

A thermal dissociation–chemical ionization mass spectrometry (TD-CIMS) technique for the simultaneous measurement of peroxyacyl nitrates and dinitrogen pentoxide

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[1] We have developed a thermal dissociation–chemical ionization mass spectrometry (TD-CIMS) technique for fast measurements of a series of peroxyacyl nitrates and dinitrogen pentoxide. Thermally generated acylperoxy radicals react with I^- to produce a carboxylate ion that is unique for each parent species. NO_3 resulting from the decomposition of N_2O_5 reacts with I^- to form NO_3^- . The measurement technique was verified for PAN and PPN during an informal comparison with a gas chromatograph (GC) equipped with an electron capture detector (ECD) in Boulder, Colorado, during October 2002. Good agreement was obtained between the two instruments with $R^2 = 0.91$ for PAN ($n = 657$) and $R^2 = 0.89$ for PPN ($n = 655$). Detection limits of 7 pptv and 4 pptv were determined for PAN and PPN, respectively, for a 1 s integration period and a signal-to-noise ratio of 3. The TD-CIMS simultaneously detected ambient PiBN and $N_2O_5 + NO_3$ in addition to PAN and PPN during the intercomparison period. We estimate a detection limit of 3 pptv in 1 s for PiBN. PnBN would be detected at the same mass, so we cannot rule out a contribution from PnBN to our PiBN estimate. Sensitivity to MPAN was found to be lower than to PAN in laboratory experiments, but a detection limit of 10 pptv can still be achieved by integrating for 15 s. Assuming the same sensitivity as for PAN, the detection limit for the sum of N_2O_5 and NO_3 was estimated to be 12 pptv in 1 s. The fast time response of the TD-CIMS combined with a sensitivity and limit of detection comparable to the GC/ECD make this a promising technique for PAN flux measurements by eddy covariance. PAN uptake by different types of vegetation could be important input for global and regional ozone models, and PAN deposition to snow is of interest in polar regions.

INDEX TERMS: 0315 Atmospheric Composition and Structure: Biosphere/atmosphere interactions; 0330 Atmospheric Composition and Structure: Geochemical cycles; 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 0368 Atmospheric Composition and Structure: Troposphere—constituent transport and chemistry; 0394 Atmospheric Composition and Structure: Instruments and techniques; **KEYWORDS:** PAN, N_2O_5 , CIMS

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1. Introduction

[2] Peroxyacyl nitrates and N_2O_5 can serve as important temporary reservoirs of reactive nitrogen oxides. Peroxyacyl nitrates are formed from association reactions between peroxyacyl radicals ($RC(O)O_2$) and nitrogen dioxide (NO_2), and N_2O_5 is produced by the association reaction of NO_2 with NO_3 . The lifetimes of both peroxyacyl nitrates and dinitrogen pentoxide are largely controlled by thermal decomposition, especially near the earth's surface [Roberts

and Bertman, 1992; Cantrell *et al.*, 1993; Atkinson *et al.*, 1999]. Photolysis becomes more important for peroxyacyl nitrates in the upper troposphere, and reaction with OH can be a factor for the more reactive analogs [Talukdar *et al.*, 1995; Harwood *et al.*, 2003; Orlando *et al.*, 2002]. Peroxyacetyl nitrate (PAN, CH₃C(O)O₂NO₂), in particular, may serve as a means for transporting NO_x to remote areas due to its abundance and relatively long lifetime (up to months) at temperatures characteristic of the middle and upper troposphere [Moxim *et al.*, 1996; Bridier *et al.*, 1991; Singh and Hanst, 1981; Cox and Roffey, 1977]. This is important because photochemical production of ozone in remote areas might increase when NO_x is released from transported PAN [Crutzen, 1979]. In fact, Singh and Hanst [1981] have suggested that transported PAN might control the photochemical production of O₃ in much of the remote marine troposphere.

1.1. Peroxyacyl Nitrates

[3] PAN is the simplest and most abundant peroxyacyl nitrate. It is formed from atmospheric degradation of a wide variety of natural and anthropogenic sources such as isoprene, acetaldehyde, acetone, methylglyoxal, and other assorted nonmethane hydrocarbons. Of the many larger analogs which have been identified, peroxypropionyl nitrate (PPN, CH₃CH₂C(O)O₂NO₂) and peroxyethacryloyl nitrate (MPAN, CH₃C(CH₃)C(O)O₂NO₂) have been singled out as especially interesting because they have distinctly different precursors. PPN is believed to be formed primarily from anthropogenic hydrocarbons, while the MPAN precursor, isoprene, is mainly biogenic in origin [Tuazon and Atkinson, 1990; Moore *et al.*, 1994; Milne *et al.*, 1995; Guenther *et al.*, 1995]. Their abundances relative to PAN can give us important information about the nature of photochemical ozone precursors [Williams *et al.*, 1997], but caution should be exercised in drawing conclusions from their relative concentrations due to differing lifetimes. Specifically, MPAN has a much shorter lifetime due to reaction with OH [Orlando *et al.*, 2002].

[4] The best developed and most commonly used technique for measuring PAN is gas chromatography with electron capture detection (GC/ECD). The original GC/ECD technique [Darley *et al.*, 1963] has been improved through the use of capillary columns [Roberts *et al.*, 1989]. It can now provide measurements of PAN; PPN; MPAN; APAN (peroxyacryloyl nitrate, CH₂CHC(O)OONO₂); and PiBN (peroxyisobutryl nitrate, CH₃CH(CH₃)C(O)O₂NO₂), a highly phytotoxic photooxidation product of gasoline vapor [e.g., Taylor, 1969; Roumelis and Glavas, 1992; Singh and Salas, 1983], every 5 min [Williams *et al.*, 2000; Roberts *et al.*, 2001] with a detection limit of 5 pptv for PAN. A sampling rate of 1 min for PAN, PPN, and PiBN (but not MPAN) with a PAN detection limit of 10 pptv has been achieved by replacing the ECD with a luminol-based detector [Gaffney *et al.*, 1999]. Recently, gas chromatography has also been coupled with negative ion chemical ionization mass spectrometry detection (GC/NICI-MS) [Tanimoto *et al.*, 1999; Tanimoto and Akimoto, 2001]. The GC/NICI-MS technique has a detection limit of 15 pptv PAN for a 10 minute sampling period. Other promising new methods for detecting PAN include proton transfer mass spectrometry (PTR-MS) [Hansel and Wisthaler, 2000], and

thermal decomposition followed by laser-induced fluorescence (LIF) of NO₂ [Day *et al.*, 2002]. Currently the PTR-MS technique is less sensitive to PAN than the GC techniques, and there is concern that peroxyacetic acid may cause significant interference [de Gouw *et al.*, 2003]. Because the thermal dissociation/LIF instrument measures the sum of all species which produce NO₂ upon thermal decomposition at a given temperature, speciation of the individual peroxyacyl nitrates cannot be achieved.

[5] The ideal peroxyacyl nitrate measurement technique for aircraft use would be comparable to the GC/ECD system in sensitivity, selectivity, and payload yet have a much shorter time response. A faster measurement, like the chemical ionization mass spectrometry technique we present here, would greatly increase the spatial resolution of the PAN data obtained from an aircraft platform. This would allow the measurement of PAN in transient features such as power plant plumes or ship plumes [Ryerson *et al.*, 2001; Neuman *et al.*, 2002].

