Monitoring Ambient Nitrate Radical (NO_3) by Open Path Cavity Enhanced Absorption Spectroscopy (CEAS)

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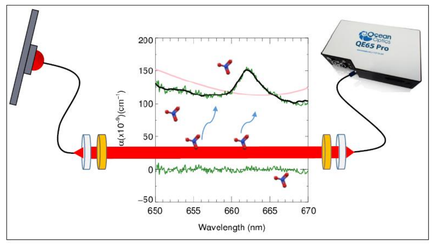
Introduction

Nitrate radical (NO_3) is one of the most important reactive nitrogen species and oxidants in the atmosphere. NO_3 contributes to the nighttime oxidation of volatile organic compounds (VOCs) and produces organic nitrate. The key role of NO_3 chemistry in regulating the NOx and VOC budget generates great interest in measuring NO_3 in the atmosphere. The closed-type CEAS suffers from the change of the transmission efficiency in field measurement, while the open path (OP) CEAS provides an alternative idea to avoid this uncertainty in measuring NO_3. Here we developed a new light emitting diode (LED)-based OP-CEAS instrument for measuring NO_3. The detailed setup of our instrument and the data processes will be introduced as well as its first field application in the Pearl River Delta, China.



Reflectivity	0.99985
Mirror distance	0.84 m
Effective Length	0.68 m
Enhanced Length	~ 5 km
Time resolution	30 s
Limit of detection	3 pptv (2σ)
Uncertainty	11-15%

Reference Spectrum and Reflectivity

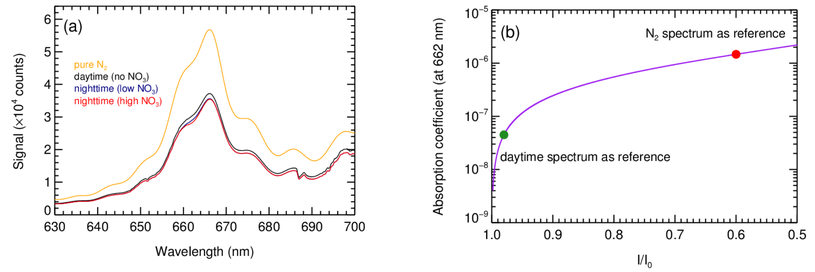


Figure 1. Reference spectrum (RS) selection. (a) Spectra of the pure N_2 and ambient samples during the daytime and nighttime (a high and a low NO_3 case). (b) Numerical calculation of the dependence of the absorption coefficient on the ratio of I to I0 (I/I0) at 662 nm. We selected daytime spectrum as RS due to the low absorption coefficient (leads to small residual spectrum) and free of retrieving H_2O absorption.

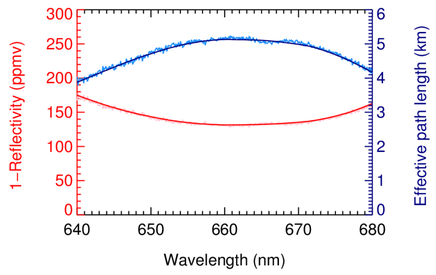


Figure 2. Reflectivity calibration. The R(λ) is determined from the difference between pure N_2 and He in Rayleigh scattering extinction. The cavity is enclosed by a detection cell with an outlet when calibrating the mirror reflectivity.

Spectral Fitting and LOD

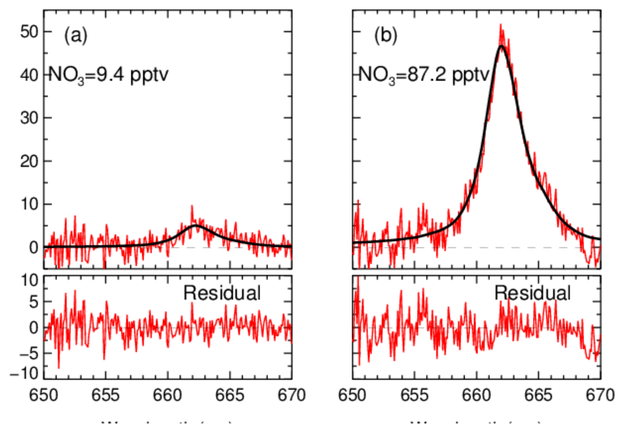


Figure 3. Spectral fitting. The measured spectral data is processed by using the DOAS Intelligent System (DOASIS) spectral fitting software. Here is an example of the spectral retrieval of low (a) and high (b) NO_3 in field measurements.

