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Techniques

A new technique for the selective measurement of atmospheric peroxy radical concentrations of HO_2 and RO_2 using a denuding method

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Abstract. A technique for the selective measurement of atmospheric HO_2 and RO_2 using peroxy radical chemical amplification coupled to laser-induced fluorescence NO_2 detection (PERCA-LIF) is demonstrated. By pulling the air through a filled pre-inlet advantage can be taken of the higher heterogeneous loss rate of HO_2 relative to CH_3O_2. Pre-inlet conditions have been found where ca. 90% of HO_2 was removed whereas the comparable CH_3O_2 loss was 15%. The dependence of loss rate on humidity and peroxy radical concentration has been investigated. When using glass beads as the surface for peroxy radical removal, the influence of the relative humidity on the removal efficiency becomes negligible. It may therefore be possible to apply this technique to the measurement of absolute concentrations of solely RO_2 as well as the sum of HO_2 and RO_2. The practical utility of the PERCA-LIF coupled to a denuder has been demonstrated with atmospheric measurements.

1 Introduction

Peroxy radicals RO_2 (with $R = H$ or C_xH_y) play an important role in the photo-oxidation cycles of the troposphere (Monks, 2005). They are produced mainly via the atmospheric oxidation of hydrocarbons and carbon monoxide by OH radicals and subsequent reactions with O_2. They can further react with NO to recycle OH radicals. This oxidation of NO via reaction with peroxy radicals is an important source of tropospheric ozone, a major constituent of photochemical oxidants that are detrimental to human health and contribute to global warming. The concentration of tropospheric ozone has significantly increased in recent years (Akimoto, 2003). To understand the mechanism of tropospheric ozone increase, precise and accurate measurements of ambient peroxy radical concentrations are essential.

Several methods have been developed for measuring atmospheric peroxy radicals and have recently been reviewed (Fuchs et al., 2008; Sadanaga et al., 2004; Heard and Pilling, 2003). Peroxy radical chemical amplification (PERCA) originated by Cantrell and Stedman (1982) is a method of measuring the total concentration of peroxy radicals, i.e. the sum of HO_2 and RO_2. In this method, peroxy radicals are converted to relatively high concentrations of NO_2 via a chain reaction by the addition of high concentrations of NO and CO in a reaction tube. The NO_2 product is then quantified by the appropriate measurement technique, e.g. luminol chemiluminescence (Parker et al., 2009), laser-induced fluorescence (Sadanaga et al., 2004) and cavity-ring-down (Liu et al., 2009) spectroscopy. In order to obtain absolute concentrations, the chain length of the amplification and the response of the NO_2 detector has to be determined in calibration experiments. Recent studies of PERCA have reported a greater wall loss rate of HO_2 relative to RO_2. For example, Mihele et al. (1999) reported a wall loss rate on a 1/4" Teflon tube of $2.8 \pm 0.2\,s^{-1}$ for HO_2 and $0.8 \pm 0.1\,s^{-1}$ for both CH_3O_2 and $C_2H_5O_2$ radicals in dry conditions. In this study, the HO_2 loss rate increased markedly with the relative humidity while the organic radicals showed no dependence.

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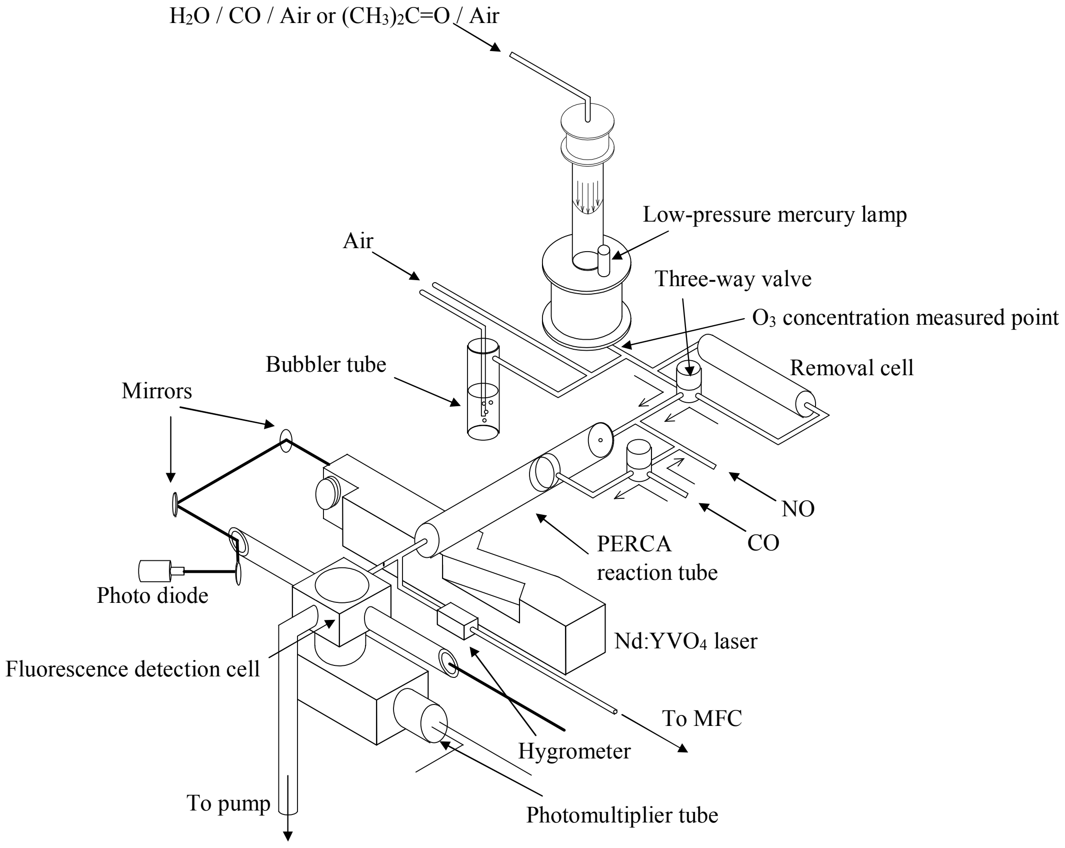

