Atmospheric
Measurement
Techniques

Large daytime signals of N_2O_5 and NO_3 inferred at 62 amu in a TD-CIMS: chemical interference or a real atmospheric phenomenon?

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Abstract. Dinitrogen pentoxide (N_2O_5) and the nitrate radical (NO_3) play important roles in atmospheric chemistry, yet accurate measurements of their concentrations remain challenging. A thermal dissociation chemical ionization mass spectrometer (TD-CIMS) was deployed to an urban site in Hong Kong to measure the sum of N_2O_5 and NO_3 in autumn 2010 based on the signals of NO_3^- at 62 amu which has also been adopted in previous studies reported in literature. To our surprise, very large signals of $N_2O_5 + NO_3$ were frequently observed at 62 amu in the daytime, with equivalent $N_2O_5 + NO_3$ mixing ratios in the range of 200–1000 pptv. To investigate this unusual phenomenon, various interference tests and measurements with different instrument configuration were conducted. It was found that peroxy acetyl nitrate (PAN) contributed to measurable signals at 62 amu, and more importantly, this interference increased significantly with co-existence of NO_2. Nitric acid (HNO_3), on the other hand, had little interference to the detection of N_2O_5/NO_3 via the NO_3^- ion in our TD-CIMS. According to the test results, the interference from PAN and NO_2 could have contributed to 30–50 % of the average daytime (12:00–16:00, local time) $N_2O_5 + NO_3$ signal at our site. On the other hand, evidence exists for the presence of elevated daytime N_2O_5, in addition to the daytime signal at 62 amu. This includes (1) daytime N_2O_5 measured via the $I(N_2O_5)^-$ cluster ion with an unheated inlet, which was subjected to minimum interferences, and (2) observation of elevated daytime $ClNO_2$ (a product of N_2O_5 hydrolysis) during a follow-up study. In view of the difficulty in accurately quantifying the contribution from the interferences of PAN and NO_2 and untested potential interfering chemicals in the real atmosphere, we caution the use of 62 amu in the TD-CIMS for measuring ambient N_2O_5 in a high NO_x environment like Hong Kong. Additional studies are needed to re-examine the daytime issue using other measurement techniques.

1 Introduction

The nitrate radical (NO_3) and dinitrogen pentoxide (N_2O_5) play important roles in the nocturnal tropospheric chemistry. NO_3 is among the most important oxidants in the atmosphere, particularly for biogenic hydrocarbons and sulfur-containing compounds (Atkinson, 1991). N_2O_5 has long been recognized as a key intermediate in the transformation of nitrogen oxides ($NO_x = NO + NO_2$) to aerosol nitrates (Riemer et al., 2003; Aldener et al., 2006; Chang et al., 2011; Brown and Stutz, 2012). Recent studies have also demonstrated an important role of N_2O_5 hydrolysis at night in chlorine activation and the subsequent effect on the next-day's ozone formation (Osthoff et al., 2008; Simon et al., 2009; Thornton et al., 2010).

Due to the low ambient abundances and high reactivity, accurate measurements of atmospheric N_2O_5 and NO_3 have been challenging. Based on the strong absorption of NO_3 in the visible spectrum at 662 nm, several optical techniques have been developed to measure the ambient NO_3, including long-path differential optical absorption spectroscopy (DOAS) (Platt et al., 1980; Atkinson et al., 1986), cavity ring-down spectroscopy (CRDS) (Brown et al., 2001, 2002),

laser-induced fluorescence (LIF) (Wood et al., 2003, 2005; Matsumoto et al., 2005), and cavity enhanced absorption spectroscopy (CEAS) (Venables et al., 2006; Langridge et al., 2008). N_2O_5 is determined by using a heated channel to decompose it into NO_3 or from the calculation according to the fast equilibrium between N_2O_5 with NO_3 and NO_2.

Another technique for detecting ambient N_2O_5 and NO_3 is chemical ionization mass spectrometry (CIMS) which combines the ion-molecule chemistry with mass spectrometry detection. This technique was originally used in the laboratory to study the heterogeneous uptake kinetics of N_2O_5 and $ClNO_2$ (e.g., Hu and Abbatt, 1997; Thornton et al., 2003; Thornton and Abbatt, 2005), and later on was applied in field measurements (Slusher et al., 2004; Zheng et al., 2008). The fundamental of this method is the reaction of I^- (the reagent ion) with N_2O_5 (and/or NO_3) forming the NO_3^- ion that can be detected at 62 amu. Previous laboratory studies suggested that the N_2O_5/NO_3 measurement at 62 amu may be subject to interferences from other N-containing trace gases such as HNO_3, HO_2NO_2, $ClONO_2$ and others (see references listed in Table 1). On the other hand, a field inter-comparison of a TD-CIMS and a cavity ring-down system showed a high degree of correlation between the two methods (Huey, 2007; Chang et al., 2011) indicating the capability of this method in measuring N_2O_5 in the atmosphere. Although non-negligible and varying background signals at 62 amu have been observed during field studies (Chang et al., 2011), there have been no reports of detailed assessment of these potential interferences under different atmospheric conditions and for different configurations of CIMS. Kercher et al. (2009) developed a method to detect N_2O_5 via the $I(N_2O_5)^-$ cluster ion at 235 amu with an unheated inlet to address the interference at 62 amu in their CIMS, however this method has its own limitations including a lower sensitivity and larger impact of water vapor than that at 62 amu.

In autumn 2010, a TD-CIMS (thermal dissociation-CIMS), which is the same type used by Slusher et al. (2004) and Huey (2007), was deployed to an urban site in Hong Kong which is characterized by large quantities of NO_x, ozone and particulate matters. Unexpectedly, large signals of $N_2O_5 + NO_3$ inferred at 62 amu were frequently observed during the daytime in our study. To investigate this unusual observation, we have conducted a series of laboratory and field tests, including testing interferences individually and in combination from PAN, NO_2, O_3, HNO_3, detection of N_2O_5 by using a cold inlet via detection of the $I(N_2O_5)^-$ cluster ion at 235 amu, and examination of daytime $ClNO_2$ which is a product of N_2O_5 hydrolysis. In this paper, we will first present the ambient observations, and then the detailed test results on interferences and other evidence for daytime N_2O_5. A surprising result from the tests is that PAN+NO_2 can contribute a large interference to the TD-CIMS signal at 62 amu, which has not been reported in previous studies. Despite large chemical interference, we show that the observed
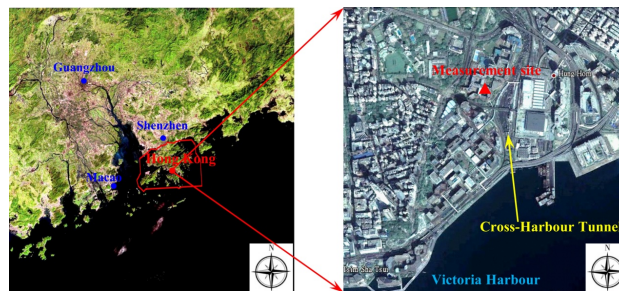

Fig. 1. Location of the measurement site and surrounding layout.

daytime N_2O_5 signal may be in part due to a real contribution from NO_3 and N_2O_5.

