

The comments of referee #1 are repeated below in black. Our replies are in blue and changed text in the revised manuscript is in red.

Overall review: This paper presents a new instrument design, using nafion drying, denuding, and thermal dissociation with cavity-ringdown detection of NO<sub>2</sub>, in order to allow quantitative measurement of particulate nitrate (both inorganic and organic). The new instrument is compared to aerosol mass spectrometry (AMS) measurements of nitrate, tested with laboratory generated NH<sub>4</sub>NO<sub>3</sub> and SOA from limonene + NO<sub>3</sub> in order to benchmark performance. The current instrument design overcomes previous challenges with humidity-dependent memory effects in the denuder. This step forward in denuder-based nitrate measurement techniques, and method validation by comparison to another technique, will be of interest to the scientific community making such measurements. The paper presentation is clear and well-written. I recommend publication after minor revisions.

We thank the referee for the comments and positive assessment of our manuscript.

Title: might be a good idea to add your instrument acronym to the end of the title, for searchability?

We have done this. The title is now:

Particle nitrate measurement using a thermal-dissociation, cavity-ringdown-spectrometer with gas-phase denuder (D-TD-CRDS)

Lines 11-13: first sentence of the abstract has 3 separate ideas in it. Suggest breaking up into 2 sentences & reword a bit: “Ambient inorganic and organic particulate nitrate has been connected to cardiovascular and respiratory illness. Accurate measurement of nitrate in both gas- and aerosol-phases is essential for understanding its partitioning and thus its impact on human health.”

We have adopted this suggestion:

Abstract. Ambient inorganic and organic particulate nitrate has been connected to cardiovascular and respiratory illness. Accurate measurement of nitrate in both gas- and aerosol-phases is essential for understanding its partitioning and thus its impact on human health.

Line 14: define NO<sub>y</sub> at first instance

We have adopted this suggestion:

“...system that reliably measured gas-phase NO<sub>x</sub> (NO and NO<sub>2</sub>) and NO<sub>y</sub> (NO<sub>x</sub> plus other reactive nitrogen species, see below) but...”

Line 28: define NO<sub>z</sub>

This is already defined. We write: “.NO<sub>z</sub>, which includes NO<sub>3</sub>, N<sub>2</sub>O<sub>5</sub>, HNO<sub>3</sub>, HONO, alkyl-nitrates, peroxy-nitrates, halogen containing nitrates and particulate nitrate (P-Nit).”

Line 30: “both NO<sub>x</sub> and OH radicals”

While HONO does indeed initially form OH radicals, this is rapidly transformed into others (HO<sub>2</sub>, peroxy radicals etc). Therefore we prefer to leave this statement more general.

Line 32: add citation after “from the gas to the particle phase”

References are given directly below. We now write:

“a substantial amount of reactive nitrogen can be transferred from the gas to the particle phase (see below).”

Line 35: don't hyphenate sodium nitrate, and mention this is due to heterogeneous reactions of HNO<sub>3</sub> on sea salt (and cite something for that). Maybe also add a sentence mentioning mineral dust inorganic nitrates (Ca, Mg), with citation, before moving to organic nitrate literature.

We have adopted this suggestion:

“sodium nitrate (formed e.g. from reaction of HNO<sub>3</sub> with sea-salt) is often present.”

Line 44-45: remove line break, continue paragraph.

We have adopted this suggestion:

Line 46: add recent Metrohm citation for MARGA, and also mention the AIM online ion chromatography system for completeness

We have added Twigg et al. (2023) as recent reference for MARGA and AIM

“Transfer of the particle nitrate to an aqueous sample as in the Monitor for AeRosols and Gases in Ambient air (MARGA), Ambient Ion Monitor (AIM), and Particle into Liquid Sampler (PILS) instruments (Khlystov et al., 1995; Twigg et al., 2023; Weber et al., 2001) is achieved.....”