[6] The response time of the chemical ionization mass spectrometer (CIMS) might also allow for the measurement of PAN fluxes by the eddy correlation technique. One application for this type of measurement is the determination of PAN uptake by vegetation. Not only is this important because PAN is phytotoxic [Taylor, 1969; Temple and Taylor, 1983; Okano *et al.*, 1990; Sun and Huang, 1995], but PAN loss near the surface may be an important input for global and regional ozone models. A variety of plants have been shown to both assimilate and emit NO₂ [e.g., Johansson, 1987; Weber and Rennenberg, 1996; Sparks *et al.*, 2001], but little is known about the flux of NO_y (sum of all reactive nitrogen species) or its non-NO_x constituents near plant canopies. Bakwin *et al.* [1990] observed a persistent downward flux of NO_y above a tropical forest canopy with a much larger deposition rate during the day than night. Net flux of PAN is also presumably toward plants, and its uptake by plants has been observed to be controlled by stomatal processes [Okano *et al.*, 1990; Sparks *et al.*, 2003]. McFadyen and Cape [1999] concluded that deposition to soil and vegetation is the largest sink for PAN in the rural UK if their parameterization of surface exchange is correct. Their assumptions about stomatal resistance are made entirely from deposition velocities measured or inferred at night [Schrimpf *et al.*, 1996; Shepson *et al.*, 1992] when stomata are mostly closed. There have been limited studies of PAN deposition velocities to grass, soil, and alfalfa [Hill, 1971; Garland and Penkett, 1976]. More direct studies of PAN deposition to forested areas, tropical plants, and other types of crops would be especially beneficial.

[7] Another area where flux measurements would be useful is over snow-covered surfaces. There has been recent speculation in the literature that PAN could play a role in NO_y transfer between snow and the air above it, potentially influencing ice core nitrate records [Dibb *et al.*, 1998; Munger *et al.*, 1999; Jacobi *et al.*, 2000; Ford *et al.*, 2002]. PAN has been suggested as a potential source of NO₃⁻ in surface snow at Summit, Greenland, where low levels of gas phase HNO₃ cannot account for observed enhancements [Dibb *et al.*, 1998]. This is somewhat controversial because PAN is not very soluble in water [Kames and Schurath, 1995] and it is not expected to readily deposit to the snow surface [Bottenheim *et al.*, 1986; Shepson *et al.*,

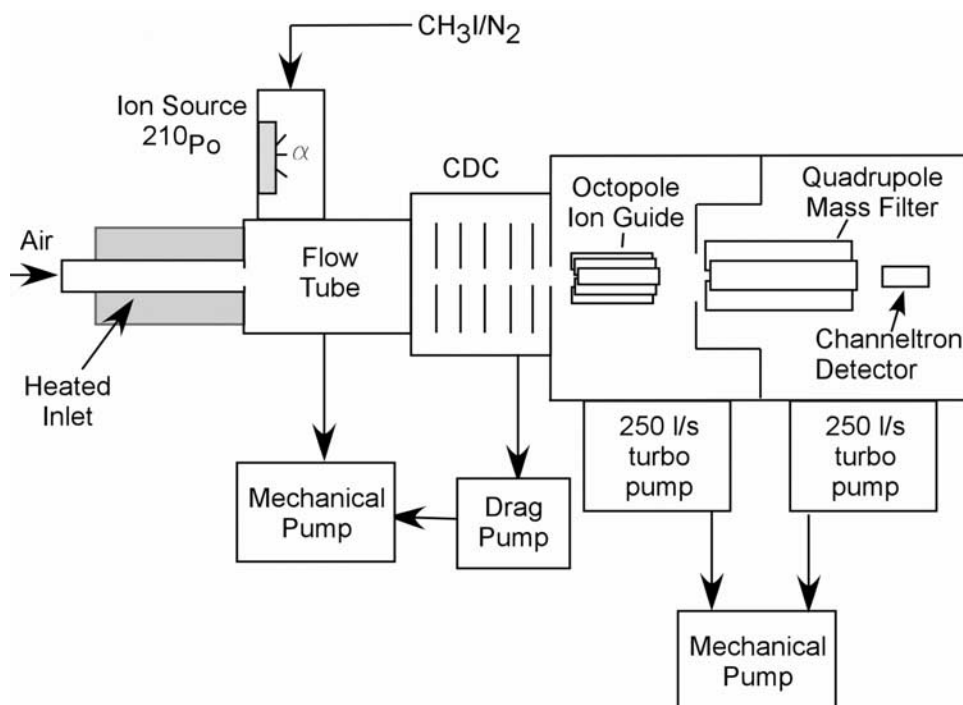


Figure 1. Instrument schematic.

1996]. However, reports of reversible PAN adsorption on ice by *Munger et al.* [1999] have been supported by chamber experiments performed by two recent studies. Chamber experiments performed by *Ford et al.* [2002] indicate weak uptake of PAN onto snow grains. *Bartels-Rausch et al.* [2002] report an adsorption enthalpy of -30 kJ mol^{-1} for PAN on crystalline ice. This falls between their measurements of the adsorption enthalpies for HNO₃ (-44 kJ mol^{-1}) and NO₂ (-20 kJ mol^{-1}), and it indicates that a relatively small fraction of gaseous PAN should partition to the snow at temperatures $\geq -27^\circ\text{C}$ (ratio of adsorbed to gas phase PAN at $-27^\circ\text{C} = 0.08$ vs. 0.30 for HONO and 90 for HNO₃). The observation of elevated concentrations of PAN in snow at Summit compared to the air above it implies an upward flux out of the snow [*Ford et al.*, 2002]. An attempt to measure PAN fluxes between snow and the air above it at Neumayer Station, Antarctica, was made by alternating measurements at two different heights, but the difference between the concentrations was frequently below the precision of the measurements and no direction could be determined [*Jacobi et al.*, 2000].

1.2. Dinitrogen Pentoxide

[8] Formation of dinitrogen pentoxide in the nocturnal boundary layer can lead to a net reduction in photochemical ozone production capacity due to its role in NO_x removal. N₂O₅ acts as a NO_x sink through heterogeneous reaction on cloud drops or aerosols [*Tuazon et al.*, 1983; *Livingston and Finlayson-Pitts*, 1991; *Hu and Abbatt*, 1997; *Schweitzer et al.*, 1998]. Hydrolysis of N₂O₅ has been shown to produce HNO₃ as efficiently at night as the reaction of OH with NO₂ during the day [*Geyer et al.*, 2001]. As a sink for NO₃, N₂O₅ removal also reduces the nighttime degradation of monoterpenes [*Gölz et al.*, 2001] and dimethylsulfide [*Winer et al.*, 1984; *Platt and Le Bras*, 1997] which might

otherwise lead to the production of peroxy radicals [*Platt et al.*, 1990; *Mihelcic et al.*, 1993]. Previous in situ measurements of N₂O₅ indicate that a fast time response is needed in order to capture its temporal variability [*Brown et al.*, 2001, 2003]. However, at the present time there are few viable methods for in situ measurement of this species [*Brown et al.*, 2001; *Wood et al.*, 2003].