2 Experiment and methodology

2.1 Measurement site

The field study was conducted in the urban center of Hong Kong (22°18′ N, 114°11′ E; ∼ 15 m above sea level). The sampling site was located on the rooftop of a seven-story teaching building (about 20 m above the ground) on the campus of the Hong Kong Polytechnic University (PolyU). To the southeast of the campus, there is a cross-harbor tunnel in the north–south direction with a large flow of vehicles, especially during rush hours (see Fig. 1). Victoria Harbor is located about 1 km south of the measurement site. Thus emissions from vehicles and marine vessels are the most important local anthropogenic sources. The sampling site is surrounded by business districts, tourism and residential areas, with no large industrial sources nearby. The field measurements were carried out from 15 October to 4 December 2010, which is the season with the most severe photochemical pollution in Hong Kong (Wang et al., 2009).

2.2 The CIMS apparatus

A TD-CIMS was deployed to measure the sum of N_2O_5 and NO_3 in this study. The system was developed at the *Georgia Institute of Technology* and is based on a soft and selective ionization process resulting from the reaction between a reagent ion and the target compounds, with the generated ions detected by a mass spectrometer. In the present study, the measurement method and operating parameters of TD-CIMS were the same as those described by Slusher et al. (2004) which was configured to simultaneously measure ambient N_2O_5 and PANs. The schematic diagram of our TD-CIMS is shown in Fig. 2. I^-, which was produced from passing a flow of 2 sccm of 0.3 % CH_3I/N_2 through an alpha ion source (Po-210), served as the reagent ion. Ambient air samples were drawn through a PFA-Teflon tube (I.D., 9.5 mm; O.D., 12.7 mm; length, 2 m) to the CIMS at a flow rate of 1.5 standard liters per minute (SLPM). To reduce the residence

Table 1. Ion-molecule reactions with product of NO_3^- and the rate constants.

Reaction	Rate constant (molecule^{-1} cm^3 s^{-1})	Comments	Reference
$I^- + HNO_3 \rightarrow NO_3^- + HI$	$< 5 \times 10^{-11}$		Fehsenfeld et al. (1975)
	No reaction		Huey et al. (1995)
$I^- + ClONO_2 \rightarrow NO_3^- + ICl$	9×10^{-10}	$\pm 40\%$	Huey et al. (1995)
$I^- + BrONO_2 \rightarrow NO_3^- + IBr$	Unknown		Hanson et al. (1996)
$I^- + HO_2NO_2 \rightarrow NO_3^- + HIO$	Unknown		Zhang et al. (1997)
$CO_3^- + HNO_3 \rightarrow NO_3^- + products$	8×10^{-10}		Fehsenfeld et al. (1975)
$CO_3^- + NO_2 \rightarrow NO_3^- + CO_2$	2×10^{-10}	$\pm 50\%$	Ikezoe and Viggiano (1987)
$CO_4^- + NO \rightarrow NO_3^- + CO_2$	4.8×10^{-11}	$\pm 30\%$	Ikezoe and Viggiano (1987)
$C_2H_2N^- + HNO_3 \rightarrow NO_3^- + CH_3CN$	1.4×10^{-9}	297 K	Ikezoe and Viggiano (1987)
$C_2H_3O_2^- + HNO_3 \rightarrow NO_3^- + C_2H_4O_2$	Unknown		Roberts et al. (2010)
$Cl^- + HNO_3 \rightarrow NO_3^- + HCl$	1.6×10^{-9}	$\pm 40\%$	Ikezoe and Viggiano (1987)
$NO_2^- + HNO_3 \rightarrow NO_3^- + HONO$	1.6×10^{-9}	$\pm 40\%$	Ikezoe and Viggiano (1987)
$NO_2^- + NO_2 \rightarrow NO_3^- + NO$	$< 2 \times 10^{-13}$		Ikezoe and Viggiano (1987)
$NO_2^- + N_2O \rightarrow NO_3^- + N_2$	$< 1 \times 10^{-12}$		Ikezoe and Viggiano (1987)
$NO_2^- + O_3 \rightarrow NO_3^- + O_2$	1.2×10^{-10}	$\pm 40\%$	Ikezoe and Viggiano (1987)
$O_3^- + NO_2 \rightarrow NO_3^- + O_2$	2.8×10^{-10}	$\pm 30\%$, 280 K	Ikezoe and Viggiano (1987)

time of air samples in the sampling tube an extra bypass flow of 7.7 SLPM was directed to the exhaust. Immediately before the flow tube, the last 14.8 cm of inlet was heated to 180 °C. The temperature of the air on the axis of the heated inlet was estimated at $\sim$ 117 °C (Slusher et al., 2004), and under these conditions more than 99 % of the N_2O_5 would decompose into NO_3 with an ambient NO_2 level of 40 ppbv. The produced and the original NO_3 then reacted with I^- to produce NO_3^- ions in the flow tube, which were subsequently detected and quantified by a quadruple mass spectrometer (Extrel 150-QC, with a FWHM resolution of 2000) at 62 amu with a temporal resolution of 6 s. The NO_3^- signal is proportional to the concentration of total NO_3, the I^- signal, the effective reaction rate constant between them, and the effective reaction time (Huey, 2007). Figure 3 depicts mass spectra of ambient air in urban Hong Kong obtained both during the daytime and at night, which clearly shows the I^- signal at 127 amu, NO_3^- signal at 62 amu, $CH_3C(O)O^-$ (PAN) signal at 59 amu, etc. The mass peak at 62 amu was well separated from that at 59 amu.

