A Simple Instrument for Measurement of NO_2 and O_3.

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WHITE PAPER

PROJECT DESCRIPTION

There is currently interest in development of specific methods for measurement of NO_2. Included among the available methods is photolysis of NO_2 to NO followed by detection of the resulting NO by $NO+O_3$ chemiluminescence. The photolysis reaction,

$$NO_2 + h\nu + O_2 \rightarrow NO + O_3$$

Also produces O_3, which can be measured by a number of means including chemiluminescence and UV absorption. Use of a UV absorption method for measurement of the resulting O_3 has the advantage of being a purely spectroscopic method that combines the absorption coefficient and quantum yield for NO_2 photolysis with the absorption coefficient of O_3 in the detection step. This white paper describes our initial characterization of an NO_2 and O_3 instrument based on these principals.

SUMMARY OF FINDINGS

Instrument description

A standard Blue Light Converter (BLC) from Air Quality Design (Wheat Ridge, CO) was used for photolytic conversion of nitrogen dioxide. This device has a cell volume of 16 mL which results in a residence time of 0.93 s at a flow rate of 1.0 l min^{-1}. The LED die in the BLC emit photons at a wavelength of 395 nm with a normal distribution half-width of 10nm The specific unit used for tests had a photolysis rate, j, of 0.84 s-1. Power consumption of the BLC is 36 W, and lifetime has been tested to at least 5000 hours of continuous use. Prior to use the BLC was conditioned with elevated levels of ozone (~300 ppb) to minimize wall losses.

A standard Model 205 Dual Beam (EPA Federal Equivalent Method) ozone analyzer from 2B Technologies (Boulder, CO) was used for measurement of ozone. A mass flow controller was added to maintain a constant flow through the system. The monitor was subject to a NIST Traceable ozone calibration prior to use.

Figure 1 shows the instrument setup for measurement of ozone and nitrogen dioxide. In this mode the ozone analyzer is set to operate in its standard configuration. Measurement of nitrogen dioxide is accomplished by first taking a measurement with the BLC off. The BLC is then turned on and a measurement is made. The difference between the two measurements divided by the conversion efficiency is the calculated amount of nitrogen dioxide.

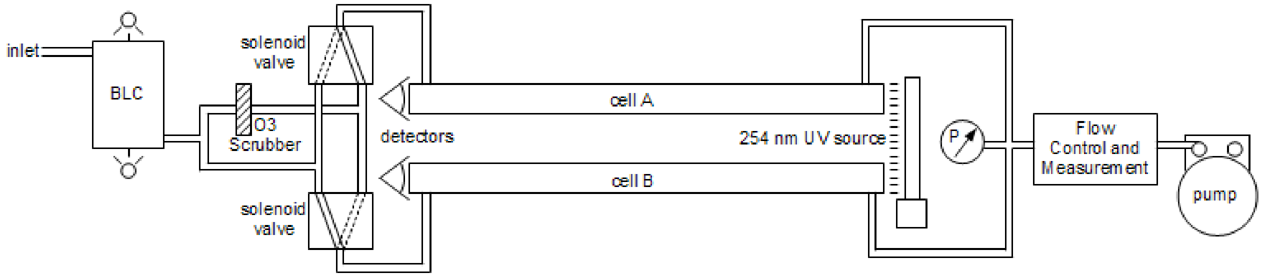

Figure 1. Instrument flow diagram with a two-cell ozone analyzer for the measurement of ozone and nitrogen dioxide

Instrument Characterization

Calibration of the unit was performed via gas phase titration. A given ozone concentration was added to excess nitric oxide in a dynamic calibration system and delivered to the instrument. Ozone was generated by photolyis of oxygen from the emission of an ozone producing mercury vapor lamp (BHK, Ontario, CA). The current provided to the lamp was controlled to produce different levels of ozone. Nitric oxide in nitrogen (Scott Marrin, Riverside, CA) and Grade 5 Zero Air (General Air, Denver, CO) were delivered via mass flow control. A TEI 42C nitric oxide (NO) analyzer that had been calibrated against a NIST traceable NO standard was used for characterizing calibration mixture.