[9] In this work, a new thermal decomposition–chemical ionization mass spectrometry (TD-CIMS) technique is described and the results of initial characterization experiments are presented. Validation of this technique for measuring PAN and PPN was performed by comparison with NCAR GC/ECD measurements. The results of this informal intercomparison conducted in Boulder, Colorado during October 2002 are included as well. We also present in situ measurements that demonstrate the ability of the TD-CIMS instrument to simultaneously detect atmospheric PiBN and N₂O₅ with the peroxyacyl nitrates listed above. The sensitivity of the TD-CIMS to MPAN is also estimated.

2. Experiment

2.1. Instrumentation

[10] This instrument has been modified from that described by *Leibrock and Huey* [2000] by the addition of a collisional dissociation chamber (CDC) [*Tanner et al.*, 1997] between the flow tube and the vacuum chamber and replacement of the ion lens stack by an octopole ion guide [*Hägg and Szabo*, 1986] as shown in Figure 1. Ambient air is sampled into the TD-CIMS through heated 0.95 cm o.d. PFA (perfluoroalkoxy alkane) Teflon tubing. The final 14.8 cm of the inlet tubing in front of the flow tube sampling orifice is heated to an external temperature of 160–180°C depending on the total flow rate through the inlet (2–3 slpm). This efficiently dissociates peroxyacyl

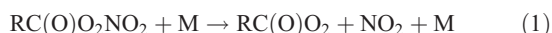
nitrites and N₂O₅ before they enter the ion-molecule reaction region. We estimate that the temperature of the gas on the axis of the inlet is 103–117°C for these experimental conditions using the method of Gilbert [1958].

[11] At an inlet pressure of 740 torr (9.87×10^4 Pa), 1.55 slpm is sampled into the flow tube and the excess inlet flow is exhausted through a diaphragm pump. The air drawn into the low-pressure (~ 20 torr or ~ 2.7 kPa) flow tube mixes with I[−] that is introduced directly from the ²¹⁰Po ion source. Ion-molecule reactions occur over the length of the flow tube. Ionized species are accelerated through the CDC via an axial electric field of approximately 25 V cm^{-1} . The CDC is maintained at <0.5 torr (<67 Pa) with a molecular drag pump (Alcatel MDP-5011). Energetic collisions inside the CDC ($\sim 50 \text{ kJ mole}^{-1}$) dissociate weakly bound cluster ions such as I[−](H₂O)_n and CH₃C(O)O[−](H₂O)_n into the core ions, resulting in simplified mass spectra. Finally, the ionized products are guided through the vacuum chamber by the octopole and analyzed with the quadrupole mass spectrometer. The combination of the actively pumped CDC and octopole ion guide led to a gain in detected ion current of roughly an order of magnitude over the previous version of the CIMS.

2.2. Ion Chemistry

[12] We use I[−] to detect the radical products of the thermal dissociation of peroxyacyl nitrates and dinitrogen pentoxide (reactions 1–4 below). I[−] is a very selective reagent ion because it is unreactive with almost all atmospheric species [Huey et al., 1995]. I[−] is synthesized by dissociative electron attachment to either CH₃I ($k \sim 1 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$ at 20°C) [Burns et al., 1996, and references within] or CF₃I ($k = 2.2 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$ at 20°C) [Burns et al., 1996]. CH₃I is preferred because it does not cluster to I[−] as strongly as CF₃I does and because CF₃I produces a significant signal due to CF₃O[−] at 85 amu, interfering with MPAN product ion (CH₂C(CH₃)C(O)O[−]) detection at that mass. For the experiments in this paper, we flowed roughly 1 sccm of a 0.5% CH₃I/N₂ mixture into the ion source with an additional 4 slpm of nitrogen.

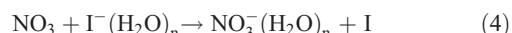
[13] PAN thermally dissociates in the inlet to form CH₃C(O)O₂ and NO₂. The CH₃C(O)O₂ reacts with I[−] to form CH₃C(O)O[−] and IO ($k = 9_{-5}^{+7} \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ in He at ~ 0.5 torr or 67 Pa) [Villalta and Howard, 1996]. Other analogs such as MPAN, PPN, and PiBN are detected in a similar manner following the general pattern:



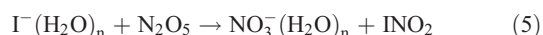
The carboxylate ion forms stronger bonds with water ($n = 1-3$) than does I[−] (J. E. Bartmess, Negative ion energetics data, in NIST Chemistry WebBook, NIST Standard Reference Database Number 69, edited by P. J. Linstrom and W. G. Mallard, National Institute of Standards and Technology, Gaithersburg, Md., 2003) (hereinafter referred to as Bartmess, NIST Chemistry WebBook, 2003). The most abundant water cluster of the acetate ion observed was $n = 2$ (product mass 95 amu) at flow tube $[\text{H}_2\text{O}] \approx 2 \times$

$10^{15} \text{ molecule cm}^{-3}$ when the instrument was used without a collisional dissociation chamber. However, the most abundant acetate cluster was $n = 0$ in the normal operation mode with the CDC.

[14] Both N₂O₅ and NO₃ are detected as NO₃[−]. Dinitrogen pentoxide forms NO₂ and NO₃ upon thermal dissociation in the inlet. Once the NO₃ enters the flow tube, I[−] charge transfers to it to form NO₃[−] [Davidson et al., 1977; Hanstorp and Gustafsson, 1992]:

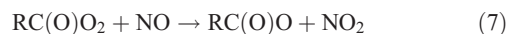
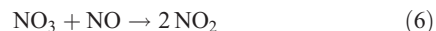


N₂O₅ also reacts directly with I[−] to form NO₃[−] [Fehsenfeld et al., 1975; Davidson et al., 1977; Huey et al., 1995]:



2.3. Background Determinations

[15] Background measurements were primarily made by adding a minimum of 1 ppmv of NO (Scott-Marrin) to the inlet to titrate both the NO₃ and the peroxyacyl radicals [Villalta and Howard, 1996; de Gouw and Howard, 1997; Froyd and Lovejoy, 1999; Maricq and Szente, 1996]:



Adding NO to the heated inlet provides a background for the combined measurement of NO₃ and N₂O₅, but it does not differentiate between them. If an unheated inlet were used, added NO would react with ambient NO₃ according to reaction (6) while N₂O₅ remained intact. Any NO₃[−] formed in the flow tube would probably be a result of reaction (5). Therefore the ambient NO₃ signal could be estimated by taking the difference between the NO₃[−] signals obtained using an experimental configuration with heated and unheated inlets. It should be noted that ClONO₂ and BrONO₂ are also detected as NO₃[−] using I[−] chemistry [Huey et al., 1995; Hanson et al., 1996], but they should not be significant interferences in the troposphere. Potential exceptions are the polar boundary layer and salt lake areas where up to 30 pptv and 176 pptv, respectively, of reactive Br species have been measured [Platt and Hönninger, 2003].