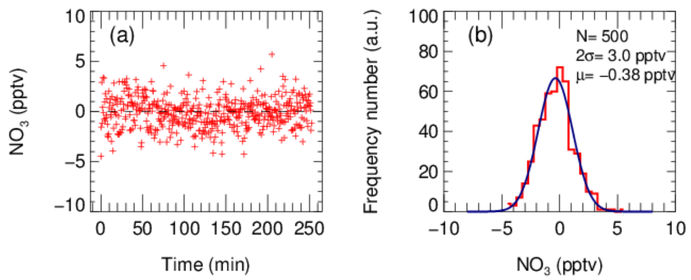


Figure 4. Limit of detection. Time series (a) and the histogram (b) of 500 ambient spectral fitting results during the daytime measurement showing that the detection limit of OP-CEAS is 3.0 pptv (2σ) in 30 s with an offset of -0.38 pptv.

Field Application

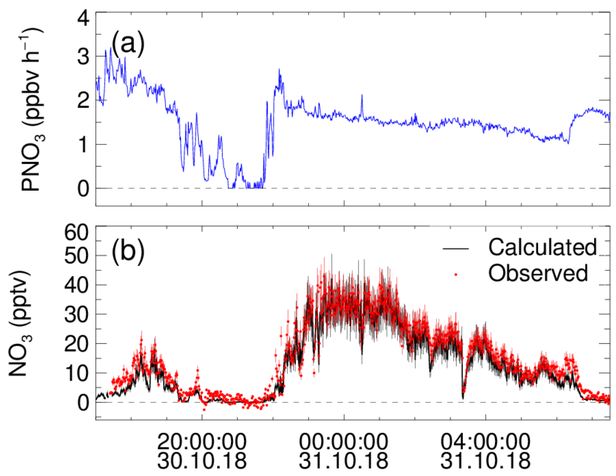


Figure 5. (a) Time series of the NO_3 production rate and measured NO_3 on the night of October 30, 2017 in a field campaign in PRD, China. (b) Time series of the measured NO_3 concentration by OP-CEAS and calculated NO_3 by the observed temperature, NO_2, N_2O_5 (with 20% uncertainty).

Applicable Environment

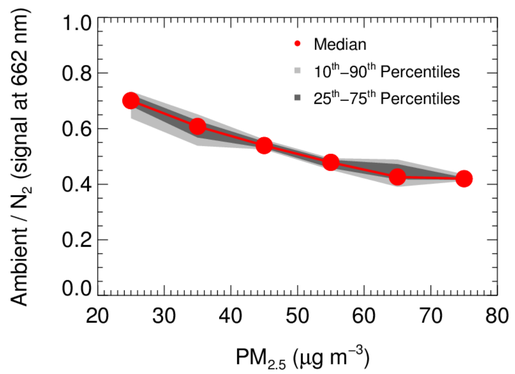


Figure 6. The functional dependence of the ratio of the spectral intensity to the N_2 spectrum on the ambient $PM_{2.5}$ in field measurement at 662 nm. To ensure the sensitivity of the instrument, our OP-CEAS configuration is applicable when the $PM_{2.5}$ below 50 μg m^{-3}. The aerosol mass loading of 50 μg m^{-3} is relatively common in the region of China where these experiments were performed, in polluted regions of Europe or in the U.S., which typically have much lower aerosol mass loadings, and OP-CEAS might be a useful alternative to closed path systems.

Take home message

1. Free of the sampling loss of the NO_3 radical by opening the optical detection path, the OP-CEAS instrument is engineered to provide sensitive and accurate measurements in field application.
2. The field measurement of NO_3 by OP-CEAS is feasible and applicable in clean or slightly polluted regions, its current configuration is better suited for a region that does not suffer from heavy PM pollution.
3. For more details of this work please visit **Anal. Chem. 2019, 91, 16, 10687-10693, or feel free to contact with H.W or K.L.**

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