The Improved Comparative Reactivity Method (ICRM): measurements of OH reactivity at high-NO$_X$ conditions in ambient air

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23 **Abstract**

24   The comparative reactivity method (CRM) has been developed more than a

25 decade to measure OH reactivity (i.e. OH loss frequency) in both laboratory and field

26 studies. However, accurate OH reactivity quantification remains challenging under real

27 ambient condition, especially for OH reactivity measurements in high-NO_X (e.g. >10

28 ppbv) environments, as ambient NO enhance regeneration of OH radicals in the CRM

29 reactor. To resolve this problem, we design a new improved CRM reactor (ICRM) and

30 add NO into the system continuously, so that the HO_2 radical concentration is

31 suppressed. We confirmed the appropriate level of NO by determining the maximum

32 decrease in the pyrrole level caused by regenerated OH radicals from $NO + HO_2$. VOC-

33 induced RO_2 radicals in the ICRM reactor were also found to react with NO, which lead

34 to the re-generation of OH radicals thus the underestimation of OH reactivity. This

35 effect was quantified by the calibration of representative VOC species at different NO

36 levels, and the correction coefficients obtained were used to correct the measured OH

37 reactivity. All these efforts resulted in reducing the uncertainty of the NO-artifact

38 correction by at least an order of magnitude compared to the original CRM system.

39 Additionally, these technological improvements also considerably reduced the

40 systematic errors from pyrrole photolysis that exists in the original system. A new

41 operation mode was proposed for ICRM, which is able to avoid the interference

42 resulting from OH radicals produced by photolysis of residual humidity and save time

43 for ambient measurement. The ICRM system was employed in a field campaign to

44 measure OH reactivity and performed well with ambient NO levels ranged from 0 to

45 50 ppbv, which were typically observed in urban and suburban atmosphere.

1 Introduction

The hydroxyl radical (OH) is the most important oxidant in the daytime troposphere. It initiates the chemically removal of primary gaseous pollutants and in turn produces a host of secondary pollutants (A. Hofzumahaus, 1991; Atkinson, 2000; Roger Atkinson, 2003). The OH reactivity is defined as the sum of all OH reactive trace gas concentrations multiplied by their respective reaction rate coefficients with OH, as shown in Eq. 1. The OH reactivity is a fundamental property of the atmosphere in that it defines the overall loss frequency of OH radicals and hence the lifetime of OH. As such it is a useful atmospheric parameter for evaluating the level of reactive pollutants and it is closely related to atmospheric oxidation capacity and formation of secondary pollutants including ozone and secondary aerosols (Sinha et al., 2012; Yang et al., 2016; Pfannerstill et al., 2019).

$$R_{OH} = k_{CO}[CO] + k_{NO}[NO] + k_{NO_2}[NO_2] + k_{SO_2}[SO_2] + k_{O_3}[O_3] + \sum_i^n k_{VOC_i}[VOC_i]$$

$$(1)$$

Equation 1 defines the OH reactivity where R_{OH} is the total OH reactivity, k_{CO}, k_{NO}, k_{NO_2}, k_{SO_2}, k_{O_3}, and k_{VOC_i} represent the reaction rate coefficients between OH radicals and CO, NO, NO_2, SO_2, O_3, and volatile organic compounds (VOCs) species i, respectively. [CO], [NO], [NO_2], [SO_2], [O_3], and [VOC_i] are the concentrations of CO, NO, NO_2, SO_2, O_3, and VOCs species i, respectively.

Currently, two general methods are used to measure OH reactivity: (1) direct measurements of OH decay rates by laser-induced fluorescence (LIF) technique; (2) measuring the relative change of a reference substance with and without ambient air present by the comparative reactivity method (CRM). The LIF based technology has been used to measure OH reactivity in a variety of different environments and has provided many new insights into the budget of OH reactivity (Kovacs et al., 2001; Kovacs et al., 2003; Sadanaga et al., 2004; Sadanaga et al., 2005; Ingham et al., 2009; Lou et al., 2010). However, the cost, complexity, and large size of LIF systems are deterrents to the widespread deployment for field measurements (Sinha et al., 2008).

Such detector systems need to be built and cannot be bought directly from a supplier. The CRM method measures OH decay rate indirectly by using the relative reaction rate of a reference substance (pyrrole) with self-generated OH radicals in the presence and absence of ambient air. The reference substance can be measured by an online instrument, such as proton transfer reaction mass spectrometry (PTR-MS) (Sinha et al., 2008; Sinha et al., 2009; Kumar et al., 2014) or a gas chromatograph (Nolscher et al., 2012a; Praplan et al., 2017a; Praplan et al., 2019b). The CRM technique has proven to be a useful supplementary technique to measure the total OH reactivity in ambient air, with a more economical and portable setup than the LIF-based systems. Based on inter-comparison between various OH reactivity techniques in the SAPHIR chamber, the LIF type-instruments are generally more sensitive and less noisy than CRM instruments (Fuchs et al., 2017).

