Thermal dissociation cavity-enhanced absorption spectrometer for measuring NO\(_2\), RO\(_2\)NO\(_2\), and RONO\(_2\) in the atmosphere

Chunmeng Li\(^1\), Haichao Wang\(^{1,2,3}\), Xiaorui Chen\(^1\), Tianyu Zhai\(^1\), Shi Yi Chen\(^1\), Xin Li\(^1\), Limin Zeng\(^1\), and Keding Lu\(^1\)

\(^1\)State Key Joint Laboratory of Environmental Simulation and Pollution Control, College of Environmental Sciences and Engineering, Peking University, Beijing, 100871, China
\(^2\)School of Atmospheric Sciences, Sun Yat-sen University, Zhuhai, Guangdong, 510275, China
\(^3\)Guangdong Provincial Observation and Research Station for Climate Environment and Air Quality Change in the Pearl River Estuary, Key Laboratory of Tropical Atmosphere-Ocean System, Ministry of Education, Southern Marine Science and Engineering Guangdong Laboratory (Zhuhai), Zhuhai, 519082, China

Correspondence: Haichao Wang (wanghch27@mail.sysu.edu.cn) and Keding Lu (k.lu@pku.edu.cn)

Received: 31 December 2020 – Discussion started: 21 January 2021
Revised: 23 April 2021 – Accepted: 29 April 2021 – Published: 3 June 2021

Abstract. We developed thermal dissociation cavity-enhanced absorption spectroscopy (TD-CEAS) for the in situ measurement of NO\(_2\), total peroxy nitrates (PNs, RO\(_2\)NO\(_2\)), and total alkyl nitrates (ANs, RONO\(_2\)) in the atmosphere. PNs and ANs were thermally converted to NO\(_2\) at the corresponding pyrolytic temperatures and detected by CEAS at 435–455 nm. The instrument sampled sequentially from three channels at ambient temperature, 453 and 653 K, with a cycle of 3 min, to measure NO\(_2\), NO\(_2\)+PNs, and NO\(_2\)+PNs+ANs. The absorptions between the three channels were used to derive the mixing ratios of PNs and ANs by spectral fitting. The detection limit (LOD, 1\(\sigma\)) for retrieving NO\(_2\) was 97 parts per trillion by volume (pptv) in 6 s. The measurement uncertainty of NO\(_2\) was 9 %, while the uncertainties of PN and AN detection were larger than those of NO\(_2\) due to chemical interferences that occurred in the heated channels, such as the reaction of NO (or NO\(_2\)) with the peroxy radicals produced by the thermal dissociation of organic nitrates. Based on laboratory experiments and numerical simulations, we created a lookup table method to correct these interferences in PN and AN channels under various ambient organic nitrates, NO, and NO\(_2\). Finally, we present the first field deployment and compare it with other instruments during a field campaign in China. The advantages and limitations of this instrument are outlined.

1 Introduction

Organic nitrates (ONs) act as temporary NO\(_x\) reservoir species, which affect atmospheric circulation and impact air quality and climate (Mellouki et al., 2015). Peroxy nitrates (PNs, RO\(_2\)NO\(_2\)) and alkyl nitrates (ANs, RONO\(_2\)) are two important kinds of organic nitrates. They are closely related to the distribution of oxidants in the atmosphere by terminating the HO\(_x\) cycle. ONs are also important precursors of secondary organic aerosols (SOAs) (Berkemeier et al., 2016; Lee et al., 2016; Ng et al., 2017; Rollins et al., 2012). Volatile organic compounds (VOCs) are oxidized by OH or O\(_3\) to produce peroxy radicals (RO\(_2\)), and then RO\(_2\) reacts with NO\(_2\) to produce PNs (Reaction R1). In addition, the aldehydes formed during the process of NO\(_3\) oxidizing isoprene at night react with NO\(_3\) to form PNs. PNs can be divided into two categories depending on the nature of the RO\(_2\) group. One is peroxy acyl nitrates (PANs) when RO\(_2\) is R′C(O)OO, among which PPN (peroxypropionyl nitrate) and PAN (peroxyacetyl nitrate) dominate PNs with percentages of 75 %–90 % due to their relatively high thermal stability. The other is some peroxy nitrates without acyl groups, which are only abundant in cold regions (Roberts, 1990; Roberts et al., 1998b; Thieser et al., 2016; Wooldridge et al., 2010). The sink pathways of PNs include deposition, thermal decomposition, photolysis, and OH oxidation, and thermal decomposition dominates in the troposphere with a temperature dependence (Reaction R2). Therefore, the lifetime of PAN varies from less than 1 h to...
In the high-NO\textsubscript{2} region, RO\textsubscript{2} reacts primarily with NO to produce ANs. ANs can also be emitted directly from biomass combustion and the ocean. Ocean emissions are regarded as the main source of short-chain ANs (C\textsubscript{1}–C\textsubscript{3}), and up to tens of parts per trillion by volume (pptv) of the species above have been measured in marine areas (Atlas et al., 1993; Chuck et al., 2002; Talbot et al., 2000). NO\textsubscript{3}-initiated ANs during the night are generally considered to be important and have a higher organic nitrate yield than OH-initiated ANs (Horowitz et al., 2007; Perring et al., 2013). During the daytime, there is a branching reaction between RO\textsubscript{2} and NO to form ANs (Reaction R3a) with a small branch ratio (1\%–30\%) (Arey et al., 2001; Reisen et al., 2005; Russell and Allen, 2005; Wennberg et al., 2018). Ambient ANs are removed by photolysis or oxidation to produce NO\textsubscript{2} or HNO\textsubscript{3}, transportation as NO\textsubscript{3} reservoirs, or deposition. ANs play a significant role in SOA formation (Lee et al., 2016; Zare et al., 2018). Monofunctional ANs are stable and account for a small proportion of ANs, among which those formed from alkanes can be tracers of human activities in remote areas (Simpson et al., 2006; Wang et al., 2003). Polyfunctional ANs are hard to detect since they are more reactive than monofunctional ANs.

\begin{align*}
\text{RO}_2 + \text{NO} + M & \rightarrow \text{RO}_2\text{NO} + M \quad \text{(R3a)} \\
\text{RO}_2 + \text{NO} + M & \rightarrow \text{RO} + \text{NO}_2 \quad \text{(R3b)}
\end{align*}

The various sources and sinks of ONs complicate their atmospheric distribution. The measurement of ANs and PNs has been developed by gas chromatography (GC). GC is used for the separation of species, and then the separated substances are quantified by electron capture detectors (ECDs), luminochemiluminescence (CL), or mass spectrometry (MS) (Atlas, 1988; Blanchard et al., 1993; Flocke et al., 2005; Gaffney et al., 1998; Hao et al., 1994; Luxenhofer et al., 1994; Tanimoto et al., 1999). These methods measure individual species accurately (Roberts et al., 2003), but the individual standards are incomprehensive. Furthermore, the methods suffer from relatively low time resolution (Blanchard et al., 1993). The strength of the bond between the NO\textsubscript{2} group and the organic group determines the temperature to pyrolyze the organic nitrates. The cleavage of the NO\textsubscript{2} group in PNs requires approximately 85–115 kJ mol\textsuperscript{-1} (Kirchner et al., 1999), while for ANs, the pyrolytic process requires approximately 160–170 kJ mol\textsuperscript{-1} (Roberts, 1990); therefore, PNs are more prone to dissociate thermally. Based on the feature of gradient pyrolysis of reactive nitrogen compounds, TD-LIF (thermal-dissociation laser-induced fluorescence) was developed to measure ANs, ANs, and gaseous HNO\textsubscript{3} indirectly by quantifying the NO\textsubscript{2} product (Day et al., 2002). Afterwards, chemical ionization mass spectrometry (CIMS), cavity ring-down spectroscopy (CRDS), and cavity attenuated phase-shift spectroscopy (CAPS) are used to quantify the pyrolytic products (Paul and Osthoff, 2010; Slusher et al., 2004; Thieser et al., 2016; Wild et al., 2014). The detection limits and response times of TD-CIMS are excellent, but \textsuperscript{13}C-labeled PAN is required as an internal standard. TD-CRDS and TD-CAPS show high spatial and temporal resolution and good measurement capability (Sadanaga et al., 2016; Sobanski et al., 2016). CEAS (cavity-enhanced absorption spectroscopy) is a powerful technology that can monitor several compounds or species simultaneously with broad absorption bands being detected (Fiedler et al., 2003) and has been applied to measure many species in field studies, such as NO\textsubscript{2}, HONO, NO\textsubscript{3}, N\textsubscript{2}O\textsubscript{5}, IO, glyoxal, and methylglyoxal (Ball et al., 2004; Barbero et al., 2020; Duan et al., 2018; Gherman et al., 2008; Jordan and Osthoff, 2020; Kahan et al., 2012; Langridge et al., 2006; Lechevallier et al., 2019; Liu et al., 2019; Min et al., 2016; Thalman and Volkamer, 2010; Vaughan et al., 2008; Venables et al., 2006; Ventrillard-Courtillot et al., 2010; Ventrillard et al., 2017; H. Wang et al., 2017; Washenfelder et al., 2016, 2008; Watt et al., 2009).