In the present study, the TD-CIMS instrument was calibrated once a week using the on-line N_2O_5 synthesis method (Bertram et al., 2009). The calibration source was generated from the reactions of NO_2 with O_3 and subsequently NO_3 with NO_2. In a glass reaction chamber in a commercially available calibrator (Model 6100, Environics) 90 sccm of 2.5 ppmv NO_2 in nitrogen gas was mixed with 480 sccm of 2.1–4.6 ppmv O_3 which was generated by UV photolysis of O_2 in zero air (Model 111, Thermo Environmental Instruments (TEI)). The reactions happened during a time period of one minute, and then the output was diluted to 6 slpm by zero air. The concentrations of the prepared N_2O_5
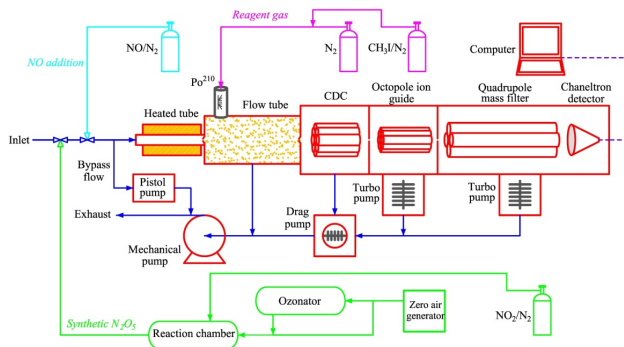
Fig. 2. Schematic diagram of the TD-CIMS deployed in this study.

were determined via the change in NO_2 concentrations after adding ozone, and conversely verified by the change in ozone after adding NO_2. Zero air that was free from moisture and aerosols served as the diluent so as to prevent the hydrolysis of N_2O_5 during the calibrations (see Fig. 2). NO_2 was monitored with a chemiluminescence analyzer equipped with a photolytic converter which ensured measurements of the true NO_2 (Ryerson et al., 2000; Xu et al., 2013). When inputting 36.7 ppbv of NO_2 and 170.4 ppbv of O_3, the generated N_2O_5 was 1.08 ppbv. Note that there could be slight overestimation in the concentration of N_2O_5 standard determined in our study, because a small fraction ($< 10\%$) of N_2O_5 could be converted into gaseous nitric acid (Bertram et al., 2009). The loss of total nitrogen in the calibration system was examined with a chemiluminescence NO_x analyzer equipped with a molybdenum converter by comparing the signal with
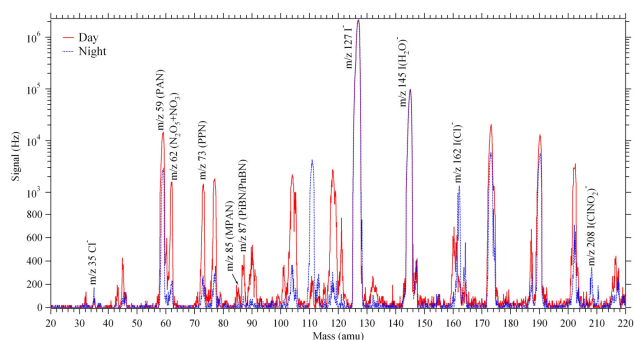
Fig. 3. Mass spectra of ambient air in urban Hong Kong at day and night by iodide TD-CIMS with heating the inlet tube to 180 °C.

and without adding O_3 to NO_2, which indicated insignificant loss.

Based on the relative standard deviation of the sample signal, the precision of our TD-CIMS was 3 % for 1000 pptv N_2O_5. The sensitivity of N_2O_5 during the campaign was 2.8 ± 0.2 (mean $\pm$ SD) Hz pptv^{-1}. The instrument background was automatically measured for 2 min once an hour by adding a small flow (5 mL min^{-1}) of NO (1000 ppm) to the sample flow (diluted to 9.2 SLPM), titrating NO_3 and thus N_2O_5. The background signal of the NO_3^- ion during this field study was 71.7 ± 36.0 (mean $\pm$ SD) Hz. Figure 4 shows the signals of NO_3^- (at 62 amu) with hourly automatic background determinations on 30 November, when the equivalent maximum concentration of $N_2O_5 + NO_3$ was inferred. Clearly, the signals exhibited relatively low background compared to ambient $N_2O_5 + NO_3$ during both day and night. According to three times the standard deviation of the background signal, the typical detection limit of N_2O_5 for 6 s average time was estimated to be 39 pptv for our TD-CIMS.

2.3 Other instruments

In addition to the TD-CIMS, a large number of other instruments were deployed concurrently. Here, we briefly describe those that were used to aid the presentation of the N_2O_5 and NO_3 data. O_3 was measured by a commercial UV photometric analyzer (Model 49i, TEI, USA). NO and NO_2 were analyzed with a chemiluminescence instrument (Model 42i, TEI) equipped with a photolytic NO_2 converter (Air Quality Design, USA) (Xu et al., 2013). Solar radiation was measured using a LI-200 Pyranometer Sensor (LI-COR, USA). The ambient RH and temperature were monitored with a RH/temperature probe (Model 41382VC/VF, M.R. YOUNG, USA). During the field measurements, the minute-average data of trace gases and meteorological parameters were collected in real time by a data logger (Model 8816, Environmental Systems Corporation, USA).
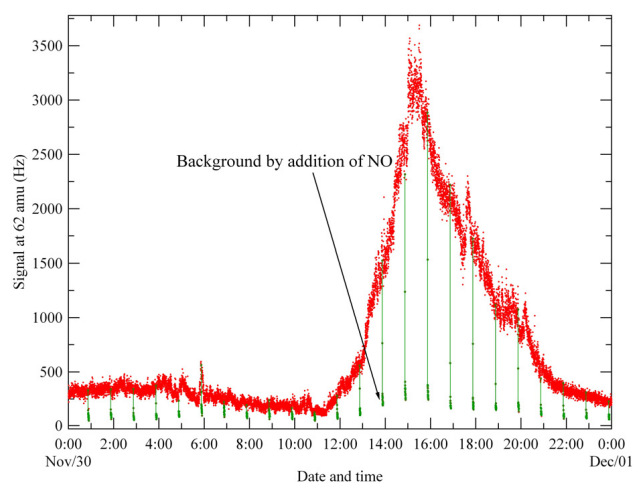

Fig. 4. Raw NO_3^- (62 amu) signal with hourly automatic background detection by adding excess NO, 30 November 2010.
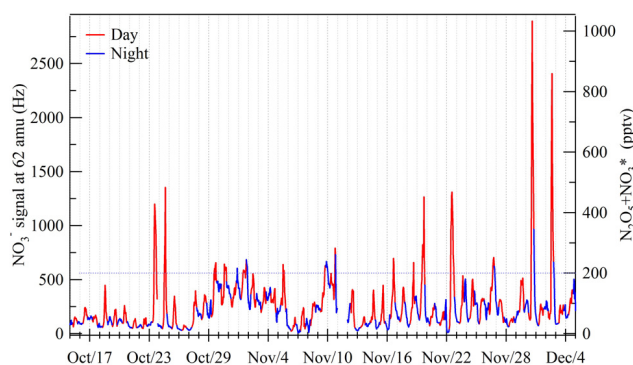

Fig. 5. Time series of hourly average NO_3^- signal at 62 amu and apparent $N_2O_5 + NO_3$ ($N_2O_5 + NO_3^*$) concentration measured in Hong Kong.

