

**Selective
measurement of
atmospheric peroxy**

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A new technique for the selective measurement of atmospheric peroxy radical concentrations of HO₂ and RO₂ using denuding method

K. Miyazaki¹, A. E. Parker², C. Fittschen², P. S. Monks³, and Y. Kajii¹

¹Department of Applied Chemistry, Graduate school of Urban Environmental Sciences, Tokyo Metropolitan University 1-1 Minami-Ohsawa, Hachioji, Tokyo 192-0367, Japan

²Laboratoire de Physico-Chimie des Processus de Combustion et de l'Atmosphère, PC2A UMR 8522, Université des Lille1, 59655 Villeneuve d'Ascq Cedex, France

³Department of Chemistry, University of Leicester, Leicester, LE1 7RH, UK

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Correspondence to: K. Miyazaki (miyazaki@atmchem.apchem.metro-u.ac.jp)

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Abstract

A technique for the selective measurement of atmospheric HO₂ and RO₂ using peroxy radical chemical amplification coupled to laser-induced fluorescence NO₂ detection (PERCA-LIF) technique is proposed. By pulling the air through a filled pre-inlet advantage can be taken of the higher heterogeneous loss rate of HO₂ relative to CH₃O₂. Pre-inlet conditions have been found where ca. 90% of HO₂ was removed whereas the comparable CH₃O₂ loss was 15%. The dependence of loss rate on humidity and peroxy radicals' concentration has also been investigated. When using glass beads as the surface for peroxy radical remove, 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 RO₂ as well as the sum of HO₂ and RO₂. The application of this technique to atmospheric measurements is suggested.

1 Introduction

Peroxy radicals RO₂ (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 O₂. They can further react with NO to recycle OH radicals. This oxidation of NO through the reaction with peroxy radicals is an important source of tropospheric ozone, a major constituent of photochemical oxidants that is detrimental to human health and contributes to global warming. The concentration of tropospheric ozone has significantly increased in recent years (Akimoto, 2003). To understand the mechanism of this 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

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Pilling, 2003). Peroxy radical chemical amplification (PERCA) is a method of measuring the total concentration of peroxy radicals, i.e. the sum of HO₂ and RO₂. In this method, peroxy radicals are converted in an inlet tube to higher concentrations of NO₂ via a chain amplification reaction by OH and HO₂ catalysed oxidation of NO to NO₂ and CO to CO₂ by the addition of excess concentrations of NO and CO. The NO₂ product is then quantified by the appropriate measurement method. In order to obtain absolute concentrations, the chain length of the amplification has to be determined in calibration experiments, as well as the response of the NO₂ detector. Recent studies of PERCA have reported a greater wall loss rate of HO₂ relative to RO₂. For example, Mihele et al. (1999) reported a wall loss rate on a $\frac{1}{4}$ " Teflon tube of $2.8 \pm 0.2 \text{ s}^{-1}$ for HO₂ and $0.8 \pm 0.1 \text{ s}^{-1}$ for both CH₃O₂ and C₂H₅O₂ radicals in dry conditions. In this study, the HO₂ loss rate increased markedly with the relative humidity while the organic radicals showed no dependence.

The greater wall loss rate of HO₂ relative to RO₂ can be actively used to separate HO₂ and RO₂ during atmospheric measurements by predominantly denuding HO₂ prior to the PERCA inlet. This makes it possible to measure the concentration of RO₂ separately from the sum of HO₂ and RO₂, and therefore obtain the ambient concentrations of HO₂ and RO₂. It will no longer be necessary to deduce the concentration of the individual radicals species from estimation of the ratio of HO₂ to RO₂ (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 HO₂ and RO₂ by use of selective destruction of HO₂ 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 HO₂ and RO₂ removal efficiency was investigated in detail for these three materials.

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2 Experimental

The experimental system is very similar to the PERCA system already described and validated in detail as described by Sadanaga et al. (2004) and is shown in Fig. 1. The system consists of (1) a peroxy radical generator, (2) a removal cell, (3) chemical amplification reaction tube and (4) LIF NO₂ detector.