Organic nitrates have a large range of mixing ratios in the atmosphere that vary from several pptv in warm and remote regions to several parts per billion by volume (ppbv) in polluted regions. Field measurements of organic nitrates have been extensively conducted in the United States and Europe (Fischer et al., 2000; Glavas and Moschonas, 2001; Kastler and Ballschmitter, 1999; Perring et al., 2009; Roberts et al., 1998a; Sobanski et al., 2017), but related studies are sparse in China (Chen et al., 2017; Song et al., 2018; Sun et al., 2018; Zhang et al., 2018). Ozone pollution in China has occurred frequently in recent years (Ma et al., 2019; Shu et al., 2019; T. Wang et al., 2009, 2017; Yin et al., 2019). Although many studies have examined the effect of PNs and ANs on regulating ozone formation (Chen et al., 2018; Ling et al., 2016; Liu et al., 2018, 2012, 2010; Zeng et al., 2019; Zhang et al., 2014), the issue has not been well studied. Here, we developed a pyrolytic measurement system based on CEAS to detect NO\textsubscript{2}, PNs, and ANs in the atmosphere. In this study, the detailed setup of the instrument, laboratory characterizations, and its first field application in China are presented.

2 Methods

2.1 Instrumentation of TD-CEAS

Our instrument is designed to measure NO\textsubscript{2}, ANs, and PNs in the atmosphere and has the characteristics of good stability, low energy consumption, and portability. The total weight of the instrument is less than 30 kg, the overall size is 110 × 60 × 50 cm, and power consumption is less than 300 W. The measurement of NO\textsubscript{2} is achieved by CEAS. Due to the
feature of gradient pyrolysis of ANs and PNs, the sample gas flowing out from three different channels contains the total amount of NO₂ at different temperatures. The gradient of NO₂ concentration absorption at different pyrolytic temperatures is used to retrieve the mixing ratio of NO₂, PNs, and ANs. The time resolution of the instrument measurement is 6 s, the measurement time of each channel is 1 min, and each cycle is 3 min.

The CEAS system has been described in detail in previous literature (Duan et al., 2018; Fiedler et al., 2003; Gherman et al., 2008; Jordan and Osthoff, 2020; Jordan et al., 2019; Langridge et al., 2006; Liang et al., 2019; Liu et al., 2019; Min et al., 2016; Tang et al., 2020; Ventrolllard-Courtillot et al., 2010; H. Wang et al., 2017; Yi et al., 2016); thus there is a brief introduction to the principle of the instrument here. NO₂ molecules have a specific absorption structure in the wavelength range of 430–460 nm (Fig. S1 in the Supplement). Based on Lambert–Beer’s law, the extinction coefficient (α) is proportional to the absorber’s concentration and optical path. Here, α is mainly contributed by molecular absorption, Rayleigh scattering, and Mie scattering. In addition, it can also be obtained by comprehensive calculations through the intensity of the sampling spectrum, reference spectrum, mirror reflectivity, and effective cavity length.

In Eq. (1), λ is the wavelength of light, I₀(λ) is the intensity of the reference spectrum, I(λ) is the sample spectrum, d_eff is the effective cavity length (see Sect. 3.2 in detail), R(λ) is the mirror reflectivity, αMie(λ) is the extinction due to Mie scattering, αRayl(λ) is the extinction due to Rayleigh scattering, and nᵢ and σᵢ(λ) are the number density and absorption cross section of i_th gas compounds, respectively. According to Eq. (1), it is necessary to quantify the mirror reflectivity, effective cavity length, and NO₂ absorption cross section.

\[
\alpha(\lambda) = \left( \frac{I₀(\lambda)}{I(\lambda)} - 1 \right) \left( 1 - \frac{R(\lambda)}{d_{\text{eff}}} \right) = \sum nᵢ × σᵢ(λ) + α_{\text{Mie}}(λ) + α_{\text{Rayl}}(λ)
\]

As shown in Fig. 1a, the optical layout of the CEAS consists of a light source, collimating optics, a cage structure, a high-finesse cavity, and a spectrometer. After filtering the PM, the gas passes through three quartz tubes, and then the alternate measurements of NO₂, NO₂+PNs, and NO₂+PNs + ANs are achieved by three-way solenoid valves.

Four stainless-steel columns are used to collimate two opposing high-mirror mounting bases. The two endplates in the middle of the cage structure further enhance the stability of the system. The light source is introduced into the system through a fiber connected to a two-dimensional adjustment frame (CX1Y, Thorlabs, Newton, NJ, USA) through a connector. The plano-convex lens (f = 30 mm) is installed in another adjustment frame, and the two adjustment frames are connected by a customized X-shaped adapter, which is fixed at the end with the light source. The center alignment of the light source, lens, and high-reflectivity module is achieved by adjusting the adjustment frame in the vertical and horizontal directions. Then, blue light is introduced into an optical cavity composed of a pair of high-reflectivity (HR) mirrors. The reflectivity of HR mirrors (CRD450-1025-100, Advanced Thin Films, CO, USA) is reported by the manufacturer to be greater than 0.9999 (440–460 nm) with a radius curvature of 1.0 m and a diameter of 25.4 mm. The high-reflectivity mirrors are installed in the groove of the special customized base and sealed by an O-ring, and then the three-dimensional microadjustment is achieved by squeezing the lens and O-ring to finely adjust their pitch and yaw. The distance between mirrors is 39.0 cm, and high-purity nitrogen (>99.999%), which passes through the small hole before the mirror base, is used as a purge gas to protect the mirror surface.

https://doi.org/10.5194/amt-14-4033-2021
The cavity system is sealed by two welded bellows, two polytetrafluoroethylene (PTFE) connecting pieces, and a stainless-steel sampling cell that is internally polished. The PTFE connecting piece connects the sampling cell and bellows and acts as a sample inlet and outlet. As shown in Fig. 1a, the distance between the inlet and outlet (d\text{in} \text{cm}) is 32.0 cm. After passing through the sampling cavity, the blue light converges through another plano-convex mirror (f = 50 mm). It enters the detector spectrometer (QE65PRO, Ocean Optics, Dunedin, FL, USA) for signal acquisition through an optical fiber. The dark current in the CCD of the spectrometer is reduced by controlling the temperature of the CCD at −20.0 °C; the width of the entrance slit is 100 µm, the corresponding wavelength resolution is 0.39 nm, and the detection wavelength range is 413.48–485.48 nm.

The schematic of the TD-CEAS is shown in Fig. 1b. The flow system mainly includes the particulate matter filter in the front end of the sampling line, quartz tubes for species pyrolytic conversion, three-way system switching module, detection module (CEAS), and flow control module. The sample gas first passes through a PTFE filter membrane (25 µm thickness, 4.6 cm diameter, and 2.5 µm pore size, Typris, China) to remove ambient aerosols. The sample gas enters the system through a 1/4 in. PFA (polytetrafluoroethylene) tube and is then divided into three channels (NO\textsubscript{2} channel, AN channel, and PN channel) by using two T-shaped PFA three-way connections. The gas flow at the end of each channel is controlled at 0.8 L min\textsuperscript{-1}, and the total flow rate (sample flow gas and purge gas) is 2.6 L min\textsuperscript{-1} maintained by mass flow controllers and a diaphragm pump.