The CRM approach has been applied to numerous field campaigns in recent years to measure OH reactivity (Dolgorouky et al., 2012; Nölscher et al., 2014; Michoud et al., 2015; Kim et al., 2016; Zannoni et al., 2016; Praplan et al., 2017b; Yang et al., 2017a; Zannoni et al., 2017; Kumar et al., 2018; Pfannerstill et al., 2018; Pfannerstill et al., 2019; Praplan et al., 2019a). However, this method is not suitable for the environment with high-level NO_X, due to the pen-ray mercury lamp used to generate OH radicals in CRM system also generates approximately equivalent amounts of HO_2 radicals that may react with sampled NO to produce additional OH radicals (Sinha et al., 2008; Yang et al., 2017a), which cause an enhanced consumption of pyrrole in the CRM system and result in an underestimation of OH reactivity in sampled ambient air when NO exceeds certain levels (Sinha et al., 2008). This NO interference prevents the CRM method from providing high-quality data in emission exhausts and urban areas with high NO levels. As a result, applications of the CRM method have been generally restricted to high reactivity/low NO_X environments, including forests (Sinha et al., 2010; Kim et al., 2011; Nolscher et al., 2012b; Praplan et al., 2019b; Pfannerstill et al., 2020), moderately polluted cities (NO < 10 ppb) (Sinha et al., 2008; Praplan et al., 2017b), pristine marine environments (Sinha et al., 2012; Zannoni et al., 2015), emission sources (e.g. gasoline

evaporation) (Wu et al., 2015), branch cuvette studies (Nölscher et al., 2013), and chamber studies (Nölscher et al., 2014) with little or no NO_x present. One solution to this issue is to deliberately remove NO, before the sampled air is introduced into the reactor. However, the present technology is not able to remove NO selectively without affecting other reactive species (i.e., VOCs). The effect of NO on measured OH reactivity can be quantified by NO-correction experiments and the resulting correction curve applied to adjust ambient measurements according to simultaneously measured NO levels (Hansen et al., 2015; Yang et al., 2017a). However, the uncertainty of measured OH reactivity due to NO correction increases with NO concentration (Hansen et al., 2015; Michoud et al., 2015). Hansen et al. (2015) reported that the total uncertainty increases by up to a factor of 3 at NO_x mixing ratios higher than 40 ppbv. Therefore, it calls for an improvement of the traditional CRM reactor for accurately quantifying OH reactivity at high NO_x conditions. In addition to the NO effect, photolysis of pyrrole and VOCs, and the humidity difference between zero air and ambient air also influence measured OH reactivity (Sinha et al., 2008; Hansen et al., 2015; Zannoni et al., 2015).

The main purpose of this study is to improve the original CRM system to make it suitable for using in high-NO_x conditions. We modified the structure of the original CRM glass reactor and add a certain amount of NO into the system to remove the generated but unwanted HO_2 radicals. We further characterized the improved CRM (ICRM) system by quantitatively evaluating the effect of the reaction of sample VOC-induced RO_2 with NO on measured OH reactivity. Additionally, the interference of pyrrole photolysis was also systematically evaluated. Finally, the ICRM system was deployed to measure OH reactivity under high-NO_x conditions (0-50 ppbv) during a field campaign in the Pearl River Delta region of China.

2 Experimental and Methodology

2.1 The original CRM reactor

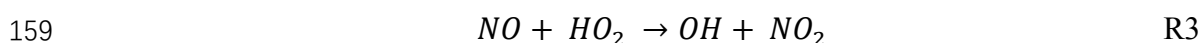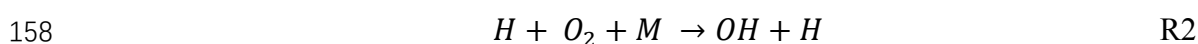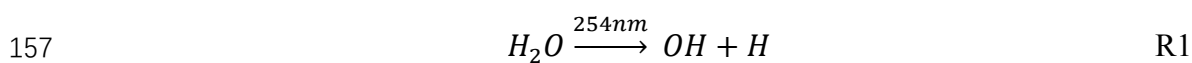The schematic of the original CRM reactor is shown in Fig. 1a. Gas-phase pyrrole

mixed with zero air or ambient air is introduced through arm C at a constant flow. Arm A consists of a pen-ray spectral mercury lamp **(Analytik Jean; 90-0012-01)**, over which nitrogen (humidified or dry) is passed through arm B at a constant flow rate. When humidified nitrogen is flowing and the mercury lamp is turned on, H_2O is photolyzed into OH and H radicals by the mercury lamp at 254 nm. The total air flow in the reactor exits through arm F and the concentration of pyrrole is monitored with a PTR-MS. A detailed description of the original CRM method has been reported by Sinha et al. (2008).

