Investigation of the Amplification Efficiency of Gases Other Than *CO* for the Measurement of Atmospheric Peroxy Radicals by Chemical Amplification

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ABSTRACT

Peroxy radicals (HO_2 and RO_2) are one of the most important key intermediates in most of the oxidation reactions taking place in the troposphere. They are produced by photolysis and oxidation of atmospheric volatile organic compounds (VOCs). Together with hydroxyl radicals (OH), they play a key role in most atmospheric oxidation mechanisms. They also contribute in tropospheric ozone formation and depletion by influencing the photochemical formation of nitrogen dioxide (NO_2) from nitrogen monoxide (NO).

The TROLAS group (Tropospheric Radical Observations and Laser Absorption Spectroscopy) at the Institute of Environmental Physics of the University Bremen (IUP-UB) have dedicated years for the measurement of peroxy radicals with peroxy radical chemical amplification (PeRCA) technology. Recently with the focus on the airborne measurement, the group joined the OMO (Oxidation Mechanisms Observations) measurement campaign in order to investigate further the atmospheric vertical distributions of peroxy radicals. Traditionally *CO* is used for PeRCA technique as the chemical amplification agent; for airborne measurement, special certification for *CO* is needed due to safety regulations. At the test mission of the OMO campaign, the certification for *CO* was not issued in time, and alternatives for amplification gases were required. In that context, the performance of C_2H_4 and CH_3CHO as potential amplification gases has been systematically characterized in this work.

With this purpose, series of calibrations for the determination of the amplification factor, the so called effective chain length (eCL) have been made for CO, C_2H_4 , and CH_3CHO as amplification agents under different conditions, where CO has been used as a reference calibration.

 C_2H_4 showed the potential of amplifying the signal, even though the eCL obtained was roughly 20% of the eCL from *CO*. Interference signals from C_2H_4 as amplification gases were identified to originate from the ozonolysis of C_2H_4 which form Criegee intermediates. The determination of the interference has been made and the valid eCL has been determined subsequently. The relative interference (interference divided by the total amplifications) from C_2H_4 does not change with within the O_3 range of concentrations investigated, being 4ppb the maximum mixing ratio of O_3 generated by the calibration source. The relative interference decreased with increasing *NO* mixing ratios, but did not change with different sampling flow rates. In the investigation of CH_3CHO as chemical amplification agent, no significant eCL was determined. The amplification signals were hardly observed beyond the detection limit under most of the conditions studied and the modulations remained negative. Potential reasons for these experimental result are discussed.

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1. INTRODUCTION AND MOTIVATION

Peroxy radicals, commonly known as hydroperoxy radical (HO_2) and organic peroxy radicals (RO_2 , where R stands for any organic chain), are short lived trace gases playing an important role in the tropospheric chemistry (Monks, 2005). As key intermediates in most oxidation reactions, peroxy radicals along with hydroxyl radical (OH) lead to the formation and depletion of tropospheric ozone, formation of aldehydes, peroxyacetyl nitrate (PAN) and acids. They are indicators of the photochemical activity of the air masses. Due to the complexity of reactions with peroxy radicals and the limited number of measurement data, there are still many unknowns regarding to the radical recycling processes (Clemitshaw et al., 2004; Hofzumahaus et al., 2009; Orlando and Tyndall, 2012). In order to understand the characteristics of the photochemical activity of the atmosphere as well as atmospheric reaction mechanisms, it is necessary to measure the peroxy radical mixing ratio at high accuracy and temporal resolution. Due to the generally low mixing ratio (peak mixing ratio up to 100pptv, Hofzumahaus et al., 2009) and short life time in the atmosphere, the measurements of peroxy radicals require sensitive techniques. Several direct and indirect measurement methods of peroxy radicals have been developed over the decades of years of pursuing by the predecessors.

Among many ways of measuring the peroxy radicals, the institute for Environmental Physics (IUP) of the University of Bremen (UB) has dedicated years to the characterisation and optimisation of the indirect method Peroxy Radical Chemical Amplification (PeRCA). The recent work is focusing on the airborne measurement. For airborne measurement purpose, the institute decided to participate in the OMO (Oxidation Mechanism Observations) measurement campaign on board the German research aircraft HALO (High Altitude LOng range) carried by DLR (German "Deutsches Zentrum für Luft- und Raumfahrt e.V."), the national aeronautics and space research center of the Federal Republic of Germany. The OMO campaign had two parts: OMO-EU and OMO-Asia. The OMO-EU campaign was a test campaign based in Oberpfaffenhofen in Germany. The OMO-Asia was a measurement campaign which was carried out in July-August 2015, based in Paphos, Cyprus and Gan, Maldives. The OMO mission aims "to determine the rates at which natural and human-made compounds are converted by oxidation processes in the upper troposphere, which in turn affect the lifetime and the global distribution of air pollutants and several greenhouse gases, including tropospheric ozone." (OMO, 2009). A main focus was the characterization of the influence of the Asian

monsoon, comprising a large scale regional system which transports pollutants from the boundary layer to the free troposphere.

The principle of PeRCA techniques requires the use of carbon monoxide (*CO*) (details in chapter 3.1). The safety regulations for airborne measurements are very strict. For the OMO mission, special certifications for using toxic and dangerous (explosive and flammable) gases on board were a mandatory requirement. A secondary containment for using *CO* gas on board was requested. For the OMO-EU campaign, the certification of using *CO* was not issued in time for the flight. Within the limited time, replacing *CO* by other gases became necessary. Two alternatives, ethylene (C_{2H4}) and acetaldehyde (CH_3CHO) were suitable candidates for replacing *CO*. Both alternatives can be transported with gas bottles; the usage was possible under toxicity, explosive and flammable level; and theoretically they can react as chemical amplifier. During the OMO-EU campaign, C_2H_4 was used instead of *CO*. The detailed characterization of C_2H_4 and CH_3CHO as chemical amplifiers were investigated later in the lab experiments and presented in this study.

2. OBJECTIVES OF THE WORK

The objective of this work is the investigation and characterization of the performance of PeRCA with C_2H_4 and CH_3CHO as amplification gases, in order to evaluate if they can become an alternative to the standard usage of *CO* for the airborne measurement of peroxy radicals.

The experimental work therefore comprises the determination of the amplification chain length for the gases selected as alternatives in comparison with the standard *CO* under controlled laboratory conditions. With this purpose, existing instruments and set-ups of the IUP TROLAS group have to be partly modified, in order to optimize the experimental performance.

Series of laboratory calibration experiments must be designed and carried out to characterize the variables affecting detector sensitivity and amplification capacity in each case. These calibrations require the generation of known mixing ratios of NO_2 and HO_2 radicals.

Finally, the results must be discussed and interpreted taking into account the expected chemistry involved in each amplification chain.

3. THEORETICAL BACKGROUND

Since the objective of the work is to investigate the performance of C_2H_4 and CH_3CHO as the amplification agent for peroxy radical peroxy radical chemical amplification techniques, the theoretical background will focus on the basics of peroxy radical chemistry in the atmosphere as well as the PeRCA techniques.

3.1. Radicals in the Troposphere

The most important radicals in the atmosphere are the peroxy radicals (hydroperoxyl HO_2 and organic peroxy radicals RO_2), hydroxyl radicals (OH), and alkoxy radicals (RO). They are the oxidation products of a series of pollutants in the atmosphere. OH, HO_2 , RO and RO_2 are sometimes summarized as RO_x , because those radicals are interconverted closely in radical cycles. The peroxy radicals change the equilibrium cycle between the NO and NO_2 (for convenience the sum of NO and NO_2 are always referred as NO_x), the co-existence of NO_x and RO_x affects the tropospheric ozone formation and depletion. Figure 1 summarizes the reaction mechanisms of radical photochemistry in the troposphere.



