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A hydroxyl radical detection system using gas expansion and fast gating laser-induced fluorescence techniques

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ABSTRACT

An OH radical measurement instrument based on Fluorescence Assay by Gas Expansion (FAGE) has been developed in our laboratory. Ambient air is introduced into a low-pressure fluorescence cell through a pinhole aperture and irradiated by a dye laser at a high repetition rate of 8.5 kHz. The OH radical is both excited and detected at 308 nm using A-X(0,0) band. To satisfy the high efficiency needs of fluorescence collection and detection, a 4-lens optical system and a self-designed gated photomultiplier (PMT) is used, and gating is actualized by switching the voltage applied on the PMT dynodes. A micro channel photomultiplier (MCP) is also prepared for fluorescence detection. Then the weak signal is accumulated by a photon counter in a specific timing. The OH radical excitation spectrum range in the wavelength of 307.82–308.2 nm is detected and the excited line for OH detection is determined to be Q₁(2) line. The calibration of the FAGE system is researched by using simultaneous photolysis of H₂O and O₂. The minimum detection limit of the instrument using gated PMT is determined to be 9.4×10^5 molecules/cm³, and the sensitivity is 9.5×10^{-7} cps/(OH·cm⁻³), with a signal-to-noise ratio of 2 and an integration time of 60 sec, while OH detection limit and the detection sensitivity using MCP is calculated to be 1.6×10^5 molecules/cm³ and 2.3×10^{-6} cps/(OH·cm⁻³). The laboratory OH radical measurement is carried out and results show that the proposed system can be used for atmospheric OH radical measurement.

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Introduction

The hydroxyl (OH) radical is known as the most potential oxidizing agent for many chemical species in the lower atmosphere. Its concentration has been estimated to be

approximately in the 1×10^6 molecules/cm³ range (Heard and Pilling, 2003; Stone et al., 2012; Amedro et al., 2012). The OH radical is involved in many atmospheric chemistry progresses through reactions with O₃, CO, CH₄, NO₂, and numerous non-methane hydrocarbons (Hofzumahaus et al.,

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2009; Whalley et al., 2010; Khan et al., 2011; Lu et al., 2013). The chemical mechanisms for the formation and consumption of OH are very complex, and understanding the various pathways involved is important to accurately model atmospheric chemistry and predict atmosphere evolution. Measuring OH radical has proven to be challenging in atmospheric chemistry because of the high reactivity, short lifetime, and extremely low concentration of this radical.

Numerous research groups have developed systems for measuring tropospheric OH radicals, resulting in the fabrication of several reliable instruments. These techniques mainly include laser-induced fluorescence (LIF) [in particular, fluorescence assay by gas expansion (FAGE)] (Kanaya et al., 2001; Novelli et al., 2014; Fuchs et al., 2016), differential optical absorption spectroscopy (DOAS) (Dorn et al., 1996; Fuchs et al., 2012), chemical ionization mass spectrometry (CIMS) (Mauldin et al., 2003), ^{14}CO oxidation (Campbell et al., 1995) and salicylic acid scrubbing (Liu and Wang, 2008). Among these methods, FAGE has been demonstrated as an effective tool in the detection of atmospheric OH radical because of its high sensitivity, good selectivity, and low detection limit. Compared to other techniques, FAGE can also measure the concentration of a series of radical like OH, HO_2 , and RO_2 , which is important means to research the radical reaction activity and its atmospheric chemical mechanism (Fuchs et al., 2008; Whalley et al., 2013; Weinberg et al., 2015).

FAGE technique used for OH radical measurement is first developed by Hard (Hard et al., 1984). Several groups have designed and improved their own instruments for more than 20 years, including techniques for instrument optimization (Holland et al., 1995; Kanaya et al., 2001; Dusanter et al. 2009a; Novelli et al., 2014), calibration studies (Hard et al., 2002; Dusanter et al., 2008), interference studies (Ren et al., 2004; Fuchs et al., 2011), and comparisons with other instruments (Dorn et al., 1996; Mauldin et al., 2003; Schlosser et al., 2009). FAGE instruments have been used in various field campaigns for different environments (Kanaya et al., 2007; Dusanter et al. 2009b; Vaughan et al., 2012). It has a detection limit of an order of magnitude of 10^5 molecules/ cm^3 and has proved to be a reliable tool to study the tropospheric OH radical. Moreover, numerous data for atmospheric chemistry modeling or further research on the mechanism of atmospheric reactions have been accumulated. Reliable FAGE systems have been developed by several universities and institutes, but few related studies have been conducted in China, where the process of atmospheric chemistry is more complicated due to its climatic conditions and industrial development. Peking University has recently performed several OH field measurements by FAGE in Beijing District and Pearl River Delta, and researched their chemistry progress combined with the local condition (Lou et al., 2010; Lu et al., 2012, 2013).

A new OH radical instrument based on FAGE is described in this paper. Each part of the FAGE instrument is designed and established in our laboratory. The OH radical is both excited and detected at 308 nm of the A-X(0,0) band. Ambient air is sampled through a pinhole and excited fluorescence in a low-pressure cell. This instrument use a gated photomultiplier (PMT) as a detector, which is actualized by a home-made gating circuit by switching the voltage applied on the dynodes of the PMT. And a commercial micro channel photomultiplier

(MCP) has also prepared for system experiment and comparison. Fluorescence signal is detected at a specific gated timing and accumulated by a photon counting card. The performance of the developed FAGE system has been detected in the laboratory and its calibration is researched. OH concentration is detected and analyzed, and the system is optimized to obtain a better sensitivity and detection limit to meet the requirement of ambient OH measurement.