[16] An alternative method for determining background concentrations is to draw (preferable) or force ambient air through a coil of hot (125°C) metal tubing upstream of the inlet heater. Thermally generated radicals are lost to the surface of the tubing. In a cursory check, no difference was observed between PAN background measurements obtained this way versus NO addition. A more thorough analysis of a statistically significant sample of

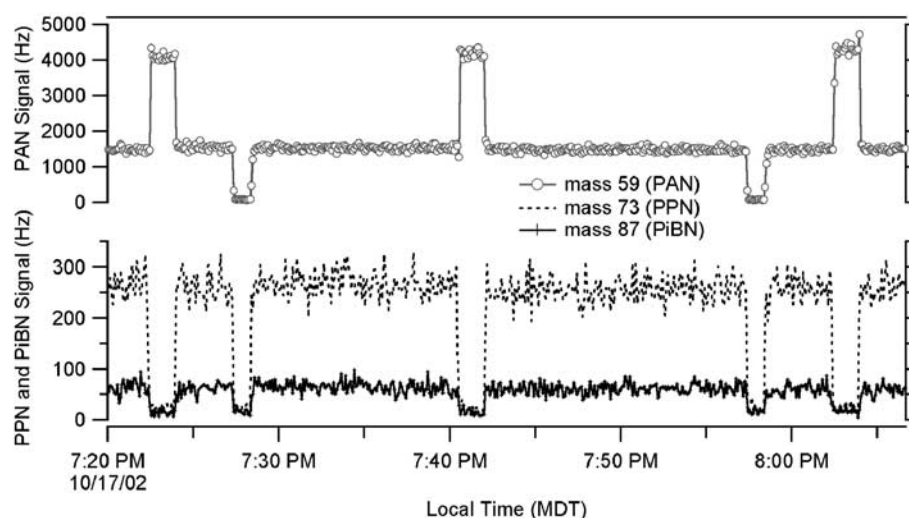


Figure 2. Raw data: 0.5 s at each mass. Shown are three PAN calibrations and two background determinations via NO addition. Note that PPN and PiBN are zeroed during PAN calibrations due to catalytic destruction on hot metal tubing.

ambient PPN and N₂O₅ + NO₃ background measurements obtained by NO addition versus thermal decomposition can be found in section 4.1.

2.4. Calibration

[17] The instrument was calibrated by periodically adding a known amount of PAN to the inlet from a photolytic source similar to that described by Warneck and Zerbach [1992]. Calibration gas was added to PAN-free air produced from ambient air pumped through hot metal tubing. As noted above, this also destroyed the other peroxyacyl nitrates and N₂O₅, thus providing a zero for other species when PAN was calibrated. The calibration source we utilized has been used successfully during the 2000 Texas Air Quality Study (TexAQS) [Roberts *et al.*, 2001] and several more recent field campaigns. The yield of PAN from this technique was assumed to be $93 \pm 3\%$ as was determined for those campaigns. Diffusion sources [Williams *et al.*, 2000] were used to verify the PAN output of the photolytic source and to provide samples of PPN and MPAN. The well-characterized response of the GC to these compounds was used to determine the output of the diffusion sources.

[18] The PAN sensitivity obtained from calibrations was used to estimate the concentrations of PAN, PPN and N₂O₅ + NO₃. The sensitivity to these species should be approximately equal assuming they react with I[−] at roughly the same rate. Future work will focus on calibrating the N₂O₅ signal with a source similar to that used in previous work [e.g., Davidson *et al.*, 1978; Fahey *et al.*, 1985; Cantrell *et al.*, 1987].

3. Instrument Characterization

3.1. Sensitivity

[19] Figure 2 illustrates the instrument sensitivity, the relatively low and stable background, and the fast time response when switching between measurement, background, and calibration modes. TD-CIMS sensitivities are summarized in Table 1 along with the typical detection limits and corresponding background concentrations observed for each species. The detection limits are defined at a signal-to-noise ratio of three where the noise is the standard deviation of the background measurement. The photolytic calibration source described above was used to determine the TD-CIMS PAN sensitivity under the measurement operating

Table 1. Summary of Typical Sensitivities and Detection Limits

Ambient Species	Thermal Decomposition Product ^a	Product Ion	Sensitivity at 1 MHz I [−] , Hz pptv ^{−1}	Typical 1 s Detection Limit, ^b pptv	Typical Background, pptv
PAN	CH ₃ C(O)O ₂	CH ₃ C(O)O [−]	4.2	7	21
PPN	CH ₃ CH ₂ C(O)O ₂	CH ₃ CH ₂ C(O)O [−]	4.2	4	6
MPAN	CH ₂ C(CH ₃)C(O)O ₂	CH ₂ C(CH ₃)C(O)O [−]	0.67	39	N/A
PiBN	CH ₃ CH(CH ₃)C(O)O ₂	CH ₃ CH(CH ₃)C(O)O [−]	4.9 ^{c,d}	3 ^{c,e}	4 ^{c,d}
N ₂ O ₅ + NO ₃	N/A	NO ₃ [−]	4.2 ^c	12 ^c	37 ^c

^aPlus NO₂.

^bSignal to noise ratio 3:1.

^cEstimated.

^dUpper limit.

^eLower limit.

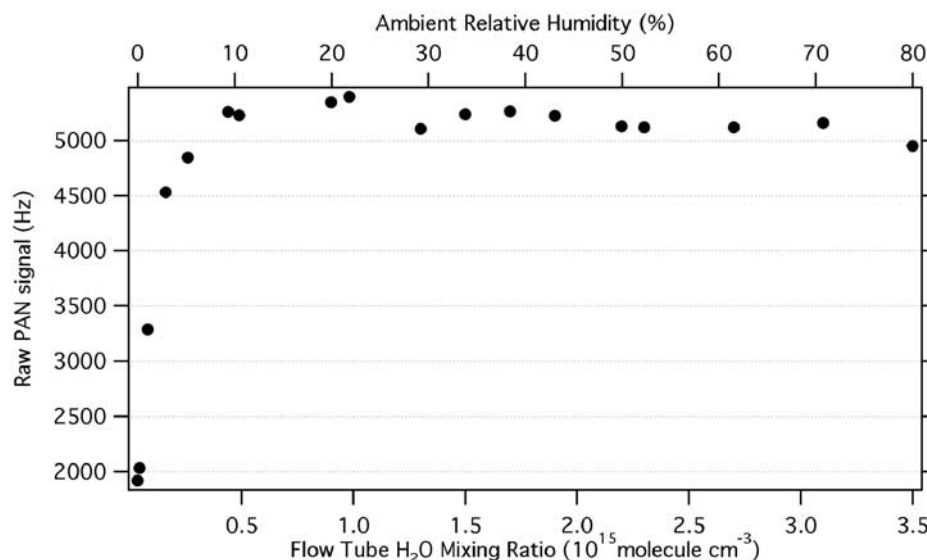


Figure 3. PAN sensitivity of TD-CIMS as a function of humidity. Ambient pressure is 740 torr (9.87×10^4 Pa). Ambient temperature is 21°C. Flow tube pressure is 20 torr (2.7 kPa).

conditions. Sensitivities to PPN and MPAN, both absolute and relative to PAN, were determined from standard addition tests that utilized diffusion sources. Equivalent sensitivity was assumed for PAN and N₂O₅ + NO₃ based on the assumption that their thermal decomposition products react at very similar rates (i.e., close to gas kinetic) with I[−]. Historical GC/ECD sensitivity to PiBN relative to PAN was used to estimate the PiBN concentrations from which the TD-CIMS sensitivity was derived.

