A new technique for the selective measurement of atmospheric peroxy radical concentrations of HO\textsubscript{2} and RO\textsubscript{2} using a denuding method

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Abstract. A technique for the selective measurement of atmospheric HO\textsubscript{2} and RO\textsubscript{2} using peroxy radical chemical amplification coupled to laser-induced fluorescence NO\textsubscript{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\textsubscript{2} relative to CH\textsubscript{3}O\textsubscript{2}. Pre-inlet conditions have been found where ca. 90% of HO\textsubscript{2} was removed whereas the comparable CH\textsubscript{3}O\textsubscript{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\textsubscript{2} as well as the sum of HO\textsubscript{2} and RO\textsubscript{2}. The practical utility of the PERCA-LIF coupled to a denuder has been demonstrated with atmospheric measurements.

1 Introduction

Peroxy radicals RO\textsubscript{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\textsubscript{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\textsubscript{2} and RO\textsubscript{2}. In this method, peroxy radicals are converted to relatively high concentrations of NO\textsubscript{2} via a chain reaction by the addition of high concentrations of NO and CO in a reaction tube. The NO\textsubscript{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\textsubscript{2} detector has to be determined in calibration experiments. Recent studies of PERCA have reported a greater wall loss rate of HO\textsubscript{2} relative to RO\textsubscript{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\textsuperscript{-1} for HO\textsubscript{2} and \(0.8 \pm 0.1\) s\textsuperscript{-1} for both CH\textsubscript{3}O\textsubscript{2} and C\textsubscript{2}H\textsubscript{5}O\textsubscript{2} radicals in dry conditions. In this study, the HO\textsubscript{2} loss rate increased markedly with the relative humidity while the organic radicals showed no dependence.

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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$_2$O at 185 nm using a low-pressure mercury lamp (Sen light, SP-5-2H). By addition of CO, generated OH is converted to HO$_2$:

\[
\text{H}_2\text{O} + h\nu \rightarrow \text{H} + \text{OH} \quad (\text{R1})
\]

\[
\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M} \quad (\text{R2})
\]

\[
\text{OH} + \text{CO} + \text{O}_2 \rightarrow \text{HO}_2 + \text{CO}_2 \quad (\text{R3})
\]

As proxy for RO$_2$, CH$_3$O$_2$ and CH$_3$C(O)O$_2$ radicals were generated in the same radical generator by photolysis of acetone (Kanto Chemical, 99.0 %):

\[
\text{(CH}_3\text{)}_2\text{CO} + h\nu \rightarrow \text{CH}_3 + \text{CH}_3\text{CO} \quad (\text{R4})
\]
CH₃ + O₂ + M → CH₃O₂ + M \quad (R5)

CH₃CO + O₂ + M → CH₃C(O)O₂ + 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 CH₃O₂ and CH₃C(O)O₂ at nearly equal concentrations ([CH₃O₂] = [CH₃C(O)O₂] ≈ 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 N₂ and O₂ (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 HO₂ 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 HO₂ and RO₂ 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/N₂ 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 NO₂ 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 HO₂ 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 NO₂ 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; 201 min⁻¹) in order to minimize the collisional quenching of the excited NO₂ molecules by air (Matsumoto et al., 2006). The second harmonic of a diode-laser-pumped solid-state pulsed Nd:YVO₄ laser (Spectra-Physics, YHP70-106Q; 5 W, 10 kHz, 532 nm) is used for NO₂ excitation. The laser power is monitored outside the detection cell by using a calibrated photodiode (Hamamatsu, S1226-5QB) 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 HO₂ is estimated by the following equation when governed by a background-limited case:

\[
\text{LOD}_{\text{HO}_2} \approx \frac{(S/N)}{S_{\text{HO}_2}} \left( \frac{1}{m} + \frac{1}{n} \right)^{1/2} \left( \frac{S_{\text{BG}}}{I \cdot \Delta t} \right)^{1/2},
\]