The quartz tubes have a length of 35 cm, which have an inner diameter of 5 mm and an outer diameter of 10 mm and are connected to the system through a 10 mm to 6.35 mm (1/4 in.) PTFE connection. The quartz tubes of the AN channel and the PN channel are heated by resistance wires, and temperature is controlled by the PID algorithm. An asbestos sleeve on the quartz tube surface is used to insulate heat exchange with the external environment. The heating powers of the PN channel and AN channel are approximately 20 and 50 W, respectively. The length of the heating module is 15 cm. According to the pyrolytic efficiency experiment (see Sect. 3.4 for details), the heating temperatures for the AN and PN channels are controlled at 380 and 180 °C, respectively. One CEAS is used to detect the NO\textsubscript{2} absorption of different channels to reduce the cross interference due to the difference of multidetectors. A solenoid valve is connected behind the quartz tube of each channel. At the same time, a time relay is used to periodically control the three T-shaped solenoid valves (71335SN2KVJ1, Parker Haminfi, USA), and the internal surface of the T-shaped solenoid valves is stainless steel. Each channel has the same constant flow rate regardless of whether the sampling air draws into the CEAS or vent. At the end of the channels, mass flow controllers are used to restrict the flow rate.

### 2.2 Laboratory experimental setup

To characterize the performance and potential interferences of this instrument, we used a photochemical PAN source in the laboratory experiments. Acetone undergoes photolysis at 285 nm from a Hg lamp and then generates excess PA radicals (peroxyacetyl radicals) in zero air. A small amount of NO reacts with PAs to form NO\textsubscript{2}, and then NO\textsubscript{2} further reacts with PAs to form PAN. We obtained a standard PAN source in this way, which generated a source at a level of 1–10 ppbv. The source was used for the laboratory experiments after the temperature of the Hg lamp stabilized at 39.0 °C, and the source level and stability were double-checked by a GC-ECD instrument. To investigate the potential interferences caused by the pyrolysis of organic radical products reacting with ambient NO and NO\textsubscript{2} in the TD-CEAS, a multigas calibrator (146i, Thermo Fisher Scientific, Inc., USA) was used to generate O\textsubscript{3} gas by photolysis of oxygen and outputted well-mixed gases by diluting NO or NO\textsubscript{2} with zero air according to the requirement of studying the potential inferences caused by ambient NO and NO\textsubscript{2}. NO (1 ppmv) and NO\textsubscript{2} (10 ppmv) bottle gases were connected to the multigas calibrator. An ozone monitor was used to detect O\textsubscript{3} levels in these experiments (49i, Thermo Fisher Scientific, Inc., USA). A NO\textsubscript{i} monitor was used to detect NO and NO\textsubscript{2} levels in these experiments (42i, Thermo Fisher Scientific, Inc., USA). Pure N\textsubscript{2} (> 99.9999 %) and He (> 99.9999 %) bottle gases were used to calibrate the mirror reflectivity of the CEAS and to purge the mirrors.

### 2.3 Box model

A box model was established to mimic the experimental results and study the potential interferences of NO and NO\textsubscript{2} in the PN and AN measurements. The chemical mechanism is based on previous work (Thieser et al., 2016). These reactions during the pyrolytic process in the box model are listed in Text S1 in the Supplement, and the reaction rate of these reactions is mainly taken from the Master Chemical Mechanism, MCM v3.3 (website: http://mcm.leeds.ac.uk/MCM, last access: March 2020) (Jenkins et al., 1997; Saunders et al., 2003). As the wall loss has an important effect on the lifetime of free radicals, we set the wall loss constant (k\text{wall}) of RO\textsubscript{2} to 0.3 s\textsuperscript{-1} (Thieser et al., 2016; Wooldridge et al., 2010). The wall loss rate coefficients of HO\textsubscript{2} and OH are selected as the values of 0.5 and 5.4 s\textsuperscript{-1}, respectively (Fuchs et al., 2008). The residence time of the sampling gas in each channel is calculated by considering the temperature distribution. The time step of the model is set to 0.001 s.
3 Instrument characterization

3.1 Mirror reflectivity

The spectra of pure N$_2$ (> 0.99999) or He (> 0.99999) filling the cavity through the purge lines are collected to calibrate the mirror reflectivity, as the Rayleigh scattering section of the two is significantly distinct; therefore, $R(\lambda)$ can be calibrated according to Eq. (2) (Chen and Venables, 2011; Min et al., 2016).

$$R(\lambda) = \frac{d}{I_{N_2}(\lambda) \times n_{N_2} \times \sigma_{Rayl,N_2}(\lambda) - I_{He}(\lambda) \times n_{He} \times \sigma_{Rayl,He}(\lambda)}{I_{He}(\lambda) - I_{N_2}(\lambda)},$$

where $d$ is the distance between two high-reflectivity mirrors, $\lambda$ is the wavelength, $I_{N_2}(\lambda)$ and $I_{He}(\lambda)$ are spectra obtained when the cavity is filled with pure N$_2$ and He, respectively, $n_{N_2}$ and $n_{He}$ are the number densities calculated at the measurement temperature and pressure in the cavity, respectively, and $\sigma_{Rayl,N_2}(\lambda)$ and $\sigma_{Rayl,He}(\lambda)$ are the Rayleigh scattering sections of N$_2$ and He, respectively (Shardanand, 1977; Sneep and Ubachs, 2005). Figure 2 shows the average of the mirror reflectivity calibration results. $R(\lambda)$ is above 0.9999 at 435–465 nm and up to 0.99992 at 450 nm. The total uncertainty of the mirror reflectivity is 5%, which comes from the uncertainty in the scattering section of N$_2$. The blue line is the average optical path length when the sampling flow rate in the cavity is 0.8 L min$^{-1}$, which is equal to $d_{eff}/(1-R)$ ($d_{eff}$ is 31.84 cm), with a value up to 5.2 km at 450 nm.

3.2 Effective cavity length

The effective length of the absorbers (named effective cavity length, $d_{eff}$) in the detection cell is shorter than the physical distance of the cavity with purge; thus, it needs to be calibrated. We performed concentration determination on the NO$_2$ standard source (130 ppbv) under two experimental settings with or without purging and then used Eq. (1) to calculate $d_{eff}$. The ratio of NO$_2$ absorption with and without purging is equal to the ratio of the effective cavity length to the physical distance $L$ between the mirrors ($d_{eff}/L$). A NO$_2$ stand was prepared from a bottled standard (5 ppmv NO$_2$) and diluted with high-purity N$_2$ in a multigas calibrator (146i, Thermo Fisher Scientific, Inc., Waltham, MA, USA). As shown in Fig. 3a, the retrieved concentration of NO$_2$ shows a general positive correlation trend with the flow rate with N$_2$ purging; the concentration of NO$_2$ is 130 ppbv without a purge.

Figure 2. Mirror reflectivity and optical path length calibrated by He (> 0.99999) and N$_2$ (> 0.99999). The red line is the average $R(\lambda)$, and the blue line is the optical path length.

Figure 3. The results of the effective cavity length. (a) The black line represents the flow rate, and the red points and brown diamonds represent the retrieved NO$_2$ concentration with and without nitrogen purge (100 sccm × 2), respectively. (b) The relationship between the ratio of the effective cavity length ($d_{eff}$) to cavity physical distance ($L$) and the sampling flow rate.
3.3 Spectral fitting

The absorption cross section of NO$_2$ measured by Voigt et al. (2002) is used to retrieve the NO$_2$ concentration in this study. The absorption cross section of NO$_2$ between 435–455 nm is selected to perform the spectral fitting. It has been reported that the NO$_2$ cross section is not sensitive to temperature changes (Vandaele et al., 2002; Voigt et al., 2002); therefore, convolution is only performed for our instrument setup at ambient temperature. The peak at 436.2 nm of the Hg spectrum measured by the spectrometer is used to generate a wavelength-dependent instrument slit function that accounts for the change in spectral resolution over the CCD pixels. The convoluted cross section of NO$_2$ is shown in Fig. S1.