Figure 1: Schematic of the radical photochemistry in the troposphere. (Fuchs, 2006)

The main source for peroxy radicals are the oxidation reactions of *OH* with carbon monoxide (*CO*) and volatile organic compounds (VOC). The hydroxyl radical *OH* is the dominant oxidant

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in the troposphere. *OH* can be mostly produced by the photolysis of O_3 . *OH* radicals can react with the *CO* and generate *H*, *H* reacts with O_2 and subsequently generate HO_2 .

$$OH + CO \to H + CO_2 \tag{R3-1}$$

$$H + O_2 \xrightarrow{M} HO_2 \tag{R3-2}$$

If NO is present, HO₂ will react with NO and regenerate OH:

$$HO_2 + NO \to OH + NO_2 \tag{R3-3}$$

The cycling between *OH* and *HO*² radicals is relatively fast in polluted areas (rich in *NO* and *NO*²). The mixing ratio of *OH* and *HO*² will reach an equilibrium, therefore *OH* and *HO*² radicals are often closely referred as HO_x . HO_x as a sum up of *OH* and HO_2 . Methane is the most abundant atmospheric VOC, which can react with *OH* and lead to the simplest RO_2 (*CH*₃*O*₂) formation.

With the presence of NO, the reaction will lead to HO₂ generation:

$$OH + CH_4 \to CH_3 + H_2O \tag{R3-4}$$

$$CH_3 + O_2 \xrightarrow{M} CH_3O_2 \tag{R3-5}$$

$$CH_3O_2 + NO \rightarrow CH_3O + NO_2 \tag{R3-6}$$

$$CH_3O + O_2 \to HCHO + HO_2 \tag{R3-7}$$

The product from reaction (R3-5) CH_3O_2 can react with HO_2 leads to the formation of methyl hydroperoxide:

$$HO_2 + CH_3O_2 \rightarrow CH_3OOH + O_2 \tag{R3-8}$$

CH₃COOH can photolysis into OH:

$$CH_3OOH \xrightarrow{hv} CH_3O + OH$$
 (R3-9)

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CH₃COOH can also react with *OH* as a source for *CH₃O₂*:

$$CH_3OOH + OH \to CH_3O_2 + H_2O$$
 (R3-10)

A more general way of expressing the reactions of VOC is shown in the following where *R* stands for organic compound:

$$RH + OH \to R + H_2O \tag{R3-11}$$

$$R + O_2 \xrightarrow{M} RO_2 \tag{R3-12}$$

$$RO_2 + NO \to RO + NO_2 \tag{R3-13}$$

$$RO + O_2 \xrightarrow{M} R'CHO + HO_2$$
 (R3-14)

R, *RO* or *RO*² in chemical reactions often represent different species. Due to the similarities of the radical reactions and the reaction rate constants, it is useful to treat the different radicals as a whole summation. So that in the equations, $RO = \sum_i R_i O$ and $RO_2 = \sum_i R_i O_2$.

OH radicals are more reactive than the peroxy radicals, so that the mixing ratio of peroxy radicals is substantially larger than *OH* radicals (generally 2 orders of magnitude). The sources and sinks of peroxy radicals are affected by the *OH* radicals' source and sinks because of the conversion relations between them.

Ozone can absorb light in two paths and generate oxygen atoms at different states, $O({}^{1}D)$ and $O({}^{3}P)$. $O({}^{3}P)$ will recombine with oxygen and form ozone; while most of the $O({}^{1}D)$ atoms are quenching by collision and deactivate to the grounded state, but a small part (about 10%) of $O({}^{1}D)$ can react with $H_{2}O$ and generate OH radicals:

$$O_3 \xrightarrow{h\nu(\lambda < 320nm)} O({}^1D) + O_2 \tag{R3-15}$$

$$O_3 \xrightarrow{hv(\lambda < 1180nm)} O({}^3P) + O_2 \tag{R3-16}$$

$$O\left({}^{3}P\right) + O_2 \xrightarrow{M} O_3 \tag{R3-17}$$

$$O({}^{1}D) \xrightarrow{M} O({}^{3}P) \tag{R3-18}$$

$$O(^{1}D) + H_2O \to 2OH \tag{R3-19}$$

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In addition, the photolysis of nitrous acid (*HONO*) in urban conditions during daytime can also produce *OH* radicals (Seinfeld and Pandis, 2012):

$$HONO \xrightarrow{hv(\lambda < 390nm)} OH + NO$$
(R3-20)

$$OH + NO \xrightarrow{M} HONO$$
 (R3-21)

Nitrate radicals (NO₃) and HO₂ react and can produce OH during the night time:

$$NO_3 + HO_2 \rightarrow OH + NO_2 + O_2 \tag{R3-22}$$

Nitrate radical is formed by the reaction of:

$$NO_2 + O_3 \to NO_3 + O_2$$
 (R3-23)

Peroxy radicals can be produced by the photolysis of formaldehyde (*HCHO*) or *HCHO* reaction with *OH*. Since *HCHO* is also a production from the oxidation process of methane and other carbonyl compounds, *HCHO* is an important source for peroxy radicals.

$$HCHO \xrightarrow{h\nu(\lambda < 360nm)} H_2 + CO \tag{R3-24}$$

$$HCHO \xrightarrow{hv(\lambda < 335nm)} H + HCO$$
(R3-25)

$$HCHO + OH \to HCO + H_2O \tag{R3-26}$$

$$HO_2 + NO \to OH + NO_2 \tag{R3-3}$$

$$HCO + O_2 \to HO_2 + CO \tag{R3-27}$$

$$H + O_2 \xrightarrow{M} HO_2 \tag{R3-2}$$

The atmospheric RO_x radicals are terminated by the reactions of radical recombination. In less polluted areas, RO_x radicals react with themselves dominating the loss processes. In polluted areas, OH react with NO_2 and producing the nitric acid (HNO_3). Nitric acid will be washed out of the wet deposition leads to the OH decreasing.

In unpolluted areas the dominant radical loss processes are:

$$HO_2 + HO_2 \to H_2O_2 + O_2$$
 (R3-28)

$$HO_2 + RO_2 \to ROOH + O_2 \tag{R3-29}$$

$$RO_2 + RO_2 \rightarrow products$$
 (R3-30)

In polluted areas *NO* reacts with *OH* and *HO*₂, *NO*₂ reacts with *OH* leads to the loss processes of radicals:

$$OH + NO_2 \xrightarrow{M} HNO_3$$
 (R3-31)

$$OH + NO \xrightarrow{M} HONO$$
 (R3-19)

$$HO_2 + NO \xrightarrow{M} HNO_3 \tag{R3-32}$$

The only known tropospheric ozone source are the photolysis of NO_2 and the subsequence reaction of the photoproduct $O({}^{3}P)$ with O_2 . NO and NO_2 reach a quasi-stationary equilibrium due to the fast reaction cycle. The amount of ozone does not increase or decrease if the reaction mechanisms with peroxy radicals are not considered. This is called the ozone null cycle:

$$NO_2 \xrightarrow{hv(\lambda < 420nm)} NO + O({}^{3}P)$$
(R3-33)

$$O\left({}^{3}P\right) + O_2 \xrightarrow{M} O_3 \tag{R3-15}$$

$$NO + O_3 \rightarrow NO_2 + O_2 \tag{R3-34}$$

In the polluted areas where *NO* is abundant, peroxy radicals will react with *NO* and produce *NO*₂:

$$HO_2 + NO \to OH + NO_2 \tag{R3-3}$$

$$RO_2 + NO \rightarrow RO + NO_2$$
 (R3-11)

The additional sources of NO_2 from reaction (R3-3) and (R3-11) will follow the reactions of (R3-32) and (R3-15) which lead to O_3 generation.

In less polluted areas (where *NO* mixing ratio is enough low so that the reaction rate for (R3-3) and (R3-11) are lower than the reaction rates of (R3-35), (R3-36), (R3-37)), peroxy radicals react with ozone leads to ozone depletion (Monks, 2005):

$$HO_2 + O_3 \to OH + 2O_2$$
 (R3-35)

$$RO_2 + O_3 \to RO + 2O_2$$
 (R3-36)

$$OH + O_3 \rightarrow HO_2 + O_2 \tag{R3-37}$$

There is a balance between photochemical ozone production and ozone depletion dependent on the mixing ratio of NO_x and HO_x . Figure 2 shows the dependence of the production of ozone on the mixing ratio of NO_x from a numerical model (Monks, 2005). Three distinctive regions are clear in terms of net ozone production vs. NO_x mixing ratio. In the region A, where NO_x mixing ratio is rather low, there is net ozone losing. The ozone net production is increasing with the increasing of the mixing ratio of NO_x until the peak value of net ozone production (A and B). Then with further increase of NO_x mixing ratio the net ozone production is decreasing (region C).