Fig. 1. Schematic diagram of the experiment. The system can be divided into 4 parts, (1) peroxy radical generator, (2) removal cell, (3) chemical amplification reaction tube and (4) LIF NO_2 detector. MFC indicates mass flow controller.

The greater wall loss rate of HO_2 relative to RO_2 can be actively used to separate HO_2 and RO_2 during atmospheric measurements by predominantly denuding HO_2 prior to the PERCA inlet. This makes it possible to measure the concentration of RO_2 separately from the sum of HO_2 and RO_2, and therefore obtain the ambient concentrations of HO_2 and RO_2. It will no longer be necessary to estimate the concentration of the individual radical species from the ratio of HO_2 to RO_2 (Cantrell et al., 1993; Clemitshaw et al., 1997; Jenkin et al., 1998).

In this paper we describe the development of a prototype instrument for the separate measurement of HO_2 and RO_2 by use of selective denuding of HO_2 prior to quantification by the PERCA technique. Three different materials have been tested as the peroxy radical remover. Also, the water and concentration dependence of the HO_2 and RO_2 removal efficiency was investigated in detail for these three materials. Further, the practical utility of the developed instrument is evaluated through atmospheric measurements of HO_2 and RO_2 radicals.

2 Experimental

The experimental system used in this work is similar to the PERCA system described and validated in detail by Sadanaga et al. (2004) (see also Fig. 1). The system consists of (1) a peroxy radical generator, (2) a removal cell, (3) chemical amplification reaction tube and (4) LIF NO_2 detector.

The peroxy radical generation system is similar to the HO_X generator described by Kanaya et al. [2001]. HO_2 radicals are generated by the photolysis of H_2O at 185 nm using a low-pressure mercury lamp (Sen light, SP-5-2H). By addition of CO, generated OH is converted to HO_2:

$$H_2O + h\,\nu \longrightarrow H + OH \tag{R1}$$

$$H + O_2 + M \longrightarrow HO_2 + M \tag{R2}$$

$$OH + CO + O_2 \longrightarrow HO_2 + CO_2 \tag{R3}$$

As proxy for RO_2, CH_3O_2 and $CH_3C(O)O_2$ radicals were generated in the same radical generator by photolysis of acetone (Kanto Chemical, 99.0 %):

$$(CH_3)_2\,CO + h\,\nu \longrightarrow CH_3 + CH_3CO \tag{R4}$$

$$CH_3 + O_2 + M \longrightarrow CH_3O_2 + M \quad (R5)$$

$$CH_3CO + O_2 + M \longrightarrow CH_3C(O)O_2 + M \quad (R6)$$

The low-pressure mercury lamp was not filtered and the photolysis of acetone will occur mainly at 254 nm from its absorption cross section (Gierczak et al., 1998). The principle products are thought to be CH_3O_2 and $CH_3C(O)O_2$ at nearly equal concentrations ($[CH_3O_2]$:$[CH_3C(O)O_2] \approx 1.1 : 0.9$) (Rajakumar et al., 2008). Peroxy radicals can be diverted either through the removal cell or through a blank cell, easy switching between both pathways is enabled by use of a Teflon solenoid three-way valve (Flon Industry, FSS-0306YN). Hereafter, we refer to these pathways as removal and blank mode respectively. In order to investigate the water dependence of the peroxy radical removal efficiency, varying quantities of dry air and humidified air (the air is humidified by passing it through a water bubbler) were mixed allowing air of varying relative humidity to be added to the flow at the exit of the radical generator as shown in Fig. 1. The relative humidity is measured at the exit of the PERCA instrument using a humidity sensor (VAISALA, HMT330). Air used in these experiments was synthesized from N_2 and O_2 (Nippon Sanso, 99.99%>) by using mass flow controllers (KOFLOC, Model3660). After passing through either the removal or blank cell the gas flow is introduced to the PERCA reaction tube.