1. Principle of FAGE technology

LIF is an efficient tool for detecting tropospheric OH radical. Based on the strong discrete line absorption spectrum of A-X(1,0) band at approximately 282 nm ($\text{A}^2\Sigma^+(\nu'=1) \leftarrow \text{X}^2\Pi(\nu''=0)$) or A-X(0,0) band ($\text{A}^2\Sigma^+(\nu'=0) \leftarrow \text{X}^2\Pi(\nu''=0)$) at approximately 308 nm, hydroxyl radicals can be selectively excited by a narrow-bandwidth laser. The amount of resonant fluorescent light subsequently emitted around 307–311 nm can be used to measure OH concentration. Most groups currently use A-X(0,0) band for excitation and detection to reduce O_3 interference.

FAGE is a pioneered improvement of the LIF technique and utilized to detect OH at low pressure. Sampling ambient air at low pressure can reduce the concentration of interference species, such as O_3 and H_2O (Stevens et al., 1994). Expanding air sample from atmospheric pressure to a few hectopascals results in an extended lifetime of OH fluorescence beyond the time region of Rayleigh, Mie, and wall scattered light. Under this condition, OH concentration is reduced to several magnitudes, and the lifetime of OH fluorescence is extended to several hundred nanoseconds (Kanaya et al., 2001; Heard, 2006). Then, the fluorescence is selectively detected by time filtering, namely a gating detector in nanosecond. Nevertheless, the main background signal is still linearly dependent on laser intensity, and the optimization is based on raising OH sensitivity while keeping the background signal as low as possible.

The major parts of this instrument include laser source combined with wavelength reference cell, fluorescence detection cell, detector, and data processing unit, which is shown in Fig. 1. The laser system is a dye laser pumped by a Nd:YVO₄ laser, which provides a 308 nm output at a high repetition rate of 8.5 kHz, and it wavelength is fixed by using a reference cell. Ambient air is introduced to the cell by a vacuum pump system, which makes the gas sampled through an inlet pinhole and expands under the nozzle, and pressure in the cell is drawn to be approximately 350 Pa. With this sampling method, this system can extend the lifetime of OH fluorescence and reduce the interference of O_3 . The laser passes the cell through the laser arm, which achieves an excitation volume with the cross of the gas flow at the midpoint of the cell. Then, the fluorescence is collected by a 4-lens system and detected by a detector, while the detector is gated off when the laser pulse appears and fast turning on for fluorescence detection after laser ends. The extremely weak and short-lifetime fluorescence signal is measured by a photon counting card, with proper timing and discrimination level. Then, OH radical concentration is further processed by a computer and analyzed after calibration.

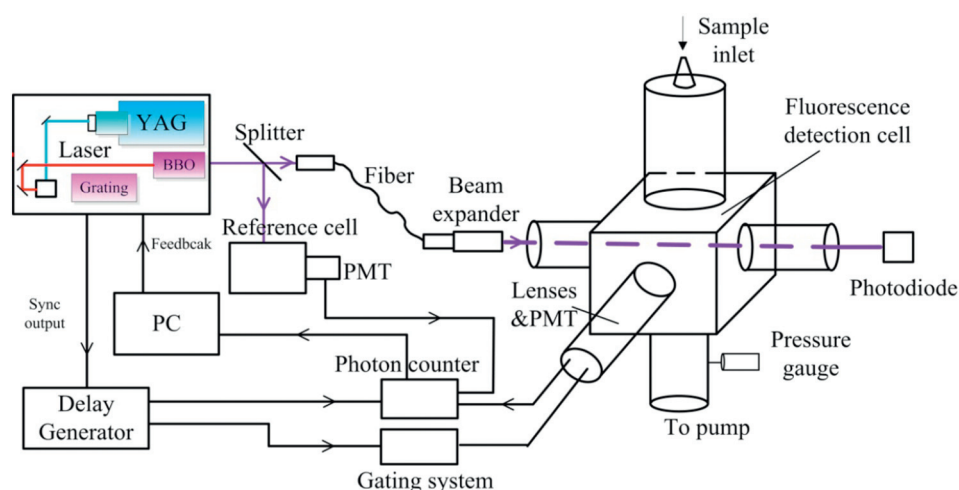


Fig. 1 – Experimental layout of fluorescence assay by gas expansion system.

2. Description of the FAGE instrument

2.1. Laser source

A combination of a Nd:YVO₄ laser (Navigator YHP40, Spectra Physics, USA) and a tunable dye laser (Sirah laser, Spectra Physics, USA) is used to obtain the 308 nm laser light corresponding to the OH A-X(0,0) band. This source is operated at a high repetition rate of 8.5 kHz for this experiment. The frequency of the diode laser-pumped Nd:YVO₄ laser is doubled to provide a 532 nm output for the dye laser excitation source. The dye solution used for the dye laser is a mixture of Rhodamine B and Rhodamine 101 in methanol solvent. The tunable dye laser light at approximately 616 nm is frequency doubled by a BBO (Barium borate) crystal to supply the required 308 nm output. The maximum average laser power produced by this laser system at 308 nm is approximately 120 mW. The tunable light at approximately 308 nm has a pulse width of 20 ns and spectral linewidth of $\sim 0.08 \text{ cm}^{-1}$, which can fit the requirement for high-efficiency OH excitation. Laser light is

divided into two beams by a beam splitter, and tiny fraction laser intensity is used by reference cell for wavelength calibration, while the main laser beam is introduced to the fluorescence cell by a long optical fiber. The diameter of the laser beam that passes through the fluorescence cell is approximately 8 mm after collimation and beam expansion.

2.2. Fluorescence detection cell

The schematic diagram of the fluorescence detection cell is shown in Fig. 2. The central part of this cell is made of an aluminum block, attached with a laser arm, sampling part, and fluorescence detection unit. Its inner and outer walls are black-anodized to reduce stray light. The air flow axis, detection axis, and laser beam are orthogonal to each other at the midpoint.