Figure 2: Schematic representation of the dependence of the net ozone production on the mixing ratio of NO_x . The magnitudes reflect clean free tropospheric conditions. (Monks, 2005)

3.2. Peroxy Radical Chemical Amplification (PeRCA)

The measurement of peroxy radicals is difficult due to their high reactivity and short life time. Highly sensitive detection instruments are required for measurement of mixing ratio of peroxy radicals which is in the magnitude of few to several pptv (part per trillion volume).

As one of the indirect measurement technique for the peroxy radicals, PeRCA was first introduced by Cantrell and Stedman (1982). It is a method that can detect the sum of all the peroxy radicals in the sampled air (all the HO_2 and all the RO_2).

The principle of PeRCA is to set up a chain reaction cycle between *OH* and *HO*₂ by adding *NO* and *CO* to the system.

$$HO_2 + NO \to OH + NO_2 \tag{R3-3}$$

$$OH + CO \xrightarrow{M} H + CO_2 \tag{R3-1}$$

$$H + O_2 \xrightarrow{M} HO_2 \tag{R3-2}$$

NO converts the sampled HO_2 into OH and generate NO_2 ; *CO* converts the OH back to HO_2 which take place the reaction (R3-1), this corresponds to the previous set of reaction. So that HO_2 is converted and amplified into NO₂. The chain length (CL) of the chain reaction defines the number of NO_2 produced by one HO_2 . The CL has limited number because the reaction cycle ends due to a series of loss reactions in the reactor.

3.4

$$RO_2 + wall \rightarrow nonradical \, products$$
 (R3-38)

$$OH + wall \rightarrow nonradical \ products$$
 (R3-39)

$$OH + NO \xrightarrow{M} HONO$$
 (R3-19)

$$OH + NO_2 \xrightarrow{M} HNO_3$$
 (R3-31)

$$HO_2 + NO \xrightarrow{M} HNO_3 \tag{R3-32}$$

$$HO_2 + NO_2 \xrightarrow{M} HO_2 NO_2 \tag{R3-40}$$

$$HO_2 + HO_2 \to H_2O_2 + O_2$$
 (R3-28)

$$OH + HO_2 \to H_2O + O_2 \tag{R3-41}$$

Since *NO* and *CO* are added in to the system with high mixing ratio, they will react with the radicals first, the radical and radical reaction loss only play a minor part. Most losses of the radicals are through the wall loss reaction. The total amplification factor is more practical (and the parameter can be determined from the series of calibrations), which is called the effective chain length (eCL). The eCL depends on the particular measurement set-ups and conditions. Due to the radical losses, the eCL is always smaller than the theoretical CL. The determination of the conversion and the amplification rate into NO_2 will be affected by other radical losses before the reactor.

The NO_2 mixing ratio can be measured by chemiluminescence detector (using luminol, $C_8H_7N_3O_2$, details in chapter 3.5) (Maeda, 1980).

Similarly, organic radicals will react with *NO* and *CO* in the chain reaction. For example, the simplest organic radicals, *CH*₃*O*₂:

$$CH_3O_2 + NO \rightarrow CH_3O + NO_2 \tag{R3-6}$$

$$CO + CH_3O \rightarrow CO_2 + CH_3 \tag{R3-42}$$

$$CH_3 + O_2 \xrightarrow{M} CH_3O_2$$
 (R3-5)

Since the mixing ratio of *OH* is much lower (generally 2 order of magnitude) than the mixing ratio of HO_2 , the measured signal should be a very good approach to the total proxy radical value. The setup for this measurement technique adds *CO/NO* and *N*₂/*NO* alternatively to the reaction area (reactor and inlet), so that the measured signal is a modulation between the correspondingly amplified signal and the background signal. When the *CO* is added in the reaction area, the chain reaction takes place and an amplified signal is detected by the *NO*₂ detector; when *N*₂ is added in the reaction area, the chain reaction area, the chain reaction area and a background signal is detected by the *NO*₂ detector.

Theoretically, the true peroxy radical mixing ratio can be calculated from the difference between the amplified signal and background signal (Figure 3) of NO_2 mixing ratio ($\Delta NO_2 = NO_{2,amplification} - NO_{2,background}$) and the eCL of the chain reaction. Therefore, the total mixing ratio of peroxy radicals can be calculated by:

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Where the total peroxy radicals are described as:

$$[RO_2^*] = HO_2 + \sum RO_2$$
 Eq.(3-2)

In Eq.3-1, $\Delta[NO_2]$ can be detected by NO_2 detector; eCL is determined as:

$$eCL = \frac{\Delta[NO_2]}{[RO_2^*]_{source}}$$
 Eq.(3-3)

Then NO_2 mixing ratio from Eq.(3-3) can be detected by the luminol NO_2 detector; $[RO_2^*]_{source}$ value is known from the peroxy radical generation from radicals source. The detailed experimental procedures and instrumental set-ups are described in chapter 4.



Figure 3: an example of the amplification signal and the background signal during the eCL calibration

3.2.1. Peroxy Radical Calibration Sources

The calibration of instruments measuring peroxy radicals uses known peroxy radical sources. The radical sources base on the photolysis of water vapor (pure water slowly pumped into synthetic air flow) at 184.9 nm with low-pressure Hg lamp (Schultz et al, 1995). Different radical concentrations can be produced by applying different lamp flux, changing the humidity in the air flow, and changing the flow rate.

$$H_2 O \xrightarrow{hv(\lambda = 184.9nm)} H + OH$$
(R3-43)

$$H + O_2 \xrightarrow{M} HO_2 \tag{R3-2}$$

CO will add additionally to the photolysis zone to convert the *OH* into *HO*₂; on the other hand, the mixture of 50% of *HO*₂ and 50% of *CH*₃*O*₂ can be generated if *CH*₄ is added to the photolysis zone instead of *CO*;

$$OH + CO \to H + CO_2 \tag{R3-1}$$

$$H + O_2 \xrightarrow{M} HO_2 \tag{R3-2}$$

$$H_2 O \xrightarrow{h\nu(\lambda=184.9nm)} H + OH$$
(R3-43)

$$OH + CH_4 \to CH_3 + H_2O \tag{R3-4}$$

$$CH_3 + O_2 \xrightarrow{M} CH_3O_2$$
 (R3-5)

In the photolysis zone, the oxygen in the synthetic air will photolyze and lead to ozone production:

$$O_2 \xrightarrow{h\nu(\lambda=184.9nm)} 2O({}^1D) \tag{R3-44}$$

$$O({}^{1}D) \xrightarrow{M} O({}^{3}P) \tag{R3-16}$$

$$O\left({}^{3}P\right) + O_2 \xrightarrow{M} O_3 \tag{R3-15}$$

3.2.2. Principle of Chemiluminescence with The Detection of *NO*₂

The chemiluminescence method for the determination of NO_2 determination based on the reaction between luminol (5-amino-2,3-dihydro-1,4-phthalazine dione, $C_8H_7N_3O_2$) and NO_2 was described by Maeda et al., 1980 and Wendel et al., 1983. NO_2 can react with luminol (R3-45 and R3-46) which emits lights (the maximum intensity is 425nm), the light is detected by a photo detector.



The light intensity from the chemiluminescence and the mixing ratio of NO_2 is linear dependent. Carbon dioxide, ozone, and sulphur dioxide can interfere the results of this method. In order to remove the interference, increasing the pH of the luminol solution (minimize the interference from carbon dioxide), and adding sodium sulphite to the luminol solution (minimize the interference from ozone and sulphur dioxide) have been performed respectively. In addition, with the presence of NO, NO_2 mixing ratio is not linearly dependent with the light intensity from the chemiluminescence, an offset of NO_2 has to be introduced to reduce this effect (Hastie et al., 1991). Furthermore, isopropanol (C_3H_7OH) is added to optimizing the sensitivity of the NO_2 .