The peroxy radical generation system is similar to the HO_x generator described by Kanaya et al. (2001). HO₂ radicals are generated by the photolysis of H₂O at 185 nm using a low-pressure mercury lamp (Sen light, SP-5-2H):



As proxy for RO₂, CH₃O₂ radicals were generated in the same radical generator by photolysis of acetone (Kanto Chemical, 99.0%):



No literature value for the quantum yield of CH₃ radicals in acetone photolysis at 185 nm could be found, but it is believed that owing to the high excess energy the quantum yield for CH₃ radical formation will be Φ_{CH₃}=2 (Somnitz et al., 2005) and therefore only CH₃O₂ radicals will be generated. 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. The relative humidity is measured at the exit of the PERCA instrument using a humidity sensor (VAISALA, HMT 330). Air used in

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these experiments was synthesized from N₂ and O₂ (Noppon Sanso, 99.99%>) by using mass flow controllers (KOFLOC, Model 3660). 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 1/2 inch diameter Teflon tube. For testing glass, spherical glass beads (GL Science, 1 mm dia.) were packed into a 5 cm long 1/2 inch glass tube. For easy comparison, the length of the removal cell was adjusted to obtain a removal efficiency of approximately 90% for HO₂ radicals.

Concentrations of HO₂ and CH₃O₂ 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 upstream 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, Model 3660) and its humidity and temperature were monitored with a humidity sensor (VAISALA, HMT330).

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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; 200 l 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:YAG 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, S1226-5BQ) in order to correct for possible drifts of the laser power. The fluorescence is collected and focused through optical lenses and passes through a sharp-cutoff 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:

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

where (S/N) is the signal-to-noise ratio for defining the LOD, S_{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_{BG} is the sensitivity of the background measurement (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 $(S/N) = 2$, $S_{\text{HO}_2} = 26$ cps ppt⁻¹ W⁻¹, $m = n = 1$, $S_{\text{BG}} = 2064$ cps W⁻¹, $I = 2.3$ W, and $\Delta t = 60$ s. Calibration of S_{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). Typically, HO₂ and CH₃O₂ 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 HO₂ radicals, while the lower part (b) is a typical example for CH₃O₂ radicals. In both cases, the signal differences between PERCA and BG mode (I_{HO_2}) is the HO₂ or CH₃O₂ concentration. The left part of each figure shows the HO₂/CH₃O₂ 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 HO₂ concentrations for each blank or removal mode can be described as follows

$$[\text{HO}_2]_{\text{dec}} \text{ or } [\text{HO}_2]_{\text{blank}} = \frac{I_{\text{HO}_2 \text{ dec}} \text{ or } I_{\text{HO}_2 \text{ blank}}}{S_{\text{HO}_2} \times C_{\text{Humid}}}, \quad (2)$$

where $[\text{HO}_2]_{\text{dec}}$ and $[\text{HO}_2]_{\text{blank}}$ indicates the concentration of HO₂ radicals in the removal and blank mode respectively and C_{Humid} indicate the correction coefficient 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. For the experiments described in this work the humidity dependence of chain length is of no importance as, ratio of signals from the blank and removal cells is measured meaning that both exhibit the same relative humidity and chain length.

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Variation in the removal of HO₂ was evaluated by defining a removal efficiency factor α as follows,

$$\alpha = 1 - \frac{[\text{HO}_2]_{\text{dec}}}{[\text{HO}_2]_{\text{blank}}} \quad (3)$$

[HO₂]_{dec} and [HO₂]_{blank} can be substituted by Eq. (2) and finally the removal efficiency α of HO₂ radicals is determined as follows:

$$\alpha = 1 - \frac{I_{\text{HO}_2 \text{ dec}}}{I_{\text{HO}_2 \text{ blank}}} \quad (4)$$

The removal efficiency of CH₃O₂ radicals can be expressed the same way:

$$\beta = 1 - \frac{I_{\text{CH}_3\text{O}_2 \text{ dec}}}{I_{\text{CH}_3\text{O}_2 \text{ blank}}} \quad (5)$$

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 ppt. Figure 3a, b and c shows 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 HO₂ at a relative humidity between 20–60%.