3 Observation results

The time series of hourly NO_3^- signals at 62 amu (after subtracting the background by adding NO) and apparent $N_2O_5 + NO_3$ mixing ratios (hereafter referred to as $N_2O_5 + NO_3^*$) from 15 October to 4 December 2010 is shown in Fig. 5. Similar to the measurement results obtained in other locations, several nighttime signal peaks of NO_3^- were noticed in our study (e.g., 31 October, 1 and 10 November). However, very large signals of $N_2O_5 + NO_3$ inferred by NO_3^- ion at 62 amu were frequently observed during the daytime (e.g., 23 and 24 October, 19, 22 and 30 November and 2 December). During the 50 day measurement period (excluding 11 November due to a lack of data), the average hourly apparent $N_2O_5 + NO_3$ concentration was 86.9 ($\pm$85.6) pptv with the maximum value of 1033 pptv recorded at 15:00 LT (local time) on 30 November. The mean daytime apparent $N_2O_5 + NO_3$ mixing ratio was 102.5 pptv (06:00–17:59 LT),
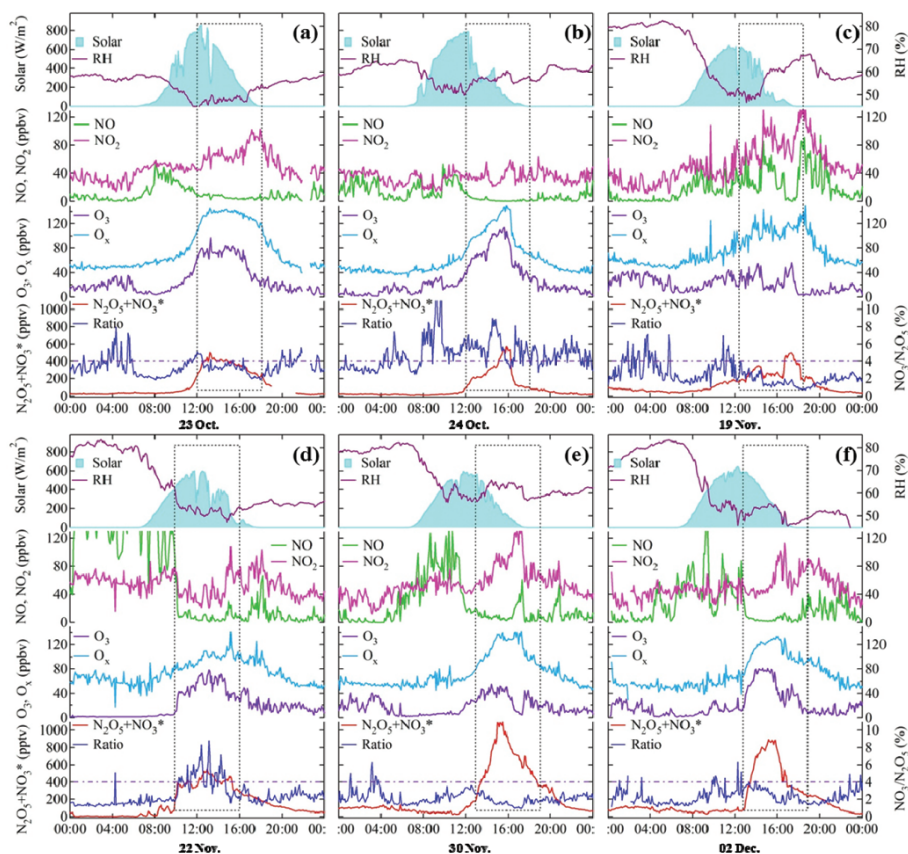
Fig. 6. Time series of apparent $N_2O_5 + NO_3$ ($N_2O_5 + NO_3^*$), NO_3 / N_2O_5 ratio, trace gases and meteorological parameters for six pollution episodes on **(a)** 23 October, **(b)** 24 October, **(c)** 19 November, **(d)** 22 November, **(e)** 30 November, and **(f)** 2 December 2010. The pollution episodes with daytime concentration peaks of N_2O_5 and NO_3 are shown in the panes.

even higher than the value of 71.3 pptv at nighttime (18:00–05:59 LT).

To learn more about the atmospheric conditions associated with the elevated daytime N_2O_5 and NO_3 signals at 62 amu, we present six cases during which the hourly apparent $N_2O_5 + NO_3$ values exceeded 400 pptv. Figure 6 presents the 5 min data of $N_2O_5 + NO_3^*$, O_3, O_x ($O_3 + NO_2$), NO, NO_2, RH, and solar radiation for these episodes. The ratio of NO_3 / N_2O_5, calculated based on the temperature dependent equilibrium among N_2O_5, NO_3 and NO_2, is also given. Inspection of the figure reveals that the daytime apparent $N_2O_5 + NO_3$ signal peaks appeared when both ozone and NO_2 were in high levels together with low levels of NO. However, daytime $N_2O_5 + NO_3$ concentrations calculated using both steady-state (Osthoff et al., 2006) and non-steady-state approaches (McLaren et al., 2010) were much lower (by a factor of 1–100) than observations. The daytime concentrations of apparent $N_2O_5 + NO_3$ in our study are also much higher than those of previous studies which reported daytime N_2O_5 and NO_3 concentrations of only a few to over 10 pptv (Geyer et al., 2003; Brown et al., 2005; Osthoff et al., 2006).

4 Chemical interferences

A major drawback of the TD-CIMS technique is that there could be potential interferences to the selected NO_3^- ion that can give rise to significant background noise at 62 amu (Chang et al., 2011). Previous laboratory studies have proposed many possible ion-molecule reactions yielding the NO_3^- ion, as summarized in Table 1. As stated earlier, the detailed results of these interferences in the real atmosphere have not been reported to date. To examine the influences of these potential interferences to our $N_2O_5 + NO_3$ measurements, a series of tests were conducted in various atmospheric conditions and in the laboratory during and after the measurement campaign.