3.3. Possible Alternatives for Chemical Amplification Agents

Besides the physical criteria which was mentioned in the introduction, the alternatives should also fit the role of "amplification" like *CO* in the PeRCA techniques. The expected theoretical amplification reactions with C_2H_4 according to previous studies (Atkinson et al., 1976, Chuong and Stevens, 2000, Mellouki et al., 2003, Cleary et al., 2005, Golden, 2012) and analogous chemistry is:

$$HO_2 + NO \to OH + NO_2 \tag{R3-3}$$

$$C_2H_4 + OH \xrightarrow{M} CH_2CH_2OH \tag{R3-47}$$

$$CH_2CH_2OH + O_2 \rightarrow CH_2CHOH + HO_2 \tag{R3-48}$$

$$CH_2CH_2OH + O_2 \rightarrow CH_2CH_2O + HO_2 \tag{R3-49}$$

$$CH_2CH_2OH + O_2 \xrightarrow{M} CH_2(OH)CH_2O_2$$
(R3-50)

$$CH_2(OH)CH_2O_2 + NO \to CH_2(OH)CH_2O + NO_2$$
 (R3-51)

NO is added into the reactor which is converted by HO_2 into NO_2 (R3-3), C_2H_4 is added into the system and reacts with the other production *OH* (R3-47). The product *CH₂CH₂OH* is believed to react with oxygen in three different paths (R3-48, R3-49, R3-50). Each of the paths can generate peroxy radicals, the radical product will react with *NO* again which triggers the chain reactions for the PeRCA. In reaction (R-48) and (R-49), the radical product is *HO₂*; in reaction (R3-50) the radical product is *CH₂(OH)CH₂O₂*. Then these peroxy radicals will follow the amplification reactions.

Similar amplification reactions with C_2H_4 for organic proxy radicals, for example CH_3O_2 :

$$CH_3O_2 + NO \rightarrow CH_3O + NO_2 \tag{R3-6}$$

$$C_2H_4 + CH_3O \xrightarrow{M} CH_2CH_2OCH_3 \tag{R3-52}$$

$$CH_2CH_2OCH_3 + O_2 \rightarrow CH_2CHOCH_3 + HO_2 \tag{R3-53}$$

$$CH_2CH_2OCH_3 + O_2 \rightarrow CH_2CHCH_3O + HO_2 \tag{R3-54}$$

$$CH_2CH_2OCH_3 + O_2 \xrightarrow{M} CH_2(OCH_3)CH_2O_2$$
(R3-55)

$$CH_2(0CH_3)CH_2O_2 + NO \to CH_2(0CH_3)CH_2O + NO_2$$
 (R3-56)

For the other possible alternative, *CH₃CHO*, the expected theoretical amplification reactions for *HO*₂ are (Moortgat, 1989, Cameron et al., 2002, Sivakumaran and Crowley, 2003):

• •

$$HO_2 + NO \to OH + NO_2 \tag{R3-3}$$

$$CH_3CHO + OH \rightarrow CH_3CO + H_2O \tag{R3-57}$$

$$CH_3CO + O_2 \xrightarrow{M} CH_3CO \cdot O_2 \tag{R3-58}$$

$$CH_3CO \cdot O_2 + NO \rightarrow NO_2 + CH_3 \cdot CO_2 \tag{R3-59}$$

$$CH_3 \cdot CO_2 \to CH_3 + CO_2 \tag{R3-60}$$

$$CH_3 + O_2 \xrightarrow{M} CH_3O_2 \tag{R3-5}$$

$$CH_3O_2 + NO \rightarrow CH_3O + NO_2 \tag{R3-6}$$

$$CH_3O + O_2 \to HO_2 + HCHO \tag{R3-61}$$

First, *NO* is converted by *HO*₂ into *NO*₂. *CH*₃*CHO* react with the *OH* from (R3-3). The product from (R3-57) will react with oxygen which generate the organic peroxy radical $CH_3CO \cdot O_2$ (R3-58). The radical will then convert *NO* into *NO*₂ (R3-59), the other product will decompose into *CH*₃ and *CO*₂ (R3-60). *CH*₃ react with oxygen and generate the peroxy radical *CH*₃*O*₂ (R3-*University of Bremen Postgraduate Programme ENVIRONMENTAL PHYSICS (PEP) 2015* 15

5). The radical CH_3O_2 can convert NO into NO_2 again (R3-6), and generate CH_3O . CH_3O react with oxygen and generate HO_2 , the HO_2 will react with NO by (R3-3). The chemical amplifications are fulfilled by the chain reactions where different peroxy radicals are generated step by step, and the amplified peroxy radicals will convert the NO into NO_2 which amplifies the NO_2 signal.

In the case of amplifying organic peroxy radicals with CH_3CHO , an example with CH_3O_2 :

 $CH_3O_2 + NO \rightarrow CH_3O + NO_2 \tag{R3-6}$

$$CH_3CHO + CH_3O \to CH_3CO + CH_3OH \tag{R3-62}$$

$$CH_3CO + O_2 \xrightarrow{M} CH_3CO \cdot O_2 \tag{R3-58}$$

- $CH_3CO \cdot O_2 + NO \rightarrow NO_2 + CH_3 \cdot CO_2 \tag{R3-59}$
 - $CH_3 \cdot CO_2 \to CH_3 + CO_2 \tag{R3-60}$

$$CH_3 + O_2 \xrightarrow{M} CH_3O_2 \tag{R3-5}$$

$$CH_3O_2 + NO \rightarrow CH_3O + NO_2 \tag{R3-6}$$

$$CH_3O + O_2 \to HO_2 + HCHO \tag{R3-61}$$

In the second step (R3-64), CH_3OH is generated instead of H_2O (R3-57). The following reactions are similar to the case with HO_2 .

3.4. Basics of Chemical Kinetics

For bimolecular reactions:

$$A + B \rightarrow product$$
 Eq.(3-4)

$$\frac{d[A]}{t} = \frac{d[B]}{t} = -k_{bi} \cdot [A] \cdot [B]$$
 Eq.(3-5)

The reaction rate for species A and B in Eq.(3-4) is expressed in Eq.(3-5) where [A] and [B] are the concentration of the species, k is the rate constant for the second order reaction. The rate constant is temperature dependent which is given in the Arrhenius form (JPL, 2011):

$$k_{bi} = k(T) = A \cdot e^{\left(-\frac{E}{RT}\right)} \qquad \text{Eq.(3-6)}$$

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Where A is the Arrhenius A-factor which specifically relates to molecular collision with the unit of $\frac{cm^3}{mol \cdot s}$, $\frac{cm^3}{mole \cdot s}$, or $\frac{cm^3}{M \cdot s}$; E is the activation energy for the reaction in $\frac{J}{mol}$; R is the universal gas constant, $8.314 \frac{J}{mol \cdot K}$; T is the reacting temperature in K. The reaction rate for the second order reaction is temperature dependent.

For termolecular reactions:

$$A + B \leftrightarrow [AB]^* \xrightarrow{M} product$$
 Eq.(3-7)

Where M is the collision partner (generally corresponds to N_2 and O_2 in the atmosphere). The concentration of the collision partner changes with the pressure. As it is showed in Eq.(3-7), the activation reaction is first a second order reaction which is temperature dependent; then the excess energy is transferred by the collision partner M, the rate coefficient is pressure dependent (Houston, 2012).

The low-pressure-limiting rate constants are given in:

$$k_0(T) = k_0^{300} (\frac{T}{300})^{-n}$$
 Eq.(3-9)

Where k_0^{300} has been adjusted for air as the third body at 300K, with unit of $\left[\frac{cm^6}{molec^2 \cdot s}\right]$; T is the temperature, K; n is the exponent factor. k_0^{300} and n is reported by experimental results or by model calculations. (JPL, 2011)

The high-pressure-limiting rate constants are given in:

$$k_{\infty}(T) = k_{\infty}^{300} (\frac{T}{300})^{-m}$$
 Eq.(3-10)

Where k_{∞}^{300} has been adjusted for air as the third body at 300K, with unit of $\left[\frac{cm^3}{molec \cdot s}\right]$; T is the temperature, K; m is the exponent factor. k_{∞}^{300} and m is reported by experimental results or by model calculations. (JPL, 2011)

The effective second order rate constant for a given condition of temperature and pressure is defined as:

$$k_f([M],T) = \left(\frac{k_0(T) \cdot [M]}{1 + \frac{k_0(T) \cdot [M]}{k_{\infty}(T)}}\right) \cdot 0.6^{\{1 + [log_{10}(\frac{k_0(T) \cdot [M]}{k_{\infty}(T)})]^2\}^{-1}} \qquad \text{Eq.(3-11)}$$

Some reactions that appear to be simple bimolecular processes proceed via bound intermediates, in this case the effective second order rate constant is:

$$k_f^{ca}([M],T) = \left(\frac{k_0(T)}{1 + \frac{k_0(T)}{k_\infty(T)/[M]}}\right) \cdot 0.6^{\left\{1 + \left[\log_{10}(\frac{k_0(T)}{k_\infty(T)/[M]})\right]^2\right\}^{-1}} \quad \text{Eq.(3-12)}$$

4. EXPERIMENTAL

The following experimental works were performed for different conditions for *CO* (pure), C_2H_4 (2% in N_2), and *CH*₃*CHO* (0.5% in N_2) respectively: the sensitivity calibration of the luminol detector, O_3 and photomultiplier (PMT) signal maximum calibration, and effective chain length calibration. The experimental setup for those calibrations comprises three parts: the radical source for the generation of peroxy radicals, the inlet and reactor where air can be sampled and the chemical amplification takes place, and the detector which detects the light intensity from the chemiluminescence.