[20] The TD-CIMS was found to have equivalent sensitivity to PPN and PAN, but MPAN sensitivity was found to be considerably lower. We are not sure why the TD-CIMS is less sensitive to MPAN than to PAN or PPN. More tests will be required to determine if peroxyacetyl radical reacts more slowly with I[−] or if it is lost efficiently to the walls or competing reactions. The limit of detection for MPAN is still low, 39 pptv in 1 s in this case, and it can be made more comparable to the other detection limits by averaging for longer periods of time. The detection limit decreases in proportion to the square root of the integration time.

[21] The sensitivity of the TD-CIMS instrument to PAN was observed to have the humidity dependence shown in Figure 3 when nitrogen with varying amounts of water was used as the inlet carrier gas. The PAN signal more than doubles between 0 and 10% relative humidity, reaching a maximum around 20%. In order to differentiate between inlet effects and ion chemistry, dry nitrogen was delivered to the inlet and water was added directly to the flow tube via the ion source. The same maximum PAN signal was obtained once the signal at 145 amu (I[−](H₂O)) reached the corresponding level in the inlet water experiment (120 Hz), indicating equivalent water concentration in the flow tube ([H₂O] $\sim 9 \times 10^{14}$ molecule cm^{−3}); therefore the enhancement appears to be due to ion chemistry rather than wall effects in the inlet.

[22] This implies that the reaction of I[−](H₂O)_n + CH₃C(O)O₂ proceeds faster than I[−] + CH₃C(O)O₂. Figure 4 shows the calculated distribution of I[−]/I[−](H₂O)

as a function of flow tube [H₂O]. In order for the kinetics of reaction (2) to account for the observed humidity dependence, the reaction of I[−](H₂O)_n + CH₃C(O)O₂ for n = 1 would have to be 2.9 times the rate when n = 0 at the lower limit (end point of error bars) of reported ΔG values and 6.9 times the rate based on the average (markers) literature ΔG values (Bartmess, NIST Chemistry WebBook, 2003). Considering that the diffusion-limited wall loss of the heavier CH₃C(O)O[−](H₂O)₂ product ion (95 amu) in the flow tube is $\sim 25\%$ less than the bare acetate ion (59 amu), the rate of reaction of I[−](H₂O) + CH₃C(O)O₂ only needs to be 5.2 times the rate derived from the average literature ΔG values. A significantly faster reaction between I[−](H₂O) and CH₃C(O)O₂ is conceivable given the error estimate of the rate coefficient for I[−] + CH₃C(O)O₂ reported by Villalta and Howard [1996] and the fact that their measurement was based on the appearance of product ion rather than disappearance of reagent ion. Their estimated uncertainty puts the lower limit for k_{I+CH₃C(O)O₂} at 4×10^{-10} cm³ molecule^{−1} s^{−1}.

[23] The slight decrease in PAN signal (<10% at 80% RH) with increasing humidity after the peak could be due to much slower reaction of CH₃C(O)O₂ with higher-order clusters of I[−](H₂O)_n. Larger I[−](H₂O)_n clusters go undetected because they dissociate in the CDC. For maximum sensitivity in areas of low absolute humidity such as the upper troposphere, water can be added directly to the flow tube via the ion source to maintain a minimum H₂O mixing ratio which can be monitored by proxy at 145 amu (I[−](H₂O)).

3.2. Selectivity

[24] The selectivity of the I[−] chemistry is illustrated in Figure 5, a mass spectrum taken of Boulder air on 16 October 2002 using CH₃I as the reagent gas. The species which is most likely to interfere with this measurement is NO, which depletes the signal through reactions (6) and (7). It is possible that NO concentrations near point sources could be high enough to react with a significant fraction of

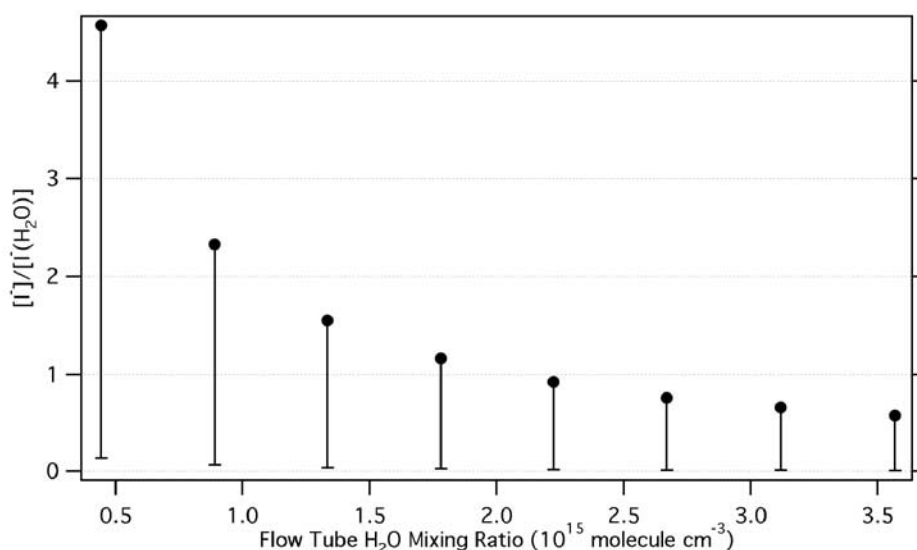


Figure 4. Calculated ratio of I⁻ to I⁻(H₂O) as a function of flow tube humidity. Markers are calculated from literature average ΔG , and error bars are calculated from lower limits (Bartmess, NIST Chemistry WebBook, 2003).

the thermally generated radicals in the inlet. Given a worst case scenario of an inlet reaction time of 30 ms and gas temperature inside the inlet of only 100°C, NO mixing ratios below 12 ppbv would cause a decrease of less than 10% in the detected ion signal for PAN [DeMore *et al.*, 1997]. A 10% reduction in the N₂O₅ + NO₃ signal would require only 7 ppbv NO due to the faster reaction of NO₃ with NO [DeMore *et al.*, 1997].

[25] Possible interfering reactions, aside from reaction with NO, are radical-radical reactions and recombination with NO₂. Over 15 ppbv CH₃C(O)O₂ would be required to cause a 10% effect due to self-reaction [DeMore *et al.*, 1997]. Ambient concentrations of acetylperoxy radicals and other peroxy radicals such as HO₂ are generally expected to

be very small compared to PAN [DeMore *et al.*, 1997]. The radicals are also unlikely to make it through the portion of the inlet upstream of the heater without special care. Thus only the peroxy radicals generated in the oven at high PAN levels are likely to lead to nonlinear behavior. In order to get 10% recombination of NO₂ + CH₃C(O)O₂ to form PAN under the same worst case conditions used above, more than 28 ppbv NO₂ would be required.