Ambient air is introduced to the cell through a molecular beam skimmer (Beam Dynamics, USA) with orifice diameter of 1 mm, and this skimmer is located at 210 mm away from the center of the cell. The skimmer is made of nickel and has ultra-thin walls and ultra-sharp orifice edges to collimate

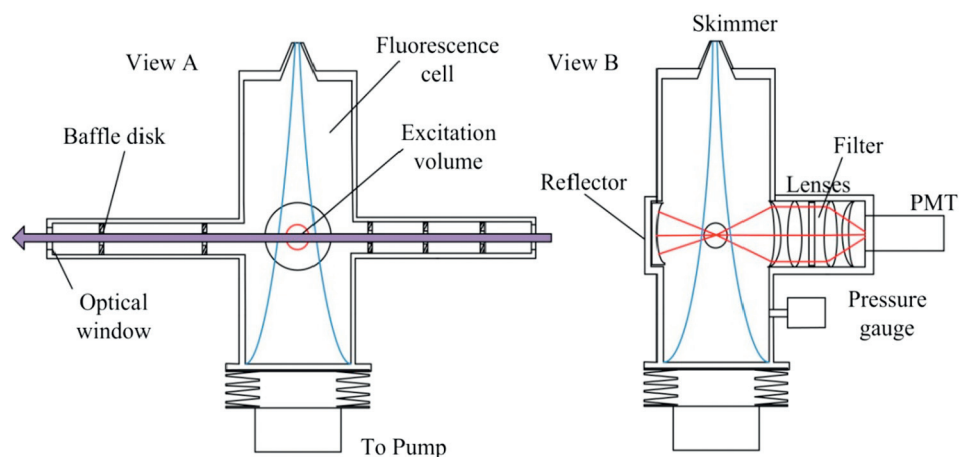


Fig. 2 – Schematic diagram of fluorescence cell and detection system. The excited volume is the overlap of laser beam and gas flow, and fluorescence is detected by lens system and PMT. PMT: photomultiplier.

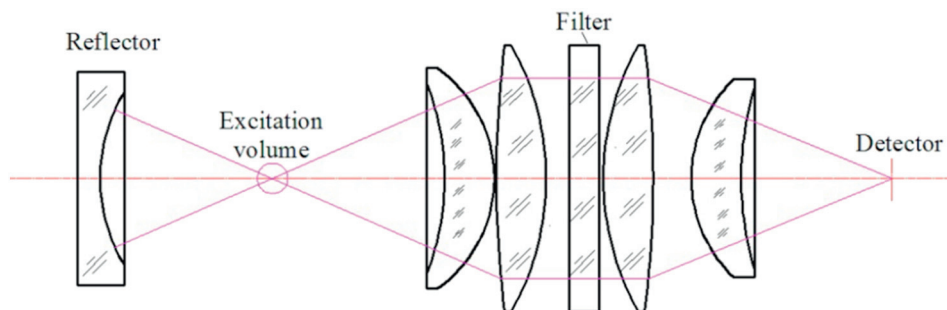


Fig. 3 – Optical system for fluorescence collecting.

the continuous supersonic molecular beams and reduce collision during sampling. Air is drawn into the cell by a mechanical booster pump (XDS35i, Edwards, UK) and rotary pump (EH250, Edwards UK), and a membrane vacuum gauge (ZDM-1v01, Reborn, China) is mounted on the cell to measure the internal pressure. The typical flow and pressure in the cell during detection are approximately 8 STP L/min and 350 Pa, respectively.

The length of the laser arm of the cell is approximately 800 mm, and several specially designed baffles are located in the arm to reduce stray light. The overlap of the laser beam and gas flow can be regarded as excitation volume. The fluorescence emitted from the excitation volume is focused on the photocathode of the PMT through four lenses, with a front lens group similar to the Kohler illumination system and a rear lens group similar to an infinite objective system. The effective aperture of the lenses is approximately 60 mm, and the magnification ratio of the whole system is 1:1. An interference bandpass filter (Barr Association, USA) is aligned between the second and third lenses to reduce stray light, where the incident angles of the collected fluorescence is not remarkably deviated. The bandwidth of the filter is 5 nm centered on 307.5 nm, and its peak transmission is 55%, with a rejection of 10^{-5} throughout a wavelength range of 200–1200 nm. A coated mirror is mounted at the opposite side of the detector to enhance the detection efficiency (Fig. 3).

2.3. Detector

Due to its weak intensity and short lifetime, the detection of fluorescence intensity is a key topic in the FAGE instrument development. Several types of detectors have been applied for fluorescence detection by FAGE groups worldwide, and a home-made gated PMT is used for OH radical measurement in our laboratory.

The gated PMT is designed based on an end window PMT (9235QB, ET Enterprises, UK), which is equipped with blue-green sensitive bialkali photocathode and 13 high-gain high-stability SbC dynodes with linear focused design. A high gain of 2.5×10^7 is achieved when a negative voltage of -1050 V is applied to the photocathode by a high-voltage power supply (PS250, Stanford Research Systems, USA). A homemade gating circuit (Fig. 4) is designed to actualize the fast tuning on/off of the PMT and detect fluorescence in a specific time sequence. The detection is actualized by switching the voltage applied on the first, third, and fifth dynodes of the PMT. The modulation voltage (V_{mod}) is a positive square-wave voltage and obtained by a fast gating circuit based on a MOSFET switch (HTS-41, Behlke, Germany). The circuit can achieve fast switching on/off in nanosecond (rising time of 20 ns), and the on/off gain (extinction) ratio is better than 10^5 , which can fit the requirement for fluorescence detection.

