Measurement of NO\textsubscript{x} and NO\textsubscript{y} with a thermal dissociation cavity ring-down spectrometer (TD-CRDS): Instrument characterisation and first deployment.

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Abstract. We present a newly constructed, two channel Thermal Dissociation Cavity Ring-Down Spectrometer (TD-CRDS) for the measurement of NO\textsubscript{x} (NO + NO\textsubscript{2}), NO\textsubscript{y} (NO\textsubscript{x} + HNO\textsubscript{3} + RO\textsubscript{2}NO\textsubscript{2} + N\textsubscript{2}O\textsubscript{5} etc.), NO\textsubscript{z} (NO\textsubscript{y} - NO\textsubscript{x}) and particulate nitrate (pNit). NO\textsubscript{y}-containing trace gases are detected as NO\textsubscript{2} by CRDS at 405 nm following sampling through inlets at ambient temperature (NO\textsubscript{x}), or at 850 °C (NO\textsubscript{y}). In both cases, O\textsubscript{3} was added to the air sample directly upstream of the cavities to convert NO (either ambient, or formed in the 850 °C oven) to NO\textsubscript{2}. An activated carbon denuder was used to remove gas-phase components of NO\textsubscript{y} when sampling pNit. Detection limits, defined as the 2\sigma precision for 1 minute averaging, are 40 pptv for both NO\textsubscript{x} and NO\textsubscript{y}. The total measurement uncertainties (at 50% RH) in the NO\textsubscript{x} and NO\textsubscript{y} channels are 11\% + 10 pptv and 16\% + 14 pptv for NO\textsubscript{z}, respectively. Thermograms of various trace-gases of the NO\textsubscript{z} family confirm stoichiometric conversion to NO\textsubscript{2} (and / or NO) at the oven temperature and rule out significant interferences from NH\textsubscript{3} detection (< 2\%) or radical recombination reactions under ambient conditions. While fulfilling the requirement of high particle transmission (> 80\% between 30 and 400 nm) and essentially complete removal of reactive nitrogen under dry conditions (> 99\%), the denuder suffered from NO\textsubscript{x} breakthrough and memory effects (i.e. release of stored NO\textsubscript{y}) under humid conditions, which may potentially bias measurements of particle nitrate.

Summertime NO\textsubscript{x} measurements obtained from a ship sailing through the Red Sea, Indian Ocean and Arabian Gulf (NO\textsubscript{x} levels from < 20 pptv to 25 ppbv) were in excellent agreement with those taken by a chemiluminescence detector of NO and NO\textsubscript{2}. A dataset obtained locally under vastly different conditions (urban location in winter) revealed large diel variations in the NO\textsubscript{z} to NO\textsubscript{y} ratio which could be attributed to the impact of local emissions by road-traffic.
1 Introduction

1.1 Atmospheric NOx and NOy

Total reactive nitrogen NOy (= NOx + NOy) consists of nitrogen oxide NO, nitrogen dioxide NO2 (NO + NO2 = NOx) and their reservoir species NOy (NO3 + 2N2O5 + HNO3 + HONO + RONO2 + RO2NO2 + XONO2 + XNO2 + pNit), where X is a halogen atom. HCN and NH3 are generally not considered to be components of NOy (Logan, 1983).

The formation of both peroxynitrates (RO2NO2, PNs) and alkyl nitrates (RONO2, ANs) requires the presence of organic peroxy radicals (RO2), which are formed e.g. in the reaction of OH radicals with volatile organic compounds (VOCs) and oxygen (reaction R1). RO2 radicals react subsequently with NO2 or NO to form peroxy-nitrates (RO2NO2, PNs) or alkyl-nitrates (RONO2, ANs, reactions R2 and R3). Reaction R3 competes with the formation of an alkoxy radical (RO) and the oxidation of NO to NO2 (reaction R4), which consumes the dominant fraction of RO2. The branching ratio between these two pathways depends on atmospheric conditions such as pressure and temperature and on the structure and length of the organic backbone (Lightfoot et al., 1992). HNO3 is produced mainly via the reaction of NO2 with OH (reaction R5).

\[ \text{OH} + \text{RH} + \text{O}_2 \rightarrow \text{RO}_2 + \text{H}_2\text{O} \] (R1)

\[ \text{RO}_2 + \text{NO}_2 + \text{M} \rightarrow \text{RO}_2\text{NO}_2 + \text{M} \] (R2)

\[ \text{RO}_2 + \text{NO} + \text{M} \rightarrow \text{RONO}_2 + \text{M} \] (R3)

\[ \text{RO}_2 + \text{NO} \rightarrow \text{RO} + \text{NO}_2 \] (R4)

\[ \text{OH} + \text{NO}_2 + \text{M} \rightarrow \text{HNO}_3 + \text{M} \] (R5)

The lifetimes of peroxy nitrates in the low troposphere are mainly governed by the temperature. PNs with an additional acyl group (PANs), such as peroxyacetyl nitrate (PAN), are generally more stable than PNs without an acyl group (e.g. pernitric acid HO2NO2), which are observed only in cold regions (Slusher et al., 2002). Thus, of the peroxy nitrates only PANs are considered able to act as transportable reservoirs for NOx. At higher altitudes in the troposphere (above ca. 7 km) photolysis becomes the most important loss process for PAN, while the reaction with OH is negligible in the entire troposphere (Talukdar et al., 1995).

The absence of photolysis reactions and low levels of the OH radical at nighttime open alternative pathways to formation of NOy species. NO2 is oxidised by O3 to produce the nitrate radical NO3, which exists in thermal equilibrium with N2O5 (reactions R6 and R7). The reaction of NO3 with hydrocarbons represents a nighttime source of alkyl nitrates (reaction R8), N2O5 can be hydrolysed on aqueous aerosol resulting in the formation of HNO3 (reaction R9) and ClNO2 (reaction R10) if particulate chloride is available (Finlayson-Pitts et al., 1989).

\[ \text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2 \] (R6)

\[ \text{NO}_3 + \text{NO}_2 \leftrightarrow \text{N}_2\text{O}_5 \] (R7)

\[ \text{NO}_3 + \text{R=R} (+\text{O}_2) \rightarrow \text{RONO}_2 \] (R8)

\[ \text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow 2 \text{HNO}_3 \] (R9)
Nitric acid formation via the reaction of NO\(_2\) and OH (reaction R5), followed by wet or dry deposition of HNO\(_3\), is considered to be the dominant daytime loss process for atmospheric NO\(_x\) (Roberts, 1990), though the reduction of NO\(_x\) may result in an increasingly important role for organic nitrates, e.g. in the USA (Present et al., 2020). As some organic nitrates are longer lived than HNO\(_3\), the atmospheric transport of NO\(_x\) to remote locations would lead to a more even distribution of NO\(_x\), instead of hotspots in polluted regions close to emission sources. Atmospheric removal processes for ANs include oxidation by OH or O\(_3\) (which may lead to a loss of the nitrate functionality), deposition to the earth’s surface and photolysis. Additionally, partitioning into the aerosol phase is possible for large and multifunctional ANs (Perring et al., 2013). Alkyl-nitrates possessing no further functionality (e.g. double bonds or hydroxyl groups) can be unreactive and have long lifetimes (Talukdar et al., 1997). On the global average, RONO\(_2\) has a lifetime of close to 3 hours (2.6 – 3 hours) with ~ 30% being lost by hydrolysis (Zare et al., 2018).

The formation of NO\(_x\) in the lower atmosphere reduces the NO\(_x\) lifetime and the partitioning of NO\(_x\) into NO\(_x\) and NO\(_2\) can provide information about the chemical history of an air-mass (Day et al., 2002; Wild et al., 2014). In regions impacted by biogenic emissions, the sources and sinks of ANs account for a large fraction of NO\(_x\) lost both during the day and night and thus control the lifetime of NO\(_x\) (Romer et al., 2016; Sobanski et al., 2017).

Laboratory experiments have shown that particulate nitrates (pNit) are formed at high yields in the atmospheric degradation of terpenoids in the presence of NO\(_x\) and play an important role in the formation and growth of secondary organic aerosol (SOA) (Ng et al., 2017; IUPAC, 2019). This has been confirmed in field studies, which provide evidence for the partitioning of organic nitrate to the aerosol phase both during day- and nighttime (Rollins et al., 2012; Fry et al., 2013; Palm et al., 2017) with formation of highly functionalised molecules and large contributions (up to 25%) of particulate organic nitrates to the total aerosol mass (Xu et al., 2015; Lee et al., 2016; Huang et al., 2019).

1.2 Detection of NO\(_x\)

Methods for the detection of NO and NO\(_2\) include Chemiluminescence (CLD), Differential Optical Absorption Spectroscopy (DOAS), Laser Induced Fluorescence (LIF) and Cavity Ring-Down Spectroscopy (CRDS). A description and inter-comparison of these methods is given in Fuchs et al. (2010) and we restrict the following discussion to an outline of the basic principles. The CLD method detects NO by chemiluminescent emission in its reaction with O\(_3\); detection of ambient NO\(_2\) by CLD follows its catalytic or photolytic conversion to NO. The best CLD devices have detection limits for NO and NO\(_2\) in single-digit pptv range (Beygi et al., 2011; Reed et al., 2016; Tadic et al., 2020). Detection of NO\(_2\) via LIF involves photo-excitation in its visible absorption band at wavelengths > 400 nm and detection of fluorescent emission at wavelengths > 600 nm, with detection limits of the order of pptv achieved for an integration time of a few seconds (Day et al., 2002; Javed et al., 2019). The structured spectrum of NO\(_2\) between ≈ 400 and 600 nm is used to detect light absorption by ambient NO\(_2\) by DOAS, using either broadband light sources (long-path DOAS, over a few km pathlength) or natural sunlight (Platt et al., 1979; Leser et al., 2003; Pohler et al., 2010; Merten et al., 2011).
The CRDS detection method for NO\textsubscript{2} also utilises its visible absorption spectrum, high sensitivity being achieved by achieving very long pathlengths for optical extinction in an optical resonator (see Sect. 2.1). Limits of detection for NO\textsubscript{2} with CRDS of < 20 pptv in 1 second integration time have been reported (Wild et al., 2014). NO can be detected as NO\textsubscript{2} following its oxidation by O\textsubscript{3} (R6) (Fuchs et al., 2009).