The following sections will explain the experimental setups and how does each calibration proceed.



Figure 4: Schematic of the instruments setup

4.1. Radical Source

For a pure HO_2 source, one H_2O molecule can produce two HO_2 radicals; each photolysis of oxygen leads to two ozone modulations. The production rate of HO_2 and O_3 can be expressed as:

$$\frac{\partial [HO_2]}{\partial t} = 2 \cdot \Theta^{184.9nm} \cdot \sigma^{184.9nm}_{H_2O} \cdot [H_2O]$$
 Eq.(4-1)

$$\frac{\partial [O_3]}{\partial t} = 2 \cdot \Theta^{184.9nm} \cdot \sigma_{O_2}^{184.9nm} \cdot [O_2]$$
 Eq.(4-2)

Where $[HO_2]$ is the mixing ratio of hydroperoxyl, $[O_3]$ is the mixing ratio of ozone, $\Theta^{184.9nm}$ is the photon flux at the photolysis zone, $\sigma_{H_2O}^{184.9nm}$ is the absorption cross section for water at 184.9nm, $\sigma_{O_2}^{184.9nm}$ is the absorption cross section for oxygen at 184.9nm, $[H_2O]$ is the water mixing ratio in the humidified air, $[O_2]$ is the mixing ratio of oxygen. Since there are no HO_2 and O_3 at the beginning of the photolysis, integrating Eq.(3-3) and Eq.(3-4) over time:

$$[HO_2] = \frac{\sigma_{H_2O}^{184.9nm} \cdot [H_2O]}{\sigma_{O_2}^{184.9nm} \cdot [O_2]} \cdot [O_3]$$
 Eq.(4-3)

In Eq.(3-5), the value of $\sigma_{H_2O}^{184.9nm}$ is used as $7.14 \times 10^{-10} [cm^{-20} \cdot molec^{-1}]$ (Cantrell et al., 1997; Hofzumahaus et al., 1997); $[H_2O]$ is calculated by the measurements of a dew point sensor; $\sigma_{O_2}^{184.9nm}$ is determined by oxygen absorption cross section calibration; $[O_2]$ is known from the information of synthetic air gas cylinder; $[O_3]$ is determined by ozone determination calibration (details in Chapter 4.4).

The water mixing ratio is determined as (Vaisala, 2013):

Where $[H_2O]$ is the water mixing ratio in ppm, $P_{ws,Tdew}$ is the saturation water vapor pressure at dew point temperature in hPa, $P_{ambient}$ is the ambient pressure in hPa.

Saturation water vapor pressure (for the condition of saturation vapor pressure over liquid water) is calculated with the formula (Laube and Höller, 1988):

$$log_{10}P_{ws,T} = 10.79574 \cdot \left(1 - \frac{T_t}{T}\right) - 5.028 \cdot log_{10}\left(\frac{T}{T_t}\right)$$

+1.50475 \cdot 10^{-4} \cdot \left(1 - 10^{\left(-8.2969 \cdot \left(\frac{T}{T_t} - 1\right)\right)}\right)
+0.42873 \cdot 10^{-3} \cdot \left(10^{(4.76955(1 - \frac{T_t}{T})} - 1\right)
+0.78614

Where $T_t = 273.16K$, T is the temperature in K, and 223K < T < 373K. Therefore, $P_{WS,T}$ is calculated with the measurement of dew point temperature.

The scheme of the radical source is shown in Figure 5. Humidified synthetic air flow in a quartz tube (the green area in Figure 5, with 20cm length and 18mm outer diameter), part of the quartz tube is placed inside the photolysis zone. Distilled water is pumped into a humidifier with peristaltic pump. The humidity is controlled by speed of the pump, and the relative humidity (RH) is calculated by measuring the dew point temperature with a dew point sensor (Vaisala DMP 248). *CO* is added prior to the photolysis zone, in order to convert the *OH* into *HO*² for

pure HO_2 source. CO can be replaced by CH_4 , so that the mixture radicals HO_2 and CH_3O_2 are produced. CO and synthetic air are controlled by mass flow controller (MFC) manually (200mln/min MKS MFC for CO, 7ln/min Bronkhorst MFC for synthetic air. "mln/min" stands for milliliter per minute flow rate at normal condition, which is 20-degree Celsius and 1atm. "ln/min" stands for liter per minute flow rate at normal condition.).



Figure 5: Schematic diagram of the radical source installed in the chamber (Kartal, 2009)

The *Hg*-lamp with 184.9nm emission is used for photolyzing the humidified synthetic air. The Hg-lamp is kept at 40-degree Celsius with a heater with temperature control. Keeping the lamp at a constant temperature means to protect the lamp from the interference of the environmental temperature change (Hofzumahaus et al., 1997).

A cylindrical lens is installed in front of the lamp to make sure that the light from the lamp goes parallel in the absorption zone.

For the purpose of ozone calibration (details in chapter 4.4.2), a shutter controlled by electric motor is added in front of the lamp. The shutter can be opened and closed automatically (controlled by the programme) and manually.

The detector of the radical source uses a photomultiplier with a spectral response between 115nm and 195 nm (Hamamatsu 1259 with MgF_2).

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An interference filter is added in front of the photomultiplier, which allows the specific transmission for the wavelength of interest at 184.9nm. The peak wavelength of the filter is $184.9nm \pm 2.5$ nm and the transmittance at this wavelength is 12.5%.

The intensity of the *Hg*-lamp is controlled by adding different mixing ratios of N_2O and N_2 (with MKS MFCs which are controlled by the programme) in the absorption cell. The N_2O has a constant absorption coefficient of 14.05×10^{-20} cm² molecule⁻¹ at 184.9 nm (Cantrell et al., 1997). Different amount of N_2O absorb the light from *Hg*-lamp which can reducing the light intensity linearly up to 90% of its maximum. All the other area in the source is purged with N_2 to avoid absorption of light from the oxygen in the ambient air.

The different mixing ratios of the radical source can be controlled by varying the N_2O/N_2 ratio in the absorption cell and/or changing the speed of peristaltic pump to change the relative humidity. In this study, the mixing ratio of radical source is controlled solely by varying the N_2O/N_2 ratio and the radical source generates pure HO_2 . The radical source will then flow directly to the inlet of the instrument (Figure 6).



Figure 6: The photo of radical source connection with the inlet of the system

4.2. Inlet and Reactor

The air is sampled through the inlet, followed with the reactor (Figure 7), this is the main place for the reactions take place (the reactions can also take place in the tube which connects reactor with the detector).



Figure 7: The photo of inlet and reactor.

There are three addition points for adding gases, two near the inlet side (adding points in the front) and the other is on the rare side (adding point in the back) of the reactor. *NO*, *CO* (or C_2H_4/CH_3CHO), N₂ are added into the reactor through MFCs (details see Table 1). *NO* is added in the front adding point constantly with a *NO* scrubber which is filled with Iron(II) Sulfate Heptahydrate (Ferrous Sulfate Heptahydrate, $FeSO_4 \cdot 7H_2O$) on the line. The scrubber removes the *NO*₂ in the *NO* line before it mixes with other gases in the reactor.