Glyoxal has strong absorption in the same optical window (Liu et al., 2019; Min et al., 2016; Thalman et al., 2015; Thalman and Volkamer, 2010; Washenfelder et al., 2008), but here we do not take glyoxal absorption into consideration in the spectral fitting. The inclusion of glyoxal in the spectral fitting would enlarge the fitting residual. Our field measurements showed that the uncertainty caused by excluding glyoxal fitting was approximately 4 % (Fig. S2). Figure 4 shows two examples of the spectral fitting of the measured absorption of high and low NO$_2$ at a 6 s integration time during the ambient measurement. The retrieved mixing ratios of NO$_2$ were 16.2 $\pm$ 0.1 and 1.8 $\pm$ 0.1 ppbv, respectively. The corresponding fitting residual, which is the difference between the measured and fitting results, is in the range of $10 \times 10^{-9}$ at 435–455 nm. A typical measurement sequence during the ambient measurement is illustrated in Fig. 5, which displays NO$_2$ mixing ratios of three channels alternatively. The mixing ratio of NO$_2$ in different channels is detected periodically, and there are several transitional points due to switching measurement phases. Therefore, we excluded the transition point of each phase and the two data points before and after the transition point to avoid measurement error. As we discuss later, the mixing ratio of ANs and PNs can be calculated by subtracting the NO$_2$ mixing ratio measured from different channels.

There are two methods to determine the mixing ratio of ONs and PNs. One is the differential concentration method (“CONC”). As shown in Eqs. (3)–(6), the $I_0$ is fixed during data analysis by using the NO$_2$ spectrum: $I_{TD380}$ and $I_{TD180}$ are the spectra obtained when the CEAS detects the AN channel and PN channel, respectively; $I_{N_2}$ is the N$_2$ spectrum obtained when the cavity is filled with N$_2$ ($> 0.99999$); $\alpha_{TD380}$ and $\alpha_{TD180}$ are absorption coefficients when setting $I_{N_2}$ as $I_0$, and setting $I_{TD380}$ or $I_{TD180}$ as $I$, respectively; and after deleting the abnormal points caused by phase switching, [ONs] is obtained by subtracting [NO$_2$]$_{TD380}$ from the average of [NO$_2$]$_{REF}$, and [PNs] is obtained by subtracting [NO$_2$]$_{TD180}$ from the average of [NO$_2$]$_{REF}$. The other method is the differential absorption method (“SPEC”), by using the dynamic background spectrum method for spectral fitting (Eqs. 7–8): $I_{REF}$ is the spectrum obtained at the reference channel, ONs can be retrieved based on $I_{TD380}$ and $I_{REF}$, and PNs can be retrieved by $I_{TD180}$ and $I_{REF}$. An intercomparison of field measurements shows that the SPEC method results in fewer outliers (Fig. 6). For the SPEC method, the shift and squeeze of the spectrum is performed only once during the spectral fitting, which reduces the uncertainty caused by the second spectral fitting. Therefore, we selected the SPEC method to retrieve the concentrations of NO$_2$, PNs, and ANs.
The occurrence of the dual-plateau phenomenon is due to the competition of pyrolysis and recombination reactions. PAN will produce NO2 when the airflow passes through the quartz tube. If PAs are not lost on the wall surface in time (Reactions R7–R8). Therefore, the thermal curve shows two plateaus as the heating temperature increases. The concentration of PAN source and wall loss rate of NO2 influence the fraction of related species. Figure 8a and c show that the gap between the two plateaus increases with PAN concentration and decreases as the wall loss rate coefficients of NO2 increase. The wall loss of NO2 competes with the recombination of PA radicals and NO2. Therefore, a high wall loss rate coefficient of NO2 reduces the recombination for PAN.

The consistency between the observed and simulated thermal efficiencies of PAN suggests that the model simulation is reliable. Without the AN source to quantify the thermal dissociation of PAN reaches the final plateau once the temperature is above 360 °C. Similarly, PAN is reported to be thermally dissociated completely at approximately 400 °C (Friedrich et al., 2020). The presence of alkyl nitrates in the PAN source has been reported before by previous studies and was regarded as the reason for the dual-plateau profile of PN dissociation (Paul et al., 2009). Here, we cannot rule out the possibility of alkyl nitrate impurities. However, the source level of PAN is equal to 92 ± 3% of NOx input, suggesting only a very small percentage (≤ 8% on average), if any, of ANs. If the PAN source is equal to 4 ppbv in the PN channel at 180 °C, as Fig. S3 shows, PAN will first dissociate completely, and then PAs will recombine with NO2 to form PAN when the airflow passes through the cooling lines.

To further study the thermal dissociation of organic nitrates in the heated channels, box model simulations were conducted to reproduce the response relationship between heating temperature and NO2 generated by pyrolysis. If the PAN source is equal to 4 ppbv in the PN channel at 180 °C, as Fig. S3 shows, PAN will first dissociate completely, and then PAs will recombine with NO2 to form PAN when the airflow passes through the cooling lines. As shown in Fig. 7, PAN gradually transforms into NO2 and CH3O2NO2 as the setting temperature increases. The simulated signals of thermal dissociation of PAN show two plateaus, which is generally consistent with the experimental results. However, there are some differences from 260 to 360 °C, which may come from simulation uncertainties such as the temperature profile in the heated channel, the follow-up reactions of PA radicals, and their reaction rates. The first plateau at 180 °C is caused by the recombination of PAs and NO2 after the pyrolysis of PAN, and the time for recombination from the end of the tube to the inlet is 297 ms. Therefore, recombination cannot be ignored when the heating temperature plateau period indicates that almost all PAN is transformed into NO2, which is due to the increase in the pyrolytic loss of PAs, and the pyrolysis of PAN is enhanced with increasing temperature.

The occurrence of the dual-plateau phenomenon is due to the competition of pyrolysis and recombination reactions. PAN will produce NO2 and PAs after thermal dissociation, but PAs will recombine with NO2 if PAs are not lost on the wall surface in time (Reactions R7–R8). Therefore, the thermal curve shows two plateaus as the heating temperature increases. The concentration of PAN source and wall loss rate of RO2 influence the fraction of related species. Figure 8a and c show that the gap between the two plateaus increases with PAN concentration and decreases as the wall loss rate coefficients of RO2 increase. The wall loss of RO2 competes with the recombination of PA radicals and NO2. Therefore, a high wall loss rate coefficient of RO2 reduces the recombination for PAN.

The consistency between the observed and simulated thermal efficiencies of PAN suggests that the model simulation is reliable. Without the AN source to quantify the thermal dissociation of PAN reaches the final plateau once the temperature is above 360 °C. Similarly, PAN is reported to be thermally dissociated completely at approximately 400 °C (Friedrich et al., 2020). The presence of alkyl nitrates in the PAN source has been reported before by previous studies and was regarded as the reason for the dual-plateau profile of PN dissociation (Paul et al., 2009). Here, we cannot rule out the possibility of alkyl nitrate impurities. However, the source level of PAN is equal to 92 ± 3% of NOx input, suggesting only a very small percentage (≤ 8% on average), if any, of ANs. If the PAN source is equal to 4 ppbv in the PN channel at 180 °C, as Fig. S3 shows, PAN will first dissociate completely, and then PAs will recombine with NO2 to form PAN when the airflow passes through the cooling lines.

To further study the thermal dissociation of organic nitrates in the heated channels, box model simulations were conducted to reproduce the response relationship between heating temperature and NO2 generated by pyrolysis. If the PAN source is equal to 4 ppbv in the PN channel at 180 °C, as Fig. S3 shows, PAN will first dissociate completely, and then PAs will recombine with NO2 to form PAN when the airflow passes through the cooling lines. As shown in Fig. 7, PAN gradually transforms into NO2 and CH3O2NO2 as the setting temperature increases. The simulated signals of thermal dissociation of PAN show two plateaus, which is generally consistent with the experimental results. However, there are some differences from 260 to 360 °C, which may come from simulation uncertainties such as the temperature profile in the heated channel, the follow-up reactions of PA radicals, and their reaction rates. The first plateau at 180 °C is caused by the recombination of PAs and NO2 after the pyrolysis of PAN, and the time for recombination from the end of the tube to the inlet is 297 ms. Therefore, recombination cannot be ignored when the heating temperature plateau period indicates that almost all PAN is transformed into NO2, which is due to the increase in the pyrolytic loss of PAs, and the pyrolysis of PAN is enhanced with increasing temperature.