where \((S/N)\) is the signal-to-noise ratio for defining the LOD, \(S_{\text{HO}_2}\) is the sensitivity of the HO₂ radical measurement, \(m\) and \(n\) are the number of measurements of the background and sample, respectively, \(S_{\text{BG}}\) is the signal of the background measurement (cps W⁻¹: count per second per Watt), \(I\) is the laser energy (W), and \(\Delta t\) 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 \((S/N) = 2, S_{\text{HO}_2} = 26 \text{ cps ppt}^{-1} W^{-1}, m = n = 1, S_{\text{BG}} = 2064 \text{ cps W}^{-1}, I = 2.3 \text{ W}, \text{ and } \Delta t = 60 \text{ s}. \) Calibration of \(S_{\text{HO}_2}\) was conducted by the method of simultaneous photolysis of O₂ and H₂O using peroxy radical generator as described above (Sadanaga et al., 2004). O₃ concentration was measured by an ozone monitor (Dylec, Model 1100) at the exit of the peroxy radical generator by changing the inlet tube. Typically, HO₂ and RO₂ 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$_3$O$_2$ + CH$_3$(O)O$_2$ radicals. In both cases, the signal differences between PERCA and BG mode is the HO$_2$ or CH$_3$O$_2$ + CH$_3$(O)O$_2$ concentration. The left part of each figure shows the HO$_2$/CH$_3$O$_2$ + CH$_3$(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

\[ [\text{HO}_2]_{\text{removal}} \text{ or } [\text{HO}_2]_{\text{blank}} = \frac{I_{\text{HO}_2\text{-removal}} \text{ or } I_{\text{HO}_2\text{-blank}}}{S_{\text{HO}_2} \times C_{\text{humid}}}, \]  

(2)

where $[\text{HO}_2]_{\text{removal}}$ and $[\text{HO}_2]_{\text{blank}}$ indicates the concentration of HO$_2$ radicals in the removal and blank mode respectively and $C_{\text{humid}}$ indicate the correction coefficient of $S_{\text{HO}_2}$ 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 $\alpha$ as follows,

\[ \alpha = 1 - \frac{[\text{HO}_2]_{\text{dec}}}{[\text{HO}_2]_{\text{blank}}}. \]  

(3)

$[\text{HO}_2]_{\text{dec}}$ and $[\text{HO}_2]_{\text{blank}}$ can be substituted by Eq. (2) and finally the removal efficiency $\alpha$ of HO$_2$ radicals is determined as follows:

\[ \alpha = 1 - \frac{I_{\text{HO}_2\text{-removal}}}{I_{\text{HO}_2\text{-blank}}}. \]  

(4)

The removal efficiency of CH$_3$O$_2$ + CH$_3$(O)O$_2$ radicals can be expressed the same way:

\[ \beta = 1 - \frac{I_{\text{CH}_3\text{O}_2+\text{CH}_3\text{(O)O}_2\text{-removal}}}{I_{\text{CH}_3\text{O}_2+\text{CH}_3\text{(O)O}_2\text{-blank}}}. \]  

(5)

Figure 3 summarizes the results of the removal efficiency measurements by plotting $\alpha$ and $\beta$ 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 $\beta$ for CH$_3$O$_2$ + CH$_3$(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, $\alpha$ 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 $\alpha$ for both materials, showing a
slightly more rapid decrease in the case of PFA compared to PTFE. In the case of CH$_3$O$_2$ + CH$_3$C(O)O$_2$, this behaviour is not observed: for both materials the removal efficiency $\beta$ 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$_3$O$_2$ and CH$_3$C(O)O$_2$ radicals is 0.15 as shown in Fig. 3. This confirms the observation reported by Mihele et al. (1999).

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, $\alpha$ decreases slightly and steadily approaching 85% at approximately 100% humidity. The removal efficiency of CH$_3$O$_2$ + CH$_3$C(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

Fig. 3. Results of the removal efficiency $\alpha$ (HO$_2$) and $\beta$ (CH$_3$O$_2$ + CH$_3$C(O)O$_2$) as a function of relative humidity using (a) PFA, (b) PTFE and (c) glass as the material in the removal cell.