The removal cell consists of a tube and beads of the same material. We have tested two different types of Teflon (PFA and PTFE) as well as glass. Cylindrical Teflon (PFA and PTFE) beads (Flon Industry, 2 dia. × 5 mm high) were packed into a 30 cm long 1.27 cm diameter Teflon tube. For testing glass, spherical glass beads (GL Science, 1 mm dia.) were packed into a 5 cm long 1.27 cm glass tube. For easy comparison, the length of the removal cell was adjusted to obtain a removal efficiency of approximately 90% for HO_2 radicals. Additionally, the length of the blank cell was set so as to have the same residence time as in the removal cell.

Concentrations of HO_2 and RO_2 radicals were measured by a chemical amplification and laser-induced fluorescence (PERCA/LIF) instrument, based on Sadanaga et al. (2004). The inlet consists of a 300 mm long glass tube of 20 mm diameter. When used in chemical amplification mode (PERCA mode), the flow from the radical generator was mixed with a NO/N_2 mixture (Nippon Sanso, 100 ppmv NO) and pure CO gas (Nippon Sanso) at the entrance of the reaction tube; flows were adjusted to obtain concentrations of NO and CO of 5 ppmV and 10% respectively. In order to measure the background NO_2 concentration (BG mode), CO was added approximately 75 mm downstream from the inlet, leading to a distance of 225 mm between second addition point and radical detection point. OH generated from the reaction of HO_2 with NO will thus have no CO with which to react and the chain cycle is terminated. By switching the CO addition and not just stopping it, the decrease of the fluorescence signal owing to CO addition (dilution of the gas mixture and fluorescence quenching) is kept constant. A Teflon solenoid valve (Flon Industry, FSS-0306YN) is used to switch between the two modes once per minute. The total flow rate in the reaction tube was set to 2 SLPM (Standard Litres per Minute). A part of the total flow was introduced into the LIF detector. The excess air flow from the reaction tube was evacuated by a diaphragm pump (ULVAC, MD-4) through a mass flow controller (KOFLOC, Model3660) and its humidity and temperature were monitored with a humidity sensor (VAISALA, HMT330).

The NO_2 fluorescence detection system was essentially the same as the instrument described in an earlier work by Miyazaki et al. (2008). The pressure inside the fluorescence detection cell is reduced to ca. 2 Torr using a critical orifice (0.3 mm id) and an oil rotary pump (Ulvac, GVD-200A; $200\,\mathrm{l\,min^{-1}}$) in order to minimize the collisional quenching of the excited NO_2 molecules by air (Matsumoto et al., 2006). The second harmonic of a diode-laser-pumped solid-state pulsed $Nd{:}YVO_4$ laser (Spectra-Physics, YHP70-106Q; 5 W, 10 kHz, 532 nm) is used for NO_2 excitation. The laser power is monitored outside the detection cell by using a calibrated photodiode (Hamamatsu, S1226-5BQ) in order to correct for possible drifts in laser power. The fluorescence is collected and focused through optical lenses and passes through a sharp cut-off glass filter (Asahi Technoglass Corp., R62) onto a photomultiplier tube (PMT; Hamamatsu, R928P). The output signal from the PMT is counted between 1.10 and 3.02 µs after the laser excitation using a photon counter (Stanford, SR400). The limit of detection (LOD) for HO_2 is estimated by the following equation when governed by a background-limited case:

$$\mathrm{LOD_{HO2}} \approx \frac{(S/N)}{S_{\mathrm{HO2}}} \left(\frac{1}{m} + \frac{1}{n}\right)^{1/2} \left(\frac{S_{\mathrm{BG}}}{I \cdot \Delta t}\right)^{1/2}, \quad (1)$$

where (S/N) is the signal-to-noise ratio for defining the LOD, S_{HO2} is the sensitivity of the HO_2 radical measurement, m and n are the number of measurements of the background and sample, respectively, S_{BG} is the signal of the background measurement ($\mathrm{cps\,W^{-1}}$: count per second per Watt), I is the laser energy (W), and Δt is the averaging interval (s) (Sadanaga et al., 2004). Under typical conditions, the LOD in dry conditions is determined to be 0.41 pptv when $(S/N) = 2$, $S_{\mathrm{HO2}} = 26\,\mathrm{cps\,ppt^{-1}\,W^{-1}}$, $m = n = 1$, $S_{\mathrm{BG}} = 2064\,\mathrm{cps\,W^{-1}}$, $I = 2.3\,\mathrm{W}$, and $\Delta t = 60\,\mathrm{s}$. Calibration of S_{HO2} was conducted by the method of simultaneous photolysis of O_2 and H_2O using peroxy radical generator as described above (Sadanaga et al., 2004). O_3 concentration was measured by an ozone monitor (Dylec, Model 1100) at the exit of the peroxy radical generator by changing the inlet tube. Typically, HO_2 and RO_2 radicals were generated at concentrations between 150–200 pptv.