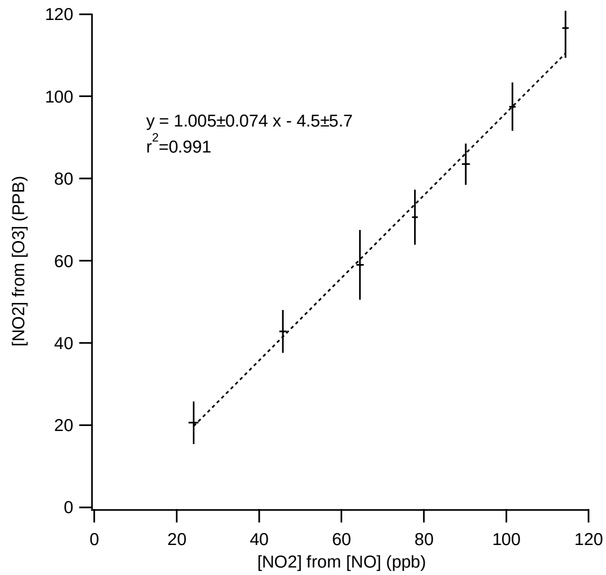

Figure 2. Nitrogen dioxide levels measured by the ozone created from photolysis and by the reduction in NO from titration. Error bars represent uncertainty in both measurements.

Figure 2 shows the correlation of different nitrogen dioxide levels measured via the production of ozone by photolysis on the ozone analyzer with the nitrogen dioxide levels measured via the decrease in nitric oxide observed on the TEI 42C analyzer. A weighted linear fit was used to compensate for the uncertainties.

Figure 3 shows 6 days of data collected at an urban location in Wheat Ridge, CO. This data shows typical levels of ozone and nitrogen dioxide for an urban Colorado site in springtime. Ozone levels are dominated by titration at night under calm conditions as seen in the early morning of March 5. Westerly winds bring in air with low levels of nitrogen dioxide and background levels of ozone as seen in the early afternoon of March 3, and around midnight of March 6. Similar levels and features were seen at a Colorado Department of Public Health and the Environment, Air Pollution Control Division site in Welby, Colorado, north of the Denver metropolitan area.

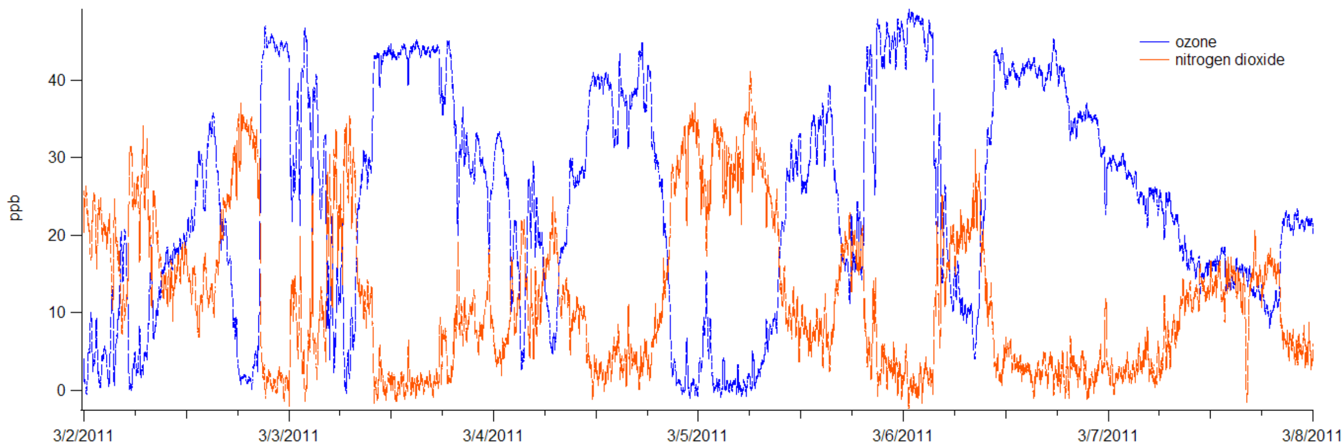

Figure 3. Levels of ozone and nitrogen dioxide in Wheat Ridge, Colorado from March 2, 2011 to March 8, 2011

CONCLUSIONS

We have demonstrated a simple instrument for measurement of NO_2 and O_3. Continuing research is focused on addition of nitric oxide (NO) to the instrument via oxidation of ambient NO to NO_2 prior to photolysis. Methods for accomplishing that oxidation include processing of the air sample through a CrO_3-based converter (room temperature, inert substrate), oxidation by O_3, and oxidation by HO_2.

The performance characteristics of the instrument are tied to those of the detector used for the ozone measurement. Thus, when a UV-absorption based ozone detector is used we can expect precision and detection limit to be on the order of 2-3 ppbv NO_2 and O_3. If we were to use the photolytic converter with one of the several chemiluminescence methods we could expect NO_2 measurement performance with precision and detection limit closer to 50 pptv or better.