1.3 Detection of NO\textsubscript{y}

The first NO\textsubscript{y} measurements were based on the conversion of all reactive nitrogen trace gases (apart from NO) to NO on catalytic metal surfaces of gold at ~ 300-320 °C or of molybdenum oxide at ~ 350-400 °C (Fahey et al., 1985; Williams et al., 1998), with subsequent CLD detection of NO. Au converters were designed to exclude particulate nitrates, while MoO setups aimed at a response towards pNit (Williams et al., 1998). In recent years, the thermal decomposition of NO\textsubscript{z} to NO\textsubscript{2} has been used to detect NO\textsubscript{z} using inlets held at temperatures high enough (> 650-700 °C) to thermally dissociate the most strongly bound reactive nitrogen trace-gas, HNO\textsubscript{3}, to NO\textsubscript{2} (Day et al., 2002; Rosen et al., 2004; Wooldridge et al., 2010; Perring et al., 2013; Wild et al., 2014) and/or using multiple inlets at intermediate temperatures (Paul et al., 2009; Paul and Osthoff, 2010; Sadanaga et al., 2016; Sobanski et al., 2016; Thieser et al., 2016). Subsequent to thermal decomposition, the NO\textsubscript{2} product can be detected using LIF (Day et al., 2002; Day et al., 2003; Rosen et al., 2004; Murphy et al., 2006; Wooldridge et al., 2010) or cavity enhanced absorption spectroscopy (Paul et al., 2009; Wild et al., 2014; Sadanaga et al., 2016; Sobanski et al., 2016; Thieser et al., 2016). These techniques are impacted to various degrees by secondary reactions at high temperatures including loss of NO\textsubscript{2} via recombination with α-carbonyl peroxy radicals or reaction with O-atoms (formed by the thermolysis of ambient O\textsubscript{3}) and the generation of extra NO\textsubscript{2} from the oxidation of NO via reactions with peroxy radicals (Day et al., 2002; Sobanski et al., 2016; Thieser et al., 2016; Womack et al., 2017). Measures to reduce potential measurement artefacts and avoid excessive data correction include operation at low pressures (Day et al., 2002; Womack et al., 2017) and addition of surfaces to scavenge peroxy radicals (Sobanski et al., 2016). Nonetheless, data correction may still be necessary, which may involve laboratory characterisation and chemical simulation of the chemical reactions within the heated inlet (Sobanski et al., 2016; Thieser et al., 2016).

In this paper we present a two-channel TD-CRDS instrument for detection of NO\textsubscript{x}, NO\textsubscript{y}, NO\textsubscript{z} and pNit which overcomes these limitations. Compared to the setups described by Thieser et al. (2016) the following changes were implemented: (1) Addition of O\textsubscript{3} for NO\textsubscript{x} detection; (2) higher oven temperature (to detect HNO\textsubscript{3}) and location directly at the front of the inlet; and (3) use of a charcoal denuder for separate measurement of pNit and gas-phase NO\textsubscript{z}. The addition of O\textsubscript{3} (after the TD-inlet) ensures that we detect NO as well as NO\textsubscript{2} and thus removes bias caused e.g. by the pyrolysis of O\textsubscript{3} and reactions of O\textsuperscript{(3P)} which reduce NO\textsubscript{2} to NO.
2 Experimental

Our TD-CRDS instrument consists of two identically constructed cavities to monitor NO$_2$ at 405 nm which are largely unchanged compared to those described by Thieser et al. (2016). In the present set-up, the two cavities are connected to three different inlets. One cavity monitors NO$_x$ via an inlet at ambient temperature, the second samples air via either of two heated inlets (one equipped with a denuder, see below) and thereby monitors either NO$_y$ or particle nitrate. A schematic diagram (not to scale) of the instrument is given in Fig. 1.

2.1 CRDS Operation principals

The optical resonator consists of two mirrors (1 m radius of curvature) with nominal 0.999965 reflectivity at 405 nm (Advanced Thin Films), which are mounted 70 cm apart. The cavity volumes are defined by Teflon (FEP) coated Duran glass tubes with an inner diameter of 10 mm.

Under normal operating conditions each cavity samples 3.0 L (STP) min$^{-1}$ (slm) of ambient air (where STP refers to 0°C and 1013 hPa). Additional purge flows (0.14 slm dry synthetic air) are introduced directly in front of each mirror to prevent surface degradation by atmospheric trace gases. The cavities are operated at pressures of 540 to 580 Torr (1 Torr = 1.333 hPa), resulting in residence time of ~1.2 s. 405 nm laser light (square-wave modulated at 1666 Hz and a 50% duty cycle) is provided by a laser diode (Laser Components), the emission of which is coupled into an optical fibre with a Y-piece for splitting into both cavities. Temperature and current control of the laser diode are achieved by a Thorlabs ITC 502 control unit. The laser emission spectrum is monitored continuously by coupling scattered light from one of the cavity mirrors into a 3648 pixel CCD-spectrograph (OMT, ~ 0.1 nm resolution).

The intensity of light exiting the cavity is measured with a photomultiplier (Hamamatsu Photonics), with ring-up and ring-down profiles recorded by a digital oscilloscope (PicoScope 3000). NO$_2$ mixing ratios are derived from the decay constant ($k$ or $k_0$) describing the exponential decrease in light intensity after the laser has been switched off:

$$[\text{NO}_2] = \frac{l}{d} \cdot \frac{1}{\sigma c} (k - k_0),$$  \hspace{1cm} (1)

where $c$ is the speed of light, $\sigma$ is the effective absorption cross-section of NO$_2$ over the emission spectrum of the laser (Vandaele et al., 2002) and $k$ and $k_0$ are the decay constant with and without NO$_2$ present in the cavity, respectively. $k_0$ is thus defined by the mirror reflectivity and light scattering by the dry, synthetic air.

The ratio $l/d$ accounts for the difference between the physical length of the cavity ($l$) and the effective optical path length ($d$) in which NO$_2$ is present, and for dilution effects. $d$ is shorter than $l$ due to the purge flows of zero air in front of the mirrors and a value of $l/d = 0.98 \pm 0.01$ was determined by adding a constant flow of NO$_2$ and varying the purge-gas flow rate (Schuster et al., 2009; Thieser et al., 2016). $k_0$ is typically determined every five minutes (for one minute) by overflowing the inlets with zero air from a commercial zero air generator (CAP 180, Fuhr GmbH) attached to a source of compressed ambient air. PTFE filters (47 mm diameter, 2 $\mu$m pore size) prevent particles entering the cavities. The filter’s efficiency, tested with laboratory air containing $1.8 \times 10^3$ particles cm$^{-3}$ and a CPC (TSI 3025 A), was > 98%.
Raw data sets (i.e. ring-down constants) undergo a few basic corrections before further analysis: 1) Interpolation of $k_0$ onto the $k$ time-grid. The first three data points after switching from sampling to zeroing are discarded, to enable stabilisation of the zero signal. The remaining data points of each zero cycle are averaged. Finally, a linear interpolation between the averaged $k_0$ values is performed, allowing subtraction of $k_0$ for each individual data point. 2) Depending on conditions of flow, pressure and inlet set-up (see sections 2.2 and 2.3), changes in flow resistance between the zeroing and sampling periods result in slight changes in the cavity pressure. The resulting change in Rayleigh scattering of the 405 nm light owing to a pressure change of 6.5 Torr was found to be equivalent to a change of ca. 300 pptv in the NO$_2$ mixing ratio, which is in accordance with earlier experiments using previous versions of this instrumental setup (Thieser et al., 2016). We have also used an alternative setup, in which the inlet is overflowed with zero air added close to the tip of the inlet (downstream of the oven), which reduces the pressure difference, but has the disadvantage that hot air is blown out of the instrument when zeroing, which may interfere with co-located inlets. Addition of zero air upstream of the quartz inlets would remove this problem but increase the complexity of the inlet and potentially result in loss of sticky molecules such as HNO$_3$.

3) A further correction is associated with the difference in the Rayleigh scattering coefficient between dry air (during zeroing) and humid air (whilst taking ambient measurements). This effect was corrected using the H$_2$O scattering cross-sections reported by Thieser et al. (2016), leading e.g. to a correction of 116 pptv at 70% RH and 20 °C.

### 2.2 Detection of NO$_x$

In order to measure NO (which does not absorb at 405 nm), it is converted to NO$_2$ by reaction (R6) with an excess of ozone (O$_3$) which was generated by passing zero air over a Hg Pen-Ray lamp emitting at 185 nm, which was housed inside a glass vessel at ca. 980 torr pressure. The gas-stream containing O$_3$ is split up equally by critical orifices and directed into two identical reaction-volumes made of 88 cm long PFA tubing (1/2 inch outer diameter, residence time 1.05 s). The concentration of O$_3$ (monitored by a commercial monitor, Model 202, 2B Technologies) was optimised in laboratory experiments in which the efficiency of conversion of NO to NO$_2$ was varied by variation of the flow of air over the Pen-Ray lamp. The maximum concentration of NO$_2$ (corresponding to 96% of the NO in the gas bottle) was observed when the flow over the pen-ray lamp was between 60 and 80 cm$^3$ (STP) min$^{-1}$ (hereafter sccm), which resulted in 19 ppmv O$_3$ in the reaction volumes. This result could be confirmed by numerical simulation (see Table S1) of the reactions involved in the formation and loss of NO$_2$ when NO reacts with O$_3$. According to the simulation, maximum conversion of NO to NO$_2$ during the 1.05 s residence time occurs between ca. 12 and 20 ppmv O$_3$. The conversion efficiency decreases at higher O$_3$ concentrations due to the formation of N$_2$O$_5$ and NO$_3$. The results from experiments to determine the optimum parameters for O$_3$ generation are summarised in Fig. S1.