Figure 1(b) shows the four work modes of the original CRM method (Sinha et al., 2009). In C0 mode, the mercury lamp is turned off and high-purity dry nitrogen is introduced into the reactor through arm B. Pyrrole is introduced into the reactor with dry zero air through arm C. In C1 mode, the mercury lamp is turned on while everything else remains the same as C0. Pyrrole concentration decreases during C1 mode due to its photolysis reaction. In C2 mode, nitrogen flow in C1 is changed to humidified nitrogen to generate OH radicals, and the pyrrole concentration decreases to C2. In the final step, ambient air is introduced to the reactor through arm C in C3 mode. Based on pseudo-first-order assumptions (i.e., [pyrrole] $\geq$ [OH]), total OH reactivity (R_{OH}) is calculated as Eq. 2:

$$R_{OH} = C1 \times k_{pyr+OH} \times \frac{C3-C2}{C1-C3} \tag{2}$$

Where k_{pyr+OH} is the rate coefficient for the reaction of pyrrole with OH radicals (1.28×10^{-10} $cm^3 \cdot molecule^{-1} \cdot s^{-1}$ (Dillon et al., 2012)), and C1, C2, and C3 represent pyrrole concentrations at the corresponding steps described above, respectively.

In C2 and C3 mode, OH radicals are produced by the photolysis of water vapor at atmospheric pressure as shown in R1. The generated H radicals from R1 reacts with O_2 of zero air or ambient air to generate HO_2 radicals, as shown in R2. When NO is present in the sampled ambient air, it can recycle OH by reacting with HO_2 (R3).

$$H_2O \xrightarrow{254nm} OH + H \tag{R1}$$

$$H + O_2 + M \rightarrow OH + H \tag{R2}$$

$$NO + HO_2 \rightarrow OH + NO_2 \tag{R3}$$

An underlying assumption of the CRM approach is that the influence of the species in ambient air on the production of OH radicals in the reactor is ignorable. The theoretical OH mixing ratio in the original CRM reactor is about $5 \sim 20$ ppbv, which depends on the introduced pyrrole concentration to ensure the Pyrrole/OH ratio is $2:1\sim3:1$. However, the additional OH radicals produced via R3 can react with pyrrole to cause an additional decrease in pyrrole relative to C2 mode, thus lead to the underestimation of OH reactivity.

2.2 The improved CRM reactor

In order to remove the interference of the reaction of HO_2 radicals with NO as discussed above, we modified the pipe structure of the original CRM reactor (Fig. 1c). We kept the length and volume of the glass reactor of the ICRM system similar to the original CRM system, but added a branch inlet G (1/4 inch OD glass; length 3 cm) in arm A to introduce steam of NO standard (Air Liquide; stated uncertainty 3%; 10.8 ppmv) mixed with zero air at a constant flow of 120 ml·min^{-1}. The typical flow rate inside the ICRM reactor is approximately 660 ml·min^{-1}. The flow rate of nitrogen (Air Liquide; 99.9995% purity) through arm B is 250 ml·min^{-1}. The input pyrrole (Linde Spectra Environment Gases; stated uncertainty 5%; 5.37 ppm) flow rate is 2.5 ml·min^{-1}. The total flow rate of pyrrole and zero air (Air Liquide; 99.9995% purity) through arm C is 290 ml·min^{-1}. With this modified structure of arm A, the HO_2 radicals, produced by the reaction of the generated H radicals near the mercury lamp and O_2 in introduced zero air, were converted to OH radicals by reacting with NO in the downstream of arm G. The interference induced by R3 can then be eliminated.

Arm A consists of one 1/2 inch OD (ID: 0.62 cm, length: 7 cm) glass tube and one 1/4 inch OD (ID: 0.32 cm, length: 5 cm) glass tube. The longer arm A is beneficial for longer reaction time of HO_2 with NO, but lower OH concentrations passing into the reactor due to wall loss. We chose an appropriate length of arm A (12 cm) to ensure appropriate OH concentration (4 ppbv) and reaction time of HO_2 with NO (~ 0.1 s). The purpose of the two-section structure is to ensure that the UV light is mostly confined within a 1/2 inch OD glass tube of arm A, as the diameter of arm A goes from