Responses to Reviewer

Reviewer #2:

This manuscript presents the development and validation of a five-channel thermal dissociation cavity-enhanced absorption spectrometer (TD-CEAS) for simultaneous, in situ measurements of gas-phase and particle-phase organic nitrates (ΣPNs and ΣANs), with a dedicated correction for NO/NO_2 interferences under high-NO_x urban conditions. The topic is timely and important for atmospheric reactive nitrogen and aerosol research. The instrument design is logical, laboratory characterization is comprehensive, field deployment is convincing, and the interference correction method is technically innovative. Overall, the manuscript is well-structured and meets the publication standards. I recommend publication after minor revisions.

General comments:

1. Please strengthen comparison with existing particle-phase TD instruments, a brief detection-limit comparison is insufficient. Please add a systematic comparison with similar instruments in terms of time resolution, phase separation, interference control, and field usability.

Response: We thank the reviewer for this constructive suggestion. We agree that a systematic comparison with existing particle-phase thermal dissociation instruments would strengthen the manuscript. In the revised manuscript, we have added a discussion of the thermal dissociation based on a systematic comparison (lines 590-600):

"*In terms of temporal resolution, single-cavity configurations are limited by channel switching, resulting in a lower time resolution. Multi-cavity designs therefore represent a promising direction for future instrumental development. Various strategies have been explored to mitigate measurement interferences, including the use of glass bead packing (which reduces but does not fully eliminate interference), correction factor lookup tables, and post-inlet ozone addition. In this study, we propose a correction model based on the NO/NO_2 ratio that accounts for the coupled effects of both interferents. Existing TD setups for particulate-phase measurements mainly employ either denuders or filter. Denuders require careful monitoring of absorption efficiency and saturation, whereas filter membranes only need to be replaced periodically, making them more convenient to use.*"

Additionally, we have added a comprehensive comparison of our five-channel TD-CEAS with the major TD-based instruments currently used for particulate organic nitrate measurements in the Table 1:

Table 1. Summary of reported 1σ detection limits (pptv) for thermal-dissociation-based measurements of gΣPNs, pΣPNs, gΣANs and pΣANs from the literature and this study, with the integration time (s) indicated in parentheses. For this study, ΣPN and ΣAN detection limits are obtained by propagating Allan-deviation-derived NO_2 precision through the channel-differencing retrieval. Reported detection limits as given in the cited studies. "/" indicates not reported. Time resolution refers to the time for all species to complete one cycle.

References	Instrument	Detection limit (pptv)				Time resolution
		gΣPNs	gΣANs	pΣPNs	pΣANs	
Day et al., 2002	TD-LIF	90 (10s)	90 (10s)	/	/	10 s
Paul et al., 2009	TD-CRDS	/	100 (1s)	/	/	1 s
Rollins et al., 2010	TD-LIF			/	45 (60s)	60 s
Sobanski et al., 2016	TD-CRDS	47 (1s)	40 (1s)	/	/	1 s
Sadanaga et al., 2016	TD-CAPS	7 (120s)	/	/	/	6 min
Thieser et al., 2016	TD-CRDS	28 (1s)	28 (1s)	/	/	/
Chen et al., 2017	TD-CRDS	/	100 (1s, RNO_2)	/	/	3 s
Keehan et al., 2020	TD-CRDS	220	220	/	/	8 min
Li et al., 2021	TD-CEAS	90 (6s)	90 (6s)	/	/	3 min
Lin et al., 2024	TD-CRDS	20.5 (1s)	18.3 (1s)	/	/	1 s
Lin et al., 2026	TD-CRDS	5.5 (30s)	6.2 (30s)	5.5 (30s)	6.2 (30s)	5 min
This study	TD-CEAS	49 (1s)	48 (1s)	49 (1s)	68 (1s)	6 min

2. The authors mention that N_2O_5 and $ClNO_2$ may interfere with nighttime gas-phase measurements. Please provide quantitative estimates of interference magnitudes or clearly define the uncertainty and applicable scope of nighttime data.

Response: We thank the reviewer for raising this important point. We have revised the manuscript so that the scope of nighttime data is now defined much more explicitly. The revised text now gives literature concentration ranges for N_2O_5 and $ClNO_2$ and states directly that nighttime gas-phase ΣPNs and ΣANs are not used for quantitative interpretation because the interference magnitude is variable and cannot be constrained from the available measurements alone.

We also clarified the status of nighttime particle-phase data. These retrievals are retained because paired-channel differencing reduces common-mode gas-phase contributions, but we now explicitly state that this reduction is not guaranteed to be complete if interfering species behave differently in the gas-only and particle-inclusive paths. Accordingly, nighttime particle-phase results are described as more robust than the corresponding gas-phase values, but still operational rather than fully interference-free.

In the revised manuscript, we have added the following statements (new Section 3.3.4, lines 538-554):

"*Ambient concentrations of* N_2O_5 *and* $ClNO_2$ *exhibit substantial variability depending on atmospheric conditions. According to the literature,* N_2O_5 *concentrations in urban environments typically range from 0.1 to 1 ppbv, with occasional peaks reaching several ppbv (Wang et al., 2017).* $ClNO_2$ *concentrations are generally lower, typically ranging from tens of pptv to several ppbv, i.e., 0.1–0.5 ppbv (Mielke et al., 2011; Riedel et al., 2014). Consequently, considerable uncertainty exists in the nighttime measurement of gaseous ΣANs and ΣPNs, and such interferences are difficult to quantify due to the variability of ambient conditions. Li et al. (2021) refrained from analyzing nighttime measurements because of these interferences. In contrast, in this study, the nighttime observational datasets were retained only to support the particulate-phase retrievals in Section 4. Because particle-phase ONs are obtained by paired-channel differencing, common gas-phase contributions are reduced substantially; however, complete cancellation cannot be guaranteed if interfering species behave differently in the gas-only and particle-inclusive paths. Nighttime pΣPNs and pΣANs should therefore be regarded as more robust than nighttime gas-phase data, but still operational rather than fully interference-free.*"

3. The manuscript uses filter configurations for gas–particle separation but does not characterize particle transmission efficiency, wall loss, or inlet adsorption effects for particulate organic nitrates. Please add discussions to quantify these artifacts.