For NO$_2$, the performance of the instrument was first described by Thieser et al. (2016), who reports a measurement uncertainty of $6\% + (20\text{ pptv}\times RH/100)$ which is dominated by uncertainty in the effective cross section of NO$_2$ and the wavelength stability of the laser diode. The NO$_x$ detection limit of 40 pptv (2σ, 1 minute average) for the present instrument (laboratory conditions) was derived from an Allan variance analysis and is worse than that reported by Thieser et al. (2016) (6 pptv at 40 s) due to degradation of the mirror reflectivity. Corrections applied to take into account humidity and pressure changes are discussed.
in Sect. 2.1. The total uncertainty in NO\textsubscript{y} will depend on the uncertainty in the conversion to NO\textsubscript{x} of both gaseous and particulate nitrate and thus depends on the individual components of NO\textsubscript{y} in the air sampled. For purely gaseous NO\textsubscript{y}, the major problem is likely to be related to loss of sticky molecules at the inlet and we choose to quote a “worst case” uncertainty of 15%.

2.3 Thermal dissociation inlets: Detection of NO\textsubscript{y}

The thermal dissociation inlets used to dissociate NO\textsubscript{y} to NO\textsubscript{2} are quartz tubes housed in commercial furnaces (Carbolite, MTF 10/15/130). The oven temperature was regulated with a custom made electronic module, which enabled spatial separation between the heating elements and insulation and the control electronics. The distance between the heated section of the quartz tubes and the point at which air was taken into the inlet was kept short (ca. 30 cm) in order to minimise losses of trace gases with a high affinity for surfaces, especially HNO\textsubscript{3} (Neuman et al., 1999). Experiments characterising the thermal conversion of various trace gases to NO\textsubscript{2} are described in Sect. 3.1. An electronic, PTFE 3-way valve (Neptune Research, Inc., type 648T032, orifice diameter 4 mm) under software control switches between the two heated inlets, one of which is equipped with a denuder. Memory effects on the valves surfaces were not observed for NO\textsubscript{2}. Bypassing the valve under normal sampling conditions led to an 0.6 Torr pressure change. The sampling flow through both heated inlets is 3.0 slm. When sampling ambient air via the denuder we expect to remove all gas phase NO\textsubscript{y} components and thus measure only particulate nitrate (pNit).

Experiments to characterise the transmission of the denuder for particles and various trace gases are presented in Sect. 3.3.

2.4 Active carbon denuder

The active carbon denuder (DynamicAQS) has a honeycomb structure with 225 quadratic channels (1mm × 1 mm) of length 10 cm in a cylindrical form (diameter 3 cm) which is housed inside an aluminium casing with ½ inch connections (see Fig. 1). The geometric surface area of the denuder is ~ 45 cm\textsuperscript{2}. Assuming a specific surface area for activated carbon of 1000 m\textsuperscript{2}g\textsuperscript{-1} (Atsuko et al., 1996), we calculate a BET (Brunauer-Emmett-Teller, Brunauer et al. (1938) surface area in the order of 10\textsuperscript{8} cm\textsuperscript{2}.

2.5 Chemicals

A stock, liquid sample of PAN in n-tridecane (98+%, Alfa Aesar) was synthesized according to the procedures described by Gaffney et al. (1984) and Talukdar et al. (1995). Samples of lower concentration (as used in the experiments described below) were produced by diluting the original sample with additional n-tridecane. Acetone (> 99%), isopropyl nitrate (> 98.0%) and (R)-(+) -limonene (97%) were obtained from Sigma-Aldrich. An ammonia permeation source (324 ng/min) was supplied by VICI Metronics. Methanol (> 99.9%) was acquired from Merck, isoprene (98%, stabilised) from Acros Organics and ethanol from Martin und Werner Mundo oHG. Both nitric acid (65%) and β-pinene (pure) were obtained from Roth. N\textsubscript{2}O\textsubscript{5} crystals were synthesized according to Davidson et al. (1978), by reacting NO (5%) with excess O\textsubscript{3} in a glass reactor. O\textsubscript{3} was produced via electrical discharge through O\textsubscript{2} using a commercial ozone generator (Ozomat Com, Anseros). The crystals were trapped and stored at -78 °C in dry-ice and ethanol.
3 Results and discussion

3.1 Trace-gas thermograms

The fractional conversion of NO\textsubscript{2} to NO\textsubscript{2} in the TD-inlets was investigated in a series of experiments in which constant flows of various NO\textsubscript{2} trace-gases were passed through the heated-inlet (bypassing the denuder) while the temperature was varied and NO\textsubscript{2} was monitored. NO\textsubscript{x} impurity levels were determined either via the simultaneous operation of the NO\textsubscript{x} channel or via the NO\textsubscript{y} channel mixing ratio at room temperature, before and after heating the inlet. By inserting a thermocouple into the middle part of the heated section under normal sampling conditions we were able to show that the temperature of the gas was \( \approx 80 \) °C lower than that indicated by the oven’s internal temperature sensor in the 200-300 °C temperature range and about 40 °C lower at a set temperature of 600 °C (see Fig. S3a)). We were unable to measure the temperatures of the gas stream at oven temperatures above about 600 °C and throughout the manuscript we refer only to the temperature indicated by the internal sensor of the oven.

We show below that the thermograms (plots of fractional dissociation of NO\textsubscript{2} to NO\textsubscript{x} versus temperature) which we measure with this instrument are broader and shifted in temperature compared to other examples found in the literature including those from this laboratory. As this instrument is built for measurement of NO\textsubscript{y} and not intended for separate measurement of e.g. PNs, ANs and HNO\textsubscript{3}, overlap of the individual thermograms does not represent a problem.

3.1.1 PAN

A stream of 200 sccm synthetic air was used to elute a constant supply of gaseous PAN from its solution (held at a constant temperature of 0 °C in a glass vessel) into the CRDS inlet. The thermogram is presented in Fig. 2, the absolute NO\textsubscript{2} mixing ratios are depicted in Fig. S2a). In this experiment the maximum amount of NO\textsubscript{2} observed (at temperatures > 400 °C) was 2.2 ppbv. At temperatures < 100 °C, there was no measureable thermal decomposition of PAN to NO\textsubscript{2}. Increasing the temperature from 100 °C to 300 °C results in a sharp increase in NO\textsubscript{2} which flattens off at temperature > 380 °C. We conclude that PAN is stoichiometrically converted to NO\textsubscript{2} at temperatures above 400 °C in our oven. The steepest part of the isotherm at \(~200 °C\), i.e. 50% conversion of PAN to NO\textsubscript{2}, is therefore shifted by ca. 80 °C compared to those reported in the literature by Wild et al. (2014), Thieser et al. (2016) and Sobanski et al. (2016). This is a consistent feature of our TD-ovens and is related to the short time available for thermal decomposition (see below) and a significantly lower gas-temperature than indicated by the oven’s internal temperature sensor.

3.1.2 Isopropyl nitrate

A 10 L stainless-steel canister containing 10.3 ppmv of isopropyl nitrate (iPN) at a pressure of 4 bar N\textsubscript{2} was prepared using a freshly vacuum-distilled liquid sample using standard manometric methods. NO\textsubscript{x} impurities were \(~4.7\) ppbv, though we note that diluted iPN stored in stainless-steel canisters for periods of several weeks degrades to form NO\textsubscript{2} and HNO\textsubscript{3}.
The thermogram is displayed in Fig. 2, the absolute concentrations in Fig. S2b). Based on the mixing ratio of iPN in the canister and the dilution flows, 10.7 ppbv represents (101 ± 11)% conversion. The shaded area around the expected iPN mixing ratio in Fig. S2b) signifies the uncertainty of this value, based on propagation of the errors during the manometric and dilution procedures (2% for flow rates, 5% for pressures measured with digital pressure gauges and 10% for the last dilution step using the analog pressure gauge of the canister).

Between 550 and 850 °C we observe a weak increase in NO2 from 10.7 to 11.2 ppbv, which is likely due to small amounts of HNO3 in the sample. For iPN, the temperature at 50% conversion is 50 °C higher than those reported by Thieser et al. (2016) and Sobanski et al. (2016). Wild et al. (2014) employed a gaseous mixture of different alkyl nitrates and also observed a broad thermogram with an initial increase in NO2 (up to 80% conversion) for temperatures < 300 °C, followed by a slower increase up to 800 °C. The alkyl nitrates thermogram of Wild et al. (2014) has been included into Fig. S2b) to illustrate this behaviour and to facilitate direct comparison.

3.1.3 HNO3

A custom-made permeation source was used to provide a constant, known flow of HNO3 (with ~ 8% NOx impurity) to the TD-CRDS inlet. The permeation source consisted of a length (≈ 1m) of PFA tubing immersed in 66% HNO3 solution held at 50 °C through which 100 sccm of dry, zero-air was passed. The concentration of HNO3 and thus its permeation rate, (1.62 ± 0.2) × 10^4 sccm, was derived by measuring the optical extinction of HNO3 at 185 nm using the absorption cross section of Dulitz et al. (2018). The uncertainty is related to uncertainty in the absorption cross-section and the reproducibility of the output. The HNO3 thermogram (Fig. 2 and Fig. S2c)) has a plateau at temperatures above ≈ 800 °C. In the plateau region of Fig. 2, the HNO3 mixing ratio measured is 13.0 ± 0.8 ppb, which (within combined uncertainties) is in agreement with the expected value (15.2 ± 1.98 ppbv) calculated from the permeation rate and uncertainty in the dilution factor. We cannot rule out some loss of HNO3 in the tubing connecting the permeation source to the TD-CRDS, through previous studies have shown that irreversible losses are ~ of 5% or less under dry conditions (Neuman et al., 1999). We note that inlet loss of HNO3 is minimized under ambient sampling conditions as only a short section (~20 cm) quartz tubing at ambient temperature is upstream of the heated section in which HNO3 is converted to NO2. Our observations are thus in accord with previous studies that found complete conversion of HNO3 to NO2 in similar set-ups (Day et al., 2002; Di Carlo et al., 2013; Wild et al., 2014; Womack et al., 2017).