[26] The best way to limit all potential radical-radical reactions is to reduce the residence time of the peroxy radicals in the inlet by increasing the flow rate and oven temperature. An effective inlet residence time of 30 ms at an inlet flow of 2.3 slpm and external oven temperature of 160°C was determined from the decay of acetate ion signal

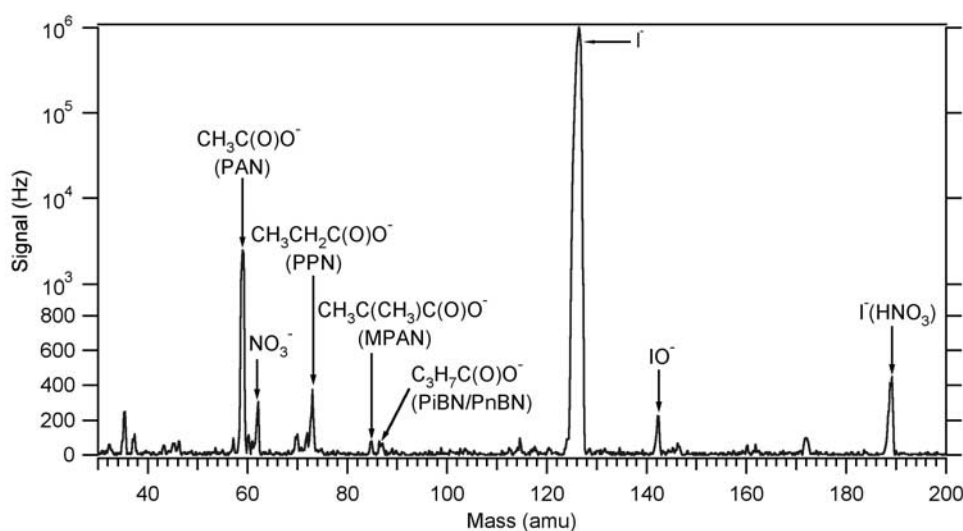


Figure 5. Mass spectrum of ambient air in Boulder, Colorado, on 16 October 2002 using I⁻. Note that the vertical scale is linear up to 1000 Hz and logarithmic above 1000 Hz. The PAN signal corresponds to ~400 pptv.

at 59 amu as a function of added NO, but residence times as short as 8 ms have been achieved with faster flows and a hotter inlet. For temperatures above ~260°C, a short length of glass tubing might be substituted for PFA Teflon tubing inside the heater. Another possible way to mitigate reactions with NO in very high NO_x environments is to add a small flow of ozone upstream of the heated portion of the inlet to titrate the ambient NO, but the increased recombination rate of CH₃C(O)O₂ with NO₂ due to the resulting [NO₂] must be carefully considered. Recombination of NO₂ and NO₃ is not as big a concern since 175 ppbv NO₂ is required in order to get 10% reformation of N₂O₅ at 100°C based on the forward rate only.

[27] The possibility of interference with the detection of PAN as CH₃C(O)O[−] from acetone, acetic acid, and peracetic acid was also considered. Laboratory tests showed no indication of interference from acetone or acetic acid at normal atmospheric levels, but a signal equivalent to ~225 pptv of PAN was obtained at acetone concentrations of 70–1000 ppmv. Acetone from the photolytic PAN calibration source, which averaged 80 ppbv, did not cause any increase in signal at 59 amu (CH₃C(O)O[−]). For concentrations of acetic acid between 0.5 and 2.3 ppmv, the signal at mass 59 was equivalent to 185–230 pptv of PAN. The acetic acid did not react with NO, so it can only serve to increase the background signal. The highest background signal observed in either Atlanta or Boulder at 59 amu was equivalent to 33 pptv of PAN. The proton transfer reaction of I[−] with acetic acid has a ΔG° of 135 kJ mol^{−1} [Cumming and Kebarle, 1978; Hanstorp and Gustafsson, 1992], which effectively rules out this pathway for making acetate. Experiments with peracetic acid have not been performed because it is a weaker acid than acetic acid and, even if peracetic acid can react with I[−] to produce CH₃C(O)O[−] in the flow tube, it should not react with NO during background determinations. Therefore it would be detected as background signal.

4. Boulder Intercomparison

4.1. Experimental Details

[28] The TD-CIMS and GC/ECD instruments were run side by side 16–21 October 2002. The procedure by which peroxyacyl nitrates were measured by the NCAR GC/ECD was similar to that described by Williams *et al.* [1997]. Both instruments sampled from a common ~10 m line made of 0.635 cm o.d. (0.32 cm i.d.) PFA Teflon tubing that extended 1 m out of a second story window near the NCAR Mesa Lab loading dock. We switched from CF₃I to CH₃I as the reagent ion precursor gas on 17 October. The TD-CIMS operating pressures were kept the same as in Atlanta except that the inlet pressure was reduced by the ratio of the surface pressures in Atlanta and Boulder (~18%). At 610 torr, (8.13 × 10⁴ Pa) the flow rate through the flow tube pinhole was 1.4 slpm. The total TD-CIMS inlet flow was maintained at 2.3 slpm. This was the maximum flow rate allowed due to limits on the combined sampling flows for the two instruments imposed by the calibration system.

[29] A sequence of TD-CIMS measurements was made every 5 s with an integration period of 0.5 s at masses 59 (PAN), 62 (N₂O₅ + NO₃), 73 (PPN), 87 (PiBN), 127 (I[−]), and 190 (I[−](HNO₃)) plus 0.275 s at masses 85 (MPAN), 95 (PAN with 2 H₂O clusters), 142 (I[−](HNO₂)), and

269 (I[−](CH₃I)). The GC/ECD sampling interval was 3 s with 5 min between data points. Each GC/ECD data point represents the average of two 2.5 min chromatograms run on separate columns. A diaphragm pump delivered calibration gas to both instruments approximately every 20 min with the exception of the period of 6:36 PM on 18 October 2002 through 9:29 AM on 20 October 2002 when only one calibration was performed. NO was added to the TD-CIMS inlet every 30 min to measure the instrument background.

[30] A PAN calibration occurred within 10 min of a background measurement via NO addition 92 times during the intercomparison. For those 92 occasions, the average difference between background levels obtained during PAN calibrations (hot metal tubing) and those obtained by the addition of NO was 1.2 pptv for PPN and 5.2 pptv for N₂O₅ + NO₃. The mean background obtained via NO addition was 5.5 pptv for PPN and 34 pptv for N₂O₅ + NO₃ versus 6 pptv and 31.5 pptv, respectively, obtained during PAN calibrations. Averaging over all 184 data points for each species, 95% of the PPN and N₂O₅ + NO₃ background measurements fall within 5.8^{+2.3}_{−2.2} pptv and 33.3^{+20.0}_{−16.2} pptv respectively. Figure 2 contains two instances of a PAN calibration and background measurement within 10 min of each other.

4.2. Peroxyacyl Nitrates

[31] The PAN and PPN levels measured by the TD-CIMS and GC/ECD were highly correlated (R² > 0.89) as shown in Figure 6. The intercepts of both correlation plots were small (−4 pptv for PAN and 2 pptv for PPN), but the TD-CIMS results were systematically higher by roughly 20% for both PAN and PPN. These results demonstrate that the TD-CIMS can selectively measure PAN and PPN in ambient air with an accuracy of at least 20%. They also indicate a ~20% calibration bias between the TD-CIMS and GC-ECD. This difference is surprising as both instruments were calibrated simultaneously with the same standard. The direction of the bias indicates diminished sensitivity for the TD-CIMS during calibrations relative to measurements. This assertion is further supported by excellent agreement (1% on average) between GC/ECD and TD-CIMS PPN measurements made of diffusion source PPN when the TD-CIMS was in PAN calibration mode to confirm PPN sensitivity relative to PAN.