Lines 48-50: Not sure I agree that mARGA type techniques can inform about organic nitrates. First, the absorbance solutions are not typically alkaline as you say (usually ultrapure H<sub>2</sub>O with a little H<sub>2</sub>O<sub>2</sub>), and hydrolysis timescale of even small, functionalized organic nitrates is likely to be too long for detection as HNO<sub>3</sub>. It certainly would not be something to trust quantitatively. So I would revise this piece to say that organic nitrate behavior in these IC systems is not well known, and omit the claim that you could use ion balance to infer org / inorg nitrates. Or, if there is literature supporting some modifications of IC systems to do this, please describe it in more detail, and cite it!

We have modified the statement in line with the comment and now write:

These wet-chemical methods are sensitive primarily to inorganic nitrates although organic nitrates that hydrolyse rapidly to HNO<sub>3</sub> may also be detected (but not quantitatively) and their behaviour in such systems is not well known.

Line 52: MARGA resolution is 1 hr.

We now state 1 hr

“...and the instrumental time resolution is generally close to 1 hour per sample.”

After line 53: Suggest to insert a line or two mentioning previous TD-based methods developed for nitrate aerosol determination: Garner et al Environ Sci Technol. 2020, Keehan et al AMT 2020. Then you can later also mention how your modifications improve on these previous methods.

We have added the citations to Garner et al. 2020 and Keehan et al. 2020 in the section where we list TD-CRDS instruments for particle-nitrate detection:

“...or cavity-ring-down spectroscopy to detect NO<sub>2</sub> rather than LIF (Brownwood et al., 2021; Friedrich et al., 2020; Garner et al., 2020; Keehan et al., 2020).”

Line 62: after citing Farmer 2010, also cite Day et al AMT 2022 (systematic re-evaluation of bulk org nitrate methods). Suggest to omit the parenthetical that follows.

We have adopted this suggestion and now write:

“The AMS can distinguish between organic nitrates and inorganic nitrates (Day et al., 2022; Farmer et al., 2010).”

Line 103: “nitrates, dissociating”

Comma added

“...especially organic nitrates, dissociating at temperatures of 200-400 °C.”

Line 105: “, 2020), a reduction in temperature is beneficial in avoiding”

Text modified as suggested.

“....a reduction in temperature is beneficial in avoiding a positive bias to NOY measurements...”

Lin 138: Can you show this effect of detecting NH<sub>3</sub> at higher temperature also on Fig. 1, by showing higher temperatures (and indicating in the figure that it is due to NH<sub>3</sub> conversion and thus a reason to keep the TD oven at lower temperature)?

We did not perform experiments at higher temperatures than already shown in the Figure. The statement is based on the Friedrich et al. (2020) work from this laboratory and the other two publications that are cited in support.

Line 145: Clarify that this means as opposed to introducing ZA downstream of the oven. Or would it be introduced even later?

We have clarified this by writing:

“In addition, we found that, when working with long inlet lines, overflowing zero-air close to the front-end of the inlet tubing (as opposed to close to the CRDS) avoided creating pressure differences when sampling ambient air or when zeroing.”

Line 159: Explain the equation for competitive absorption in a bit more detail. What are the  $K_{Lang}$ 's for relevant NO<sub>y</sub> species?

The values of  $K_{Lang}$  for H<sub>2</sub>O and NO (or the other NO<sub>y</sub> that are denuded) are not known for the active-carbon denuder. The statement intends only to highlight the fact that the relative degree of binding to the surface depends on both a partition coefficient and the gas-phase concentration. We now write:

“...the relative strength of interaction of H<sub>2</sub>O or the trace gas with the active carbon surface as defined by a gas-surface partition coefficient such as the Langmuir equilibrium coefficient ( $K_{Lang}$ ).”

Line 181: replacing every 45 hours is still pretty frequent ... How low does the RH actually need to be? Earlier you mentioned effects above 20% RH. Good if you can make a recommendation for how often to regenerate in field applications

We have modified the text and now mention how much molecular sieve was used and indicate a replacement interval and how this can be extended:

This is a conservative approach to avoid even low levels of denuder breakthrough and implied that, for ambient measurements in the mid-latitude boundary layer (with 30% < RH < 90%), the molecular sieve was replaced every 4-5 days. In principal this interval could be lengthened by using a larger molecular sieve drier.