3 Results and discussion

Figure 2 shows an example of the removal efficiency measurement: the upper part a of the figure illustrates the measurement of HO_2 radicals, while the lower part b is a typical example for $CH_3O_2 + CH_3C(O)O_2$ radicals. In both cases, the signal differences between PERCA and BG mode is the HO_2 or $CH_3O_2 + CH_3C(O)O_2$ concentration. The left part of each figure shows the $HO_2/CH_3O_2 + CH_3C(O)O_2$ concentration after passing through the blank cell, while the right part of the graph shows the signal obtained after passing the gas mixture through the removal cell prior to entering the PERCA inlet, also in PERCA and BG mode. The connecting tubing in the blank cell path and in the removal cell path are made of the same material: the path in the blank cell (and therefore the residence time) is approximately 10 times shorter than the tubing in the removal cell path. Simple calculations show that radical loss is insignificant ($< 3\%$) under the experimental conditions in this part of the experimental set-up and no correction was required. The HO_2 concentrations for each blank or removal mode can be described as follows

$$[HO_2]_{\text{removal}} \text{ or } [HO_2]_{\text{blank}} = \frac{I_{\text{HO2\_removal}} \text{ or } I_{\text{HO2\_blank}}}{S_{\text{HO2}} \times C_{\text{humid}}}, \quad (2)$$

where $[HO_2]_{\text{removal}}$ and $[HO_2]_{\text{blank}}$ indicates the concentration of HO_2 radicals in the removal and blank mode respectively and C_{humid} indicate the correction coefficient of S_{HO2} for humidity. It has been shown by several authors (Mihele and Hastie, 1998; Reichert et al., 2003; Salisbury et al., 2002) that the chain length of the chemical amplification decreases with increasing humidity: this correction factor accounts for this characteristic. Our PERCA-LIF instrument also experiences chain length variations with changing humidity as reported by Sadanaga et al. (2004), in which the method of determining the correction factor is also described. However, for the experiments described in this work the humidity dependence of the chain length is of no importance as only the ratio of signals from the blank and removal cells is measured: both blank and removal path exhibit the same relative humidity and chain length and therefore the correction factor cancels.

Variation in the removal of HO_2 was evaluated by defining a removal efficiency factor α as follows,

$$\alpha = 1 - \frac{[HO_2]_{\text{removal}}}{[HO_2]_{\text{blank}}}. \quad (3)$$

$[HO_2]_{\text{dec}}$ and $[HO_2]_{\text{blank}}$ can be substituted by Eq. (2) and finally the removal efficiency α of HO_2 radicals is determined as follows:

$$\alpha = 1 - \frac{I_{\text{HO2\_removal}}}{I_{\text{HO2\_blank}}} \quad (4)$$

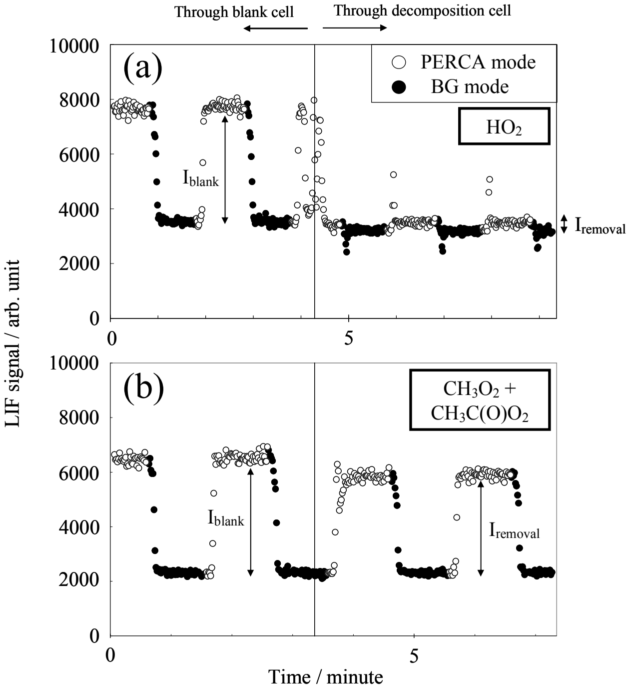

Fig. 2. An example of removal efficiency measurements showing PERCA/BG mode for both blank (left side) and removal (right side) mode. PERCA/BG mode are switched every minute. Upper panel **(a)** shows HO_2, lower panel **(b)** is $CH_3O_2 + CH_3C(O)O_2$.