[32] For these reasons, we investigated how the CIMS sensitivity might have changed between measurements and the automated calibration mode. Two likely mechanisms for the bias are the small pressurization of the common sampling inlet above ambient pressure during the calibrations and matrix effects due to passing the calibration carrier gas through a diaphragm pump and flow controller. The first mechanism was found to increase the sensitivity of the TD-CIMS due to higher pressures and number densities in the flow tube. However, the sensitivity of the TD-CIMS decreased when the sampled air was delivered to the inlet by a diaphragm pump and mass flow controller. The net decrease in sensitivity for flow conditions identical to the Boulder intercomparison, including the pressurization, was 25%. Although we did not use the same pump and flow controller from Boulder, this effect is consistent with the observed calibration bias. It is likely that matrix effects such as a small decrease in humidity are responsible for the

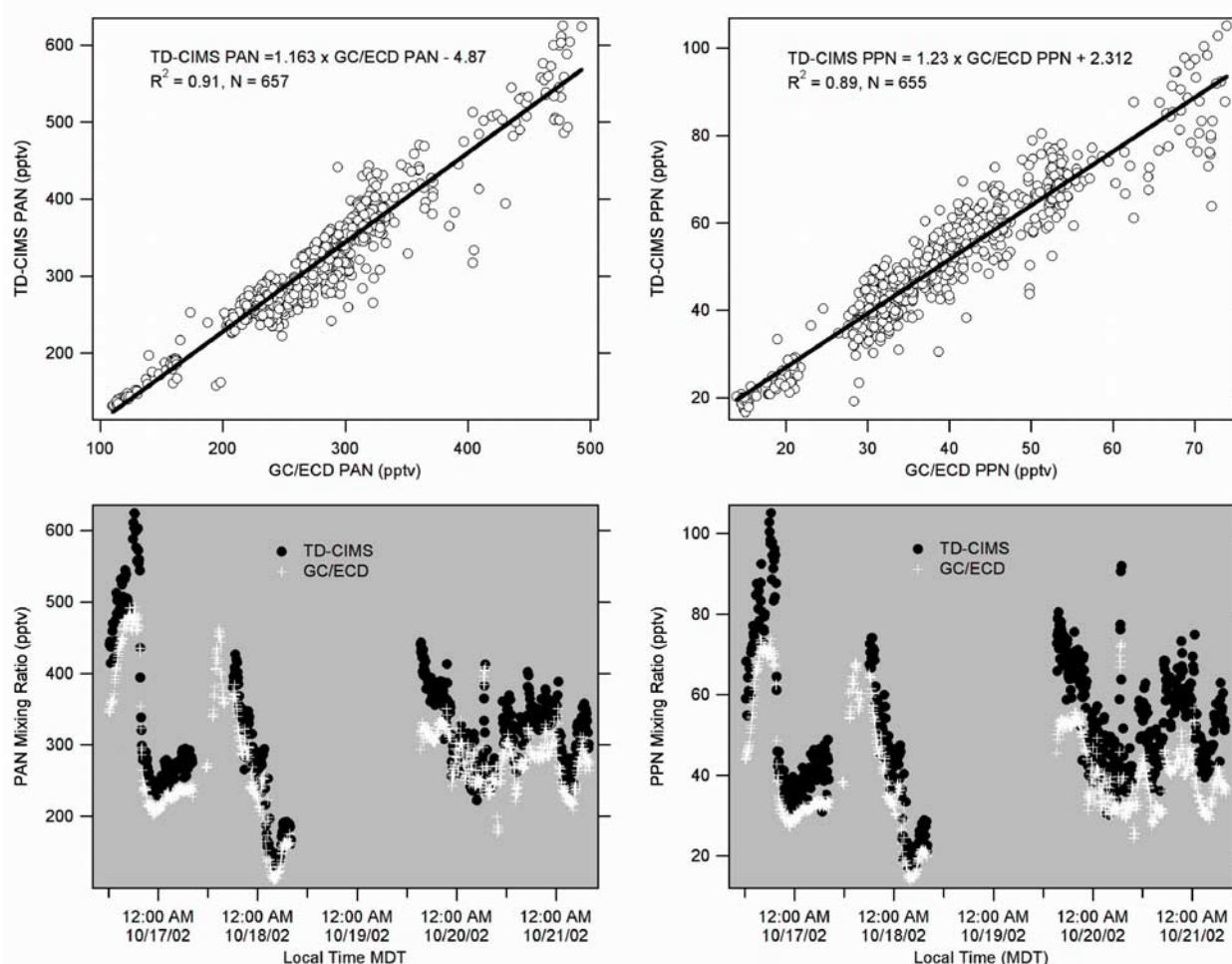


Figure 6. Correlation of TD-CIMS and GC/ECD PAN and PPN measurements.

decreased sensitivity. We concluded from this investigation that it is best to keep the TD-CIMS inlet at a constant pressure and to calibrate via standard additions to air that is sampled directly into the inlet.

[33] Peroxy-*n*-butyryl nitrate (PnBN, CH₃CH₂CH₂C(O)O₂NO₂) and peroxyisobutyryl nitrate would both be detected at 87 amu with the TD-CIMS. According to the GC retention time, PiBN was present during the intercomparison. Retention of PnBN on the GC column is longer than the 2.5 min window monitored during the intercomparison so it is not certain whether or not any PnBN was present. PiBN was not calibrated, but the known GC/ECD sensitivity of PiBN relative to PAN was used to estimate the concentrations. According to the GC/ECD, the amount of PiBN shown in Figure 2 is 9.2 pptv, which gives us a TD-CIMS sensitivity of 4.9 Hz pptv⁻¹. The ratio of the PiBN and PAN sensitivities should be proportional to the rate constants for their associated radical reactions with I⁻/I⁻(H₂O). That the ratio is close to 1 indicates they are similar, but further testing will be needed for confirmation.

The average flow tube H₂O mixing ratio during the intercomparison period, estimated at 7.6×10^{14} molecule cm⁻³ (17% RH in Figure 3) from ambient dew points, was sufficient to ensure measurements were made near the maximum sensitivity. The maximum and average PiBN concentrations observed during the intercomparison period of 17.8 pptv and 4.8 pptv, respectively, should be taken as upper limits due to possible contribution from PnBN. The TD-CIMS detection limit at 87 amu of 2.8 pptv for PiBN was achieved by averaging the data for 1 s.

4.3. Dinitrogen Pentoxide

[34] The product mass (NO₃⁻) corresponding to N₂O₅ and NO₃ was monitored with the TD-CIMS between 12 and 21 October 2002. It was sufficiently cold that N₂O₅ could be expected to accumulate each night in a much higher concentration than NO₃. The 0.5 s data for the night of 14 October and morning of 15 October is shown in Figure 7 (top). Figure 7 (bottom) is an enlarged view of the morning of 15 October with the thermal decay rate of N₂O₅ calcu-

Figure 7. (top) Background-corrected 0.5 s signal at 62 amu 14–15 October 2002. (bottom) Expanded morning of 15 October 2002. N₂O₅ thermally decomposes after sunrise at 7:11 AM. Assuming equivalent PAN and N₂O₅ + NO₃ sensitivities, the signal just before 5 AM represents 438 pptv N₂O₅ + NO₃, and the signal at sunrise corresponds to 197 pptv.