“....which was loaded with circa 0.9 kg of either dry silica-gel (AppliChem A7220, 1000 grained orange) or molecular sieve (Roth, type 564, 0.3 nm).”

Line 190: End of section 2.3: One question that came up for me reading this: can you show the (lack of) effect on HNO<sub>3</sub> measured of these inlet components? Could pulling off HNO<sub>3</sub> in the denuder / drying affect the partitioning of NH<sub>4</sub>NO<sub>3</sub> in the instrument?

The thermal decomposition of ammonium nitrate is too slow (at room temperature) for this to occur significantly in our drying system. We have added this statement (in section 2.4) to the paper:

“At a flow of 2.1 SLM, the residence time in the drying system and denuder is ~3 s and thus comparable to that found between the differential mobility analyser (DMA) and AMS-inlet in AMS calibration systems for which loss of ammonium nitrate through thermal decomposition to HNO<sub>3</sub> and NH<sub>3</sub> is known to be insignificant.”

Line 193: “2020), which however”

The “who” refers to Friedrich et al. and should not be replaced by a “which”

Line 214: “loss is negligible.”

“Inefficient” has been replaced by “negligible”

“...for which electrostatic loss is negligible.”

Line 236: Suggest expanding section header title, something like “Gas-phase breakthrough and reactivation of the denuder”

Section 2.3 already refers to “breakthrough” We prefer to keep the original section header.

Lines 256-260: I think this error propagation could be better conveyed using a few inline equations, rather than just embedding in the paragraph text.

We prefer to keep the explanatory text, which we think is useful.

Line 264-272: same. Also nice to briefly show / mention the conversion factor for the ppb <-> ug m<sup>-3</sup> conversion. For particulate nitrate, do you assume the MW of NO<sub>3</sub> group only? Or NO<sub>2</sub>?

This is now mentioned:

Taking 2σ to define the LOD, this corresponds to 0.12 μg m<sup>-3</sup> of particulate nitrate (conversion factor of pptv NO<sub>2</sub> to μg m<sup>-3</sup> nitrate is 2.50 x 10<sup>-3</sup> for 298 K and 1 bar and using a molecular weight of 62 g mol<sup>-1</sup> for nitrate).

Line 268: What does “Under laboratory conditions” mean in this context?

This is now defined:

“Under ideal, laboratory conditions (i.e. in a stable temperature, draft and vibration-free location)..”

Line 305: explain what d(v) = 38.5 means. Diameter in nm?

The volume weighted mode maximum diameter d(v) is defined two lines above. The unit (nm) was however missing. We now write:

“Smaller particles with e.g. d(v) = 38.5 nm were associated..”

Lines 325-326: Can you demonstrate this by including a timeseries panel of SMPS / RH?

The emphasis here is not on the relative humidity but on the particle size. As the deviation from the slope is at very low particle mass and is close to the LOD of the D-TD-CRDS this would be difficult to prove experimentally and we prefer to refer to this as being a “potential” explanation. We have removed the reference to “dry” as this was perhaps confusing. We now write:

The change in slope at the lowest nitrate mass could thus potentially be associated with a lower AMS inlet transmission and detection efficiency for the smallest particles, compared to the D-

TD-CRDS collection and detection efficiency, which is less affected by very small particle sizes.

Lines 330-332: how do you interpret this  $>1$  slope? If there is an interpretation for it, could include the above small-particle hypothesis, if not, maybe omit both?

We state that the deviation of the slope from unity is within the combined uncertainty of the two instruments. It makes little sense to speculate on the origin of something that is not statistically significant.

Related to figure 6: why is the D-TD-CRDS trace intermittent?