Response: We sincerely thank the reviewer for this critical and constructive suggestion. We fully agree that systematic characterization of particle transmission efficiency, wall losses, and inlet adsorption effects is essential for rigorous gas-particle separation validation. In the revised manuscript, we added a literature-based discussion of these factors and, equally importantly, reframed them as a current limitation rather than as a resolved issue (lines 244-260):

"*According to a study by Rollins et al. (2010), particulate transmission experiments using non-volatile NaCl particles revealed significant loss of small-particle-size (≤100 nm) particles, while the transmission efficiency for particles larger than 100 nm exceeded 85% (represent a lower limit to the transmission and detection efficiency for semi volatile particles). As for volatile particles, they rapidly evaporate and thermally decompose into NO_2 within the TD. In addition, Garner et al. (2020) performed a cross-validation of $NaNO_3$ aerosols using TD-CRDS and SMPS, the correlation coefficient between $NaNO_3$ and the NO_2 produced by its quantitative conversion was 0.98 ± 0.03, which further demonstrates the high transmission efficiency of the particles. Although there may be transmission losses for small particles, these losses are generally acceptable. One line of evidence suggesting that wall losses of organic nitrates (ONs) are negligible is that the uncertainty in the recovery of 2-EHN is below 4 % (Fig. 4). This indicates that ANs rapidly decompose into NO_2 during transmission through the TD inlet, and that no significant back-reaction loss of RO radicals with NO2 occurs. Of course, for high-molecular-weight ONs, wall loss effects are largely dependent on compound volatility, tubing material, and temperature. In this study, we used PTFE tubing and ambient-temperature sampling to minimize such effects.*"

Minor comments:

1. Improve readability of some figures (axis labels, legends, units).

Response: We thank the reviewer for this constructive suggestion. We agree that improving the readability of figures is essential for clear communication. In the revised manuscript, we revised the figures to enhance clarity, with particular attention to:

(1) We have increased the font size of the axis labels, axis titles and legend in new Figure 2.

(2) We have corrected the x-axis title in revised Figure 3 to "PAN measured by TD-CEAS (ppbv)" and the y-axis title to "PAN measured by GC-ECD (ppbv)".

(3) We have increased the font size of the axis labels, axis titles and legend in revised Figure 4.

(4) We have corrected the spelling error "Slpoe" to "Slope" in revised Figure 5b.

2. Shorten some repetitive descriptions in the Introduction and Conclusion.

Response: We thank the reviewer for this helpful suggestion. We agree that some descriptions in the Introduction and Conclusion are repetitive and can be streamlined. In the revised manuscript, we reviewed both sections and removed redundancy while preserving clarity and completeness. Specifically:

(1) We shortened "TD has been combined with a range of sensitive NO_2 detectors, including" to "Measurement techniques include" on lines 76-77.

(2) We shortened "A central challenge in TD-based ΣPNs measurements is that thermal dissociation does not simply convert the analyte to NO_2; it also produces radical intermediates that can participate in secondary chemistry within the heated inlet. In particular, dissociation of peroxy nitrates yields RO_2 radicals, which can react with NO to form additional NO_2, biasing ΣPNs high, or recombine with NO_2 to re-form peroxy nitrates, biasing ΣPNs low" to "A central challenge in TD-based ΣPN measurements is

that thermal dissociation of peroxy nitrates generates RO_2 radicals, which can react with NO (positive bias) or recombine with NO_2 (negative bias)" on lines 90-92.

(3) We have deleted "The direction and magnitude of the bias depend on the chemical regime in the inlet and are therefore expected to be especially important under high-NOx conditions, where NO and NO_2 coexist at elevated concentrations and vary rapidly. This issue is not merely a calibration detail: for TD instruments deployed in polluted urban air, inaccurate treatment of NO/NO_2-dependent chemistry can directly compromise the quantitative retrieval of ΣPNs.", and merged with the following paragraph, and shortened "In ambient air, NO and NO_2 generally vary simultaneously rather than independently, and the relative importance of the competing pathways is governed by the chemical regime rather than by either species alone. In addition, PAN standards are commonly generated photochemically from acetone-containing systems, which may introduce excess peroxyacetyl radicals and other secondary products that complicate the interpretation of separate NO and NO_2 addition experiments (Wüst et al., 2025). Under high-NOx conditions, where both interferences may occur simultaneously, treating NO and NO_2 effects independently may therefore be insufficient." to "The net bias depends on the chemical regime in the inlet and becomes particularly important under high-NO_2 conditions, where NO and NO_2 coexist in ambient air. In addition, PAN standards are commonly generated photochemically from acetone-containing systems, which may introduce excess peroxyacetyl radicals and other secondary products that complicate the interpretation of separate NO and NO_2 addition experiments (Wüst et al., 2025). Inaccurate treatment of this interference can compromise quantitative ΣPN retrieval in polluted urban air." on lines 116-129.

(4) We have shortened "Laboratory characterization supported the selection of operational TD temperatures, with PAN (proxy for ΣPNs) exhibiting near-complete conversion at 250 °C and alkyl nitrate standards (proxies for ΣANs) reaching stable conversion at 450 °C for the residence time and reactor geometry employed" to "Laboratory characterization of PNs and ANs standards supported the selection of operational TD temperatures" on lines 717-718.

References:

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