3.1.4 N2O5

A sample of N2O5 was prepared by flowing 80 sccm of synthetic air over N2O5 crystals, kept at -70 °C, with further dilution with 20 slm synthetic air. An 8.5 cm long Nylon tube was used to reduce HNO3 impurity. Two distinct dissociation steps can be observed in Fig. 2, the first between 50 °C and 185 °C (in which NO2 increases to 4.2 ppbv, see Fig. S2d)) is due to the dissociation of N2O5 to NO2 + NO3. In the second step, in which NO3 is dissociated to NOx between 450 °C and 800 °C, the NO2 mixing ratio was 9.2 ppbv. As the amount of N2O5 derived from the first dissociation step was in accord with simultaneous
measurements of N$_2$O$_5$ using a further TD-CRDS set-up (Sobanski et al., 2016) we conclude that some HNO$_3$ was present in the sample, presumably the result of N$_2$O$_5$ hydrolysis. Our thermogram is similar to that reported by Womack et al. (2017) who also observed two steps, the first with a plateau at T > 100 °C and the second at T > 650 °C. The shift in temperature (100-150 °C) compared to our results is rationalised in Sect. 3.1.8.

3.1.5 HONO

Gaseous HONO was produced by flowing HCl in air (22 ppbv, relative humidity RH ca. 50 %), over a bed of continuously stirred sodium nitrate crystals (Wollenhaupt et al., 2000). In our setup, the thermal dissociation of HONO to NO starts at ~400 °C and reaches a plateau (6.2 ppbv) between ca. 800 °C and 850 °C (Fig. 2). We did not have access to independent instrumentation to characterise the concentrations of HONO and potential impurities generated using this method. Previous investigations report that HONO thermally dissociates between 450 and 650 °C (Perez et al., 2007), and between 200 and 700 °C (Wild et al., 2014). The reasons for such large divergence in the positions and widths of the thermograms may be partially related to the presence of impurities in the HONO samples used, though the details of the ovens used to thermally dissociated HONO also play an important role as described in see Sect. 3.1.8.

3.1.6 ClNO$_2$

ClNO$_2$ was generated by passing Cl$_2$ (33 ppbv in air) over sodium nitrate at room temperature. The thermogram, depicted in Fig. 2 has two steps, one with an apparent plateau at ~500 °C and a second at ~ 800°C. The lower temperature plateau in which ClNO$_2$ dissociates to NO$_2$ corresponds to that reported previously (Thaler et al., 2011; Sobanski et al., 2016; Thieser et al., 2016). The observation of further NO$_2$ formation at higher temperature is consistent with the observations of Wild et al. (2014). We hypothesize, that the second dissociation step might be associated with the presence of ClNO which dissociates to NO (and would therefore not have been detected by instruments that monitor NO$_2$ rather than NO$_3$). Even at temperatures > 850 °C, we still see an increase in NO$_2$ signal. However, as ClNO is not considered to be an important atmospheric trace gas, this has no repercussions for deployment of the instrument.

3.1.7 NH$_4$NO$_3$ and NaNO$_3$ particles

NH$_4$NO$_3$ and NaNO$_3$ particles were generated from an aqueous solution (ca. 1 g in 500 mL deionized water) using an atomizer (TSI 3076). The particles were dried prior to size selection (DMA, TSI 3080), diluted in a total flow of 6 slm synthetic air which was split between a CPC and the heated TD-CRDS inlet (after further dilution). The relative thermogram for NH$_4$NO$_3$ is displayed in Fig. 2 and, similar to HNO$_3$, displays a plateau region at temperatures above 830 °C. The shift in the thermogram when comparing HNO$_3$ and NH$_4$NO$_3$ (which we expect to detect in a two-step process in which NH$_4$NO$_3$ first decomposes to HNO$_3$) may be related to the time required to fully thermally decompose particles (e.g. of 200 nm diameter) containing several million molecules. Particle numbers (in cm$^{-3}$) detected by the CPC were converted to molar-mixing ratios via the diameters and densities of the dry particles (1.72 g cm$^{-3}$ for NH$_4$NO$_3$, and 2.26 g cm$^{-3}$ for NaNO$_3$). The fraction of NH$_4$NO$_3$ detected as
\[ \text{NO}_x \] following passage through the oven is illustrated in Fig. S5 which indicates values between \( \approx 60\% \) and 120\% depending on particle size. The total uncertainty in the concentration was estimated as 41\%, which includes 10\% uncertainty in the particle diameter (based on measured size distributions of Latex calibration particles), 20\% uncertainty in the particle number (including the error in the multiple charge correction) and 10\% uncertainty in the density, due to possible differences between single crystal and bulk density. As the particle mass scales to the third-order with the particle diameter, the correction for double charged particles introduces a large uncertainty in the calculated mixing ratios, the effect being largest in the size range between 100 to 150 nm, which probably explains the lower \( \text{NH}_4\text{NO}_3 \) detection efficiencies in this range. We consider the data obtained at 200 nm to be the most reliable and conclude that, similar to other TD-instruments (Womack et al., 2017; Garner et al., 2020), ours also detects \( \text{NH}_4\text{NO}_3 \) particles as \( \text{NO}_2 \) with close to 100\% efficiency. In contrast, our experiments using \( \text{NaNO}_3 \) resulted in much smaller \( \text{NO}_x \) concentrations despite identical experimental conditions in back-to-back experiments and resulted in detection efficiencies of close to 25\%. While the inefficient detection of \( \text{NaNO}_3 \) is consistent with previous reports suggesting that \( \text{NaNO}_3 \) would not be detected in TD-inlets (Womack et al., 2017) it contrasts strongly with the very recent result of Garner et al. (2020) who observe quantitative conversion of \( \text{NaNO}_3 \) to \( \text{NO}_2 \) at 600 °C. The difference may be related to residence times in the heated section of the inlet.

3.1.8 Summary of thermograms

The thermograms obtained by the present instrument deviate from others reported in the literature, the temperatures required for 50\% dissociation being generally higher by e.g. 80 °C for PAN, 50 °C for iPN and 150 °C for HNO\(_3\), respectively (Day et al., 2002; Wild et al., 2014; Sobanski et al., 2016; Thieser et al., 2016; Womack et al., 2017). This lack of agreement with other setups is not unexpected as the degree of dissociation of a trace gas at any temperature depends not only on the temperature but also on the time over which the molecule is exposed to that temperature (Womack et al., 2017). To illustrate this, based on rate coefficients (related to bond-dissociation energies, BDE) for the thermal dissociation of PAN (Bridier et al., 1991), iPN (Barker et al., 1977), HNO\(_3\) (Glänzner and Troe, 1974), \( \text{N}_2\text{O}_5 \) (IUPAC, 2019), ClNO\(_2\) (Baulch et al., 1981), and HONO (Tsang and Herron, 1991), we calculated the theoretical 50\% conversion temperature for each molecule as a function of residence time inside the oven (see Fig. S3b)). At short residence times the dependence on temperature is very steep (especially for large BDEs) which partially explains the differences between our short heated section inlet and longer ones. However, in practise, we know neither the precise average temperature of the gas at the centre of the oven, nor can we characterise the axial and radial gradients in temperature in the quartz tubes so that calculations of fractional dissociation (or complete thermograms) based on bond-dissociation energies are at best only a rough guide. We note that use of different flows, oven diameters and operational pressures will strongly affect heat transfer from the oven walls to the gas, so that reporting the temperature of the external oven-wall (as done here and in all reports in the literature) to some extent precludes comparison between different setups. The width of the thermograms (i.e. the temperature difference between e.g. 10\% and 90\% dissociation) will also depend on details of axial and radial temperature gradients in the tubing located within the oven and also in the downstream section of tubing, which represents a transition regime between oven and room temperature. The impact
of temperature gradients inside the quartz tube was explored by calculating the HNO$_3$ thermogram using an Arrhenius expression for its thermal dissociation and the gas residence time within the quartz tube. First we assumed that all HNO$_3$ molecules experience the same temperature and then compared this to the situation in which 20% of the HNO$_3$ molecules are 80 °C lower in, and 20% are 80 °C higher in temperatures. The resultant thermograms are displayed in Fig S3c) and indicate that the presence of temperature gradients results in an increase in the width of the thermogram from 250 °C to 350 °C.

The thermograms we report here serve only to determine the temperature needed to ensure complete maximum conversion of each trace gas to NO$_2$. This is achieved in the present setup with a temperature of 850 °C. Where possible, we have verified that operation at the plateau of the thermogram resulted in quantitative conversion of the traces gases and particles studied, with one exception, NaNO$_3$ particles. We further note that, in an instrument designed only to measure NO$_y$, there is no need to ensure separation (in temperature) of the thermograms for different classes of molecules.

3.1.9 Detection of NH$_3$

As described previously (Wild et al., 2014; Womack et al., 2017) ammonia represents a potential interference in NO$_y$ measurements. In order to quantify this interference, we measured NO$_2$ formation in air containing 131 ppbv NH$_3$ delivered by a calibrated permeation source (VICI METRONICS, permeation rate 324 ng min$^{-1}$ at 45 °C). The results are summarised in Fig. 2. In NH$_3$ – air mixtures, we observe a small NO$_2$ signal, increasing at first slowly and then (from ≈ 700 °C) rapidly with temperature; the amount of NO$_2$ observed at 850 °C corresponds to a fractional conversion of NH$_3$ to NO$_2$ of 0.006 ± 0.002. This result is in broad agreement with Wild et al. (2014), who found a conversion efficiency of < 0.01 at 700 °C. In experiments with NH$_3$ in zero-air with relative humidities of 17%, 31% and 53% we were unable to observe conversion of NH$_3$ to NO$_2$, again consistent with humidity related suppression of NO$_2$ formation observed by Wild et al. (2014).

In additional experiments, we investigated the potential influence of ozone on the NH$_3$ to NO$_2$ conversion efficiency in zero-air containing O$_3$. The addition of O$_3$ results in a significant increase in NO$_2$ with a linear dependence on the O$_3$ mixing ratio (Fig. 3) with up to 11.4% conversion of NH$_3$ to NO$_2$ at 200 ppbv O$_3$. This was not reduced measurably by the addition of water vapour to the air / O$_3$ mixture. In further experiments we spiked air with the head-space of various organic liquids (acetone, methanol, ethanol, beta-pinene, limonene and isoprene). The gas-phase mixing ratios of the organic trace gases were unknown but in each case the formation of NO$_2$ was suppressed or completely stopped. A more quantitative investigation was carried out using a known concentration (1 ppmv gas bottle) of isoprene. We found that addition of 30 ppbv isoprene to zero-air (containing 330 ppbv O$_3$) did not significantly reduce the NH$_3$-to-NO$_2$ conversion efficiency under dry conditions, but reduced it by a factor of two when the RH was increased to 50%.