The D-TD-CRDS is frequently zeroed to correct for baseline drifts in the ring-down-constant. These are the gaps in the trace, which are now mentioned in the caption.

“The data-gaps in the D-TD-CRDS dataset are periods when the instrument was zeroed.”

Line 347: Can reiterate that MARGA time resolution is 1 hr

This is now mentioned again:

(~ 1 hr, which may limit deployment to non-mobile platforms)

Line 347: non-**detection** of organic nitrates

Modified as follows

“...non-quantitative detection of organic nitrates, high instrument costs and large weight/size...”

Data availability: cite public database and remove parenthetical

I did not find a link to the supplement.

The data will be made accessible and the link to the SI will be available when the article is published

Figure 1: “NO<sub>x</sub> **and** NO<sub>y</sub>” (not or). Also explain the filters (mention with symbol in caption, material); state temperature the TD inlets are heated to in caption.

“or” replaced by “and”. The TD temperature and filters are now mentioned in the caption.

“TD1 and TD2 are the thermal dissociation inlets consisting of 70 cm long quartz tubes with a ~40 cm long section heated by resistive wire to 700 °C. The filters are PTFE membrane filters (Pall Corporation, R2PJ047).”

Figure 2: Make left axis match right, “NO<sub>2</sub> from HNO<sub>3</sub>”

Figure modified as suggested

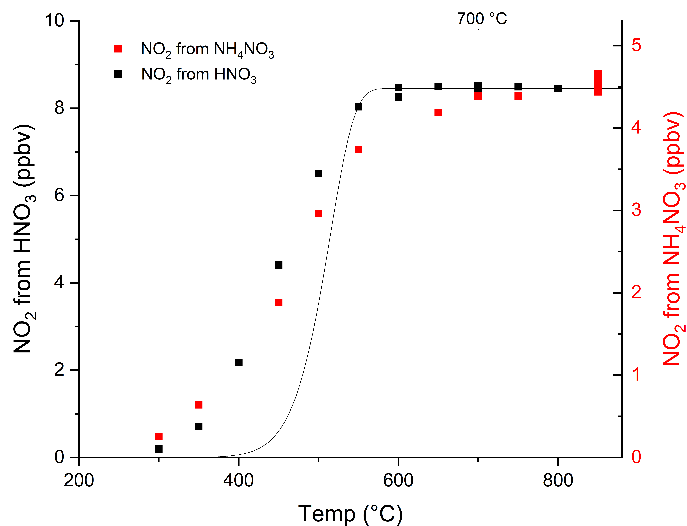


Figure 4: all occurrences of “poly / mono dispersed” should be “polydisperse”

All occurrences of “dispersed” have been replaced by “disperse”

Transmission of polydisperse (mainly multiply charged) ammonium sulphate particles (red lines) and charge neutralized (mainly single charged), monodisperse particles (red data points) through the Nafion drier. The transmission of the monodisperse particles through the complete inlet system (Nafion drier, molecular sieve drier and denuder) is given as black data points. The dotted line is the average transmission ( $96.9 \pm 6.6$  %) for mono-disperse particles of diameter  $\sim 50$  nm. For the experiments using polydisperse aerosol, the transmission is indistinguishable from 100 % at the larger diameters

Figure 6: “1:1 line” not agreement

Modified as suggested

The dashed black line is the 1:1 line.

The comments of referee #2 are repeated below in black. Our replies are in blue and changed text in the revised manuscript is in red.

This paper presents a further development of a CRD instrument previously presented, modified such that it can detect particulate NO<sub>y</sub> through thermal desorption after the use of a stripper to remove gas phase NO<sub>y</sub>. This is an interesting concept and offers an alternative method of integrated quantification of particulate NO<sub>y</sub> compared to other techniques such as semicontinuous IC and AMS. Two specific conceptual advantages this has over the AMS is the lack of a size cutoff and the fact that this has a more direct quantification of atomic nitrogen, rather than electron ionisation fragments. The advantages over IC is the reduced complexity of the measurement and ability to measure total organic particulate reactive oxidised nitrogen.