The background determination by adding excess NO provided a first examination of the interferences. Such determined background reflects the interferences from compounds that are unreactive to NO, including most potential ones other than PAN and HO_2NO_2. As stated above, the background was periodically measured once an hour throughout the campaign. A considerable background signal in our CIMS measurements at 62 amu was indeed seen
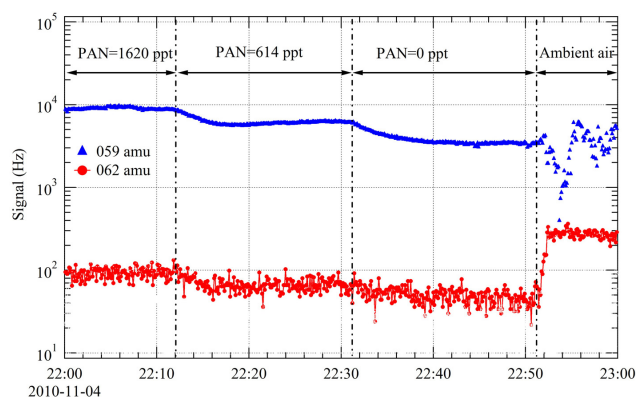
Fig. 7. Changes of signals at 59 and 62 amu when diluted synthetic PAN was introduced to the TD-CIMS.

Fig. 8. Changes of raw signals of $CH_3C(O)O^-$, NO_3^-, $C_3H_7C(O)O^-$, $I(H_2O)^-$ detected by I^- TD-CIMS when adding trace amounts of PAN, HNO_3, or their mix to the ambient air.

during the present study, and they also exhibited a diurnal pattern with higher values in the late afternoon (see Fig. 4). This indicates that the $N_2O_5 + NO_3$ measurements via the 62 amu channel in our TD-CIMS were subject to some interference during the present study. However, the background signals were much lower than the total signal in ambient air. For the six cases with daytime $N_2O_5 + NO_3$ concentrations exceeding 400 pptv, the instrument background on average only accounted for 10 % of the ambient values. This background signal is due to most of the gases shown in Table 1 and has been accounted for (i.e., subtracted from the total signals at 62 amu) in our final data. The interference from PAN and HO_2NO_2 could not be determined because they also reacted with NO during zeroing. Their interferences are addressed below.

4.1　Interference of PAN

PAN is the most possible compound to interfere the TD-CIMS measurements in this study, not only due to its relatively high ambient abundances but also because it can escape from background determination by adding NO. In the previous studies of using a different technique of CRDS, higher N_2O_5 signals than the steady-state predictions were usually observed with elevated mixing ratios of PAN (Brown et al., 2005; Osthoff et al., 2006). The interference from PAN to the NO_3^- signals in our TD-CIMS was evaluated post field campaign by adding synthetic PAN to zero air and in the ambient air samples. The PAN was generated from a PAN calibrator (Meteorologie Consult GmbH), which is based on the reaction sequence of NO and acetone in ultrapure air with a Penray lamp. The concentrations of PAN that were added to the CIMS were quantified simultaneously by a NO_y analyzer (TEI 42CY). We also generated PAN using a conventional wet chemistry method by reacting peracetic acid with HNO_3 (Gaffney et al., 1984). The test results from the two PAN sources are consistent, thus this study only shows the result which used the PAN generated from the photolytic source.
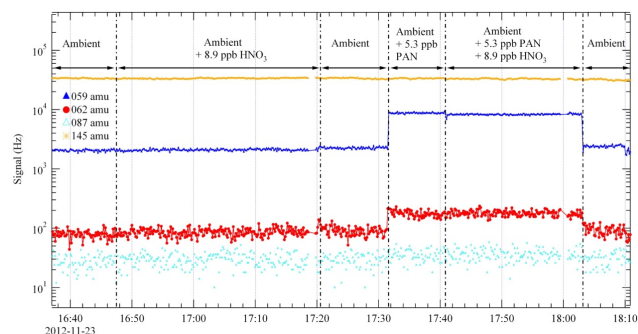
For tests of PAN in zero air and in relatively clean ambient air at a coastal site (Hok Tsui), a measurable interference from PAN was observed at 62 amu. The result in zero air (i.e., the response of 62 amu signal to the PAN standard) indicates 23 ± 4 pptv of apparent $NO_3 + N_2O_5$ signal per ppbv of PAN (one example is shown in Fig. 7). Adding PAN to ambient air at the coastal site yielded similar results. Table 2 shows the results from four tests conducted with varying ambient pollution levels and meteorological conditions. Introducing 5.6–6.3 ppb of PAN to the ambient air resulted in an increase in the NO_3^- signal of 42–75 pptv of $NO_3 + N_2O_5$ in our TD-CIMS, again indicating interference from PAN to the field NO_3/N_2O_5 measurements via the NO_3^- by TD-CIMS. The mechanism for the interference of PAN on the NO_3^- signal is unclear. Some researchers proposed that the $CH_3C(O)O^-$ ion (produced from the reaction of I^- with $CH_3C(O)O_2$ – the product of PAN thermo-dissociation) likely reacts with HNO_3 to produce NO_3^- (Veres et al., 2008; Roberts et al., 2010). This appeared not to be the case in our CIMS as additions of both PAN and HNO_3 didn't lead to any increase at 62 amu compared to the addition of PAN alone (see Fig. 8).

A surprising finding was much larger interferences at 62 amu when the same spike tests were conducted at the PolyU site, which has very high NO_x concentrations, and the interference appeared to increase with ambient NO_2 suggesting that reaction between PAN and NO_2 leads to significant interference at 62 amu. To confirm this, a series of tests were conducted by mixing different levels of NO_2 with synthetic PAN (see an example in Fig. 9). Figure 10 shows the signal at 62 amu as a function of PAN and NO_2 concentrations in zero air, which clearly shows that the interference increases with both PAN and NO_2. For example, at 5 ppbv of PAN, adding 60 ppbv of NO_2 produces a 400 ppt equivalent N_2O_5/NO_3 signal, compared to 150 pptv without NO_2, indicating an amplifying effect of NO_2 on the previously reported PAN interference. The exact chemical reaction that leads to the interference is not clear. We believe that interference of PAN + NO_2 is related to the thermal dissociation of
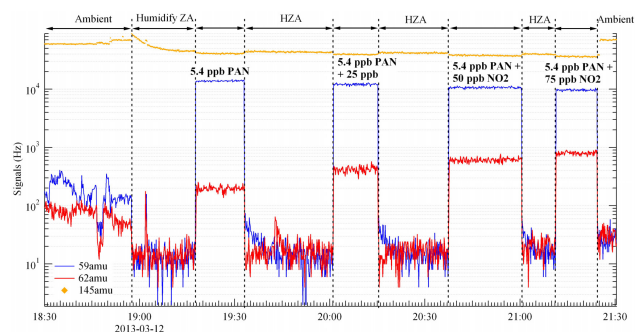
Fig. 9. Changes of signals at 59 and 62 amu when NO_2 was added to the sample flow of synthetic PAN.
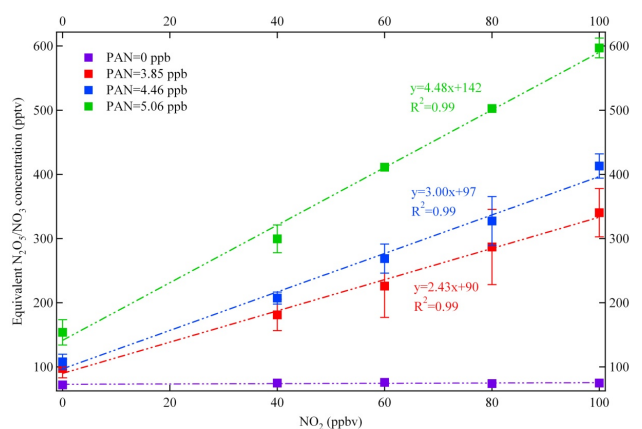

Fig. 10. Interference of NO_2 to equivalent NO_3^- concentration under different levels of PAN. Vertical bars are standard deviations of tests results.