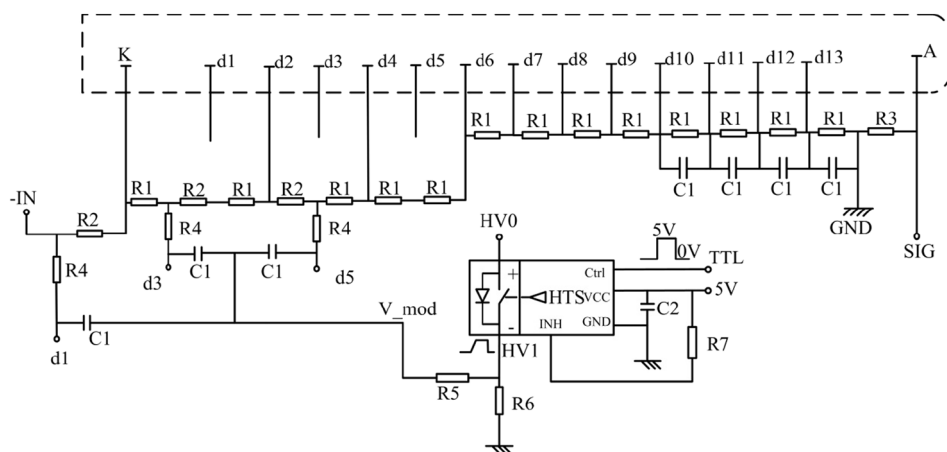


Fig. 4 – Gating circuit of the PMT system. Gating is actualized by switching the voltage applied on first, third and fifth dynodes. K, dn, and A represents the photocathode, dynode, and anode of the PMT, respectively. ($-In = -1085$ V, $HV0 = V_{mod} = +175$ V, $R_1 = 330$ k Ω , $R_2 = 165$ k Ω , $R_3 = 100$ k Ω , $R_4 = 2$ M Ω , $R_5 = 100$ Ω , $R_6 = 2$ k Ω , $R_7 = 5.1$ k Ω , $C_1 = 10$ nF, $C_2 = 100$ μ F). PMT: photomultiplier.

The fluorescence photons reach the photocathode of the PMT and are converted to current signals. These signals are amplified by a fast-timing preamplifier and sent to a gated photon counter (PMS400A, Becker & Hickl GmbH, Germany) for further processing. The photon counter is integrated in a computer. The timing of the gated PMT and gated photon counter is controlled by a transistor-transistor logic pulse provided by a digital delay generator (DG645, Stanford Research Systems, USA) triggered externally by the synchronous output of the laser system (T_0) (Fig. 5). The laser appears at $T_0 + 890$ ns with a pulse width of 20 ns. The timing of the gated PMT and photon counter are carefully considered. The PMT is fully turned on at 190 ns after laser ends, and the counting gate width is set to be 500 ns for fluorescence detection. Then, the intensity of the fluorescence is calculated by a data processing program, and the OH radical concentration is analyzed after calibration.

In order to further study the performance of the FAGE system, a commercial micro channel multiplier (PMT325, Photek Ltd., UK) has also been prepared in our lab for fluorescence detection and comparison, which has integrated an ultra fast gating system. The MCP has many advantages in the weak signal detection and time correlated photon counting. It has a quite low dark counts and high gain up to 1×10^7 , and its gating module has a pulse rise times to 50 ps and can provide gated speeds to 2 ns. The FAGE system can alter the detectors between gated PMT and MCP conveniently, just have some slightly difference in the experimental parameters matching the detector.

2.4. Wavelength reference cell

During the experiment, the laser wavelength fixed at the excited line can drift because of the change in environmental

temperature, which will affect the fluorescence intensity as a result of the narrow excitation line. A reference cell is established for wavelength calibration to protect the output of the laser system from drifting (Fig. 6) (Wennberg et al., 1994; Hofzumahaus et al., 1996).

Synthetic gas is introduced from the top of the cell by a vacuum pump, and the gas flow and pressure in the cell are controlled by the Mass Flow Controller (MFC) and mechanical valve. The laser beam crosses the cell and is perpendicular to the gas flow. An alumel filament is aligned 5 mm right above the laser beam. A sufficiently stable concentration of OH radical is produced by thermal dissociation of H_2O , and fluorescence is excited by the 308 nm laser in a low-pressure cell (350 Pa and similar to the fluorescence cell). Fluorescence is collected by several lenses and detected by a PMT (H10720, Hamamatsu Photonics, Japan) and a high-speed data acquisition card, while the laser light is monitored by a photodiode. The signals are sent to the computer and further analyzed by the LabVIEW program.

The effects of humidity, oxygen concentration, and mass flow on fluorescence intensity and lifetime are studied at the excited line to optimize system parameters and achieve a high signal-to-noise (S/N) ratio. Different mixtures of synthetic gases, which consist of different proportions of N_2 , O_2 , and N_2 bubbled through a water trap, are used for these tests. The results show that, at a total flow of 1 STP L/min, the system can achieve the strongest fluorescence at 25% v/v O_2 and 30% v/v N_2 bubbled through a water trap, and this condition is similar to typical ambient air. In the actual measurement, the fluorescence intensity using ambient air in the reference cell is tested to be sufficiently stable and can be used for wavelength calibration.

The two-step wavelength correction procedure includes the following. First, laser output wavelength is scanned in a