Fig. 4. Removal efficiency $\alpha$ 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.
strongly on the initial concentration over ambient HO₂ 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 CH₃O₂ + CH₃C(O)O₂ 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 HO₂ radicals at HO₂ concentrations of ~150 pptv, allowing for an easy comparison. However, some improvement on the removal cell is necessary for observations under ambient HO₂ concentrations because the removal efficiency for HO₂ decreases steeply over the typical ambient HO₂ concentration range. If the HO₂ loss reaction occurs through bimolecular reaction on the surface, relatively high removal efficiency for HO₂ 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 HO₂ 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 HO₂ 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 HO₂ radicals. Denuder 2 is twice as long as Denuder 1. As can be seen, the removal efficiency still depends on initial HO₂ 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 HO₂ 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 HO₂ can be obtained even under the ambient concentration range by increasing the residence time. As for the removal efficiency for CH₃O₂ 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, CH₃O₂ radicals were generated by the photolysis of CH₃I by using the radical generator described above. The low-pressure mercury lamp was not filtered and the photolysis of CH₃I will occur mainly at 254 nm to generate mainly CH₃O₂ radical (Clemitshaw et al., 1997). This results shows that the removal efficiency for CH₃C(O)O₂ is relatively higher than that for CH₃O₂. Considering the result of the acetone photolysis experiment, a removal efficiency of at least 0.27 for the CH₃C(O)O₂ 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 CH₃O₂ was used as that for RO₂ (R = C₂H₅) in this study.

Further tests show that the removal efficiency for HO₂ does not depend on the presence of RO₂ radicals. In some experiments, C₂H₅H₂ was added to photolysis gas instead of CO: now OH radicals will be converted to C₂H₅O₂ and equal amounts of HO₂ and C₂H₅O₂ radicals will be generated. The LIF signal obtained through these experiments was consistent with an LIF signal calculated using separately premeasured removal efficiencies for HO₂ and RO₂.

As discussed above, the LOD for HO₂ and RO₂ measurements was calculated to be 1 pptv in dry conditions considering the removal efficiencies for HO₂ and RO₂ 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 HO₂ and RO₂ can then be described using LIF signal S as follow:

\[
S_{\text{HO}_2} \left[ \text{HO}_2 \right]_{\text{blank}} + S_{\text{RO}_2} \left[ \text{RO}_2 \right]_{\text{blank}} = \frac{I_{\text{blank}}}{C_{\text{humid}}}, \tag{6}
\]

\[
S_{\text{HO}_2} \left[ \text{HO}_2 \right]_{\text{removal}} + S_{\text{RO}_2} \left[ \text{RO}_2 \right]_{\text{removal}} = \frac{I_{\text{removal}}}{C_{\text{humid}}}, \tag{7}
\]

where \( S_{\text{HO}_2} \) and \( S_{\text{RO}_2} \) indicate the sensitivity for HO₂ and RO₂ respectively. \( I_{\text{blank}} \) and \( I_{\text{removal}} \) indicate the LIF signal in the blank and removal mode, respectively. Here, \( \left[ \text{HO}_2 \right]_{\text{removal}} \) is described by \( \left[ \text{HO}_2 \right]_{\text{blank}} \) in consideration of
K. Miyazaki et al.: A new technique for the selective measurement of atmospheric peroxy radical concentrations

the combination of first and second order reactions for HO$_2$ as below:

$$[\text{HO}_2]_{\text{removal}} = \frac{[\text{HO}_2]_{\text{blank}}}{F_1} \times \frac{[\text{HO}_2]_{\text{blank}} + F_2}{},$$

(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, $[\text{RO}_2]_{\text{removal}}$ can be described by $[\text{RO}_2]_{\text{blank}}$ because the constant removal efficiency for RO$_2$ can be obtained:

$$[\text{RO}_2]_{\text{removal}} = (1 - \beta) [\text{RO}_2]_{\text{blank}},$$

(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 two measurement modes and the calibration factors, if the factor $C_{\text{Humid}}$, 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 $S_{\text{HO}_2}$ and $S_{\text{RO}_2}$. More selective and precise measurements of HO$_2$ and RO$_2$ concentrations can therefore be possible using this technique.

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$_3$O$_2$. 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$_3$O$_2$ and CH$_3$C(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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References


