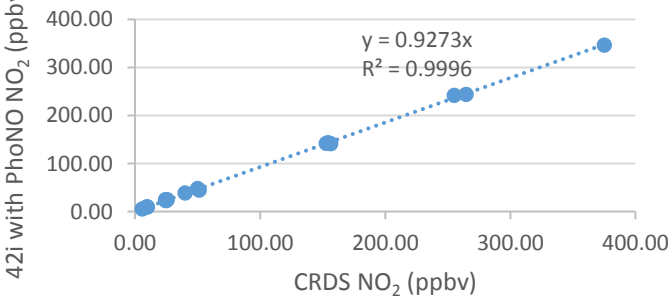

Fig. 3: Shows a calibration of a PhoNO-Thermo42i system with CRDS NO_2 measurement

A correlation plot of the PhoNO calibration with CRDS is shown in Fig. 3. The slope showed NO_2 conversion efficiency of 93%. This is consistent with all other validation experiments such as GPT which were performed on the PhoNO prototype. A newer model of the PhoNO prototype is being developed and would be discussed in this abstract.

Field Deployment

Preliminary analyses of the deployment of PhoNO at Fort Saskatchewan are shown in the time series plot below. The site is close to a major roadway hence rapidly changing NO_2, NO mixings ratios were evident (Fig. 4). During the period of deployment, the ambient temperatures averaged -11 ^oC. Daily zero and span NO and NO_2 mixing ratios were completed to ensure quality assured data. NO_2 showed much variations on days where vehicular emissions likely impacted the site (Fig. 4). In each plot is a 1 minute averaged data. In some of the days, NO_2 showed anti-correlation with ambient ozone where the early morning and evening maxima recorded within that day correlates well with NO-O_3 titration events as described by the NO-NO_2-O_3 photostationary state model.[6]

Fig. 4: Time series of NO, NO_2 mixing ratio during Fort Saskatchewan deployment

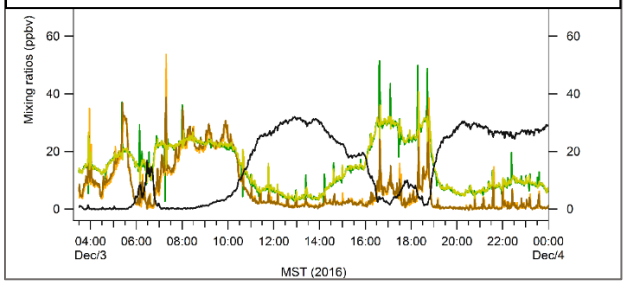

Fig. 4b: Time series of NO_2 mixing ratio during LMOS deployment on June 3, 2017

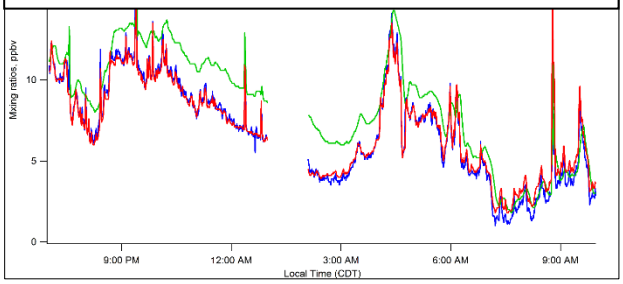

Fig. 4a: (Green): NO_2 measured by PhoNO-Thermo 42i system, (Yellow): NO_2 measured by Thermo 17i, (Brown and Orange): NO measured both instruments respectively, (Black): Ozone. 4b: NO_2 mixing ratios of PhoNO (blue) compared to CAPS (red) and FRM (green) instruments. CAPS and PhoNO match closely while FRM NO_2 reads higher mixing ratios

This means biogenic VOC emissions were suppressed and the main the main driver of NO_2 processing was influenced either by time of day, wind direction as well as photochemistry anthropogenic activities. The expectation from this deployment was that both instruments, the NO_2 mixing ratio of the analyzer using a photolytic converter and the Thermo 17i which uses the Molybdenum converter should match closely since higher-oxidation nitrogen oxides are expected to be absent or negligible under such cold winter conditions. Fig. 4a shows also, the fast response of the PhoNO between 16:00 MST to 18.30 MST when temporal erratic NO_2 mixing ratios impact the site. The observed spikes in the data in Fig 4 correlated well with the same spikes in the NO data. These spikes were evidently absent in the NO_2 data from the heated metal converter system. Since the PhoNO works in the gas phase while converting the NO_2 to NO, the matrix effects as well as memory effects from other sticky interference species such as water vapor and nitric acid are absent.

Fig 4b shows a preliminary raw data time series of NO_2 data from the PhoNO, CAPS and FRM instruments deployed at Sheboygan, Michigan, during summer of 2017. The observations from the data show that the CAPS and PhoNO match closely whiles the FRM NO_2 is elevated due to the use of the heated metal converters. This means these existing instruments can be retrofitted with the PhoNO and even operated at higher data acquisition rates compared to the Molybdenum converters and these instrument will perform well in accurate NO_2 readings.

Since the deployment of these first generation prototypes, a newer model has been developed and tested.

Fig. 5: Calibration plot of high efficiency PhoNO

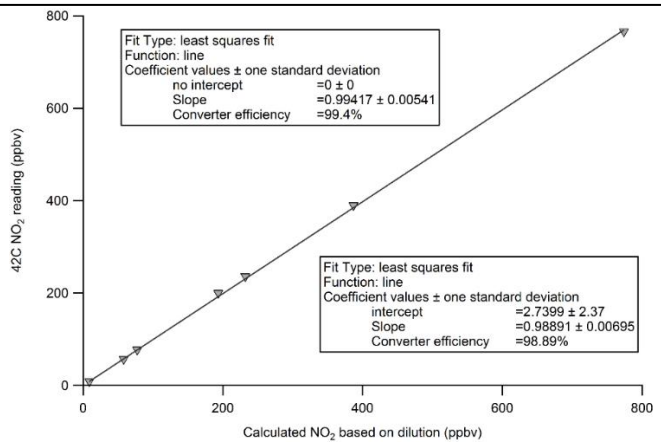

Fig. 5: High efficiency PhoNO calibration plot

Fig. 5 shows the most recent upgrade of the device which has shown improved performance. On average, the PhoNO has shown conversion efficiency of greater than 96% of NO_2 to NO. There was no degradation of light output during all the deployment periods. The PhoNO has also shown a quick response to changing air mass concentration and maybe suitable for deployment for near road monitoring of nitrogen dioxide.

SUMMARY

Here, we have demonstrated through laboratory and field evaluations of a novel standalone selective photolytic NO_2 converter. We have seen very good agreement between the PhoNO-Chemiluminiscence system with direct CRDS/CAPS systems as well as a regular FRM heated metal molybdenum NO_2 converter instruments. Results from field deployment also show a fast response of the photolytic system compared to the heated metal converter system. Results from the 2017 summer months are underway to ascertain NO_2 overestimation by the heated metal converters as well evaluating its performance in the presence of potential interference species such as multifunctional alkyl nitrates. The PhoNO was further evaluated during the Lake Michigan Ozone Study in June 2017. Data Analyses are currently ongoing. These results together with further interference testing would be beneficial in the certification process of this PhoNO device.

ACKNOWLEDGEMENT

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