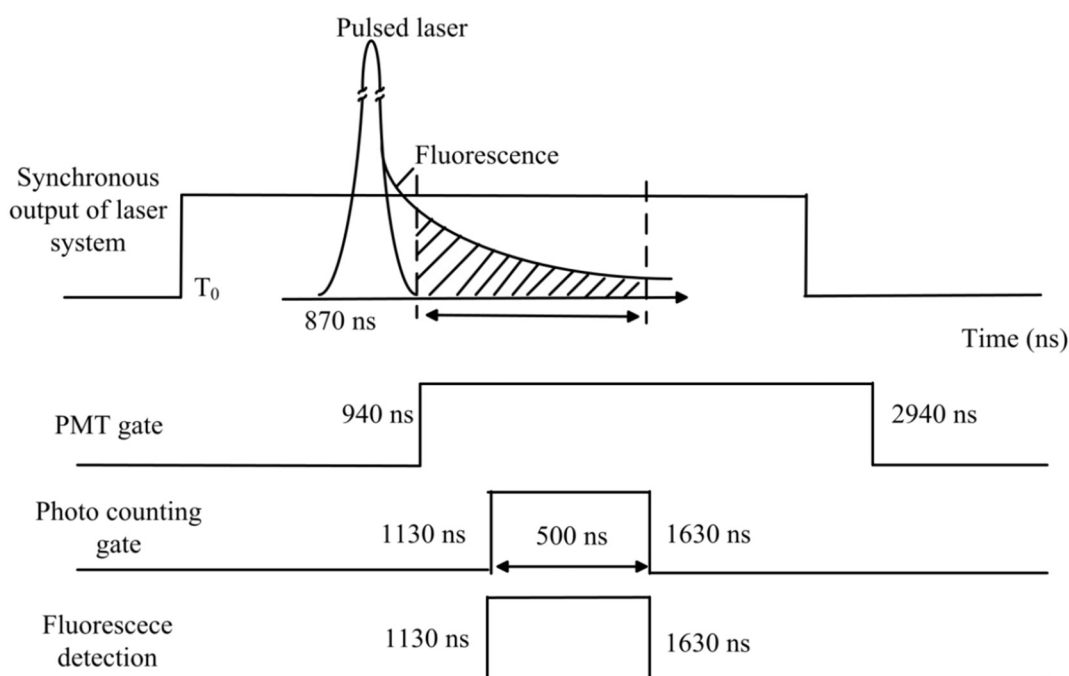


Fig. 5 – Timing chart of FAGE instrument by using gated PMT. TTL pulse is offered by a digital delay generator triggered externally by the synchronous output of the laser system. Fluorescence is detected at 190 ns after laser ends and counting gate is opened for 500 ns. FAGE: Fluorescence Assay by Gas Expansion; PMT: photomultiplier; TTL: Transistor-Transistor Logic.

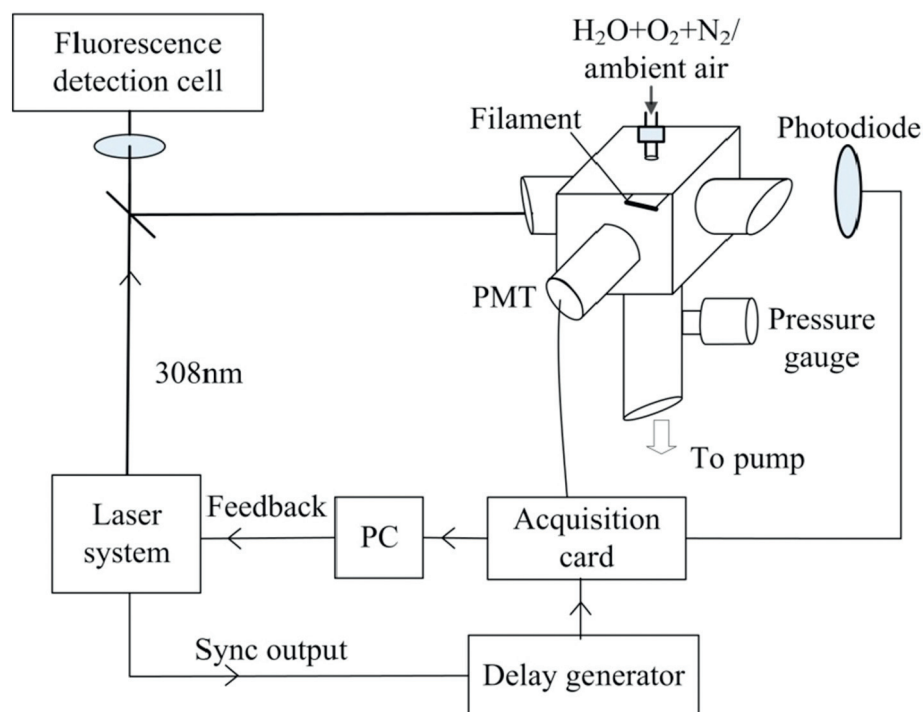


Fig. 6 – Schematic diagram of the reference cell for wavelength calibration. OH radical is produced by thermal dissociation of H_2O , and excited line is fixed by the feedback of peak fluorescence intensity.

small range around the excited line to determine the exact exciting line and record the maximum fluorescence intensity. Second, laser output is rescanned and stopped when the fluorescence signal reaches 95% of the maximum. During the experiment, the correction procedure is restarted when the intensity fluctuates over a certain range or after a proper time interval (typically 8–10 min). The wavelength correction procedure is implemented many times and the results show that the systematic error of the instrument is less than 0.1 pm (Xing et al. in press).

3. Experiments and result analysis

3.1. Determination of the excited line for OH detection

A relatively high-concentration OH radical is measured to test the response and sensitivity of the gated PMT system for fluorescence detection, and the OH excited line at approximately 308 nm is obtained. This experiment can also be used to determine the excited line for OH radical detection. OH radical is supplied by simultaneous photolysis of H_2O and O_2 by 185 nm line of Hg lamp. The Hg lamp is set at the top of the aperture and the concentration of OH radical is estimated to be $1\text{--}5 \times 10^9$ molecules/ cm^3 , and this OH radical is introduced into the cell through the sampling aperture.

The laser power used in this experiment is approximately 20 mW, and the diameter of the laser beam is approximately 8 mm. The output wavelength of the laser is scanned from 308.2 nm to 307.82 nm with a constant speed of 0.0001 nm/s. Fluorescence is detected as the timing of that described in Section 3.3. Using an integration time of 1 sec and a proper

discrimination voltage of the photon counter, the OH excited line is observed at approximately 308 nm (Fig. 7). Application of the gating system avoids the PMT from nonlinear response and afterpulse caused by laser stray light. Under the selected integral time and photon pulse threshold, the peak value of fluorescence intensity is more than 2000 counts, and average background signal is approximately 6 counts. The background signal mainly consists of dark counts, laser stray light, and Hg lamp light. The excitation spectrum is simulated by the PGOPHER program. A nicely matched observed and simulated rotational excitation spectrum of the (0,0) band is demonstrated in Fig. 7. And the rotational temperature has resumed to room temperature at the sufficient long distance from the sampling aperture to the excited midpoint, while the distance is also helpful for stray light suppression. The fluorescence has good S/N ratio and meets the requirements for fluorescence detection. The $\text{Q}_1(2)$ excitation line can be further applied to monitor the OH radical in lower concentration because of its high intensity and narrow linewidth.