The occurrence of the dual-plateau phenomenon is due to the competition of pyrolysis and recombination reactions. PAN will produce NO2 and PAs after thermal dissociation, but PAs will recombine with NO2 if PAs are not lost on the wall surface in time (Reactions R7–R8). Therefore, the thermal curve shows two plateaus as the heating temperature increases. The concentration of PAN source and wall loss rate of RO2 influence the fraction of related species. Figure 8a and c show that the gap between the two plateaus increases with PAN concentration and decreases as the wall loss rate coefficients of RO2 increase. The wall loss of RO2 competes with the recombination of PA radicals and NO2. Therefore, a high wall loss rate coefficient of RO2 reduces the recombination for PAN.

The consistency between the observed and simulated thermal efficiencies of PAN suggests that the model simulation is reliable. Without the AN source to quantify the thermal dissociation of PAN reaches the final plateau once the temperature is above 360 °C. Similarly, PAN is reported to be thermally dissociated completely at approximately 400 °C (Friedrich et al., 2020). The presence of alkyl nitrates in the PAN source has been reported before by previous studies and was regarded as the reason for the dual-plateau profile of PN dissociation (Paul et al., 2009). Here, we cannot rule out the possibility of alkyl nitrate impurities. However, the source level of PAN is equal to 92 ± 3% of NOx input, suggesting only a very small percentage (≤ 8% on average), if any, of ANs. If the PAN source is equal to 4 ppbv in the PN channel at 180 °C, as Fig. S3 shows, PAN will first dissociate completely, and then PAs will recombine with NO2 to form PAN when the airflow passes through the cooling lines.

To further study the thermal dissociation of organic nitrates in the heated channels, box model simulations were conducted to reproduce the response relationship between heating temperature and NO2 generated by pyrolysis. If the PAN source is equal to 4 ppbv in the PN channel at 180 °C, as Fig. S3 shows, PAN will first dissociate completely, and then PAs will recombine with NO2 to form PAN when the airflow passes through the cooling lines. As shown in Fig. 7, PAN gradually transforms into NO2 and CH3O2NO2 as the setting temperature increases. The simulated signals of thermal dissociation of PAN show two plateaus, which is generally consistent with the experimental results. However, there are some differences from 260 to 360 °C, which may come from simulation uncertainties such as the temperature profile in the heated channel, the follow-up reactions of PA radicals, and their reaction rates. The first plateau at 180 °C is caused by the recombination of PAs and NO2 after the pyrolysis of PAN, and the time for recombination from the end of the tube to the inlet is 297 ms. Therefore, recombination cannot be ignored when the heating temperature plateau period indicates that almost all PAN is transformed into NO2, which is due to the increase in the pyrolytic loss of PAs, and the pyrolysis of PAN is enhanced with increasing temperature.

The occurrence of the dual-plateau phenomenon is due to the competition of pyrolysis and recombination reactions. PAN will produce NO2 and PAs after thermal dissociation, but PAs will recombine with NO2 if PAs are not lost on the wall surface in time (Reactions R7–R8). Therefore, the thermal curve shows two plateaus as the heating temperature increases. The concentration of PAN source and wall loss rate of RO2 influence the fraction of related species. Figure 8a and c show that the gap between the two plateaus increases with PAN concentration and decreases as the wall loss rate coefficients of RO2 increase. The wall loss of RO2 competes with the recombination of PA radicals and NO2. Therefore, a high wall loss rate coefficient of RO2 reduces the recombination for PAN.

The consistency between the observed and simulated thermal efficiencies of PAN suggests that the model simulation is reliable. Without the AN source to quantify the thermal dissociation of PAN reaches the final plateau once the temperature is above 360 °C. Similarly, PAN is reported to be thermally dissociated completely at approximately 400 °C (Friedrich et al., 2020). The presence of alkyl nitrates in the PAN source has been reported before by previous studies and was regarded as the reason for the dual-plateau profile of PN dissociation (Paul et al., 2009). Here, we cannot rule out the possibility of alkyl nitrate impurities. However, the source level of PAN is equal to 92 ± 3% of NOx input, suggesting only a very small percentage (≤ 8% on average), if any, of ANs. If the PAN source is equal to 4 ppbv in the PN channel at 180 °C, as Fig. S3 shows, PAN will first dissociate completely, and then PAs will recombine with NO2 to form PAN when the airflow passes through the cooling lines.

To further study the thermal dissociation of organic nitrates in the heated channels, box model simulations were conducted to reproduce the response relationship between heating temperature and NO2 generated by pyrolysis. If the PAN source is equal to 4 ppbv in the PN channel at 180 °C, as Fig. S3 shows, PAN will first dissociate completely, and then PAs will recombine with NO2 to form PAN when the airflow passes through the cooling lines. As shown in Fig. 7, PAN gradually transforms into NO2 and CH3O2NO2 as the setting temperature increases. The simulated signals of thermal dissociation of PAN show two plateaus, which is generally consistent with the experimental results. However, there are some differences from 260 to 360 °C, which may come from simulation uncertainties such as the temperature profile in the heated channel, the follow-up reactions of PA radicals, and their reaction rates. The first plateau at 180 °C is caused by the recombination of PAs and NO2 after the pyrolysis of PAN, and the time for recombination from the end of the tube to the inlet is 297 ms. Therefore, recombination cannot be ignored when the heating temperature plateau period indicates that almost all PAN is transformed into NO2, which is due to the increase in the pyrolytic loss of PAs, and the pyrolysis of PAN is enhanced with increasing temperature.
losses of NO

Previous studies have shown that the filter losses and wall depositing, suggesting that the memory effects on the inlet and cavity tubing were insignificant. As shown in Figs. 5 and S6, the filter loss and sampling tube are negligible. The transmission efficiency for PAN is > 97% if there is a fresh filter membrane in the holder. We propose that changing the filter once a day can ensure a high transmission efficiency of the species to be detected. However, isoprene nitrates are prone to hydrolysis (Vasquez et al., 2020), which is more likely to be lost during sampling. We have no evaluation of the sampling loss of isoprene nitrates, and the wall loss of isoprene nitrates is likely to be reduced by increasing the frequency of filter changes. In the heated channels, organic nitrates will be thermally dissociated to produce NO2, but some simultaneous reactions will affect the NO2 mixing ratio. The potential interferences mainly come from the following reactions: formation of NO2 via NO and O3, pyrolysis of O3, reactions of organic radicals with NO and NO2, and pyrolysis of other reactive nitrogen oxides.

The formation of NO2 in a dark reaction between NO and O3 should be considered in NO2 measurements. If the reaction has continued for a certain time (t) during sampling, the amount of NO2 formed [NO2]t can be calculated: [NO2]t = k × [NO] × [O3] × t, where k is the rate coefficient for Reaction (R4) and is given as 2.07 × 10−12 exp(−1400/T) cm3 molecule−1 s−1 (Atkinson et al., 2004). According to the temperature distribution and airflow temperature measurements changing with the distance after the heating quartz tube, the heated channel temperature profiles under normal sampling are shown in Fig. S7. Based on the temperature profile, the reaction of NO and O3 in the three channels can be calculated. As the residence time of airflow in the three channels is short and similar (0.806 s in the reference channel, 0.697 s in the AN channel, and 0.730 s in the PN channel), the simulation results show that the interference is small. For example, during an ozone pollution day with O3 = 100 ppbv, NO = 2 ppbv, and NO2 = 5 ppbv, the NO2 produced by the reaction of NO and O3 in the reference channel is 0.07 ppbv, corresponding to 1.3% of atmospheric NO2. Similarly, the interferences in the AN channel and PN channel are 0.14 ppbv (2.7% of NO2) and 0.10 ppbv (2.0% of NO2), respectively. The interferences are within 3% in the typical case, which is smaller than the uncertainty of the NO2 measurement. Therefore, the interference is ignored in the measurement correction.

The thermal degradation of O3 occurs at high temperatures, which reduces NO2 to NO via O(3P) (Reactions R5–R7). Interference has been ignored before in the process of PN and AN pyrolysis (Day et al., 2002). However, subsequent studies have shown that the reaction can cause significant negative deviations in the measurements of NO2 at higher temperatures, and the degree of interference is closely related to the temperature change of the pyrolytic module (Lee et al., 2014; Thieser et al., 2016). To determine the reduction reaction effect, we performed experiments in which NO2 was detected in three different channels when various amounts of NO2 and O3 were added. The experimental results are shown in Table 1 with various amounts of NO2.
Figure 8. Model-simulated thermal decomposition profiles of PAN and MeN with different amounts of PAN or MeN under different wall loss rate coefficients of RO$_2$. Panels (a) and (b) show the NO$_2$ signals of PAN and MeN when the wall loss rate coefficient of RO$_2$ is 0.3 s$^{-1}$. Panels (c) and (d) show the NO$_2$ signals of PAN and MeN when the wall loss rate coefficient of RO$_2$ is 5 s$^{-1}$.