A tentative chemical mechanism, based partially on Womack et al. (2017) to explain the formation of NO$_2$ from NH$_3$ and O$_3$ at high temperatures and the processes that suppress it is given in reactions (R11 to R15). In this scheme, the oxidation of NH$_3$ is initiated and propagated by O($^3$P), formed from the thermal dissociation of O$_3$ (Peukert et al., 2013). This leads to formation of NO and HNO (R13a and R13b), both of which can be oxidised to NO$_2$ (R14 and R15). Forward and reverse rate coefficients for reaction (R11) indicate that O$_3$ is converted almost stoichiometrically to O($^3$P) in the ≈ 10 ms reaction time in the heated
inlet. The rate constants (at 1123 K) for the subsequent reactions involving O(3P) are: \( k_{12} = 4.4 \times 10^{13} \text{ cm}^3 \text{molec}^{-1} \text{s}^{-1} \) \( k_{13a} = 8.3 \times 10^{12} \text{ cm}^3 \text{molec}^{-1} \text{s}^{-1} \) and \( k_{13b} = 7.5 \times 10^{11} \text{ cm}^3 \text{molec}^{-1} \text{s}^{-1} \) (Cohen and Westberg, 1991). Reaction (R12) converts 0.3% of the initial NH3 molecules to NH2 within 10 ms (at 100 ppbv O3 and 1123 K).

\[ \begin{align*}
5 & \quad \text{O}_3 + \text{M} \rightarrow \text{O}(3P) + \text{O}_2 + \text{M} \quad \text{(R11)} \\
\text{O}(3P) + \text{NH}_3 & \rightarrow \text{NH}_2 + \text{OH} \quad \text{(R12)} \\
\text{NH}_2 + \text{O}(3P) & \rightarrow \text{NO} + \text{H}_2 \\
& \quad \rightarrow \text{HNO} + \text{H} \quad \text{(R13a)} \\
\text{HNO} + \text{O}(3P) / \text{OH} / \text{H} & \rightarrow \text{NO} + \text{OH} / \text{H}_2\text{O} / \text{H}_2 \quad \text{(R14)} \\
10 & \quad \text{NO} + \text{O}(3P) + \text{M} \rightarrow \text{NO}_2 + \text{M} \quad \text{(R15)}
\end{align*} \]

The experimental results obtained in zero-air indicate that reactions involving O(3P) from O3 thermolysis can result in the conversion of NH3 to NO and NO2. These results could however not be reproduced when adding NH3 to ambient air sampled from outside of the building. In this case, the addition of NH3 (at 50-60 ppbv O3) did not result in a measureable increase in NO2, which was in accord with the observations of Womack et al. (2017). The scavenging of NH2 radicals and O(3P) by both volatile organic compounds and H2O provides a likely explanation for this. Womack et al. (2017) also found that addition of 100 ppbv CO can reduce the conversion of NH3 to NOx.

In summary, our experiments indicate that the conversion of NH3 to NO2 is suppressed in ambient air samples, or in synthetic air with added VOCs and water. The ambient air used in these experiments was from an urban and polluted environment (typical NOx levels between 10 and 50 ppbv, see Sect. 4.2). As high levels of atmospheric NH3 are associated with agricultural activity (Langford et al., 1992; Schlesinger and Hartley, 1992) and are often accompanied by high NOx and VOC levels, the NH3 interference under these conditions is most likely to be small compared to ambient NOx levels. Long term measurements of NH3 have additionally found a positive correlation between NH3 concentrations and ambient temperature (Yamamoto et al., 1988; Wang et al., 2015; Yao and Zhang, 2016), the latter promoting the presence of high levels of biogenic VOCs, such as isoprene (Tingey et al., 1979), which would also help to minimize the NH2-related interference.

### 3.2 Bias caused by secondary reactions in the TD-ovens

Thermal dissociation techniques coupled to CRD-systems for measurement of organic nitrates suffer bias to different degrees owing to reactions of organic peroxy radicals with NO and NO2 (Sobanski et al., 2016; Thieser et al., 2016). According to previous studies (Day et al., 2002; Rosen et al., 2004; Thieser et al., 2016), in experiments using iPN at an oven temperature of 450 °C, an overestimation of ANs in the presence of NO is caused by reactions of the initially formed alkoxy radical, C3H7O, which results in the formation of both HO2 and CH3O2 (R16-R21).

\[ \text{C}_3\text{H}_7\text{ONO}_2 + \text{M} \rightarrow \text{C}_3\text{H}_7\text{O} + \text{NO}_2 + \text{M} \quad \text{(R16)} \]
\[
\begin{align*}
\text{C}_3\text{H}_5\text{O} + \text{O}_2 & \rightarrow \text{CH}_3\text{C}(\text{O})\text{CH}_3 + \text{HO}_2 \quad (\text{R17}) \\
\text{C}_3\text{H}_5\text{O} + \text{M} & \rightarrow \text{CH}_3 + \text{CH}_3\text{CHO} + \text{M} \quad (\text{R18}) \\
\text{CH}_3 + \text{O}_2 + \text{M} & \rightarrow \text{CH}_3\text{O}_2 + \text{M} \quad (\text{R19}) \\
\text{CH}_3\text{O}_2 + \text{NO} & \rightarrow \text{CH}_3\text{O} + \text{NO}_2 \quad (\text{R20}) \\
\text{HO}_2 + \text{NO} & \rightarrow \text{HO} + \text{NO}_2 \quad (\text{R21}) \\
\text{CH}_3\text{C}(\text{O})\text{O}_2\text{NO}_2 + \text{M} & \rightarrow \text{CH}_3\text{C}(\text{O})\text{O}_2 + \text{NO}_2 + \text{M} \quad (\text{R22a}) \\
\text{CH}_3\text{C}(\text{O})\text{O}_2 + \text{NO}_2 + \text{M} & \rightarrow \text{CH}_3\text{C}(\text{O})\text{O}_2\text{NO}_2 + \text{M} \quad (\text{R22b}) \\
\text{CH}_3\text{C}(\text{O})\text{O}_2 + \text{M} & \rightarrow \text{CH}_3\text{CO} + \text{O}_2 + \text{M} \quad (\text{R23a}) \\
\text{CH}_3\text{C}(\text{O})\text{O}_2 & \rightarrow \text{CH}_3\text{C}(\text{O})\text{OOH} \quad (\text{R23b}) \\
\text{OH} + \text{NO}_2 + \text{M} & \rightarrow \text{HNO}_3 + \text{M} \quad (\text{R24})
\end{align*}
\]

In order to investigate the potential bias in the measurement of ANs under the present experimental conditions, a set of experiments was conducted in which NO (up to 12 ppbv) was added to various amounts of iPN. The NO mixing ratio was determined by modulating the addition of O\(_3\). The results (Fig. 4a), show that NO\(_2\) derived from the thermal decomposition of iPN increases with the amount of NO added and results in overestimation (factor of \(\sim 1.6\)) at 12 ppbv NO, which is consistent with the observations by Thieser et al. (2016). This disappears when 19 ppmv ozone is added in front of the cavity so that NO\(_x\) rather than NO\(_2\) is measured (blue data points). This is readily explained by the compensation of the additional NO\(_2\) formed via reactions of NO with RO\(_2\) by an equal loss in NO, which is only detected when introducing O\(_3\). This is illustrated graphically in Fig. S4.

We also explored the potential for bias caused by the recombination of CH\(_3\)C(O)O\(_2\) and NO\(_2\) (reaction R22b), following the thermal decomposition of PAN (reaction R22a). Thieser et al. (2016) reported that PAN was underestimated by a factor 0.45 when adding 10 ppbv NO\(_2\) to an air sample containing PAN at 200 °C. This behaviour was not apparent at 450 °C, which is related to the decomposition (reaction R23a) or isomerisation (reaction R23b) of CH\(_3\)C(O)O\(_2\) at the higher temperature. The results of a similar experiment with our 850 °C inlet are presented in Fig. 4b). In this plot, the measured NO\(_2\) relative to the input PAN is plotted versus the mixing ratio of added NO\(_2\). For PAN concentrations from 1.5-2.2 ppbv no effect was observed for NO\(_2\) concentrations of up to 10 ppbv. This is consistent with the reaction scheme presented by Thieser et al. (2016) at 450 °C.

A potential source of bias when measuring HNO\(_3\) includes its reformation via the reaction of OH and NO\(_2\) (reaction R24). Compared to the RO and RO\(_2\) radicals formed in the thermal dissociation of PNs and ANs, OH exhibits a higher affinity for surfaces and is likely to be efficiently removed at the oven wall. Day et al. (2002) estimated that wall losses are the dominant OH sink and that the resulting underestimation of HNO\(_3\) would be < 2%, for NO\(_y\) levels < 5 ppbv. At our oven temperature, the diffusion coefficient for OH \((D_{\text{OH}})\) can be calculated according to Tang et al. (2014):

\[
D_{\text{OH}}(1123 \text{ K}) = D_{\text{OH}}(296 \text{ K}) \cdot \frac{296^{-1.75}}{T}.
\]
Using an average of the literature values for $D_{OH}$ at room temperature from Ivanov et al. (2007) (165 Torr cm$^2$s$^{-1}$) and Bertram et al. (2001) (192 Torr cm$^2$s$^{-1}$), a value of $D_{OH}(1123 \text{ K}) = 1841$ Torr cm$^2$s$^{-1}$ was derived. The maximum rate constant for OH wall loss (assuming laminar flow) can subsequently be approximated according to Zasypkin et al. (1997): 

$$k_{\text{wall}} = \frac{D_{\text{OH}} 3.66}{r^2 p},$$

(3)

With the radius of the oven quartz tube $r$ (0.45 cm) and the pressure $p$ (760 torr), the maximum value of $k_{\text{wall}}$ is 44 s$^{-1}$. The first-order loss rate coefficient for reaction of OH with NO$_2$ is given by $k_{(OH + NO_2)[NO_2]}$, where $k_{(OH + NO_2)}$ is the rate coefficient for reaction between OH and NO$_2$ at 1123 K ($\sim 5 \times 10^{-14}$ cm$^3$ molecules$^{-1}$s$^{-1}$ (IUPAC, 2019) and $[NO_2] = 6.5 \times 10^{10}$ molecule cm$^{-3}$ the concentration of 10 ppb NO$_2$ at the pressure and temperature of the oven. The first-order loss rate of OH via reaction with NO$_2$ is then $3 \times 10^{-3}$ s$^{-1}$. Clearly, the efficiency of uptake of OH to the wall would have to be very low in order to reduce the maximum value of 44 s$^{-1}$ to values that are comparable to reaction with NO$_2$, which is very unlikely. We conclude that reformation of HNO$_3$ via reaction (R24) will not bias measurements of HNO$_3$ with the present set-up.