3.2. OH radical generation

Fluorescence intensity is detected by FAGE technology, and the instrument should be optimized and calibrated using a standard sample with known concentration. However, no stable standard gas is available for OH radicals, because OH radicals are very reactive, and their atmospheric lifetime is approximately 1 sec. OH radical should be generated based on some chemical reactions under a specific condition.

In this study, OH radical is generated based on the simultaneous photolysis of H_2O and O_2 . This technique has been applied as a calibration method in many FAGE instruments

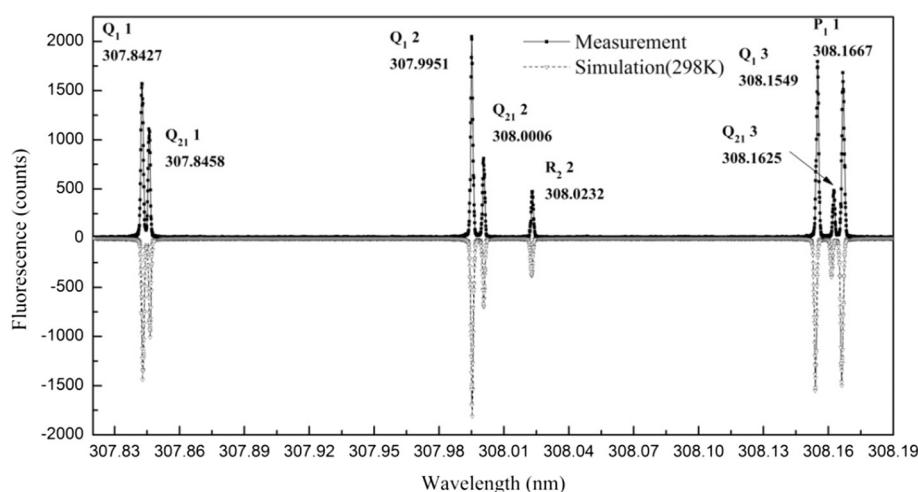
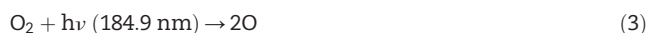


Fig. 7 – Excited line of OH radical at approximately 308 nm. The excitation spectrum is simulated by PGOPHER program and have a nicely agreement with the observed rotational excitation.

(Creasey et al., 1997; Kanaya et al., 2001). The gas flow of purified air containing known H_2O and O_2 in N_2 buffer gas is irradiated by 184.9 nm light from a mercury low-pressure pen-ray lamp (SP-5-2H, Sen Lights Corporation, Japan). The OH radical is mainly generated via the following reactions (Bloss et al., 2004):



where M represents the constituents of air.

A schematic diagram of the OH calibration cell is shown in Fig. 8. The mixed gas is introduced to a quartz tube at a constant flow (typically 15–20 STP L/min), which mainly contains three parts, namely, high purity O_2 ($\geq 99.99\%$, Nanjing Specialty Gases, China), high purity N_2 ($\geq 99.99\%$, Nanjing Specialty Gases, China), and N_2 bubbled through a water trap. Each gas flow is separately controlled by a MFC (CS200, Sevenstar, China). The quartz tube has a length of 600 mm and an inner diameter of 20 mm, and the Hg lamp is set at 90 mm upstream of the inlet aperture and horizontally irradiates the gas flow. The generation cell is aligned at the top of the fluorescence cell, and the gas at the center portion from the nozzle is sampled for detection. The total flow through the aperture is approximately 8 L/min, and the pressure of

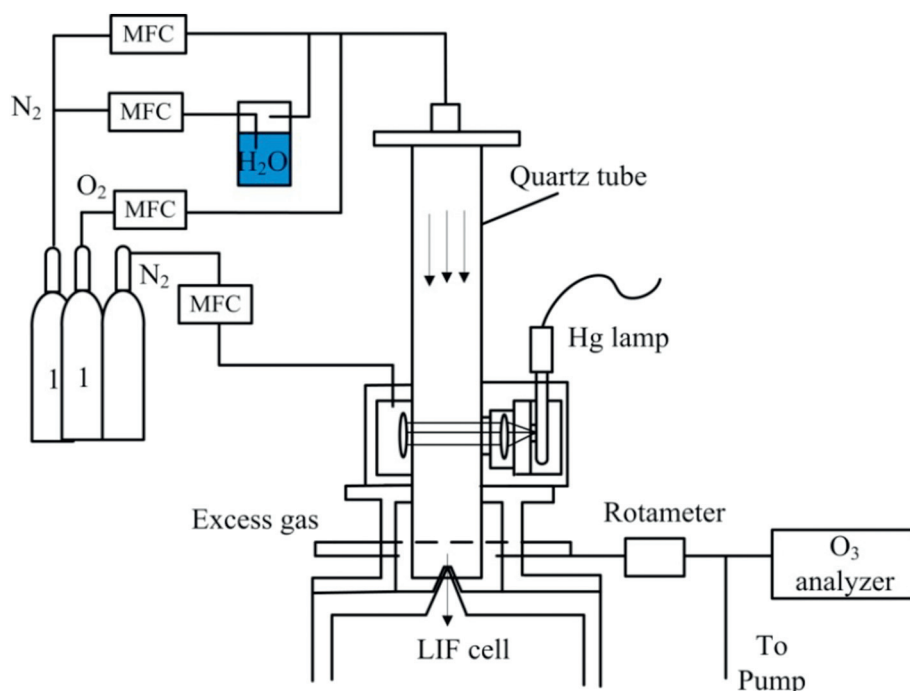


Fig. 8 – Schematic diagram of OH calibration cell based on simultaneous photolysis of H_2O and O_2 .

the fluorescence cell is kept at 350 Pa. The excess gas is exhausted from the side of the quartz tube with the assistance of a mechanical pump.

