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Supplement of

A five-channel cavity ring-down spectrometer for the detection of NO₂, NO₃, N₂O₅, total peroxy nitrates and total alkyl nitrates

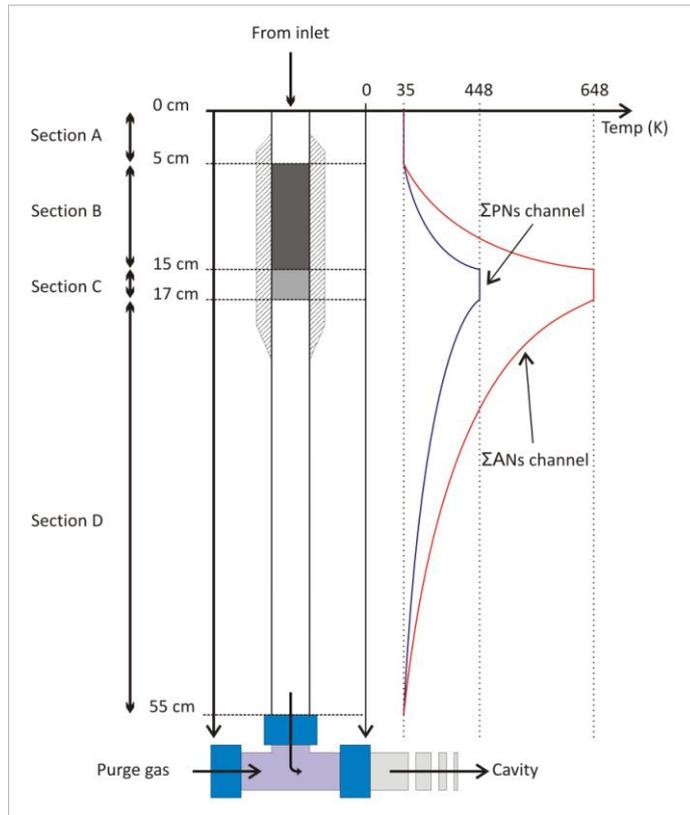
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Heated inlets for the Σ PNs and Σ ANs channels

The following schematic diagram outlines the construction of the heated inlets. Air at ambient temperature flows through section A before being heated in section B, which is filled with glass beads of ~ 0.5 mm diameter which rest on a glass frit support (section C). The temperature profile downstream of the heated volume (section D) was measured by insertion of a thermocouple, whereas those of sections B and C are estimated.



l-to-d ratio

The distance between the cavity mirrors (d , optical length) is the same for all five cavities (approximately 93 cm). However, the length over which the sampled air circulates (l , absorbing length) is shorter and corresponds roughly to the distance between the inflow and outflow T-pieces (≈ 72 cm). For all five channels, the ambient air flowing through the cavity mixes with the purge gas stream and is thus diluted by a factor that depends on the relative flow rates of air and purge gas. The modification of the absorber length and dilution effects caused by using purge gas to protect the mirrors can be combined into one single correction factor which can be determined experimentally by comparing the NO_2 concentration in two channels, one being operated normally (with purge gas) while the second one is modified so that the NO_2 / air sample completely fills the cavity including the purge gas volume. The value l/d was found to be 0.69 ± 0.02 for the channels

detecting at 405 nm and 0.77 ± 0.04 for the channels detecting at 662 nm. These numbers are entirely in accord with simple calculations based on the construction of the cavities (i.e. distances between mirrors and inlet/outlet T-pieces) and purge gas flow rates suggesting that there is negligible mixing of purge gas and ambient air close to the mirrors.