As can be seen from Fig. 3, the removal efficiency β for CH₃O₂ is approximately 15% for all three materials and only slightly depends on the relative humidity. However, the removal efficiency of HO₂ 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 HO₂ 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

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slightly more rapid decrease in the case of PFA compared to PTFE. In the case of CH_3O_2 this behaviour is not observed: for both materials the removal efficiency β increases slightly and steadily with relative humidity. This confirms the observation already 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, α decreases slightly and steadily approaching 85% at approximately 100% humidity. The removal efficiency of CH_3O_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 when getting to low radical concentration. 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. 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.

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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:

$$S_{\text{HO}_2}[\text{HO}_2] + S_{\text{RO}_2}[\text{RO}_2] = \frac{I_{\text{blank}}}{C_{\text{humid}}}, \quad (6)$$

$$(1 - \alpha_{[\text{HO}_2]})S_{\text{HO}_2}[\text{HO}_2] + (1 - \beta_{[\text{CH}_3\text{O}]})S_{\text{RO}_2}[\text{RO}_2] = \frac{I_{\text{dec}}}{C_{\text{humid}}}, \quad (7)$$

where S_{HO_2} and S_{RO_2} indicate the sensitivity for HO₂ and RO₂ respectively. I_{blank} and I_{dec} indicate the LIF signal in the blank and removal mode, respectively. $\alpha_{[\text{HO}_2]}$ and $\beta_{[\text{RO}_2]}$ indicate the removal efficiency for HO₂ and RO₂ at a given initial concentration, respectively. Equations (6) and (7) were solved for [HO₂] and [RO₂] leading to the following expressions:

$$[\text{HO}_2] = \frac{(1 - \beta_{[\text{RO}_2]})I_{\text{blank}} - I_{\text{dec}}}{(\alpha_{[\text{HO}_2]} - \beta_{[\text{RO}_2]})S_{\text{HO}_2}C_{\text{humid}}}, \quad (8)$$

$$[\text{RO}_2] = \frac{(1 - \alpha_{[\text{HO}_2]})I_{\text{blank}} - I_{\text{dec}}}{(\beta_{[\text{RO}_2]} - \alpha_{[\text{HO}_2]})S_{\text{RO}_2}C_{\text{humid}}}. \quad (9)$$

Equations (8) and (9) show that the concentrations of HO₂ and RO₂ can 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 with relative humidity, has been determined. Furthermore, using this method it is not necessary to correct for the sensitivity of HO₂ and RO₂ on the hypothesis of an abundance ratio of HO₂ and RO₂, i.e. the concentrations of HO₂ and RO₂ can be corrected by separate sensitivity factors of S_{HO_2} and S_{RO_2} . More selective and precise measurements of HO₂ and RO₂ concentrations can therefore be possible using this technique.

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4 Conclusions

An improvement to the well-established PERCA technique allowing the selective measurement of HO₂ and RO₂ radical concentrations has been described in this paper. Advantage is taken of different heterogeneous removal efficiencies for HO₂ and RO₂ 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 HO₂ over the entire relative humidity range, compared to only 15% removal efficiency of CH₃O₂. The investigation of the dependence of the removal efficiency on the concentration at a given relative humidity has been tested for HO₂ 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. Again, glass seems to be the more suited material, as it does not show any dependence on the relative humidity. However, this characteristic needs to be carefully investigated before applying this technique to atmospheric measurements.

The results presented in this work are very promising and indicate the possibility of selective measurement of peroxy radicals. It has been shown that the concentrations of HO₂ and RO₂ 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 RO₂, but we think that this technique has the potential of increasing the precision of atmospheric peroxy radical measurements in the future.