The water vapor concentration of the mixed gases is detected by a digital humidity-temperature probe (HL-NT-V3, Rotronic, Switzerland) and calibrated by an ammonia/water vapor analyzer (911-0016, LGR, USA). O₃ concentration is detected by an O₃ analyzer (49i, Thermal Fisher, USA) by sampling part of the excess gases. The O₃ concentration of the center portion for sampling is estimated to be half of the average value of the excess gas by considering the laminar gas flow and the position of Hg lamp light irradiation (Stevens et al., 1994; Heard and Pilling, 2003).

The concentration of the OH radical after photolysis can be calculated by the following relationships based on the Reactions (1) and (2):

$$[\text{OH}] = [\text{HO}_2] = [\text{H}_2\text{O}] \cdot \sigma_{\text{H}_2\text{O}} \cdot \Phi_{\text{HO}_2} \cdot F \cdot \delta t \quad (5)$$

where $\sigma(\text{cm}^2)$ is the absorption cross sections at 184.9 nm, Φ is the photodissociation quantum yield, $F(\text{mol}/(\text{cm}^{-2} \cdot \text{sec}^{-1}))$ is the photon flux of the lamp at 184.9 nm and δt (sec) is the photolysis exposure time. The absorption spectrum of H₂O at 184.9 nm has been measured by several groups and the value of $\Phi_{\text{HO}_2}=1$ is well established. Then the main error of [OH] (molecules/cm³) comes from $F \cdot \delta t$, which is difficult to quantitatively measure it accurately. Then an indirect method is used to obtain the $F \cdot \delta t$ by considering the photolysis of O₂ in the flow tube (Reactions (3) and (4)). The O₃ concentration can be determined as:

$$[\text{O}_3] = [\text{O}_2] \cdot \sigma_{\text{O}_2} \cdot \Phi_{\text{O}_3} \cdot F \cdot \delta t \quad (6)$$

Considering that OH and HO₂ are produced at a quantum yield of 1 and O₃ is produced at a quantum yield of 2 (Kanaya et al., 2001), the OH radical can be calculated by the following formula:

$$\frac{[\text{OH}]}{[\text{O}_3]} = \frac{1 \sigma_{\text{H}_2\text{O}} [\text{H}_2\text{O}]}{2 \sigma_{\text{O}_2} [\text{O}_2]} \quad (7)$$

At known concentrations of H₂O and O₂, the OH radical concentration can be determined by measuring the produced

O₃ concentration. In this study, $\sigma_{\text{H}_2\text{O}}$ and σ_{O_2} are used at $(7.1 \pm 0.2) \times 10^{-20} \text{ cm}^2$ (Cantrell et al., 1997) and $(1.2 \pm 0.12) \times 10^{-20} \text{ cm}^2$ (Hofzumahaus et al., 1997). The uncertainty of OH concentration generated by this method mainly consists the uncertainties of the O₂ photodissociation cross section (10%), H₂O cross section (3%), and the measurements of O₃ concentrations (15%, including system error and measurement error) and H₂O concentrations (10%), then the total uncertainty is calculated to be approximately $\pm 21\%$ for OH.

3.3. System calibration

The FAGE system is applied for OH radical measurement in the laboratory, and its calibration is carried out by the OH calibration cell. Instrument sensitivity and detection limit have been theoretically calculated.

Measurement is performed using the calibration cell with a relatively low concentration OH radical. In the total 15 STP L/min mixed gas flow of the OH generation cell, O₂ is 20% v/v and N₂ bubble through water trap is about 4.5% v/v, resulting in water vapor concentration of 640 ppm, and O₃ is detected as 0.2 ppb after irradiation from the Hg lamp. Based on Eq. (7), the OH concentration is calculated to be 5.0×10^7 molecules/cm³ with an uncertainty of $\pm 21\%$. The laser power used in this experiment is approximately 20 mW, and the wavelength of the laser output is fixed at the Q₁(2) line (307.9951 nm). Fluorescence is detected by gated PMT and the gating timing is set as Fig. 5, and measured results are shown in Fig. 9(a). The background counts are detected at the irradiation of laser light at 307.9800 nm, where the resonance fluorescence is not excited. At an integration time of 60 sec, the measured fluorescence intensity is approximately 2900 counts.

During the experiment, a calibration procedure is tested to relate the fluorescence signal to OH concentration. Measurement is performed using a low-concentration OH radical, and the fast radical cross reaction ($\text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$) can be quite small. Moreover, the concentration is much closer to the ambient condition, which makes the calibration more accurate. The O₃ concentration is fixed, and the H₂O mixing fraction is varied to produce a wide-ranged OH concentration, generating OH radical ranging in 2.9×10^7 – 1.2×10^8 molecules/cm³. OH radical with

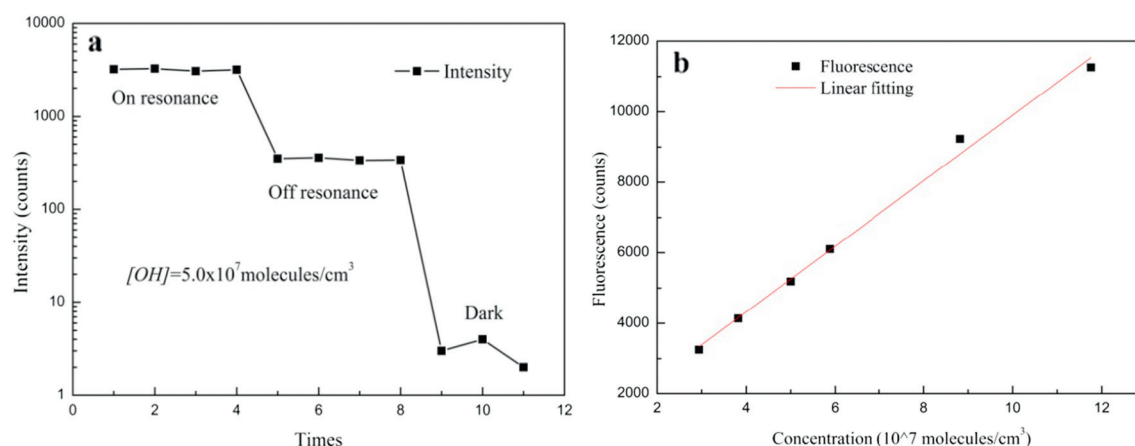


Fig. 9 – Fluorescence measured by FAGE instrument using gated PMT. a) On/off resonance intensity and b) OH radical calibration curve with varied OH concentrations. FAGE: Fluorescence Assay by Gas Expansion; PMT: photomultiplier.

varied concentrations is detected, and the experiment shows remarkable linearity (Fig. 9b). The calibration factor can be used for OH radical calibration.