NO₃ and N₂O₅ losses in the filter changer

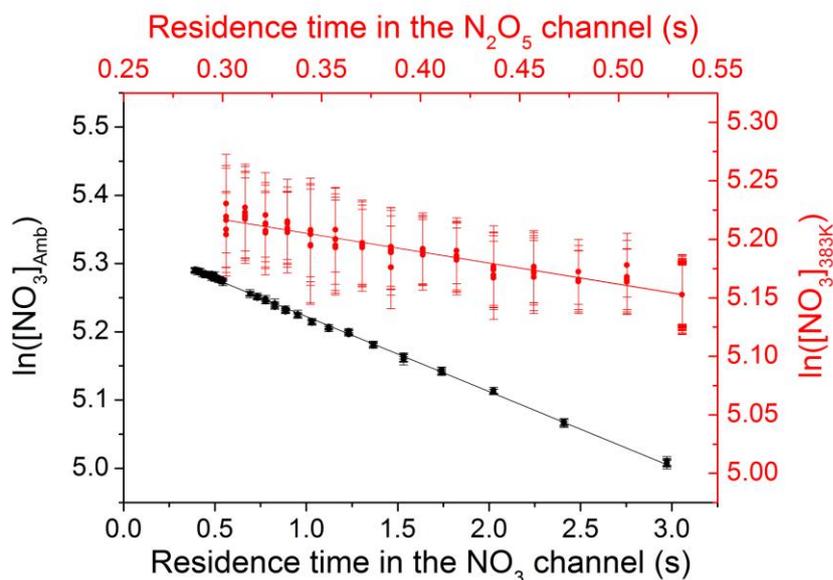
The custom-built filter changer used in this instrument consists of a circular plate that transports filters from a supply stack in a cylinder (flushed with dry synthetic air or N₂) to a holder and from the holder to a used-filter-dump. The holder is made of two conical, FEP coated stainless steel parts that are pressed together by springs to hold the filters and forced apart pneumatically during filter changes.

Typically, filters are changed every hour during field deployment of the instrument, which has been sufficient to minimise the loss of NO₃ or N₂O₅ on contaminated filters (Dorn et al., 2013). Measurement of the loss of NO₃ and N₂O₅ on passing through the filter holder equipped with a fresh filter was performed by flowing a sample of NO₃ in synthetic air alternatively through the filter changer or through a short PFA bypass line. NO₃ was generated by mixing NO₂ and photochemically produced O₃. Under typical flow conditions (15 slm passing through the filter holder at ≈ 850 mbar) the loss of NO₃ was $30 \pm 3\%$ (statistical error) assuming no losses in the PFA $\frac{1}{4}$ " bypass line. No losses of N₂O₅ on passage through the filter holder were observed.

NO₃ and N₂O₅ losses in the cavities

The cavities as well as the NO₃ titration volume and the N₂O₅ decomposition reactor are all coated with FEP. However, losses of radicals (especially NO₃) to surfaces during passage through the inlets and cavities remain non negligible. Different methods of estimating these losses are found in the literature (Dubé et al., 2006; Fuchs et al., 2008). The method used here consists of varying the individual flows of an NO₃ / synthetic air sample through both channels while keeping the total flow (and thus the NO₃ mixing ratio) constant. In this way, losses in the main inlet of the instrument and in the filter changer remain constant while the residence time in each channel is varied. The results of such an experiment are displayed in Fig. S2, which shows an exponential decrease in [NO₃] in both channels as a function of the residence time. In this case, values of $0.1101 \pm 0.0006 \text{ s}^{-1}$ (2σ) and $0.28 \pm 0.01 \text{ s}^{-1}$ were obtained for the NO₃ and the N₂O₅ channels, respectively. The values obtained are enhanced above that for wall loss alone by the reaction of NO₃ with NO₂, which is present in the gas-mixture used to generate NO₃. To account for this, a simulation of NO₃ loss processes using the initial [NO₂] value and rate constants for the reaction of NO₂ with NO₃ (R2) and

the thermal decomposition of N_2O_5 (R3) was performed. The resulting wall loss rate was calculated to be 0.06 s^{-1} for the NO_3 channel. This value is retained to correct $[\text{NO}_3]$ field data. The effective value of 0.28 s^{-1} can be used to correct the NO_3 losses in the N_2O_5 channel directly, as the loss of NO_3 via formation of N_2O_5 is offset by the large thermal dissociation rate constant of N_2O_5 at 383 K in comparison with the formation reaction of N_2O_5 . The value 0.28 s^{-1} for the N_2O_5 channel was obtained using a reduced range of residence times due to the degradation of the signal when running this channel at flow rates lower than 4 slm. This effect is not documented in the literature and is thought to be specific to our instrument design and is likely due to flow patterns resulting in enhanced turbulence under some conditions. The wall loss rates obtained are of the same order of magnitude as previous values obtained for NO_3 uptake on Teflon coated surfaces or PFA tubing (Schuster et al., 2009). The difference in loss rate between the cold and the hot channel is likely due to enhanced rates of transport of NO_3 to the walls in the more turbulent conditions and to the increases uptake coefficient. Finally, the transmissions for NO_3 in the NO_3 and N_2O_5 channels are $97.4 \pm 2.5 \%$ and $90.2 \pm 5 \%$, respectively. The error of both values is a conservative estimation based on the variability of wall loss rate constants over time (i.e. prior to and after a campaign), which may reflect variation in the reactivity of the inlet and cavity walls after sampling different air masses.



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