The technique is described in detail and some initial validation work comparing against an AMS is presented resulting in very favourable correlations, so this is within scope for AMT. While I have a number of technical queries and corrections, this should not detract from the fact that this presents a novel approach to what has always been a tricky measurement in atmospheric science, so I am happy to recommend publication with minor corrections.

We thank the referee for these comments and positive assessment of our manuscript.

Major comments:

One major conceptual point not directly addressed is the propensity for ammonium nitrate to dissociate to ammonia and nitric acid at low relative humidities, which may happen to an extent during the drying stage, after which they would then be removed by the denuder. This process has previously caused artefacts with HTDMA systems (e.g. <https://doi.org/10.5194/acp-7-6131-2007>) and seems dependent on how long the particles were subjected to a low RH for. This potential issue needs addressing and the typical time particles spend at low RH after being sampled should be specified. Note that the time spent in the chamber at low RH prior to sampling is a separate issue, but this will affect the AMS and D-TD-CRDS equally.

The thermal decomposition of ammonium nitrate in the HTDMA that the reviewer refers to happens over a period of ~ 1 minute. This is much longer than the residence time in our drying system (a couple of seconds). We have added a statement (in section 2.4) to the paper.

“At a flow of 2.1 SLM, the residence time in the drying system and denuder is ~3 s and thus comparable to that found between the differential mobility analyser (DMA) and AMS-inlet in AMS calibration systems for which loss of ammonium nitrate through thermal decomposition to HNO<sub>3</sub> and NH<sub>3</sub> is known to be insignificant.”

Minor comments:

Line 77: The other techniques summarised here only cover a specific subset of methods for the measurement of bulk oxides of nitrogen in aerosol, but other techniques are used, such as molecule-resolving techniques like CIMS, ESI and liquid/gas chromatography, or spectroscopic techniques such as NMR, FTIR and UV-Vis. While I would not expect a comprehensive review here, the authors should be more specific about the types of technology they are comparing their technique against.

We have specified “online” techniques that measure ambient air “in-situ” (i.e. we do not discuss methods in which samples are collected and stored (e.g. on filters) for later spectroscopic or spectrometric analysis.

“A number of online techniques are available to measure (in-situ) the nitrate content of ambient aerosol....”

Line 80: Are there problems with NO<sub>2</sub> photolysis at 405 nm, or extinction caused by the O<sub>3</sub>? I'd like to assume not, but I couldn't find references to either in the Friedrich et al. (2020) paper, so it would be good to have these confirmed.

Photolysis of NO<sub>2</sub> is not an issue (for any of the CRDs that measures NO<sub>2</sub>): The in-cavity light intensity is too low and this is well established. O<sub>3</sub> does not represent an interfering trace gas as its cross-section at 405 nm is too low.

Line 175: The technical details of the RH sensors must be specified, because the capacitance probes typically used for atmospheric work lose accuracy at lower humidities. Although it is noted that the RH thresholds referred to here are purely operational, so the absolute accuracy of the RH measurements probably isn't important.

The information has been added to the caption of Figure 1.

“The flow through the relative humidity (RH) sensors (iST, type-HYT939P, 0-100% RH, accuracy 1.8 %) was regulated by needle valves to ~ 20 sccm”

Line 283: What orientation was the t-piece in? If there was an asymmetric 10:1 split in flows (as implied) this could lead to an uneven transmission of particles over the two flows, as the centreline of a laminar flow could be exclusively following the major flow. If the minor flow was taken from the centreline using a subsampling tube (a common feature on AMS systems), this should be specified.

The T-piece was oriented such that the minor flow (to the AMS) was straight, whereas the 1 L flow was at a right-angle. This is mentioned in the text:

“...a stainless-steel T-piece was connected in front of the AMS inlet. The 100 sccm flow to the AMS passed straight through the T-piece with 1 SLM drawn through the T at 90°.”