The removal efficiency of $CH_3O_2 + CH_3C(O)O_2$ radicals can be expressed the same way:

$$\beta = 1 - \frac{I_{\text{CH3O2+CH3C(O)O2\_removal}}}{I_{\text{CH3O2+CH3C(O)O2\_blank}}} \quad (5)$$

Figure 3 summarizes the results of the removal efficiency measurements by plotting α and β as a function of relative humidity for the three different materials tested in this study: for all experiments, the initial radical concentration was kept constant at around 150 pptv. Figure 3a–c show the results for PFA, PTFE and glass. Error bars indicate the 95% confidence interval. As mentioned above, the lengths of the removal cells have been adjusted as to obtain around 90% removal efficiency for HO_2 at a relative humidity between 20–60%.

As can be seen from Fig. 3, the removal efficiency β for $CH_3O_2 + CH_3C(O)O_2$ is approximately 15% for all three materials and only slightly depends on the relative humidity. However, the removal efficiency of HO_2 is more sensitive to the relative humidity and shows different behaviours for the three materials tested in this work. When using Teflon (PFA, PTFE), the removal efficiency of HO_2 radicals decreases rapidly with decreasing humidity and is only around 10% in dry conditions. With increasing humidity, α increases for both materials and approaches the maximum of 90% at humidities of around 20%. Further, increasing the humidity leads to a slow decrease of α for both materials, showing a

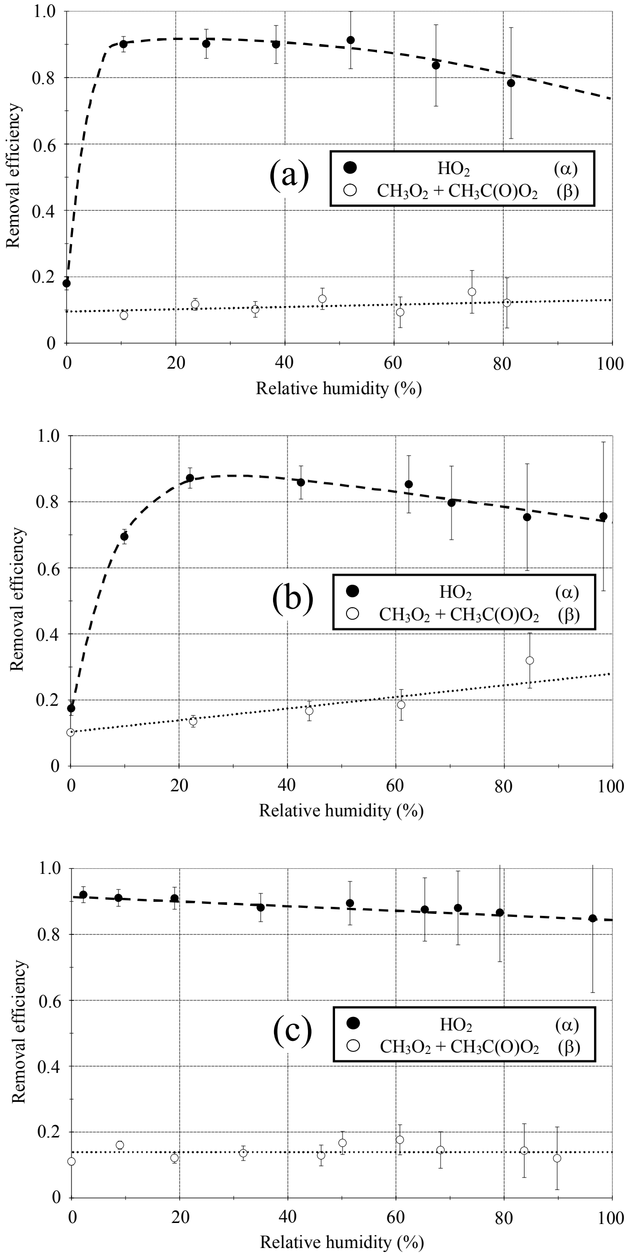

Fig. 3. Results of the removal efficiency α (HO_2) and β ($CH_3O_2 + CH_3C(O)O_2$) as a function of relative humidity using **(a)** PFA, **(b)** PTFE and **(c)** glass as the material in the removal cell.

slightly more rapid decrease in the case of PFA compared to PTFE. In the case of $CH_3O_2 + CH_3C(O)O_2$, this behaviour is not observed: for both materials the removal efficiency β increases slightly and steadily with relative humidity. Though the removal efficiency of RO_2 might depend on the structure of R, the average removal efficiency for both CH_3O_2 and $CH_3C(O)O_2$ radicals is 0.15 as shown in Fig. 3. This confirms the observation reported by Mihele et al. (1999).