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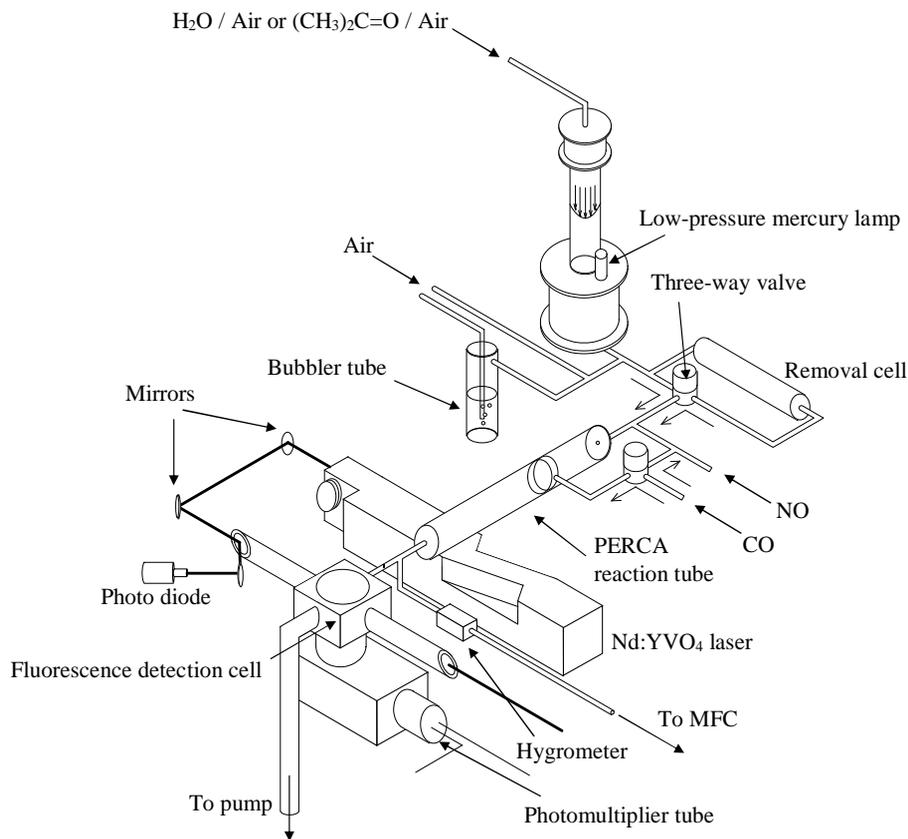


Fig. 1. Schematic diagram of the experiment. The system can be divided into 4 parts, (1) peroxy radical generator, (2) removal cell, (3) chemical amplification reaction tube and (4) LIF NO₂ detector. MFC indicates mass flow controller.

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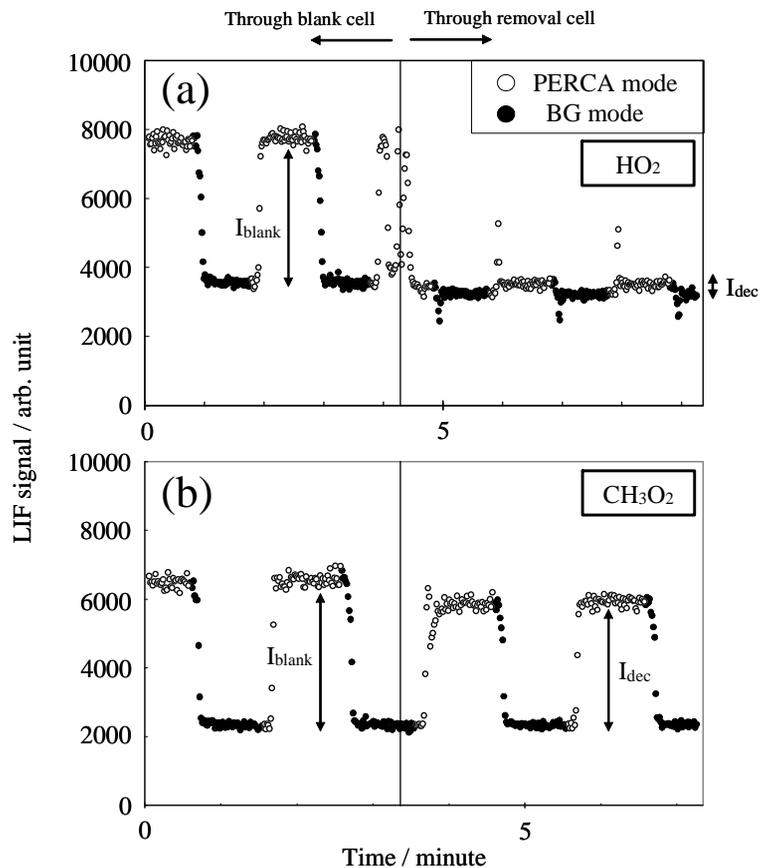


Fig. 2. An example of removal efficiency measurements showing PERCA/BG mode for both blank (left side) and removal (right side) mode. PERCA/BG mode are switched every minute. **(a)** shows HO₂, **(b)** is RO₂.