Controlled flow	Maximum flow rate	Manufacture
NO	20mln/min	MKS
CO	1000mln/min	MKS
C2H4	500mln/min	MKS
СНЗСНО	1000mln/min	MKS
N2	500mln/min	MKS
Sampling flow	7ln/min	Bronkhorst

Table 1: Flow controllers related to the reactor

CO (or C_2H_4/CH_3CHO) and N_2 are added into the reactor alternatively in the front adding point or the back adding point with the switch of two 3-way magnetic valves (MV). When CO (or C₂H₄/CH₃CHO) is adding in the front, N₂ is adding in the back (amplification mode, see chapter 3.2); N_2 is adding in the front, CO (or C_2H_4/CH_3CHO) is adding in the back (background mode, see chapter 3.2). The MVs are controlled by a Labview programme through a data acquisition card, so that different modes can be controlled. Then the sampled air will flow to the NO_2 luminol detector.

The sampling flow is controlled by a MFC and pumped out continuously to the exhaust by a vacuum pump. Since CO is toxic and explosive gas, NO₂ and NO are toxic gases, additional CO and NO_x scrubbers are installed before the sampling flow reaches the exhaust line. The CO scrubber contains Pt/Al pellets and activated charcoal, when the scrubber is heated up to 200degree Celsius, a catalytic reaction converts CO into CO_2 . The NO_x scrubber is filled with active coal which removes NO and NO₂ in the line. The NO_x scrubber is placed prior to the CO scrubber before the air reaches the exhaust line.

An additional scrubber contains activated charcoal and iodine, for CO line, was installed to remove nickel and iron carbonyls from the CO gas bottle before the MFC. The reason of installing a CO scrubber is to prevent the possible interference to the luminol and NO_2 reaction.

4.3. NO₂ Luminol Detector

The inner view of luminol NO₂ detector is shown in Figure 8. Inside the detector, the sampling air flows through a Whatman glass fiber filter which is homogeneously soaked with luminol solution. The luminol solution is pumped continuously from a bottle filled with luminol with a peristaltic pump. A photodiode (Hamamatsu Si-1248, detection range 400-500nm) is placed in the center of the NO_2 detector behind the filter, the light emitted by chemiluminescence (from luminol and NO₂ reaction) can be detected by the photodiode which gives an output signal in voltage. The NO_2 signal output will be saved through the acquisition card by Labview programme and use for the later calculation.

The luminol solution contains 0.866g C8H7N3O2, 22.4g KOH, 63.02g Na2SO3, and 30ml C₃H₇OH dissolved in 10L distilled water.

As it is mentioned in chapter 3.5, NO₂ is added into the system as an offset to the detector right before the gas flow in connection point in Figure 8. University of Bremen Postgraduate Programme ENVIRONMENTAL PHYSICS (PEP) 2015



Figure 8: Inner view of the NO_2 luminol detector. The reaction zone and the photodiode are separated with a quartz glass, the white and red arrows indicating the flow direction (Kartal, 2009)

4.4. Calibration Procedure

4.4.1. Calibration of the Sensitivity of NO₂ Luminol detector

In the NO_2 calibration, several known mixing ratios of NO_2 were added to the luminol detector. The different mixing ratios of NO_2 are given to the system using a MFC. The MFC is mixing a certain flow of NO_2 from cylinder which has known mixing ratio to the sampling flow. The MV is kept at the background mode; the instrument is running with all the gases which are required for the PeRCA technique. The mixing ratio of NO_2 has a linear relationship to the signal (Voltage) of NO_2 luminol detector when the correct value of NO_2 offset is taken into account. In the previous studies 45ppb NO_2 offset is sufficient for the NO_2 luminol detector. (Hastie, 1991; Kartal, 2009)

$$[NO_2] = a \cdot V_{detect} + b \qquad \text{Eq.(4-6)}$$

Where *a* is the slope for the linear equation [ppb/volts], 1/a is the sensitivity of the *NO*₂ detector [volts/ppb] and *b* is the intercept for the linear equation [ppb] can be determined with linear regression calculation. The actual *NO*₂ value is calculated from the sampling flow rate and *NO*₂ mixing ratio from the *NO*₂ cylinder.

The actual NO₂ mixing ratio is by calculated the voltage output from the NO₂ MFC:

$$[NO_2]_{actual} = \frac{\frac{MR_{NO_2} \times \frac{V}{V_{max}} \times Q_{max}}{Q_{SF}}}{Eq.(4-7)}$$

Where MR_{NO_2} is the mixing ratio of NO_2 in the gas cylinder in ppb; V is the current voltage output for the MFC; V_{max} is the voltage output at the maximum flow rate for the MFC; Q_{max} is the maximum flow rate for the MFC; Q_{SF} is the sampling flow rate. The sampling rate of the MFC voltage was 1 point/s, the mixing ratio of NO_2 in the cylinder is 10.34 ppm.

An example of the NO_2 calibration performed on 2015-02-23, is presented in Figure 9 and Figure 10, the NO_2 offset is 45ppb. Different NO_2 mixing ratios were given by controlling the MFC, the NO_2 signal responses were saved accordingly. The offset and intercept of the linear equation can be calculated. During the work, 130 sets of NO_2 luminol sensitivity calibrations were made in the laboratory, the selected results and details are described in chapter 5.





Figure 10: The linear relation between NO2 mixing ratio and NO2 luminol detector signal 2015-02-23

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The output signal of NO_2 MFC, the output signal of sampling flow MFC, the positions of the MVs, the NO_2 signal from the luminol detector are saved in the hard disk through acquisition card by the Labview programme. Other gases such as CO, NO, and N_2 are controlled manually and the data are not saved.

4.4.2. Determination of Effective Chain Length

For the calibration of the chemical amplifier, it is necessary to determine the effective chain length. The effective chain length is calculated by:

$$eCL = \frac{\Delta[NO_2]}{[RO_2^*]_{source}}$$
 Eq.(3-3)

The different mixing ratios of NO_2 can be measured by NO_2 luminol detector, different mixing ratios of peroxy radicals are generated by the radical source (Figure 11). Figure 12 shows an example of eCL calculation. By plotting the NO_2 mixing ratio from the modulation against the HO_2 mixing ratio, the slope of the linear relation is the eCL. During this work, pure HO_2 radicals were generated by the source.



Figure 11: An example of eCL determination calibration, HO2 generation and NO2 signal detection over time



Figure 12: An example of eCL determination, the slope corresponds to eCL

The procedure for the eCL calibration follows the following steps:

- 5 or 7l/min of synthetic air is humidified with the humidifier into the source (RH 3%-4%, controlled by programme);
- Humidified air is photolyzed in the photolysis zone where pure *HO*₂ radicals were generated by adding additional *CO* (20ml/min) into the source;
- Different *HO*₂ radicals are generated by adding different mixtures of *N*₂/*N*₂*O* gasses into the absorption cell of the source;
- $\Delta[NO_2]$ is determined by measuring the amplification and background signal (switch the MVs) from the NO_2 luminol detector;
- The eCL is calculate using Eq.(3-3).

53 sets of eCL calibrations have been performed during this work for different conditions for CO, C_2H_4 , and CH_3CHO , the details of results and discussions will be listed in chapter 5

4.4.3. Determination of Ozone Production

The ozone production at the radical source can be determined from the signal of the NO_2 detector. The radical source generates HO_2 and ozone at the same time in the photolysis zone. During the eCL calibrations, the NO_2 background signal corresponds to the NO_2 produced from O_3 generation from the source which react with NO in the reactor (R3-34).

$$NO + O_3 \rightarrow NO_2 + O_2 \tag{R3-34}$$

When applied the different light intensities during the calibration for the determination of the eCL, slight variations of O_3 are generated. O_3 will convert NO into NO_2 and will be detected by the NO_2 luminol detector. In order to increase the accuracy of the O_3 determination the linear relationship between the maximum O_3 generation and the maximum lamp intensity is described as:

$$\frac{O_{3 detected}}{O_{3 max}} = \frac{I_{detected}}{I_{max}}$$
 Eq.(4-8)

The maximum ozone value and maximum light intensity can be determined by the ozone and PMT maximum calibration. For this, the shutter in front of the Hg-lamp closes and opens for a certain time repeatedly (an example shown in Figure 13). The light intensity of the lamp is measured by the PMT in the source. The NO_2 detector detects a maximum NO_2 signal when the shutter is opened, and detects a minimum NO_2 signal when the shutter is closed. This NO_2 signal corresponds with the O_3 generation in the source. The ozone generation at any point in the radical source can be therefore calculated as:

$$O_{3 detected} = \frac{I_{detected}}{I_{max}} \cdot O_{3 max} \qquad \qquad \text{Eq.(4-9)}$$

In this work 74 sets of O_3 and PMT maximum calibrations were performed in laboratory for different conditions, the results and discussion are described in chapter 5.