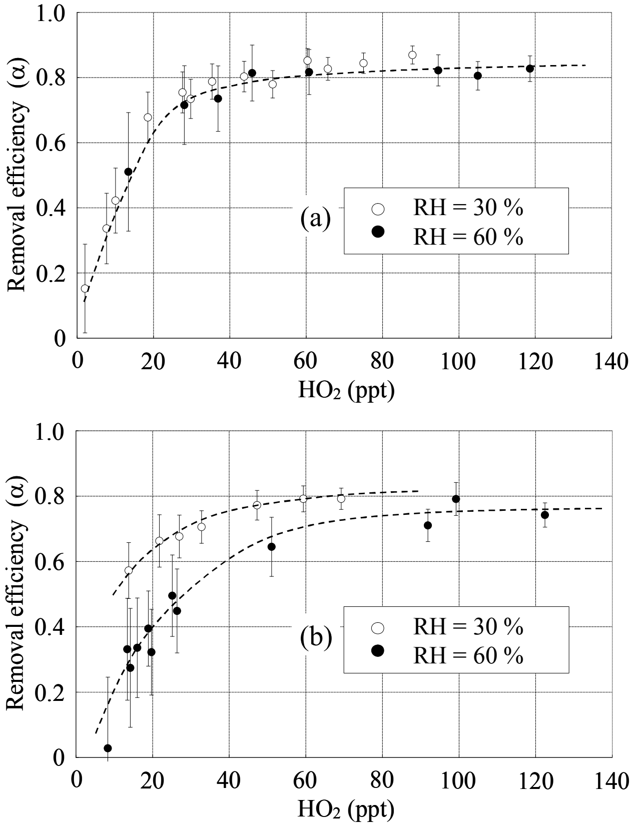

Fig. 4. Removal efficiency α for two different relative humidities as a function of initial HO_2 radical concentration: panel **(a)** shows the results with glass as filling material, panel **(b)** is for PFA.

Results change markedly when using glass as material in the removal cell: even in dry conditions a removal efficiency of about 90% for HO_2 is observed. With increasing relative humidity, α decreases slightly and steadily approaching 85% at approximately 100% humidity. The removal efficiency of $CH_3O_2 + CH_3C(O)O_2$ radicals was found to be almost constant at around 15% across the entire range of relative humidity.

These results indicate clearly that the removal efficiency variation is affected by the surface structure of the material within the removal cell. The removal efficiency has almost been constant for several days of experiment, i.e. no saturation effect has been observed. Therefore, HO_2 and RO_2 radicals seem to be removed from the gas phase not by a simple absorption process, but probably react at the surface to generate non-radical products. Furthermore, HO_2 radicals seem to be absorbed by hydrophilic surface sites since the removal efficiency of HO_2 radicals is high when using glass, even under dry conditions.

We have further investigated the removal efficiency of HO_2 radicals as a function of initial radical concentration: the results are summarized in Fig. 4 for glass (Fig. 4a) and PFA (Fig. 4b). As can be seen, the efficiency depends strongly on the initial concentration over ambient HO_2 concentration range. For glass as filling material, the removal efficiencies do not depend on the relative humidity, while for PFA the efficiency is somewhat higher at lower relative humidity. The concentration dependence of the removal is probably connected to the removal mechanism, for example a bimolecular reaction on the surface between two absorbed radicals. On the other hand, the constant removal efficiency for $CH_3O_2 + CH_3C(O)O_2$ was obtained at a concentration range of ∼150 pptv. Further work is needed to understand the removal mechanism. The concentration dependence of α has of course an impact on the applicability of this experimental technique to atmospheric measurements and needs to be taken into account when developing a field instrument. In this experiment, the geometry of the removal cell was designed to achieve a removal efficiency of approximately 90% for HO_2 radicals at HO_2 concentrations of ∼150 pptv, allowing for an easy comparison. However, some improvement on the removal cell is necessary for observations under ambient HO_2 concentrations because the removal efficiency for HO_2 decreases steeply over the typical ambient HO_2 concentration range. If the HO_2 loss reaction occurs through bimolecular reaction on the surface, relatively high removal efficiency for HO_2 even under the ambient concentration range can be obtained by increasing the residence time or controlling the surface temperature. Some optimization is necessary for ambient measurements to be made with high precision.

In order to improve the removal efficiency for HO_2 radicals under typical ambient concentrations, a longer removal cell with an increased surface was applied to the measurement. The results are summarized in Fig. 5. The removal efficiency α for two different long removal cells was plotted as a function of initial HO_2 radical concentration. Unlike the previous removal cells that were used for earlier experiments, these cells have a honeycomb structure in that many narrow pyrex glass tubes are packed in the cell. The length of Denuder 1 was adjusted to obtain a removal efficiency of approximately 90% for HO_2 radicals. Denuder 2 is twice as long as Denuder 1. As can be seen, the removal efficiency still depends on initial HO_2 concentrations as in Fig. 4. However, as can be seen in Fig. 5, high removal efficiencies can be obtained even in the lower range of typical ambient HO_2 radical concentration range. Compared with Denuder 1 results, Denuder 2 shows higher removal efficiency for the same radical concentrations. This result suggests that a high removal efficiency for HO_2 can be obtained even under the ambient concentration range by increasing the residence time. As for the removal efficiency for CH_3O_2 by using these Denuder 1 and 2, the constant lower removal efficiency of 0.05–0.06 can be obtained for both denuders. In this experiment, CH_3O_2 radicals were generated by the photolysis of CH_3I by using the radical generator described above. The low-pressure mercury lamp was not filtered and the photolysis of CH_3I will occur mainly at 254 nm to generate mainly CH_3O_2 radical (Clemitshaw et al., 1997). This results shows that the removal efficiency for $CH_3C(O)O_2$ is relatively higher than that for CH_3O_2. Considering the result of the acetone photolysis experiment, a removal efficiency of at least 0.27 for the $CH_3C(O)O_2$ radical can be obtained. This result indicates that the removal mechanism might be affected by the peroxy radical structure. Further experiment is needed for other types of peroxy radicals, but the removal efficiency for CH_3O_2 was used as that for RO_2 ($R = C_xH_y$) in this study.