3.3 Denuder characterisation

The efficiency of removal of NO$_y$ trace gases and transmission of submicron particles was determined in a series of experiments, which are described below.

3.3.1 Transmission of ammonium nitrate particles (10 – 414 nm)

In order to characterise the transmission of the denuder for particles of different diameter a constant flow of particles was generated by passing 3.3 slm of nitrogen through an atomizer (TSI 3076) containing an aqueous solution of ammonium nitrate. The flow rate (3.3 slm) was matched to the typical sampling flow through the denuder. 0.28 slm of the flow was sampled into an SMPS/CPC system (TSI 3080 and TSI 3025A) to measure the number density and size distribution (10 – 414 nm) of the ammonium nitrate particles. The flow was delivered either directly to the SMPS/CPC via straight metal tubing (length 27 cm, inner diameter 0.9 cm), for which we assume 100% particle transmission, or via the denuder. The ratio of the particle numbers in each size bin thus represents the size-dependent denuder transmission. As shown in Fig. 5, the transmission of the denuder is > 80% for particles between 30 and 400 nm diameter. As expected, some diffusive loss is observed for particles < 20 nm diameter and loss due to impaction/settling is observed for particles > 300 nm. The particle transmission $T$ as a function of particle diameter $d$ can be represented by the following empirical expression:

$$T(\%) = \frac{d(nm)^{-5.79}}{0.035 + 0.010 \cdot (d - 5.79)^2 + 1.78 \times 10^{-6} \cdot (d - 5.79)^2}$$

(4)

The particle transmission through the denuder channels was also calculated using the Particle Loss Calculator (PLC) developed by von der Weiden et al. (2009). The results of this calculation are also plotted in Fig. 5. The observed loss of particles smaller than 40 nm are not replicated by the PLC, which was developed for cylindrical piping and not the square honeycomb shape of the denuder and also does not take into account losses due to impact at the finite surface area which the
gas/particle flow is exposed to at the entrance to the honeycomb. The PLC does a better job in predicting a reduction in transmission for the largest particles which we measured and indicates a transmission of 74% at 1 µm and 45% at 2 µm. In certain environments, nitrate associated with coarse mode particles thus represents a potential bias for TD-CRDS measurements of NO₃.

### 3.3.2 Efficiency of removal of NOₓ trace gases.

The efficiency of removal of trace gases in the denuder under typical flow conditions (3.3 slm) was investigated for NO, NO₂, PAN, iPN, HONO, N₂O₅, ClNO₂ and HNO₃ as representative NOₓ species. The efficiency of removal of each trace gas (generally present at 5-40 ppbv) was determined by measuring its relative concentration when flowing through the denuder (pNit-channel) and when bypassing the denuder (NOₓ channel). The results (Fig. 6) indicate that, in dry air, all of these trace gases were removed with an efficiency of close to 100%. However, when the main dilution flow was humidified significant, RH-dependent breakthrough of NO was observed, with only 60% stripped from the gas-phase at RH close to 100%. HONO was removed with 85% efficiency at an RH of 46%, and ClNO₂ with 75% efficiency at an RH of 60%. In contrast, humidification had only a marginal effect on the scrubbing efficiency for NO₂, iPN and HNO₃ for which an efficiency of ≥ 95% was observed. The precise values from which the removal efficiencies in Fig. 6 were determined are listed in Table S2.

In further experiments, we examined the potential for re-release of NOₓ that had previously been stored in the activated carbon substrate of the denuder. In these experiments, in which either NOₓ or NOᵧ was continuously monitored, the denuder was exposed to a flow of 9.5 ppm iPN in dry nitrogen for 90 minutes during which 2.30 x 10¹⁷ molecules of iPN were stripped from the gas phase and deposited onto the denuder. This exposure is equivalent to a month-long exposure to 20 ppb of iPN. The air passing through the denuder was subsequently humidified to RH = 65%. The results (Fig. 7a)) indicate a high initial (11:40 – 11:50) rate of release of NOₓ under humid conditions (resulting in a maximum mixing ratio of 2 ppbv at 11:45). At 11:50, humidification of the air was stopped and the rate of release of NOₓ dropped gradually towards zero. During a second period, in which the air was again humidified (from 11:50 on), NOₓ was released from the denuder, albeit at a lower rate than during the first humidification. From 12:25 onwards, the oven behind the denuder was heated to 850 °C so that NOᵧ was added. No significant increase in NO₂ was observed indicating that the trace-gas(es) species released from the denuder surface upon humidification are predominantly NOₓ. During this experiment, 2.55 x 10¹⁵ molecules of NOₓ desorbed from the denuder, indicating that the major fraction of iPN molecules remained stored on the denuder surface upon humidification.

Similar denuder exposure experiments were performed with HNO₃ and NO₂. For HNO₃, no evidence for desorption of NOₓ or NOᵧ during exposure to humidified air was observed, whereas NO₂ exhibited a similar behaviour to iPN (Fig. 7b)). After loading the denuder with 5 sccm from a 0.831 ppm NO₂ gas bottle for 4.8 days (a total of 7.60 x 10¹⁷ molecules were deposited as derived from the flow rate, the exposure time and the gas bottle mixing ratio), the effect of passing humidified air through the denuder was to release NOₓ, which was observed at concentrations up to ≈ 39 ppbv. While the relative humidity was kept constant at close to 100%, the NOₓ released decreased over time so that after 30 minutes, 3.2 ppbv NOₓ could still be detected. By switching the O₃ source off (at ≈ 10:45) the NO₂ measured went to ≈ zero indicating that predominantly NO was released.
Integrating these results over time yielded a value of $1.63 \times 10^{16}$ molecules desorbed NO from the denuder surface in humid air. Qualitatively similar results, i.e. humidity induced formation and release of NO\(_x\) from the denuder, were observed when the denuder was exposed for periods of weeks to variable levels of NO\(_x\) (i.e. up to 20 ppbv) under dry conditions. Clearly, adsorption of water molecules onto the denuder surface can initiate / catalyse chemical transformation at the surface than convert stored NO\(_x\) into forms than can desorb and be detected as NO\(_x\). To further our understanding of underlying processes that occur upon humidification, a series of experiments were conducted to examine the adsorption of water on the denuder. In these experiments the denuder was first dried by exposing it to dry air for several hours until the relative humidity of the air exiting the denuder was close to zero. Subsequently, humidified air was passed through the denuder and the RH of air exiting it was continuously monitored. The results of an experiment in which the air was humidified to 68% are shown in Fig. 8a). After 77 minutes of exposure to this humidity, the RH of the air exiting the denuder acquired a maximum value of 64%. After switching back to dry synthetic air (at 09:37 UTC), ~60 minutes passed before the RH dropped to values close to zero. In this period, the RH did not decrease monotonically, the rate of change of relative humidity exiting the denuder revealing a number of discreet steps. Figure 8b) plots the derivatives (dRH/dt) of the drying phases of a series of experiments in which the initial RH was varied between 47 and 75%. A similar pattern emerges for each experiment with the greatest desorption rates occurring at the beginning of the drying phase followed by a minimum in the desorption rate and a second maximum (at ≈ 15% relative humidity). This behaviour is a clear indication that H\(_2\)O is bound to more than one chemically or physically distinct surface sites on the activated-activated carbon.

By measuring the change in RH of the air flowing into and out of the denuder we can derive an equilibrium adsorption isotherm for H\(_2\)O at the active carbon surface. An example is given in Fig. 9 where it is also compared to a literature isotherm for adsorption of water vapour on activated carbon fibre (Kim et al., 2008). The data of Kim et al. (2008) have been scaled, by matching the number of adsorbed water molecules at 65.9% RH to our observed value at 67.2% RH. The exposure of carbonaceous surfaces to inert gases at high temperatures (2000 °C) reduces the capacity for water uptake, whereas functionalising the carbon surface with oxygen containing groups (e.g. from HNO\(_3\)) enhances the water adsorption capacity (Dubinin et al., 1982; Barton and Koresh, 1983; Liu et al., 2017). In our experiments, the uptake of gas-phase NO\(_y\) is thus expected to generate oxygenated sites on our denuder surface, which in turn will influence water uptake and thus further trace-gas accommodation.

The chemistry leading to the formation of gas-phase NO\(_x\) from NO\(_y\) trace-gases adsorbed at the denuder surface under humid conditions cannot be elucidated in detail with our experimental setup. However, a strong humidity dependence in the heterogeneous generation of HONO and NO from NO\(_2\) adsorbed on soot particles has been reported (Kalberer et al., 1999; Kleffmann et al., 1999). Formation of HONO from NO\(_x\) has also been observed on wet aerosol and ground surfaces in field studies (Lammel and Perner, 1988; Notholt et al., 1992). Previous investigations report the adsorption of NO\(_2\) on activated carbon at ambient or close to ambient temperatures (30-50 °C), followed by its reduction to NO, with the simultaneous oxidation of the carbon surface (Shirahama et al., 2002; Zhang et al., 2008; Gao et al., 2011). These results are consistent with
our observation of e.g. conversion of NO₂ to NO at the denuder surface under humid conditions. In our experiments, we observed that NO₂ was converted to NO (rather than HONO) at the denuder surface. It is possible that the initial step is formation of HONO (e.g. by the surface catalysed hydrolysis of NO₂ or iPN) which undergoes further reduction on the surface to NO. Release of HONO and NO has also been observed from soil, after the nitrification of NH₃/NH₄⁺ or the reduction of NO₃⁻ (Su et al., 2011; Pilegaard, 2013; Meusel et al., 2018). Oswald et al. (2013) found comparable HONO and NO emission fluxes from non-acidic soils, providing another example of heterogeneous formation of HONO from other atmospheric nitrogen species, followed by the gas phase release of NO.