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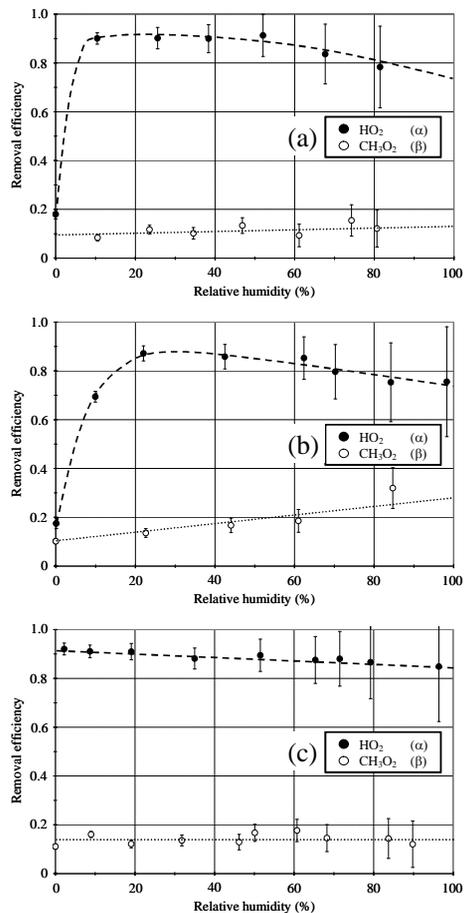


Fig. 3. Results of the removal efficiency α (HO_2) and β (CH_3O_2) as a function of relative humidity using (a) PFA, (b) PTFE and (c) glass as the material in the removal cell.

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Selective
measurement of
atmospheric peroxy

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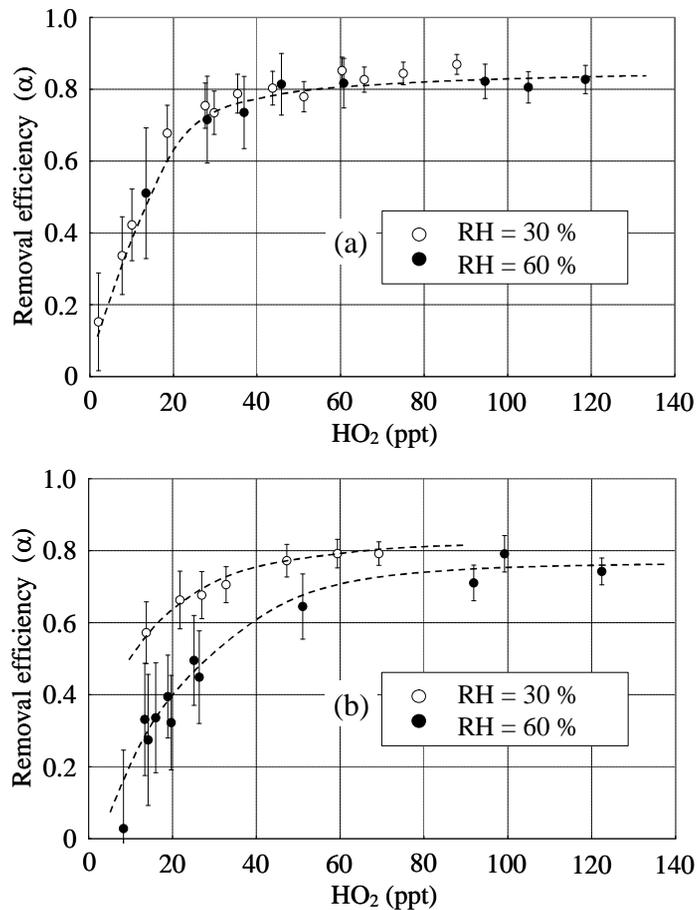


Fig. 4. Removal efficiency α for two different relative humidities as a function of initial HO_2 radical concentration: **(a)** shows the results with glass as filling material, **(b)** is for PFA.

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