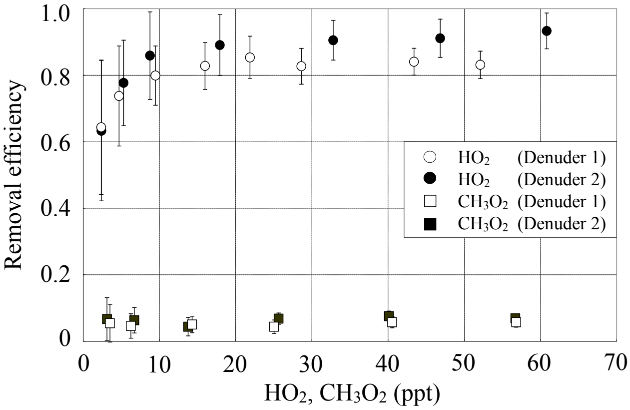

Fig. 5. Removal efficiency α for two different long denuders as a function of initial HO_2 radical concentration: Denuder 2 is twice as long as Denuder 1.

Further tests show that the removal efficiency for HO_2 does not depend on the presence of RO_2 radicals. In some experiments, C_2H_6 was added to photolysis gas instead of CO: now OH radicals will be converted to $C_2H_5O_2$ and equal amounts of HO_2 and $C_2H_5O_2$ radicals will be generated. The LIF signal obtained through these experiments was consistent with an LIF signal calculated using separately premeasured removal efficiencies for HO_2 and RO_2.

As discussed above, the LOD for HO_2 and RO_2 measurements was calculated to be 1 pptv in dry conditions considering the removal efficiencies for HO_2 and RO_2 under experimental conditions.

Since the effect of humidity on removal efficiency can be minimized by using glass, this material seems to be a good choice as material for the removal cell. By using the removal efficiency factors, the concentrations of HO_2 and RO_2 can then be described using LIF signal S as follow:

$$S_{\mathrm{HO2}}\,[\mathrm{HO_2}]_{\mathrm{blank}} + S_{\mathrm{RO2}}\,[\mathrm{RO_2}]_{\mathrm{blank}} = \frac{I_{\mathrm{blank}}}{C_{\mathrm{humid}}}, \tag{6}$$

$$S_{\mathrm{HO2}}\,[\mathrm{HO_2}]_{\mathrm{removal}} + S_{\mathrm{RO2}}\,[\mathrm{RO_2}]_{\mathrm{removal}} = \frac{I_{\mathrm{removal}}}{C_{\mathrm{humid}}}, \tag{7}$$

where S_{HO2} and S_{RO2} indicate the sensitivity for HO_2 and RO_2 respectively. I_{blank} and I_{removal} indicate the LIF signal in the blank and removal mode, respectively. Here, $[\mathrm{HO_2}]_{\mathrm{removal}}$ is described by $[\mathrm{HO_2}]_{\mathrm{blank}}$ in consideration of the combination of first and second order reactions for HO_2 as below:

$$[HO_2]_{\text{removal}} = \frac{[HO_2]_{\text{blank}}}{F_1 \times [HO_2]_{\text{blank}} + F_2}, \tag{8}$$

where F_1 and F_2 are correction factors obtained by fitting the data in Fig. 5 using Eq. (8).

In the same way, $[RO_2]_{\text{removal}}$ can be described by $[RO_2]_{\text{blank}}$ because the constant removal efficiency for RO_2 can be obtained:

$$[RO_2]_{\text{removal}} = (1 - \beta)\, [RO_2]_{\text{blank}}, \tag{9}$$

Equations (6)–(9) were solved for $[HO_2]$ and $[RO_2]$ to give HO_2 and RO_2 concentrations. This methodology allows the concentrations of HO_2 and RO_2 to be described separately by the LIF signals obtained in the two measurement modes and the calibration factors, if the factor C_{humid}, i.e. the variation of the chain length only with relative humidity, independent of the radical concentration, has been determined in separate experiments. Furthermore, using this method it is not necessary to correct for the sensitivity of HO_2 and RO_2 based on the hypothesis of an abundance ratio of HO_2 and RO_2, because now the concentrations of HO_2 and RO_2 can be corrected by separate sensitivity factors of S_{HO2} and S_{RO2}. More selective and precise measurements of HO_2 and RO_2 concentrations can therefore be possible using this technique.