Table 1. Measurements of the NO$_2$ mixing ratio in three channels of the TD-CEAS with different added amounts of NO$_2$ and O$_3$.

<table>
<thead>
<tr>
<th>Order</th>
<th>[NO$_2$] [ppbv]</th>
<th>[O$_3$] [ppbv]</th>
<th>[O$_3$] × [NO$_2$] [ppbv × ppbv]</th>
<th>[NO$_2$]_TD380 [ppbv]</th>
<th>[NO$_2$] − [NO$_2$]_TD380 [ppbv]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>7.45 ± 0.27</td>
<td>48.19</td>
<td>359</td>
<td>7.79 ± 0.27</td>
<td>−0.34</td>
</tr>
<tr>
<td>1</td>
<td>7.89 ± 0.27</td>
<td>67.47</td>
<td>532</td>
<td>8.17 ± 0.28</td>
<td>−0.28</td>
</tr>
<tr>
<td>2</td>
<td>15.58 ± 0.29</td>
<td>48.19</td>
<td>751</td>
<td>15.84 ± 0.28</td>
<td>−0.26</td>
</tr>
<tr>
<td>3</td>
<td>8.23 ± 0.27</td>
<td>96.38</td>
<td>793</td>
<td>8.22 ± 0.28</td>
<td>0.01</td>
</tr>
<tr>
<td>4</td>
<td>15.77 ± 0.25</td>
<td>67.47</td>
<td>1064</td>
<td>15.94 ± 0.27</td>
<td>−0.17</td>
</tr>
<tr>
<td>5</td>
<td>8.43 ± 0.27</td>
<td>144.57</td>
<td>1218</td>
<td>8.64 ± 0.28</td>
<td>−0.21</td>
</tr>
<tr>
<td>6</td>
<td>16.18 ± 0.28</td>
<td>96.38</td>
<td>1559</td>
<td>16.20 ± 0.28</td>
<td>−0.02</td>
</tr>
<tr>
<td>7</td>
<td>16.28 ± 0.30</td>
<td>144.57</td>
<td>2354</td>
<td>16.26 ± 0.31</td>
<td>0.02</td>
</tr>
</tbody>
</table>

and O$_3$ added. No significant NO$_2$ mixing ratio difference was observed between the reference and AN channels. We showed negligible interference here, which is different from previous reports (Lee et al., 2014; Thieser et al., 2016). This is likely caused by the much lower temperature setting of our AN measurement channel. Since the pyrolytic rate constant of O$_3$ is highly temperature-dependent, the lower temperature would largely reduce the level of O atoms as well as this interference.

\[
\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 \quad \text{(R4)}
\]
\[
\text{O}_3 \rightarrow \text{O} + \text{O}_2 \quad \text{(R5)}
\]
\[
\text{O} + \text{O}_2 + M \rightarrow \text{O}_3 + M \quad \text{(R6)}
\]
\[
\text{O} + \text{NO}_2 \rightarrow \text{O}_2 + \text{NO} \quad \text{(R7)}
\]
The RO₂ recombines with NO₂ or reacts with NO to interfere with the measurement of ANs and PNs. Taking PAN as an example, organic radicals may trigger interference, as described below (Reactions R8–R15). The PAs produced after thermal dissociation of PAN (Reaction R8) can recombine with NO₂ (Reaction R9). PAs can oxidize NO to produce NO₂ while generating another organic radical (Reaction R10). CH₃O₂ can further initiate a series of reactions that affect the distribution of NO₂ (Reactions R11–R15). Therefore, the lifetime and fate of PAs generated by PAN pyrolysis will cause interference, and atmospheric NO and NO₂ will affect the degree of measurement interference.

\[
\begin{align*}
\text{CH}_3\text{C(O)O}_2\text{NO}_2 + M &\rightarrow \text{CH}_3\text{C(O)O}_2 + \text{NO}_2 + M \quad \text{(R8)} \\
\text{CH}_3\text{C(O)O}_2 + \text{NO}_2 + M &\rightarrow \text{CH}_3\text{C(O)O}_2\text{NO}_2 + M \quad \text{(R9)} \\
\text{CH}_3\text{C(O)O}_2 + \text{NO}(-\text{O}_2) &\rightarrow \text{NO}_2 + \text{CH}_3\text{O}_2 + \text{CO}_2 \quad \text{(R10)} \\
\text{CH}_3\text{O}_2 + \text{NO} &\rightarrow 0.999 \times (\text{CH}_3\text{O} + \text{NO}_2) \\
&+ 0.001 \times \text{CH}_3\text{O}_2\text{NO}_2 \quad \text{(R11)} \\
\text{CH}_3\text{O} &\rightarrow \text{HCHO} + \text{HO}_2 \quad \text{(R12)} \\
\text{CH}_3\text{O}_2 + \text{NO}_2 &\rightarrow \text{CH}_3\text{O}_2\text{NO}_2 \quad \text{(R13)} \\
\text{HO}_2 + \text{NO} &\rightarrow \text{OH} + \text{NO}_2 \quad \text{(R14)} \\
\text{OH} + \text{NO}_2 &\rightarrow \text{HNO}_3 \quad \text{(R15)} \\
\text{CH}_3\text{NO}_3 &\rightarrow \text{CH}_3\text{O} + \text{NO}_2 \quad \text{(R16)}
\end{align*}
\]

A set of laboratory experiments was conducted to measure the interference in PN channels with different NO, NO₂, and PAN levels. Figure 9a shows the measured and simulated results of different PAN concentrations mixed with different concentrations of NO. With the increase in NO added, the detected PN mixing ratio (the signal difference between the PN channel and REF channel) also gradually increased. More NO reacted with PA radicals generated during thermal dissociation to produce additional NO₂ within the residence time in the PN channel, which led to measurements higher than the PAN source level. In contrast, as shown in Fig. 9b, the measured PNs were lower than the PAN source level when NO₂ was added to the source, and the bias increased with the increase in NO₂ added. The addition of NO₂ to the system improves the overall concentration of NO₂ in the PN channel, promoting regeneration to PAN.

We conducted numerical simulations by a box model to mimic observations and to check the chemical reactions in the PN channel. Figure 9a shows that the simulations have good consistency with the experimental results under different NO levels. Figure 9b shows that the model can capture the trend of experimental results on NO₂ interferences, except in the case of a PAN source of 4.5 ppbv, which may be due to the reaction of small excess RO₂ in the PAN source line and extra NO₂ added to the instrument to generate additional PAN before sampling. Overall, these experiments proved that NO and NO₂ interfere with the measurement of PNs. However, the agreement of the experimental and model results indicates that the interference of NO and NO₂ for PN measurements can be corrected. In the field measurements, the correction factor refers to the ratio between the real value and the measured value of PNs. For example, in a typical case during field measurements where PNs = 3 ppbv, NO = 8 ppbv, and NO₂ = 5 ppbv, the difference between the PN channel and reference channel is equal to 4.54 ppbv (equivalent to the measured PNs), which requires a correction factor of 0.66. Here, nearly 40 000 simulations are performed under various initial concentrations of NO (0–70 ppbv), NO₂ (0–60 ppbv), and PAN (0–10 ppbv) to obtain the correction factor lookup table for our first field measurement (detailed in Sect. 4.3). The correction factor (C1) for PN measurements in the PN channel can be determined from the lookup table according to atmospheric NO and NO₂ and the raw data of PN measurements using linear interpolation. According to Eq. (9), the corrected PN mixing ratios are derived by the raw PN measurements ([NO₂_180]) and C1.

\[
[P\text{Ns}_\text{real}] = [NO_2\text{ }180] \times C1
\]
between the NO\(_2\) signal in the AN channel and reference channel for different PAN sources with different amounts of NO (a) and NO\(_2\) (b). The error bars show 1 standard deviation.