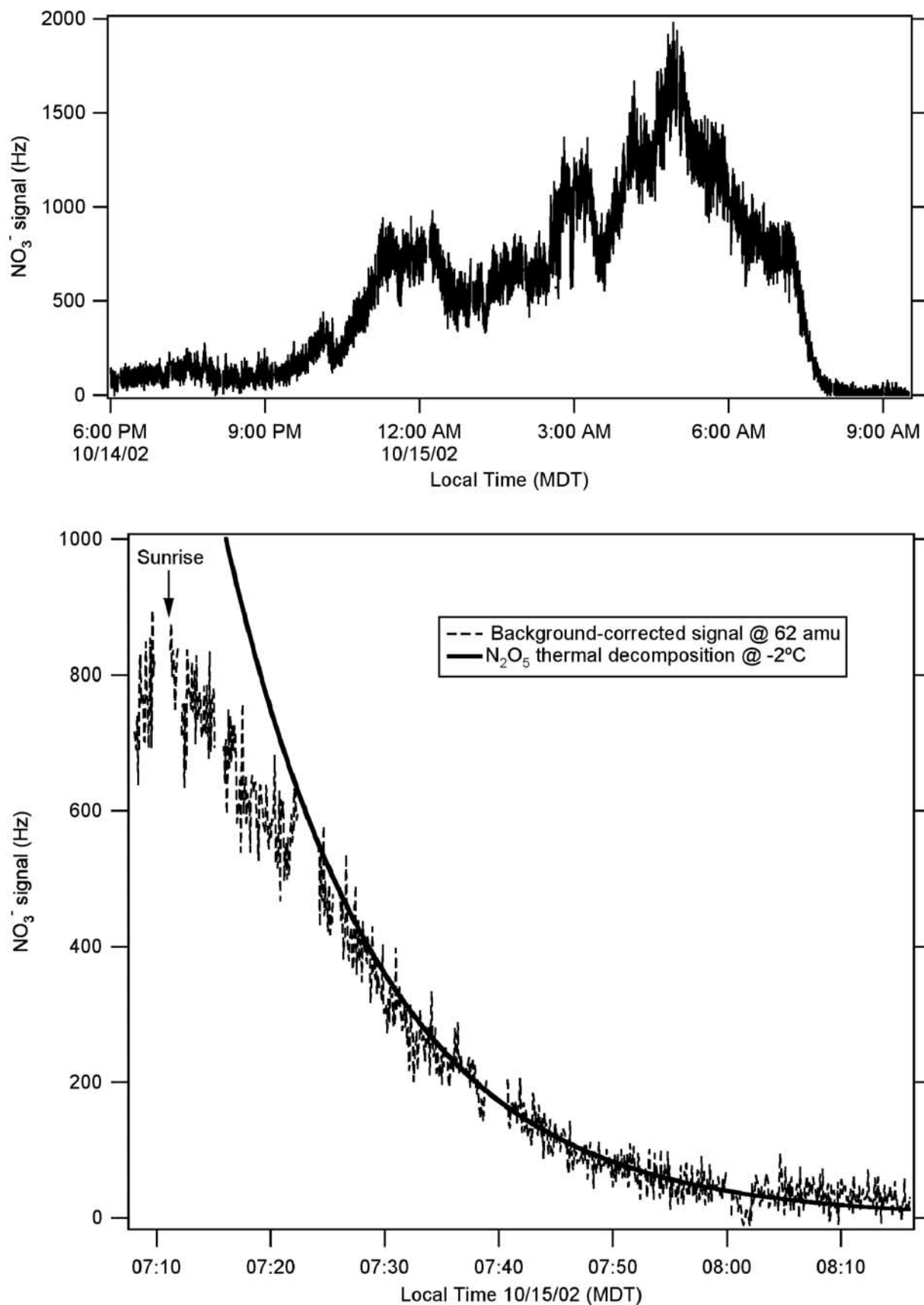


Figure 7

lated at -2°C [DeMore *et al.*, 1997] superimposed. Figure 7 shows that N₂O₅ was lost at its thermal decay rate as the NO₃ product rapidly photolyzed after sunrise. The NCAR Mesa Lab weather station was not in operation during our measurement period, but the temperature at the nearby Broomfield airport, was 1°C at 5:45, 6:45 and 7:45 AM. The same pattern was observed on the mornings of 13 and 17 October.

[35] Although no standard for NO₃ or N₂O₅ was available, we expect the TD-CIMS sensitivity to NO₃[−] was similar (within a factor of 2) to that observed for CH₃C(O)O[−] because NO₃[−] should be produced at close to the gas kinetic rate from I[−] chemistry. The reaction of NO₃ with I[−], reaction (4), is exothermic by 84 kJ mol^{−1} [Davidson *et al.*, 1977; Hanstorp and Gustafsson, 1992]. Using the PAN sensitivity puts the average mixing ratios for the total N₂O₅ + NO₃ we observed around 95 pptv, with the spike just before sunrise on 20 October 2002 at 1270 pptv, and the maximum otherwise at 600 pptv. These results are consistent with observations by Brown *et al.* [2001, 2003] in Boulder. Like Brown *et al.*, we also observed considerable variability in the concentration of NO₃ + N₂O₅ throughout the measurement period with a trend toward a buildup at night followed by a fast drop-off just after sunrise. This underscores the need for fast measurements of these species.

5. Conclusions

[36] This CIMS technique can provide sensitive and selective detection of PAN and PPN in a fraction of a second. It is also a very sensitive detector for NO₃ + N₂O₅. Sensitivity to PiBN is excellent as well, but it cannot be distinguished from PnBN with the TD-CIMS. Even quantitation of the sum of these two species would provide important information about the contribution of larger hydrocarbons to the photochemistry of air masses in which they are detected. MPAN sensitivity appears to be significantly lower, but a detection limit comparable to that of PAN in 1 s can be achieved by integrating for 30 s. A minimum amount of water must be maintained in the flow tube for maximum sensitivity.

[37] The only significant interference that has been identified is due to high levels of NO. Negative interference from NO mixing ratios above ~ 12 ppbv can be mitigated by shortening the reaction time in the heated inlet or, possibly, by the addition of ozone. For these reasons, we believe the new CIMS technique will yield robust measurements of many peroxyacyl nitrates and N₂O₅ in almost all tropospheric environments. The TD-CIMS technique appears to be suitable for aircraft-based experiments and PAN flux measurements by eddy covariance given its fast time response and a detection limit comparable to that of the GC/ECD. Preliminary measurements of the eddy flux of PAN, PPN, and MPAN in a coniferous forest with a TD-CIMS have been reported by Turnipseed *et al.* [2003].

[38] Future development work will be conducted to increase the sensitivity of the TD-CIMS while reducing its size and power consumption. Additional characterization studies will determine whether or not other peroxyacyl nitrates such as peroxybenzoyl nitrate (PBzN), hydroxyl peroxyacetyl nitrate (HPAN), or peroxyacryloyl nitrate (APAN) can be measured with this detection scheme.

Further work on the NO₃/N₂O₅ system is also needed to calibrate and speciate these compounds.

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