4 Ambient measurement

Ambient measurements were performed using the newly developed PERCA-LIF set-up coupled to the denuder instrument during July 2010 at our campus located in Hachioji, Tokyo, Japan. Denuder 1 in Fig. 5 was used during the observations. The instruments were set up on the roof container of the ninth building of Tokyo Metropolitan University. The site is located in the suburbs of Tokyo.

Figure 6 shows an example of the measured diurnal profiles of HO_2 and RO_2 radical concentrations. Data averaged over 2 min are plotted in Fig. 6 and the error bars represent 1 σ precisions of the data points. Each solid line in Fig. 6 indicates a 10 points moving average data.

A typical diurnal variation was observed for both HO_2 and RO_2 radicals, and a maximum concentration value of 50pptv for RO_2 ($R = C_x H_y$) and 25 pptv for HO_2 was observed at noon time. A removal efficiency for CH_3O_2 of 0.05 was used for the analysis. The variations in RO_2 and HO_2 are highly correlated, and the concentrations of the HO_2 radical were half the magnitude of that of the RO_2 radical. The concentrations of HO_2 obtained in this study are similar to concentrations previously observed (Kanaya et al., 2007). The practical utility of our PERCA-LIF coupled to the denuder instrument has been demonstrated for atmospheric measurements.

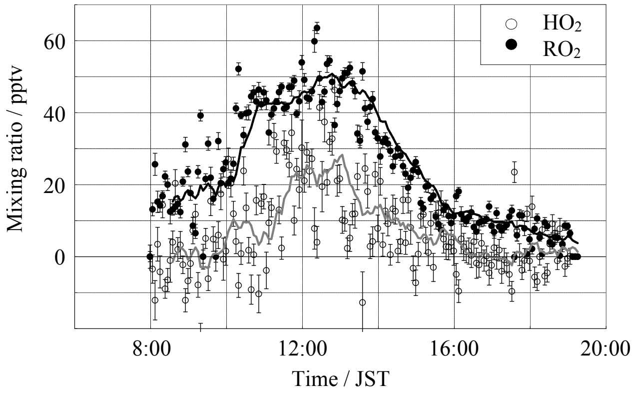

Fig. 6. In situ measurements of HO_2 and RO_2 radical concentrations with 1 σ precision error bars. Each solid line indicates the 10 points moving average data. The measurements were obtained on 23 July 2010 in Hachioji, Tokyo.

5 Conclusions

An improvement to the well-established PERCA technique allowing the selective measurement of HO_2 and RO_2 radical concentrations has been described in this paper. Advantage is taken of different heterogeneous removal efficiencies for HO_2 and RO_2 radicals prior to the inlet of the PERCA reaction cell. Three different materials have been tested to investigate the variation of the removal efficiency as a function of relative humidity. From these results, glass has been found to be best suited as the material for the removal cell as it shows very low dependence on relative humidity, the difference of removal efficiency seems to be linked to the surface structure. The removal cell filled with glass showed about 90% removal efficiency of HO_2 over the entire relative humidity range, compared to only 15% removal efficiency of CH_3O_2. The investigation of the dependence of the removal efficiency on the concentration at a given relative humidity has been tested for HO_2 radicals on glass and PFA as filling material. Both materials show a pronounced dependence on the concentration, i.e. the removal efficiency decreases steeply at low initial radical concentrations, probably due to the removal mechanism. On the other hand, the constant removal efficiency for CH_3O_2 and $CH_3C(O)O_2$ was obtained at a concentration of ~150 pptv. In order to improve the removal efficiency for HO_2 under ambient concentrations range, a longer removal cell with increased surface to volume ratio was applied to the instrument. Using a longer removal cell a higher removal efficiency can be obtained at lower radical concentrations demonstrating a high removal efficiency for HO_2. LOD for both HO_2 and RO_2 measurements was calculated to be 1 pptv in dry conditions considering the removal efficiencies for HO_2 and RO_2 under experimental conditions. This performance could be applicable to field measurements. The first ambient measurements were performed by the newly developed PERCA-LIF coupled to the denuder instrument in summertime of Tokyo, Japan. Typical diurnal variations were observed for both HO_2 and RO_2 radicals, and the maximum concentration value of 50 pptv for RO_2 and 25 pptv for HO_2 was observed at noon time. The practical utility of our PERCA-LIF coupled to the denuder instrument has been demonstrated for atmospheric measurements.

The results presented in this work are promising and indicate the possibility of selective measurement of peroxy radicals. It has been shown that the concentrations of HO_2 and RO_2 can be independently corrected by separate sensitivities of S_{HO2} and S_{RO2}. Clearly, there is more work needed in order to generalise these observations to other types of RO_2, but we think that this technique has the potential to increase the precision of atmospheric peroxy radical measurements in the future.

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