PAN followed by radical reactions with NO_2 in the heated inlet. The radical reactions might serve as a source of NO_3 and N_2O_5, or the products could react with I^- to produce NO_3^- ions which is detected at 62 amu. We will evaluate the possible contribution of PAN + NO_2 to the observed high daytime N_2O_5 + NO_3 for the 2010 autumn study in Sect. 5.

4.2 Interference of HNO$_3$

Another possible source of interference to the NO_3^- ion is HNO_3 since it has a NO_3 group. Several studies have proposed the production of NO_3^- from ion-molecule reactions involving HNO_3, with somewhat inconsistent results. Huey and co-workers showed that the reaction of I^- with HNO_3 (producing NO_3^-) was rather inefficient. Thornton and coworkers on the other hand found a significant background signal (10–50 Hz) at the NO_3^- mass in a cold iodide CIMS under conditions of long ion-molecule reaction time, and attributed this to the reaction of HNO_3 with I^- (Thornton et al., 2003; Thornton and Abbatt, 2005). Roberts and coworkers reported that the HNO_3 was sensitive to the acetate ions and react to produce NO_3^- ions at the 62 amu (Veres et al., 2008; Roberts et al., 2010).

The relatively low background signals by adding NO in our study suggest insignificant interference from HNO_3 to our CIMS, which has been corrected during data reduction. This was further confirmed by the addition of HNO_3. The test was carried out three times for varying ambient conditions to check the repeatability of the results, which are listed in Table 2 with an example being shown in Fig. 8. It can be seen that after introducing a trace amount of HNO_3 to the inlet tube of our TD-CIMS, there was no significant increase in the NO_3^- signal compared to the ambient air. Additionally, adding HNO_3 to a trace level of PAN which resulted in an acetate ion signal of $\sim 0.9 \times 10^4$ Hz, the NO_3^- signal showed no apparent change compared to that for only adding PAN. These results suggest that the HNO_3 itself and its mixture with acetate ions have no significant interference to the detection of N_2O_5 + NO_3 via the NO_3^- ion in our TD-CIMS. It should be noted that the result of non-reactivity

of HNO_3 to the acetate ion in our TD-CIMS is different from that obtained by Roberts and coworkers using a NI-PT-CIMS (negative-ion proton-transfer CIMS) (Veres et al., 2008; Roberts et al., 2010), possibly due to different configurations and operation conditions.

4.3 Interference of other possible compounds

$ClONO_2$, $BrONO_2$ and HO_2NO_2 also react efficiently with I^- to produce NO_3^- (Huey et al., 1995; Hanson et al., 1996; Zhang et al., 1997; Amelynck et al., 2001). Again, the relatively low instrument background indicated small interference from $ClONO_2$ and $BrONO_2$ and any interference from them would have been corrected in our measurements because they cannot be removed by adding NO. The zeroing would not work for HO_2NO_2. However, it is impossible for HO_2NO_2 to pass through the heated inlet tube in our TD-CIMS considering its thermally unstable nature.

In addition, the NO_3^- ion may also come from the ion-molecule reactions involving Cl^- (35 amu), $C_2H_2N^-$ (40 amu), NO_2^- (46 amu), O_3^- (48 amu), CO_3^- (60 amu), and CO_4^- (76 amu) (listed in Table 1). These reagent ions were observed in quite low levels (i.e., < 20 Hz for 40 and 48 amu, and 10–500 Hz for 35, 46, 60 and 76 amu) in our TD-CIMS during the field measurements (see Fig. 3). Therefore, the ion-molecule reactions induced by Cl^-, $C_2H_2N^-$, NO_2^-, O_3^-, CO_3^- and CO_4^- are also believed to have no significant influence to the NO_3^- detection based on the relationship between the product ion and reactants.

In summary, according to the above tests and discussions, reactions between PAN and NO_2 in the heated inlet are found to have significant interference to signal at 62 amu in our TD-CIMS, while HNO_3 and other compounds are not believed to have contributed to signal at 62 amu, although our tests are not exhaustive for including all other chemicals.

Table 2. Summary of the interference tests for the TD-CIMS.

Test	Ambient conditions				Standard addition*		CIMS response	
	NO_y (ppb)	O_3 (ppb)	T (°)	RH (%)	ΔPAN (ppb)	ΔHNO_3 (ppb)	ΔN_2O_5 (ppt)	$\Delta S_{62}/\Delta S_{59}$ (cps/cps)
1	3.5	69	25	83	6.3	0	75	0.014
2	4.8	71	25	87	5.8	0	42	0.009
3	4.5	60	23	83	5.9	0	69	0.014
4	14.0	35	22	69	5.6	0	62	0.013
5	7.2	70	24	81	0	1.4	1	n.a.
6	6.2	76	24	64	0	9.1	1	n.a.
7	15.2	38	22	69	0	8.9	2	n.a.
8	12.8	41	21	68	5.3	8.9	62	n.a.

* The concentrations of PAN and HNO_3 that were added to the ambient air were determined by a NO_y analyzer.

5 Contribution of interference to daytime concentrations

As indicated above, laboratory and field tests revealed significant interference from PAN and NO_2 to 62 amu in our TD-CIMS. The contribution from this interference to the observed daytime $N_2O_5 + NO_3$ in this study was examined and corrected based on the tests results in Fig. 10. During the field campaign at PolyU, PAN was concurrently measured by the same TD-CIMS and a GC-ECD instrument (gas chromatography with an electron capture detector). For the six episodes shown in Fig. 6, the interference would contribute to 41.3–67.0 %, 29.0–39.8 %, 32.2–73.2 %, 25.6–49.2 %, 19.4–43.4 %, 20.4–77.8 % of the daytime signals in the 6 episodes (two examples on 23 October and 30 November are shown in Fig. 11). The remaining daytime signal after correction may be a real contribution from N_2O_5 and NO_3, but interferences from other untested chemicals (e.g., organic nitrates in addition to PAN) cannot be ruled out. As interferences at the 62 amu channel are large and variable, and some of them may not have been identified in our tests, it is difficult to determine the fraction of real signal from $N_2O_5 + NO_3$ in our study at 62 amu.