Figure 13: An example plot of PMT signal and *NO*₂ detector signal vs. time for *O*₃ calibration University of Bremen Postgraduate Programme ENVIRONMENTAL PHYSICS (PEP) 2015
4.4.4. Calibration of *O*₂ Cross Section at 184.9nm

The O_2 absorption cross section at 184.9 nm lays in the Schumann-Runge bands, which is a highly structured band (Murry, 2012). In reality, the oxygen absorption cross section is very sensitive to the emission spectrum of the Hg-lamp. The emission spectrum of the Hg-lamp is affected by the lamp current, working temperature, and oxygen column, therefore each lamp has a "unique" spectrum for each instrumental setup. (Landzendorf et al., 1997; Hofzumahaus et al., 1997; Cantrell et al., 1997) Thus, it is necessary to determine effective oxygen absorption cross section which represents the local "effectiveness" of the oxygen absorption cross section for each instrument setups.

From the Lambert-Beer Law:

$$\sigma_{O_2,app}(x) = (\frac{1}{x}) \cdot ln(I_0/I(x))$$
 Eq.(4-10)

The apparent absorption cross section results in the integration of effective absorption cross section through oxygen column x:

$$\sigma_{O_2,eff}(x) = \sigma_{O_2,app}(x) + \frac{d\sigma_{O_2,app}(x)}{dx} \cdot x \qquad \qquad \text{Eq.(4-11)}$$

The idea for this determination is to add different mixing ratios of oxygen (by mixing synthetic air and N_2) to the photolysis zone. I₀ is the light intensity measured when no oxygen is in the mixing gas. Then $\sigma_{O_2,app}(x)$ and x are known values. The value of $\sigma_{O_2,eff}(x)$ and $\sigma_{O_2,app}(x)$ can be calculated.

The calibrations for each conditions follows the procedure: 1. Calibration of the sensitivity of NO_2 luminol detector, 2. Calibration of O_3 maximum and PMT maximum, 3. Determination of eCL, and 4. Calibration of the sensitivity of NO_2 luminol detector after eCL calibration.

5. RESULTS and DISCUSSION

Different series of measurements have been performed along with this master thesis. The calibration works started at the beginning of the master work. After the familiarization with the measurement technique and the set-up, the calibrations from the 12^{th} of February to the 31^{st} of March 2015 focused on the investigation of C_2H_4 by comparing with the *CO* standard configuration. From the 1^{st} of April to the 20^{th} of June, the experimental characterization was interrupted due to the preparation of the OMO campaign (see chapter 1). From the 23^{rd} of June till the 6^{th} of August, the system was restarted again for the calibration focusing on the investigation of *CH₃CHO* as the amplification agent. The set-up has been gradually tested and optimized. New sets of calibrations with an optimizing performance of the instrument have been performed during November 2015.

Two parameters determine at the most performance of PeRCA:

- the *NO* mixing ratio which affects the sensitivity of the *NO*₂ luminol detector as well as some of the chemical amplification reactions;
- the sampling flow rate which affects the retention time for the reactions taking place from the inlet to the *NO*₂ detector.

These parameters have been used as reference for the evaluation of the performance of C_2H_4 and CH_3CHO as amplifying agents. Consequently, the *NO* mixing ratio and the sampling flow rate have been varied systematically in the series of measurements carried out.

The calibrations were performed at 3ppm, 6ppm, and 9ppm *NO* mixing ratio, and at 11/min and 21/min sampling flow rates using *CO*, C_2H_4 , and *CH₃CHO* as the amplification agents. The flow rate for *CO* was chosen in order to dilute pure *CO* into 9% in the sampling flow, N_2 was used at the same flow rate as *CO* respectively at different conditions. The flows of C_2H_4 and *CH₃CHO* were adding 2% of C_2H_4 in N₂ and 0.5% of *CH₃CHO* in *N₂* respectively at the same flow rates as *CO* in different conditions.

This chapter will focus on the calibrations which were made in November and in comparison with selected previous calibrations. Table 2 presents the selected sets of calibrations for the analysis.

Date	Amplification	Sampling flow	NO mixing ratio
	agent	rate [l/min]	[ppm]
2015-11-28	СО	1	3
2015-11-30	СО	1	6
2015-11-27	СО	1	9
2015-02-23	СО	2	6
2015-11-24	C_2H_4	1	3
2015-11-25	C_2H_4	1	6
2015-11-26	C_2H_4	1	9
2015-03-05	C_2H_4	2	3
2015-03-04	C_2H_4	2	6
2015-11-23	CH ₃ CHO	1	3
2015-11-20	CH ₃ CHO	1	6
2015-11-19	CH ₃ CHO	1	9

Table 2: Selected sets of calibrations

5.1. NO₂ Luminol Detector Sensitivity

A suggested offset value for the *NO*² luminol detector is 45ppb from previous studies. This value was used by many previous works at IUP under similar conditions and instrumental setups (Kartal, 2009; Safadi, 2013). For 2l/min sampling flow, 8.7ml/min *NO*² from the gas cylinder is needed for 45ppb offset; correspondingly, for 1l/min sampling flow, half of *NO*² flow is needed to generate the 45ppb offset. At the beginning of the thesis work, a 50mln/min MFC (MKS mass flow controller) has been used to control the *NO*² flow. The *NO*² sensitivity calibration showed different errors under the same conditions but different sampling flow rates.

Figure 14 and Figure 15 show two calibrations plots. Table 3 shows the corresponding mean NO_2 mixing ratio and standard deviation values for the calibration. These two calibrations were made within 3 days under the same conditions except the sampling flow and the corresponding NO_2 offset flow rates, so that results are comparable.



Figure 14: NO2 mixing ratio and luminol detector signal at 04-03-2015



Figure 15: NO2 mixing ratio and luminol detector signal at 06-03-2015

2l/min sampling flow (04-03- 2015)			11/min sampling flow (06-03- 2015)			
mean	sd NO ₂	error NO ₂	mean	sd NO ₂	error NO ₂	
NO ₂	MR(ppb)	MR (%)	NO ₂	MR(ppb)	MR (%)	
MR(ppb)	· · · · ·		MR(ppb)			
45.65	1.05	2.3	44.45	2.65	6.0	
46.61	0.95	2.0	45.65	2.81	6.1	
50.84	1.02	2.0	49.47	2.95	6.0	
55.77	1.16	2.1	54.46	2.84	5.2	
60.86	1.16	1.9	59.51	3.07	5.2	
66.04	1.17	1.8	64.68	3.09	4.8	
55.82	1.05	1.9	54.60	2.94	5.4	
50.74	1.09	2.1	49.48	2.88	5.8	
46.67	0.99	2.1	45.52	2.74	6.0	
45.65	1.01	2.2	44.47	2.82	6.3	

Table 3: NO2 mixing ratio mean and standard deviation for 21/min and 11/min sampling flow

The error in Table 3 stands for the percentage of standard deviation to the mean NO_2 mixing ratio from the NO_2 MFC. At 2l/min sampling flow, the error for NO_2 mixing ratio varies from 1.8% to 2.3%; at 1l/min sampling flow, from 4.8% to 6.3%. If the set flow of the MFC is less than 10% of the maximum MFC controlling range, the flow becomes unsteady leading to higher errors. In order to improve the performance, a more accurate MFC (Bronkhorst) with 20mln/min maximum range was tested for the NO_2 sensitivity calibration. Under the same conditions as the calibration made on 06-03-2015, the result improves and the error for the NO_2 mixing ratio at 11/min sampling flow varies from 1.1% to 1.6%.