We conclude that the use of this denuder type (and assumption of complete removal of gaseous NOₓ) may potentially result in a positive bias in measurements of particle nitrate owing to variable breakthrough and release of NOₓ (dependent on the historical exposure of the denuder and relative humidity). Our findings may be applicable (at least in a qualitative sense) to similar denuders using activated carbon surfaces, and careful characterisation of the capacity to adsorb, breakthrough and release of NOₓ components should be carried out prior to use in the field.

Reliable surface re-activation techniques for similar denuders would be useful to ensure continuous, efficient scrubbing of NOₓ and NOₓ and circumnavigate the potential overestimation of pNit. In this regard, attempts to “reactivate” the denuder by cleaning with distilled water, drying at 50 °C and exposure to ca. 300 ppbv O₃ for one hour did not result in an improvement of the direct NO-breakthrough or in the background pNit signal upon humidification. Surface sensitive, spectroscopic investigation of the water-induced transformation of organic and inorganic NOₓ to NOₓ (and its subsequent release to the gas-phase) on denuder surfaces would be useful in resolving these issues.

3.4 Comparison of the TD-CRDS with existing methods for NOₓ and NOᵧ and instruments

In this section, our instrument’s performance is compared to other methods for NOₓ and NOᵧ detection. We consider only instruments which measure NOₓ and / or NOᵧ and not those that measure individual trace-gases from each family.

NOₓ has traditionally been measured by two-channel CLD instruments (one channel each for NO and NO₂) in which NO is detected by chemiluminescence from its reaction with O₃ and NO₂ is reduced converted to NO on a molybdenum converter or by photolysis at wavelengths close to 390 nm. Examples of this type of instrument and the reported LODs and overall uncertainties are listed in Table 2. In this Table we also list the LOD and uncertainty of a recently developed CRDS setup which is similar in principal of operation to the one described here (Fuchs et al., 2009).

NOᵧ has frequently been measured by CLD instruments with Au/MoO-coated thermal dissociation inlets that reduce NOₓ to NO which is detected as described above for CLD-NOₓ instrument. Although such instruments have very low detection limits, they have been shown to be vulnerable to degradation of the NOᵧ conversion efficiency and suffer from interferences by HCN, CH₃CN and NH₃ (Kliner et al., 1997), as well as loss of NOᵧ in the inlet (Zenker et al., 1998; Parrish et al., 2004). Table 2 summarises the LODs and uncertainties reported by other NOᵧ instruments.
Table 2 indicates that the total uncertainty of the present instrument is comparable to those reported for both NO\textsubscript{x} and NO\textsubscript{y}. Our present detection limit for both NO\textsubscript{x} and NO\textsubscript{y} is however worse than that reported (for NO\textsubscript{2}) for the same instrument in 2016 (Thieser et al., 2016), which is a result of mirror degradation since that study.

4 Application of the instrument in field experiments

4.1 NO\textsubscript{x} intercomparison and pNit measurements during the AQABA campaign

The first deployment of the instrument was during the AQABA (Air Quality and climate change in the Arabian Basin) ship campaign in summer 2017. From the 31\textsuperscript{st} of July to the 2\textsuperscript{nd} of September, the ship “Kommander Iona” followed a route from southern France via the Mediterranean Sea, the Suez Channel, the Red Sea, the Arabian Sea and the Arabian Gulf to Kuwait and back. The instrument was located in a container in front of the ship, with the inlet ovens located in an aluminium box on the roof of the container. The (unheated) tips of quartz inlet tubes protruded about 15 cm from the side of the aluminium box. Here we compare the NO\textsubscript{x} and pNit measurements with other measurements of these parameters made during the campaign. During AQABA, NO\textsubscript{x} levels ranged from a few pptv (maritime background) up to several tens of ppbv in heavily polluted air masses in shipping lanes or in harbours. In Fig. 10a) we compare NO\textsubscript{x} measured with the TD-CRDS with the results of a chemiluminescence detector (CLD 790 SR, ECO Physics, Tadic et al. (2020)), which measured NO and NO\textsubscript{2}. The data points represent 1 minute averages for the entire campaign, excluding air-masses which were contaminated by the ships exhaust. Additionally, periods with very high NO\textsubscript{x} variability were not included, a data point being discarded whenever the differences in mean values exceeded 2 ppbv for consecutive data points.

A bivariate fit to the datasets (York, 1966), which incorporates total uncertainties for both instruments (CLD: 8.6%; TD-CRDS; 11% + 20 pptv*RH/100) resulted in a slope of 0.996 ± 0.003 and an intercept of -1.3 pptv. The very good agreement, serves to underline the general applicability of the TD-CRDS in NO\textsubscript{x} measurements even under difficult conditions (e.g. a non-static platform). In this context we note that the deployment on a ship resulted in a degradation in performance (LOD was ≈ 100 pptv) owing to the ship’s motions, especially in heavy seas, which resulted in drifts in the instrument zero.

Figure 10b) shows a ca. 10 hours time frame with pNit measurements from the denuder channel of the TD-CRDS. Unfortunately, the TD-oven of the denuder channel broke down very early in the campaign and was not operational afterwards. The data from the pNit channel are presented together with the NO\textsubscript{x} and NO\textsubscript{y} measurements along with particulate nitrate mass concentrations measured by an aerosol mass spectrometer (Aerodyne HR-ToF-AMS; DeCarlo et al. (2006), Brooks et al. (2020)). The night-to-day transition is indicated via NO\textsubscript{2} photolysis rates $J_{NO2}$ derived from a spectral radiometer (Metcon GmbH), the relative humidity was > 80 % throughout the period shown. During the two periods when, apart from some short spikes, NO\textsubscript{x} was very low (21:10-23:45 UTC and 02:20-03:40 UTC), TD-CRDS data indicate the presence of 300-400 pptv of pNit, which would then constitute ~80% of NO\textsubscript{y}. Such mixing ratios of particulate nitrate are not commensurate with those measured by the AMS, which, on average, are a factor 6-8 lower. As the AMS does not detect particles larger than ~600 nm with high efficiency (Drewnick et al., 2005), the difference could potentially indicate that a significant fraction of the
particulate nitrate is associated with coarse mode aerosol. In the lower panel of Fig. 10b) we plot coarse mode aerosol mass concentration determined from measurements of an optical particle counter (OPC) that measures particles between 0.2 and 20 μm. In the two low NO\textsubscript{x} periods outlined above, the OPC-derived aerosol mass concentrations were between 3 and 5 μg m\textsuperscript{-3}. If 10% of this coarse mode aerosol mass concentration were nitrate, which is a typical value in the Mediterranean (Koulouri et al., 2008; Calzolai et al., 2015; Malaguti et al., 2015), this would account for 100-200 pptv of the pNit observed by the TD-CRDS and not by the AMS. However, the time profile of pNit measured by the TD-CRDS is not consistent with those of either the OPC or the AMS, but rather resembles the NO\textsubscript{x} mixing ratios. This strongly suggests that the large difference between pNit reported by the TD-CRDS and the AMS does not result from the non/detection of supermicron particulate nitrate by the AMS, but result from the denuder artefacts described in Sect. 3.3.2. This short case-study serves to highlight the potential positive bias in denuder based, TD-CRDS measurements of pNit under humid field conditions.

4.2 Ambient NO\textsubscript{x} and NO\textsubscript{y} measurements in an urban environment (Mainz, Germany)

NO\textsubscript{x} and NO\textsubscript{y} mixing ratios were obtained in air sampled outside the Max-Planck-Institute for Chemistry (MPIC). The MPIC (49°59'27.5"N 8°13'44.4"E) is located on the outskirts of Mainz but within 200 m of two busy 2- and 4-lane roads and within 500 m of additional university buildings as well as commercial and residential areas. The city of Mainz (217k inhabitants) is located in the densely populated Rhine-Main-Area together with the cities of Frankfurt (753k) and Wiesbaden (278k) and the air is strongly influenced by local pollution. The sampling location was on the top floor of a three story building (ca. 12 m above ground level). Air was sub-sampled to the inlets of the instrument from a ~1 m long 0.5 inch outer diameter PFA tube which was connected to a membrane pump / flow controller to generate a 20 slm bypass flow. Aerosol transmission was probably < 100% in these measurements.

Figure 11a) summarises the 8-days of measurement (data coverage 82%) as a time series for NO\textsubscript{x}, NO\textsubscript{y}, NO\textsubscript{z}, (10 min averages) wind speed (1 hour averages) and the NO\textsubscript{z}/NO\textsubscript{x} ratio. The NO\textsubscript{x} and NO\textsubscript{y} mixing ratios were highly variable throughout this period, with NO\textsubscript{x} mixing ratios between 0.7 and 148.3 ppbv (mean and median values of 22.1 and 6.9 ppbv, respectively). Traffic-related morning rush-hour peaks in NO\textsubscript{x} were observed on all weekdays (14\textsuperscript{th}, 16\textsuperscript{th}, 17\textsuperscript{th} and 20\textsuperscript{th}) between 5:00 and 10:00 UTC. The morning NO\textsubscript{x} peak is reduced or absent on the weekends (18\textsuperscript{th} and 19\textsuperscript{th}). NO\textsubscript{x} levels stayed above 50 ppbv for nearly a full day from 18:00 UTC on the 16\textsuperscript{th} of January until 18:00 UTC on the 17\textsuperscript{th} of January, which coincides with constantly low wind speeds and sampling of air masses that were predominantly local, and thus highly polluted. NO\textsubscript{z} mixing ratios were usually between 0.5 and 2.5 ppbv (minimum < LOD, maximum 3.1 ppbv, mean 1.0 ppbv and median 0.9 ppbv), with NO\textsubscript{z}/NO\textsubscript{x} ratios below 0.5. These values indicate that the air masses have been impacted by recent (local) NO\textsubscript{x} emissions. The NO\textsubscript{z}/NO\textsubscript{x} ratio can be used as indicator for the degree of chemical processing of an air mass. In Fig. 11b) a median diel profile (including all measurement days) for the NO\textsubscript{z}/NO\textsubscript{x} ratio from the ambient measurement is shown. The diel profile displays two distinct minima in NO\textsubscript{z}/NO\textsubscript{x} during the morning and evening rush hour, where NO\textsubscript{z} only makes up 5-10% of the total NO\textsubscript{x}. This fraction increases up to 15% during midday and up to 25% during nighttime during which emissions of NO\textsubscript{x} are reduced. The diel profiles of NO\textsubscript{z}/NO\textsubscript{x} are strongly influenced by fresh emissions of NO\textsubscript{x}. As the measurement location is
strongly influenced by traffic, there is a decrease in NO\(_x\) (and increase in NO\(_2/\)NO\(_3\)) at nighttime. Nighttime increases in NO\(_z\) (13\(^{th}\)-14\(^{th}\), 15\(^{th}\)-16\(^{th}\), 18\(^{th}\)-19\(^{th}\) and 19\(^{th}\)-20\(^{th}\) of January 2020) may also be partially caused by formation of N\(_2\)O\(_5\) as previously observed (Schuster et al., 2009) and which would have been favoured by the low nighttime temperatures (< 10 °C) in winter. These measurements serve to illustrate the applicability of our TD-CRDS over a wide range of NO\(_x\) and NO\(_y\) concentrations under realistic field conditions and in the investigation of processes that transform NO\(_x\) into its gas- and particle-phase reservoirs.