To compare the observed signals with the concentrations predicted by known chemistry, Fig. 12 shows the source strength and loss frequency of NO_3, the predicted $N_2O_5 + NO_3$ levels for the six polluted episodes, together with corrected $N_2O_5 + NO_3$ data (i.e., subtracting the interference due to PAN + NO_2). In brief, the reaction of NO_3 with NO is the dominant loss pathway at the study site. In most cases, the NO concentration was relatively high, and the calculated values using steady-state assumption (see SI) were much lower than the observed values (after correction for interference due to PAN + NO_2). There is one exception in the late afternoon on 24 October. At 16:00 on this day when O_3, NO_2 and NO concentrations were 96.1, 49.1 and 0.3 ppbv, respectively, the predicted NO_3 and N_2O_5
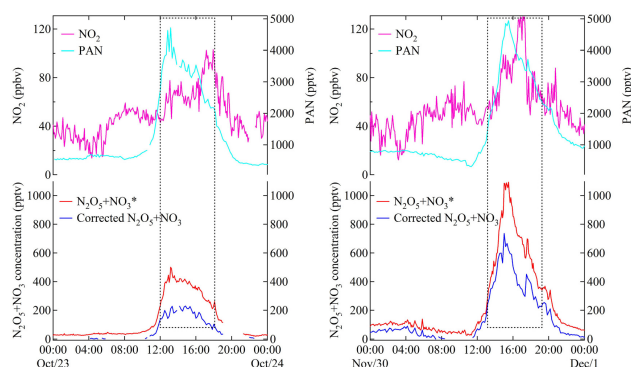

Fig. 11. Time series of corrected $(N_2O_5 + NO_3^*)$ and uncorrected $N_2O_5 + NO_3$, PAN, NO_2 and NO on 23 October and 30 November 2010.

concentration (5 min average) could reach 321 pptv if all major removal pathways are considered. In comparison, the measured $N_2O_5 + NO_3$ concentration was 286.5 pptv (with correction for PAN + NO_2 interference). The agreement between observation and prediction under the condition of very low NO in this case indicates that the elevated N_2O_5 in daytime is possible at the study site. The significant discrepancy in most cases may be attributed to other unknown measurement interference (e.g., chemical interference from organic nitrates in addition to PAN), unknown NO_3 source(s) (e.g., chemical reactions between Criegee intermediates and NO_2 suggested by recent studies (Welz et al., 2012; Ouyang et al., 2013), and invalidity of the steady-state assumption for air masses receiving fresh injection of NO). Further studies are required.

6 Other evidence of daytime $NO_3 + N_2O_5$ in Hong Kong

To check the measurement results at 62 amu, we attempted to measure ambient N_2O_5 with a cold version of CIMS
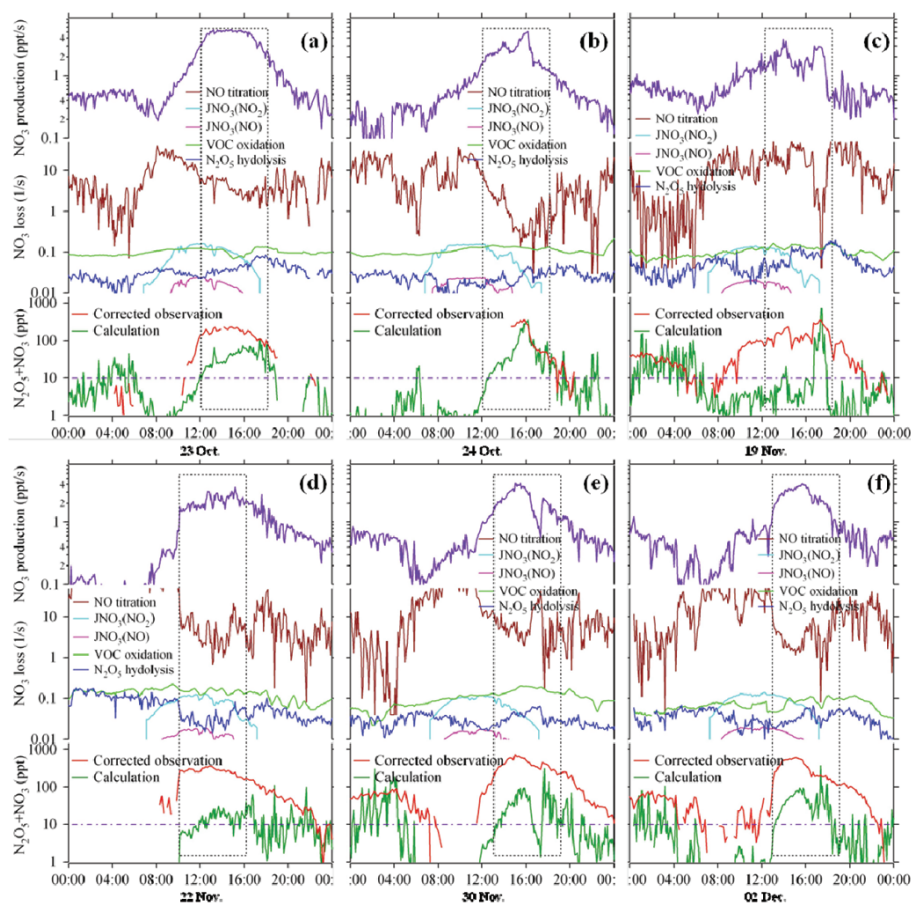
Fig. 12. NO_3 production rate from NO_2 and ozone, loss frequency of NO_3 from NO reaction, photolysis, VOC oxidation and N_2O_5 hydrolysis, steady-state calculated $N_2O_5 + NO_3$ and observed $N_2O_5 + NO_3$ after correction (for the interference from $PAN + NO_2$) for the six pollution episode days.

immediately after the present campaign at the same site. The CIMS was configured similar to that described by Kercher et al. (2009). When an unheated inlet tube is used, the reactions of N_2O_5 with I^- produce both the NO_3^- and $I(N_2O_5)^-$ cluster ions. The $I(N_2O_5)^-$ ion (at 235 amu) is thought to be free from the chemical interferences that can perturb the NO_3^- ion, and thus provides a better measure of N_2O_5 (Kercher et al., 2009). However, the $I(N_2O_5)^-$ sensitivity is influenced by the abundance of the water content in the sample flow. Similar to the setup with the heated inlet and the detection at 62 amu by TD-CIMS, signal at 235 amu with the cold CIMS also showed a daytime peak. Figure 13 gives an example of the ambient $I(N_2O_5)^-$ signal (in Hz) and related trace gases taken on 20 December 2010. The 235 amu signal exhibited generally good correlation with the 62 amu signal during both daytime and nighttime (figure not shown here). Calibration of the cold CIMS with the N_2O_5 standard in dry synthetic air gave a sensitivity of 0.55 ± 0.003 Hz pptv^{-1}. But the true sensitivity for ambient air with moderately high humidity during study is believed to be larger, possibly by a factor of two or more, according to our recent lab tests.