The detection sensitivity C (cps/(OH·cm⁻³)) is given as the OH fluorescence signal divided by the OH concentration (Kanaya et al., 2001; Faloona et al., 2004), as follows:

$$C = \frac{S_{OH}}{[OH]} \quad (8)$$

And the OH detection limit ($[OH]_{min}$) can be calculated by the following formula:

$$[OH]_{min} = \frac{S}{N} \sqrt{\frac{1}{m} + \frac{1\sqrt{S_{BG}}}{n C \sqrt{t}}} \quad (9)$$

where S/N is the signal-to-noise ratio at the detection limit, m and n are the numbers of fluorescence and background measurement, and S_{BG} (cps) is the background signal count rate. Under the condition of the laboratory experiment by using the gated PMT, these parameters are determined as follows: $S/N = 2$, $m = n = 1$, $S_{BG} = 6$ cps, and the C is estimated to be 9.5×10^{-7} cps/(OH·cm⁻³), the $[OH]_{min}$ is calculated to be 9.4×10^5 molecules/cm³ at a accumulation time of 60 sec. And the system could improve a better detection limit by increasing the integration time.

A similar test has been carried out by using MCP for comparison. Most experimental parameters are the same, and there are just some slightly differences in the gate timing and threshold which is accord with the MCP. The detection sensitivity and OH detection limit is calculated to be 2.3×10^{-6} cps/(OH·cm⁻³) and 1.6×10^5 molecules/cm³, respectively. The result shows that the gated PMT has a slightly worse performance compared to the MCP, which might mainly be caused by the afterpulse of the PMT. But it still meets the needs of the OH radical measurement in smoke chamber or some ambient condition, and it also has lower cost and is more flexible for system test.

3.4. System performance

In order to test the performance of the whole FAGE system, an OH detection experiment is carried out in the laboratory. A 5w mercury low-pressure pen-ray lamp is set near the top side of the inlet aperture, which provides an OH radical source by photolysis of H₂O and O₂. By controlling the distance between the lamp and the aperture, several kinds of relatively stable OH radial similar to the ambient air is produced, and its concentration is detected by the gated PMT. The room temperature and relative humidity is 20°C, and 30%, respectively.

Based on the calibration results, average concentration of three kinds of OH radial during the experiment are calculated to be approximately 3.4×10^6 molecules/cm³, 6.7×10^6 molecules/cm³ and 1.15×10^7 molecules/cm³ (Fig. 10). The results show that the FAGE system with gated PMT meets the needs of the OH radical measurement in smoke chamber or most ambient condition. The system can also make some optimization to improve the detection limit and sensitivity, like increasing integration time and suppressing stay light, and applied for ambient OH radical measurement.

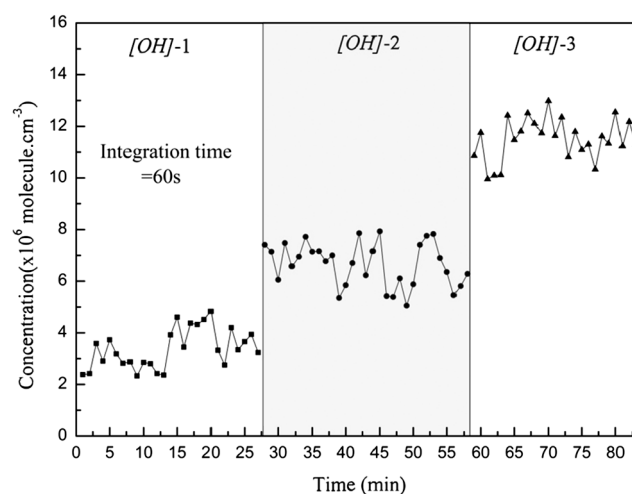


Fig. 10 – Laboratory OH radical measurement of three kinds of concentration.

4. Conclusions

An OH radical detection system using FAGE technique is constructed in our laboratory, and its performance is tested. Ambient air is introduced to the low-pressure fluorescence cell, and fluorescence is both excited and detected at 308 nm. The instrument includes a home-made gating PMT as the detector, which has a performance comparison with the MCP, and fluorescence is counted by a photon counting card with a specific time filtering system. The OH excited line at approximately 308 nm is obtained using the OH radical supplied by the generation cell. The Q₁(2) line is chosen for OH radical excitation based on the excitation spectrum. The sensitivity and detection limit is tested using an OH radical with known concentration generated by using simultaneous photolysis of H₂O and O₂, and the calibration for OH radical measurements is researched. By using the gated PMT as the detector, the sensitivity of the system is estimated to be 9.5×10^{-7} cps/(OH·cm⁻³), and the minimum detection limit is estimated to be 9.4×10^5 molecules/cm³, while these parameters is 2.3×10^{-6} cps/(OH·cm⁻³) and 1.6×10^5 molecules/cm³ by using MCP. These values are better than typical tropospheric OH concentrations (order of 10⁶ molecules/cm³). Combining with the calibration procedure, a laboratory measurement of OH radical is carried out, and the results show a good sensitivity. Thus, the instrument with FAGE technology developed in this study can be used for tropospheric OH measurements, and the instrument also needs further optimization to improve the detection limit for further field application.

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