5 Conclusions

We report on the development, characterisation and first deployment of a TD-CRDS instrument for the measurement of NO\(_x\), NO\(_y\), NO\(_z\) and pNit. Our laboratory experiments suggest that the different gas-phase NO\(_z\) species investigated (PAN, iPN, N\(_2\)O\(_5\), HONO, ClNO\(_2\), HNO\(_3\)) are converted with near stoichiometric efficiency to NO\(_x\) at an oven temperature of 850 °C. NH\(_4\)NO\(_3\) particles of diameter 200 nm are also detected quantitatively as NO\(_x\), whereas the efficiency of detection of NaNO\(_3\) particles of similar diameter was closer to 25%. The efficiency of detection of coarse mode particles will be further reduced by their lower transmission through the denuder.

The potential for NH\(_3\) to bias NO\(_y\) measurements was assessed and found to be insignificant in ambient air or synthetic air containing VOCs and water. The conversion to NO\(_2\) (by reaction with O\(_3\)) of atmospheric NO, and also NO formed in the heated inlet circumvents bias resulting from O\(_3\) thermolysis (leading to an NO\(_2\) overestimation) and secondary processes, initiated by the thermal dissociation of organic nitrates.

For our activated carbon denuder, we observed > 90% transmission for ammonium nitrate particles with diameters between 40 and 400 nm. Under humid conditions the denuder suffered from direct breakthrough of NO and the re-release of previously stored iPN and NO\(_2\) in the form of NO, indicating a potential bias of pNit measurements using this technique and potentially limiting its deployment to low-NO\(_x\) and low-NO\(_z\) environments. When using comparable denuders, we recommend regular checks with humidified zero air to characterize potential breakthrough. Our experiments demonstrated that the release of NO\(_x\) from the denuder exposed humid zero-air for several hours can decrease to values below 1 ppbv, which, in a first approximation could be treated as an offset. Cycling between multiple denuders would help in reducing the size of any bias.

The performance of the instrument under field conditions was demonstrated by measurements in Mainz, Germany and during the AQABA ship campaign. NO\(_x\) measurements with the new instrument were in good agreement with those from an established, independent CLD-based instrument.

Author contributions

NF developed the TD-CRDS, performed all laboratory and campaign measurements, evaluated the data sets and wrote the manuscript. IT and HF provided the AQABA CLD NO\(_x\) measurements. JS designed the heated inlet system and performed
actinic flux measurements on AQABA. JB, ED and FD provided AMS and OPC measurements from AQABA. JL and JNC
designed and supervised the study and the campaigns. JNC, JL and FD contributed to the manuscript.

**Competing Interests**

The authors declare that they have no conflict of interest.

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Table 1: Comparison of NO\textsubscript{x} and/or NO\textsubscript{y} measurements.

<table>
<thead>
<tr>
<th>Species</th>
<th>Reference</th>
<th>Method</th>
<th>2\sigma Level of detection (integration time)</th>
<th>Uncertainty (%)</th>
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<td>NO\textsubscript{x}</td>
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<td>CLD</td>
<td>20 pptv (1 s)</td>
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<td></td>
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<td>This Study</td>
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<td>~ 1.0 pptv (60 s)</td>
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<td>CRDS</td>
<td>40 pptv (60 s)</td>
<td>15 \textsuperscript{a}</td>
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</table>

Notes: \textsuperscript{a}Refers to gas-phase NO\textsubscript{y} only.
Figure 1: Schematic diagram of the TD-CRDS instrument (not to scale). NO\textsubscript{x} and pNit are detected via the heated channel, NO\textsubscript{x} via the ambient channel. Ozone is generated via a Pen-Ray lamp (185 nm) and serves to convert NO to NO\textsubscript{2}. TD = Thermal Dissociation, FC = flow controller. The flows listed are those used under normal operating conditions, p = pressure sensor, Ex = membrane pump and exhaust, Amb = ambient air outside of the chamber, V = electronically switchable PTFE valve. Filter = PTFE filter, 2 \( \mu \)m pore size). The inset (photo) shows the honeycomb structure of the activated carbon denuder. The critical orifices have diameters of \( \approx 0.05 \) mm.
Figure 2: Thermograms of the NO₂ species PAN, iPN, HNO₃, NH₄NO₃, N₂O₅, HONO, ClNO₂ and the potential interference NH₃ (without added O₃). The NH₃ fractional conversion is calculated relative to the calibrated output of the employed permeation source, all others relative to the observed mixing ratio at maximum conversion. Error bars are derived from the normed standard deviations during the averaging intervals. At the set temperature of 850 °C PAN, iPN, NH₄NO₃, N₂O₅ (x2), HONO and HNO₃ are converted quantitatively to NO₂, while the NH₃ interference is negligible under common ambient conditions.
**Figure 3:** NH$_3$ to NO$_x$ conversion in the heated inlet channel of the instrument in the presence of O$_3$. The fractional conversion of NH$_3$ to NO$_x$ is calculated from the 13.1 ppmv of NH$_3$ from the permeation source.
**Figure 4:** Investigation of bias caused by reactions of NO with HO$_2$ and RO$_2$ when measuring iPN. 

*a)* NO varied for two initial iPN mixing ratios in the presence (blue data points) and absence (orange data points) of added O$_3$. The NO$_x$ background signal from the iPN cylinder was subtracted from the iPN mixing ratios.

*b)* Investigation of bias caused by the recombination of RO$_2$ and NO$_2$ during the thermal decomposition of PAN. In both experiments the oven temperature was 850 °C. In both plots, the error bars indicate standard deviation over the averaging interval.
**Figure 5:** Transmission of ammonium nitrate particles through the denuder inlet. Relative transmissions are derived by dividing the number size distribution when sampling through the denuder by a size distribution obtained without the denuder. Error bars are based on the standard deviation of three consecutive measurements with and without the denuder. An aerosol flow of 3.3 slm was directed through the denuder (diameter 3 cm, see Sect. 2.4) and subsequently a DMA sampled 0.3 slm from the stream exiting the denuder. The plot also includes a fit of the experimental (solid, black line) data and a theoretical transmission distribution computed with the *Particle Loss Calculator (PLC)*.
Figure 6: Removal efficiency of the denuder for various NO\textsubscript{y} trace-gases as a function of RH. Units of the inset are identical to the main graph. See Table S2 for the exact values and information on the error determination.
Figure 7: a) Release of NO$_x$ from the denuder in humid air after exposure to 9.5 ppmv iPN for 1.5 hours. Relative humidity was measured before passing through the denuder. The blue shaded area signifies the period in which the inlet oven was heated to 850 °C. Changes in RH are achieved by flowing parts of the zero air stream through deionized water. b) Release of NO$_x$ from the denuder in humid air after exposure to 0.83 ppmv NO$_2$ for 4.8 days. O$_3$ addition was switched off during the blue shaded period.
Figure 8: a) RH of humidified zero air after passing through the denuder. The initial RH was determined by bypassing the denuder before and after the experiment. Zero air was humidified by flowing a fraction of the stream through deionized water stored in a glass vessel. The time at which the experiment was conducted is given on the x-axis. Until ca. 09:35 UTC, zero-air with constant humidity (RH ca. 68%) was sent through the denuder. Afterwards the denuder was exposed to dry zero air. b) Derivative of the measured RH during the drying period. The step during the drying phase occurs in a higher RH area when starting the drying from a larger RH value.
Figure 9: Number of adsorbed water molecules onto the denuder surface at equilibrium versus RH. The red line represents (scaled) results from a study on activated carbon fibre (Kim et al., 2008).
Figure 10: a) Correlation between the TD-CRDS NO$_x$ measurements (1 min averages) and an independent CLD NO$_x$ instrument from the AQABA. Data obtained during phases of very high NO$_x$ variability have been excluded (see Sect. 4.1). See Fig. S6 for a histogram of the NO$_x$ data points. b) pNit measurements using the denuder channel (blue data points) during AQABA and comparison with particulate NO$_3^-$ from an AMS. The discrepancy towards the AMS and the correlation with the NO$_x$ mixing ratios indicate a positive bias in the pNit measurements, caused by humidity effects on the denuder surface. OPC measurements are added in the lower panel to assess the potential influence of coarse mode aerosol nitrates.
Figure 11: a) Time series of NO\textsubscript{x}, NO\textsubscript{y}, NO\textsubscript{z}, NO\textsubscript{y}/NO\textsubscript{z} and wind speed from ambient measurements in Mainz, Germany in January 2020. Highly variable NO\textsubscript{x} (between 0 and 150 ppbv) and moderate NO\textsubscript{z} (between 0 and 3 ppbv) mixing ratios were observed, identifying the sampled air masses as dominated by anthropogenic emissions. Wind speed data was obtained from Agrarmeteorologie Rheinland-Pfalz (wetter.rlp.de) b) Diel profile of the NO\textsubscript{y}/NO\textsubscript{z} ratio including all measurement days, showing distinct minima during the morning and evening rush hours. Shaded areas signify the time between sunset and sunrise.