Line 298: A 10% error on the airbeam correction factor seems very high, especially for a discrete experiment such as this. How is this derived?

The reviewer is correct, this uncertainty was overestimated. We have modified the text and Figure 5.

“The uncertainty associated with the inorganic nitrate mass concentrations is ~16 %, which is related mainly to uncertainty in IE (16%) with a minor contribution from variability in the air beam correction factor (3%).”

Line 307: Strictly, the LOD should be determined based on filtered air, not the ‘beam blocked’ signal, as there may be gas phase interferences. Although this is likely to be minor for m/z 30, but if the authors have this data they should use that instead.

We do not have data using a filter for these experiments

Line 358: Not commented on is whether this instrument could be of use for more refractory nitrate species such as sodium or calcium nitrate, but given the desorption tube operates at a temperature higher than the boiling point of both, one might expect this to be the case. If it is able to, this would offer another potential benefit over the AMS, so should be mentioned.

As described in Friedrich et al, when operated at higher temperatures, the TD inlets detect NaNO<sub>3</sub> (albeit with low efficiency). With the lower TD-Inlet temperatures used here, we do not expect to detect sodium or calcium nitrate. This is now mentioned in section 2.1:

We note that the reduction in temperature will also make the instrument even less sensitive to sodium nitrate than the ~ 15 % conversion efficiency reported by Friedrich et al. (2020).

Technical corrections:

Line 25: Technically the biggest source of reactive nitrogen to the atmosphere is  $\text{NH}_3$ . It would be truer to refer to combustion  $\text{NO}_x$  as the biggest source of “reactive oxides of nitrogen”. This terminology should also be used when referring to  $\text{NO}_z$  further down.

We have modified the text appropriately:

“Combustion-related, anthropogenic emissions (mainly as  $\text{NO}$ ) are the primary source of reactive oxides of nitrogen to the atmosphere.”

Line 35: The statement about sodium nitrate is overly simplistic. Technically the nitrate salt is formed with other marine cations such as potassium, calcium, magnesium, etc. Furthermore, calcium nitrate can also be formed from nitric acid reacting with calcium carbonate minerals in wind-blown dust.

We have added some more information in line with this comment:

“...whereas in coastal regions with anthropogenic influence, sodium, potassium magnesium nitrates (formed from reaction of  $\text{HNO}_3$  with sea-salt) is often present. Calcium nitrate can also be formed e.g. in the interaction of mineral dust with  $\text{HNO}_3$  and mineral dust.”

Line 64: The AMS is capable of sub-second time resolution in 'fast' mode, which has been successfully used in eddy covariance and aircraft measurements, among other applications.

We have adopted this statement:

“The time resolution of the AMS is usually a few seconds, although it can be used in “fast mode” with sub-second time-resolution for some applications.”

Line 282: Different models of aerodynamic lens are now available, so it should be specified that this is using the ‘Standard’ Aerodyne design. Recommend citing <http://doi.org/10.1080/02786820701422278>

We have modified the text:

“The HR-ToF-AMS instrument we used samples ambient air with  $\sim 0.1 \text{ L min}^{-1}$  through a “Standard” Aerodyne aerodynamic lens (Liu et al., 2007) that focuses particles into the vacuum system...”

Line 323: I wouldn't refer to the shrinkage of ammonium nitrate as “thermal decomposition” because this implies an irreversible chemical transformation similar to the desorption tube. What's more likely to happen is that the ammonia and nitric acid will be in dynamic equilibrium with the gas phase, but because the chamber walls are microscopically ‘flat’, the condensed phase will favour this surface over the particles in the chamber due to the Kelvin effect.

The decomposition of ammonium nitrate to  $\text{HNO}_3$  and  $\text{NH}_3$  is a thermal process that is enhanced in rate at high temperatures and slows at low temperatures. In line with this comment we now write:

“...substantial shrinkage of the ammonium nitrate particles (resulting from thermal decomposition and loss of  $\text{HNO}_3$  and  $\text{NH}_3$  to the chamber walls).....”