Another independent piece of evidence for the daytime $N_2O_5 + NO_3$ in Hong Kong is concurrent increase in the mixing ratios of $ClNO_2$ (a product of N_2O_5 hydrolysis) observed in a follow-up study in western Hong Kong (Tung Chung; see SI for the experiment information). At this site, elevated $N_2O_5 + NO_3$ signals were also found at 62 amu at daytime during photochemical episodes, with the $ClNO_2$ signals (208 amu) showing concurrent increases. Figure 14 shows an example for 28 August 2011. On that day, apparent $N_2O_5 + NO_3$ inferred from 62 amu exhibited an afternoon peak of 670 pptv (uncorrected 5 min average), and $ClNO_2$ had a concurrent enhancement to 120 pptv. To estimate the levels of N_2O_5 that would be needed to sustain such amount of $ClNO_2$, we assumed a photostationary steady state for $ClNO_2$ in the afternoon with an uptake coefficient of 0.03 for N_2O_5 hydrolysis on aerosol surfaces and a $ClNO_2$ yield of 10 % with consideration of relatively low content of sea salt in aerosols at the site. The photolysis rate of $ClNO_2$ was estimated as 7.8×10^{-4} s^{-1} using the method by Simon et al. (2009), and the aerosol surface area was 979 mm^2 m^{-3} from concurrent measurements of aerosol size
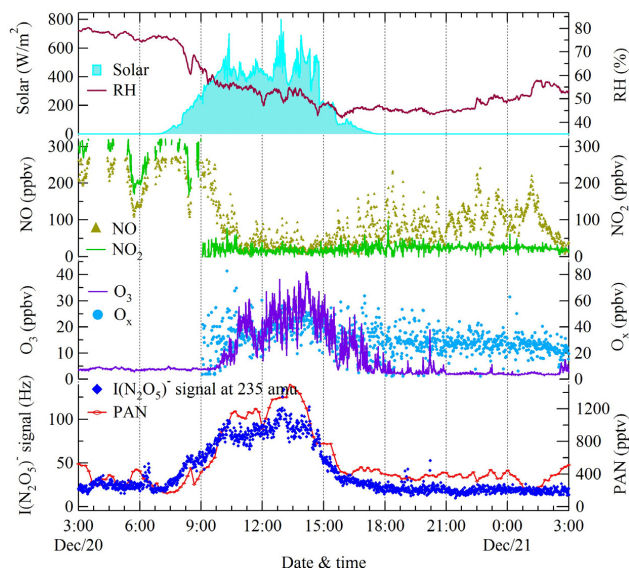
Fig. 13. Time series of $I(N_2O_5)^-$ signal at 235 amu, solar radiation and relative humidity in urban Hong Kong on 20 December 2010.
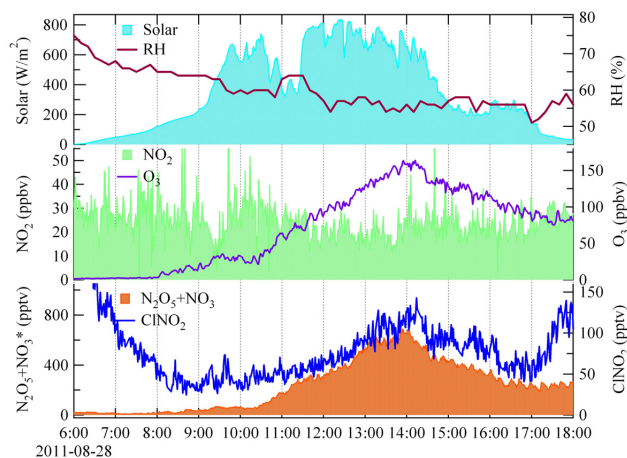

Fig. 14. A case showing concurrent increase of $ClNO_2$ and N_2O_5 at daytime during a photochemical episode at a suburban site (Tung Chung) in western Hong Kong.

distribution. The calculation showed that to produce the observed 120 pptv of $ClNO_2$, at least 518 pptv of N_2O_5 would be required. This result, although is not an absolute proof, supports the possibility of elevated daytime concentrations of $N_2O_5 + NO_3$ in Hong Kong. On this day the peak concentration of $ClNO_2$ was ∼ 600 pptv at night and the $ClNO_2$ concentration exhibited good correlation ($R^2 = 0.78$) with the observed NO_3^- signals at 62 amu (figures not shown here).

7　Conclusions

A TD-CIMS technique, which has been previously applied to field measurements in the US, was deployed to measure ambient NO_3 and N_2O_5 in urban Hong Kong in a photochemical season. Surprisingly, large signals of $NO_3 + N_2O_5$ inferred from 62 amu were frequently observed in daytime, which is in contrast to our current understanding of reactive nitrogen chemistry. Subsequent laboratory and field tests provide new insights into chemical interferences in the TD-CIMS. In particular, we have discovered that reaction between NO_2 and PAN can amplify the interference from PAN at 62 amu. This interference could have contributed 30–50 % to the average daytime NO_3 and N_2O_5 at our site. It is possible that the additional interferences from untested chemicals may have also contributed to the daytime signal at 62 amu. On the other hand, evidence exists to suggest that the elevated daytime signals at 62 amu may be in part due to real contribution from NO_3 or N_2O_5. In viewing of the large and variable interferences at 62 amu and difficulty in correcting them, we conclude that it is not suitable to use the TD-CIMS to measure NO_3 or N_2O_5 at 62 amu in a high NO_x environment like the present study site. Adoption of either 235 amu with a cold

inlet or an optics-based technique is recommended. We also suggest more studies to examine the abundance of daytime NO_3 and N_2O_5 in similar urban areas with co-existence of high ozone and NO_2.

Supplementary material related to this article is available online at http://www.atmos-meas-tech.net/7/1/ 2014/amt-7-1-2014-supplement.pdf.

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