In the AN channel, the thermal dissociation of PA radicals is rapid, and the regeneration of PAN is also suppressed at higher temperatures. Therefore, there is a different relationship between PANs and ambient NO\(_x\) in the AN channel. Similar to PNs, the measurement of ANs could be affected by NO\(_x\). We derived the PNs corrected by \(C_1\) and \(\text{[NO}_2\_180\] as mentioned above. To determine the corrected concentrations of ANs as Eqs. (10)–(11) show, we need to apply another correction factor \(C_2\) to determine the contribution of PNs to ONs, in which this is subtracted from the raw ON measurement \(\text{[NO}_2\_380\] \text{[PNs_real]}\), and finally the third correction factor \(C_3\) is applied to obtain corrected AN measurements. Figure 10 displays the interference of NO and NO\(_2\) with the PAN measurements in the AN channel. The laboratory experiments showed that the measured signal difference increased with NO (Fig. 10a). Hence, the presence of NO still led to higher measurement results of ONs compared with the source value. However, the interference was weakened compared with the measured results in the PN channel at the same NO and PAN source levels (Fig. 9a). Similarly, the experiments with added NO\(_2\) showed underestimated measurements of ONs, and the interference was significantly weakened compared with that in the PN channel. We used the same box model except for updating the temperature distribution and the corresponding residence time in the AN channel to simulate the interference of NO or NO\(_2\) under different PAN source levels. However, there are still some uncertainties about the reaction mechanism and reaction rate for the thermal dissociation of PAN at these high temperatures. We performed sensitivity tests on the follow-up reactions of PAs, similar to the simulation results of Thieser et al. (2016), and found that the isomerization of PAs to CH\(_2\)C(O)OOH has a great effect on the consistency of the experiments and simulation results. If the reaction rate of the branching reaction is set to zero, as shown in Fig. 10, the simulation results capture the trend well when NO\(_2\) or NO is added. Many factors affect the NO\(_2\) signal produced by the thermal dissociation of PAN; therefore, the mechanism scheme mentioned above provides a reasonable assumption for the interference process. Overall, the box model predicts the interference of PAN measurement caused by NO and NO\(_2\) in the AN channel. Next, the correction factors \(C_2\) of different cases under various amounts of NO, NO\(_2\), and PAN added in the AN channel are simulated to form the second lookup table.

\[
\text{[NO}_2\_380\] = \frac{\text{[PNs_real]}}{C_2} + \frac{\text{[ANs_real]}}{C_3}
\]  

(10)

The raw ON mixing ratio \(\text{[NO}_2\_380\]) is determined by the difference between the AN channel and reference channel based on the SPEC method. According to Eq. (10), it is necessary to quantify the interference caused by ambient NO/NO\(_2\) for AN measurements. Due to the lack of AN sources, we use box models to study the interferences by setting MeN as the representative ANs. Methyl nitrate is pyrolyzed to produce NO\(_2\) and CH\(_3\)O in the AN channel (Reaction R16), and CH\(_3\)O is an important intermediate product of the reactions of PAs (Reactions R10–R12). Therefore, the mechanism scheme regarding PAN applies to interference simulations of NO\(_x\) for AN measurements. Similarly, the different cases under various NO, NO\(_2\), and MeN additions were simulated to form the third lookup table for the corrections of AN measurements in the AN channel. According to Eq. (10), the raw concentration of ANs is the difference between the raw ON measurements \(\text{[NO}_2\_380\]) and the signal contribution of PNs \(\frac{\text{[PNs_real]} \text{[PNs_real]}}{C_2}\) in the AN channel. The correction factor \(C_3\) is determined by the third lookup table and then multiplied by \(\text{[ANs]}\) to obtain the corrected AN mixing ratio \(\text{[ANs]\_CI}) by Eq. (11).

\[
\text{[ANs_real]} = \left(\frac{\text{[NO}_2\_380]}{C_2} - \frac{\text{[PNs_real]} \text{[PNs_real]}}{C_2}\right) \times C_3
\]  

(11)

In addition to the interference mentioned above, other nitrogen compounds may undergo pyrolysis to generate NO\(_2\) in the heated channels, such as N\(_2\)O\(_5\) and CINO\(_2\) (Li et al.,
4.2 Uncertainty and detection limit

The uncertainty of the CEAS measurement of NO$_2$ is contributed by the absorption cross section, mirror reflectivity, effective cavity length, and spectral fitting. The absorption cross section of NO$_2$ is taken from Voigt et al. (2002), whose uncertainty is approximately 4% (Voigt et al., 2002); the uncertainty of mirror reflectivity is approximately 5%, determined by the error of the scattering cross section of N$_2$; the uncertainty of effective cavity length is approximately 4.5%; and the uncertainty of spectral fitting when omitting the cross section of glyoxal is 4%. According to Gaussian error propagation, the associated uncertainty of the ambient NO$_2$ measurement is ±9% based on the above parameters. The precision of the CEAS can be assessed by the Allan deviation and standard deviation (Duan et al., 2018; Langridge et al., 2008; H. Wang et al., 2017). Figure 11 shows the variance analysis of 21077 continuously measured N$_2$ spectra when the cavity was filled with N$_2$ under purge. The integration time was 3 s, and the sampling time was 6 s, as every two spectra were averaged before saving. The first 100 N$_2$ spectra collected were averaged as $I_0$, and all spectra were analyzed based on $I_0$. The dataset was divided into 300 gradients for Gaussian fitting, and 1σ was 97 pptv, as shown in Fig. 11a. The 21 077 N$_2$ spectra mentioned above were averaged at different time intervals (from 6 to 11 400 s), and then the Allan deviations at different time intervals were calculated. As shown in Fig. 11b, the Allan deviation decreases as the sampling time increases when the sampling time is smaller than 1300 s, and the minimum is 5 pptv. When the sampling time is 6 s, the Allan variance can reach 90 pptv, close to 1σ. ANs and PNs are detected by the same CEAS system and calculated by the dynamic $I_0$ (SPEC) method; therefore, their precision is identical to the NO$_2$ measurement. The uncertainty of [ANs] and [PNs] mainly comes from spectral fitting to derive the concentration of NO$_2$ and the interference correction in heated channels, which should be larger than 9%.

As summarized in Table 2, there are several typical technologies to measure organic nitrates based on the thermal dissociation method. TD-LIF is the pioneer to determine organic nitrates by measuring NO$_2$ produced through pyrolysis (Day et al., 2002), and the technology has been developed well and deployed in considerable campaigns (Di Carlo et al., 2013; Farmer et al., 2006). TD-LIF has a high time resolution and low detection limit, but the determination of NO$_2$ has to rely on extra calibration. TD-CIMS has a similar limitation to TD-LIF, and the method can measure some individual species of PNs, which need corresponding standards to be calibrated one by one (Slusher et al., 2004). CRDS, CAPS, and CEAS are all cavity-enhanced techniques with high sensitivity and time resolution, of which CRDS and CAPS have been applied to detect NO$_2$ after ON pyrolysis. Specifically, in this study, the ONs and PNs are determined directly through broadband absorption measurement by CEAS, which can avoid the uncertainty caused by multiple spectral fitting and subsequent differential calculations. Overall, TD-CEAS has a detection capacity similar to that of TD-LIF and others. Recently, thermal dissociation peroxy radical chemical amplification (TD-PERCA)-CRDS was developed to indirectly determine PNs by measuring NO$_2$ through chemical amplification, which also showed high sensitivity, but the technology for atmospheric measurements needs to be studied further.

4.3 Performance in field observations

TD-CEAS deployed the first field observations in Xining County, Chengdu, China, in 2019, referred to as the CHOOSE campaign (Yang et al., 2020). As shown in Fig. S8, there is a residential area 5 km northwest of the site; the sur-
Table 2. Typical thermal dissociation methods to measure organic nitrates.

<table>
<thead>
<tr>
<th>Method</th>
<th>Targets</th>
<th>Time resolution</th>
<th>Detection limit</th>
<th>Accuracy</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>TD-LIF</td>
<td>ANs, PNs</td>
<td>10 s</td>
<td>90 pptv</td>
<td>10%–15%</td>
<td>Day et al. (2002)</td>
</tr>
<tr>
<td>TD-LIF</td>
<td>ANs, PNs</td>
<td>1 s</td>
<td>18.4, 28.1 pptv</td>
<td>22%, 34%</td>
<td>Di Carlo et al. (2013)</td>
</tr>
<tr>
<td>TD-CIMS</td>
<td>PAN, PPN</td>
<td>1 s</td>
<td>7, 4 pptv</td>
<td>20%</td>
<td>Slusher et al. (2004)</td>
</tr>
<tr>
<td>TD-CRDS</td>
<td>ANs, PNs</td>
<td>1 s</td>
<td>100 pptv</td>
<td>6%</td>
<td>Paul et al. (2009)</td>
</tr>
<tr>
<td>TD-CAPS</td>
<td>PNs, ONs</td>
<td>2 min</td>
<td>7 pptv</td>
<td>NA</td>
<td>Sadanaga et al. (2016)</td>
</tr>
<tr>
<td>TD-CRDS</td>
<td>ANs, PNs</td>
<td>1 s</td>
<td>28 pptv</td>
<td>6% + 20 pptv</td>
<td>Thieser et al. (2016)</td>
</tr>
<tr>
<td>TD-CRDS</td>
<td>ANs, PNs</td>
<td>1 s</td>
<td>59, 94 pptv</td>
<td>8% + 10 pptv</td>
<td>Sobanski et al. (2016)</td>
</tr>
<tr>
<td>PERCA-CRDS</td>
<td>PNs, PAN</td>
<td>1 s</td>
<td>6.8, 2.6 pptv</td>
<td>13%</td>
<td>Taha et al. (2018)</td>
</tr>
<tr>
<td>TD-CEAS</td>
<td>ANs, PNs</td>
<td>6 s</td>
<td>90 pptv</td>
<td>9%</td>
<td>This work</td>
</tr>
</tbody>
</table>

Figure 12. Time series of the observed mixing ratios of PNs, ANs, and NO$_2$ during ozone pollution from the CHOOSE campaign in 2019. The yellow regions indicate the daytime period. (a) The black lines represent the raw measurements of PNs, and the red lines are the corrected measurements of PNs according to the lookup table. (b) The blue lines represent the raw measurements of ANs, and the orange lines are the corrected measurements of ANs according to the lookup tables. (c) Measurements of NO$_2$ in the reference channel.

The value of $C_1$ was generally greater than 1.0 (except during the morning), suggesting that the role of NO$_2$ was more significant than that of NO at this site. The tendency of $C_2$ and $C_3$ was consistent with $C_1$ during measurements, but the daily changes of $C_2$ and $C_3$ were relatively smaller as the sensitivity of interferences in the AN channel decreased, as mentioned above. Figure 12c shows that NO$_2$ constantly increased at night, reaching a peak near the early morning and maintaining a high value to approximately 11:00 (UTC+8) local time. High mixing ratios of PNs were observed during the measurement, and the diurnal variation of PNs was clear. The peak of ANs appeared in the noontime and several hours before that of PNs. However, when the ambient NO$_2$ changed drastically at night during the campaign, the difference in NO$_2$ between adjacent measurement phases in a cycle was great, resulting in unfeasible measurements (Fig. S10). Simultaneous measurements showed that the N$_2$O$_5$ mixing...
Figure 13. Comparison of the TD-CEAS and PL-CLD in the CHOOSE campaign. Panel (a) shows the time series of NO\(_2\) measurements. Orange points represent the results from the TD-CEAS, and the blue line represents the results from the PL-CLD. Panel (b) shows the NO\(_2\) correlation between the two instruments. Comparison of the PNs measured by the TD-CEAS and the PAN measured by the GC-ECD. Panel (c) shows the time series of PNs and PAN, orange points represent the results from the TD-CEAS, and blue line represents the results from the GC-ECD. Panel (d) shows the PN correlation of the two instruments.

ratio during nighttime was low and zero during the daytime. Therefore, the interferences of N\(_2\)O\(_5\) were negligible for the N\(_2\) measurements during the daytime during the CHOOSE campaign. Nevertheless, the observed ANs may have been subject to the interference from CINO\(_2\).

A photolytic conversion chemiluminescence detector (PC-CLD) was used to measure NO and NO\(_2\) during the campaign. The time series of NO\(_2\) measured by the TD-CEAS and PL-CLD with a 5 min average is shown in Fig. 13a, which were from 9 to 16 August. The trend of NO\(_2\) measured by the two instruments agrees well, but the results of the PL-CLD are higher when the mixing ratio of NO\(_2\) was low at noon. Figure 13b shows that the correlation coefficient of the NO\(_2\) concentration measured by the two instruments is 0.99. The results of the TD-CEAS are slightly higher than the results of the PL-CLD, as the slope is 0.95, which is reasonable when considering instrument uncertainties. The time series of PNs (TD-CEAS) and PAN (GC-ECD) is shown in Fig. 13c, and the trends are relatively consistent, but the results of PNs are higher than the results of PANs measured by the GC-ECD, especially at noon. This result is reasonable since PAN concentration is the highest but is not equal to the total concentration of PNs. The correlation between the two instruments is good, as the correction coefficient is up to 0.85 (Fig. 13d), suggesting our instrument’s feasibility in PN measurement.

5 Conclusions and outlook

We developed a new and robust TD-CEAS instrument to measure PNs, ANs, and NO\(_2\) in the atmosphere with high accuracy and sensitivity. The advantage of this equipment is that only one detector is used for measuring NO\(_2\) at 435–
455 nm, which reduces the potential for cross interference caused by multiple detectors and has a lower cost and simpler operation. One measurement cycle of the instrument is 3 min, with an LOD of 97 pptv (1σ) at 6 s. The short cycle period meets the atmospheric lifetime requirements of organic nitrates and NO\textsubscript{2} in general. The measurement interferences are characterized under different NO, NO\textsubscript{2}, and organic nitrates (PAN or MeN) by laboratory experiments and model simulations. A lookup table method was established to correct the PN and AN concentrations.

The instrument was first deployed for field measurements in Chengdu, China, and the PNs measured by the TD-CEAS showed good consistency with PAN measured by a GC-ECD during the daytime. However, when the ambient NO\textsubscript{2} in the sampled air masses changes drastically, there will be great errors for the measurement of ANs and PNs, as the NO\textsubscript{2} mixing ratio between adjacent measurement phases in a cycle will be definitely different. Adding another NO\textsubscript{2} CEAS in parallel in the instrument for continuous NO\textsubscript{2} measurement will avoid this limitation. In addition, the observed PNs and ANs may be subject to interference from other reactive nitrogen species, such as N\textsubscript{2}O\textsubscript{5} and ClNO\textsubscript{2}, which can be corrected with simultaneous measurements in the future. Overall, this instrument is suitable for measuring NO\textsubscript{2}, PNs, and ANs in chamber studies or ambient measurements with relatively stable air masses free of intensive NO\textsubscript{2} emissions. We highlight the impact of interference reactions in heated channels for accurately measuring PNs and ANs. Although the lookup table can correct the interferences, the best way to reduce them is to quench RO\textsubscript{2} during the sampling process by improving the instrument design, such as by increasing the wall loss of RO\textsubscript{2} in the heated channel.

Data availability. The datasets used in this study are available from the corresponding author Keding Lu upon request (k.lu@pku.edu.cn).

Supplement. The supplement related to this article is available online at: https://doi.org/10.5194/amt-14-4033-2021-supplement.

Author contributions. KL and HW designed the study, CL and HW set up and characterized the instrument, analyzed the data, and wrote the paper with input from KL. All authors contributed to the field measurements and discussed and improved the paper.

Competing interests. The authors declare that they have no conflict of interest.

Acknowledgements. The authors thank the CHOOSE team for establishing and maintaining the Xinjin site and the synchronized data used in the article.

Financial support. This project is supported by the Beijing Municipal Natural Science Foundation for Distinguished Young Scholars (grant no. JQ19031), the special fund of the State Key Joint Laboratory of Environment Simulation and Pollution Control (grant no. 21K02ESPCP), the National Natural Science Foundation of China (grant no. 21976006), and the National Research Program for Key Issue in Air Pollution Control (grant no. DQGG0103-01).

Review statement. This paper was edited by Bin Yuan and reviewed by three anonymous referees.

References


Vaughan, S., Gherman, T., Ruth, A. A., and Orphal, J.: Incoherent broad-band cavity-enhanced absorption spectroscopy of the ma-