The determination of the NO_2 offset required to keep the luminol detector response linear with the NO_2 mixing ratio was performed after the new MFC was installed in the system. The result is shown in Figure 16:



Figure 16: Offset calibration for NO2 luminol detector

Starting from 62ppb NO_2 , the response of NO_2 signal and NO_2 mixing ratio becomes linearly dependent. The NO_2 offset was set to 65ppb for the calibrations performed after November 2015. Even though 65ppb offset is a most accurate value, as a matter of fact the result of NO_2 detector sensitivity obtained with a 45 ppb offset is not expected to be significantly different.

The NO_2 luminol detector sensitivity calibration is the most basic and important calibrations among all the calibrations, such as O_3 and the radical calibrations. The results of the sensitivity calibration affect the accuracy of other calibrations. Therefore, NO_2 calibrations were carried out at the beginning and at the end of each day of experiments. All the selected dates for the analysis have stable NO_2 detector sensitivity and the calibration results are reproducible. All the NO_2 sensitivity calibration plots for the selected dates are given in the Annex.

The results regarding to the NO₂ luminol detector sensitivity are summarized in Table 4:

Date	Amplification	Sampling flow	NO mixing ratio	Sensitivity 1/a
	Agent	rate [l/min]	[ppm]	[volts/ppb]
2015-11-28	СО	1	3	0.075 ± 0.002
2015-11-30	СО	1	6	0.039 ± 0.001
2015-11-27	СО	1	9	0.021 ± 0.001
2015-02-23	СО	2	6	0.064 ± 0.002
2015-11-24	C_2H_4	1	3	0.076 ± 0.003
2015-11-25	C_2H_4	1	6	0.038 ± 0.001
2015-11-26	C_2H_4	1	9	0.021 ± 0.001
2015-03-05	C_2H_4	2	3	0.142 ± 0.003
2015-03-04	C_2H_4	2	6	0.061 ± 0.002
2015-11-23	$CH_{3}CHO$	1	3	0.114 ± 0.002
2015-11-20	CH ₃ CHO	1	6	0.065 ± 0.002
2015-11-19	CH ₃ CHO	1	9	0.045 ± 0.001

Table 4: NO₂ luminol detector sensitivity calibration results

The sensitivity of the NO_2 detector was tested for the three amplification gases investigated. The plot in Figure 17 shows the sensitivity of three amplification agent gases versus the NO mixing ratio for 11/min sampling flow.



Figure 17: NO2 detector sensitivity versus NO mixing ratio at 11/min sampling flow

The sensitivity decreases with the increasing *NO* mixing ratio for all amplification agent gases. This agrees with other experiments obtained with the chemiluminescence reaction between NO_2 and luminol (Maeda, 1980; Clemitshaw, 1997). *CO* and C_2H_4 follow the same trend line. The sensitivities for *CO* and C_2H_4 at different *NO* mixing ratios are very similar within the error. For the NO_2 luminol detector, the sensitivity of the detector determines how the detector reacts with different NO_2 mixing ratios. The similar sensitivity indicates both amplification agents have the same ability to measure NO_2 , therefore, C_2H_4 does not interfere in the NO_2 detection.

 CH_3CHO has similar sensitivity trend as CO when NO mixing ratio is increased. The sensitivity results for CH₃CHO are higher than the obtained with CO. The NO_2 signals at each NO_2 level for CH_3CHO are also higher than CO. The NO_2 response for a NO_2 offset of 65ppb are shown in Table 5.

NO mixing ratio	CO, NO2 signal at offset	CH ₃ CHO, NO ₂ signal at offset
Зррт	3.65V	5.98V
бррт	1.93V	3.05V
9ppm	1.20V	2.09V

Table 5: NO₂ signal at offset with CO/CH₃CHO in the system

Furthermore, during the NO_2 luminol detector sensitivity calibrations with CH_3CHO in the system, the NO_2 signal was often not reproducible for the same NO_2 mixing ratio. The NO_2 signal often varied randomly during the calibration. The instrumental conditions were kept stable and any instrumental failure was ruled out after several performance tests. An example is shown in Figure 18, where 45ppb, 46ppb, 50ppb, 55ppb, 56ppb, 50ppb, 46ppb, 45ppb NO_2 was sampled (from left to right). The NO_2 detector does not reproduce the same values at 45ppb and 46ppb levels.



Figure 18: NO2 detector sensitivity calibration on 21-07-2015 with CH3CHO

A possible reason for these variations is the chemiluminescence reaction reported by Deluca and McElroy, 1981. According to their description, CH₃CHO will react with the KOH from the luminol solution (chapter 4.3) and emits light with a maximum at 400nm, which can be detected by the photodiode of the luminol detector used (detection range 400-500nm). Because of this reaction, the chemiluminescence efficiency is also higher, which results in the observed higher sensitivity of the detector. Another potential effect from the CH3CHO and KOH reaction is that the NO2 signal is likely to become very sensitive to the homogeneity of the distribution of the luminol solution on the filter inside the detector. This luminol distribution depends on the filter quality and on the stability of the luminol. Inhomogeneity in the distribution of the luminol solution on the filter might explain the low reproducibility of the NO2 signals. Additionally, CH3CHO may decompose by photolysis with a maximum near 290nm (absorption spectrum in Figure 19). In the instrumental setup used, CH₃CHO was added into the reactor in a transparent tube of a few meter length. Although it is not expected to be significant variation of daylight condition in the laboratory, some overlaps for the absorption spectrum of CH₃CHO and the emission of a typical daylight fluorescent lamp (spectrum is shown in Figure 20) might have introduced additional instabilities during the experiments.



Figure 19: The absorption spectrum of acetaldehyde obtained with 0.08 nm wavelength resolution (Moortgat et

al., 2010)



Figure 20: Spectrum from a 48" Philips F32T8 natural sunshine fluorescent light (RicHard-59, 2011)

Concerning the variation of the *NO*₂ sensitivity with sampling flow rate, the Table 6 shows the *NO*₂ sensitivity calibration results for *CO* and *C*₂*H*₄ at *NO* 6ppm for 1 and 2l/min sampling flow rates. For *CO*, the sensitivity increases at 2l/min sampling flow rate from 0.039 ± 0.001 to 0.064 ± 0.002 [volts/ppb] and for *C*₂*H*₄, from 0.038 ± 0.001 to 0.061 ± 0.002 [volts/ppb]. It is likely that when the sampling flow is increased, the surface of the filter is more homogeneously covered by the air flow. As a consequence, the reaction is more effective and the light output obtained from the chemiluminescence is higher. *University of Bremen Postgraduate Programme ENVIRONMENTAL PHYSICS (PEP) 2015* 38

Date	Amplification	Sampling flow	NO mixing ratio	Sensitivity 1/a
	Agent	rate [l/min]	[ppm]	[volts/ppb]
2015-11-30	СО	1	6	0.039 ± 0.001
2015-02-23	СО	2	6	0.064 ± 0.002
2015-11-25	C ₂ H ₄	1	6	0.038 ± 0.001
2015-03-04	C_2H_4	2	6	0.061 ± 0.002

Table 6: NO2 luminol detecrot sensitivity calibration results at NO 6ppm

5.2. Determination of Ozone Maximum and PMT Maximum

As explained in chapter 4.4.3 the O_3 generated at the source during the radical calibrations is calculated on the basis of the PMT signal obtained at a maximum O_3 production by the radical source.

Table 7 summarizes the results of the ozone maximum and PMT maximum intensity calibrations obtained during the present work.

Date	Amplification	Sampling	NO mixing	Ozone	PMT	Ozone _{max} /
	Agent	flow rate	ratio [ppm]	maximum	maximum	PMT _{max}
		[l/min]		[ppb]	[V]	[ppb/V]
2015-11-28	СО	1	3	3.57±0.20	2.31±0.02	1.55±0.09
2015-11-30	СО	1	6	3.63±0.37	2.36±0.02	1.54±0.16
2015-11-27	СО	1	9	3.43±0.53	2.33±0.02	1.47±0.23
2015-02-23	СО	2	6	4.13±1.22	4.03±0.05	1.03±0.30
2015-11-24	C ₂ H ₄	1	3	3.85±0.25	2.41±0.04	1.60±0.11
2015-11-25	C ₂ H ₄	1	6	3.36±0.38	2.39±0.02	1.41±0.16
2015-11-26	C ₂ H ₄	1	9	3.46±0.67	2.41±0.04	1.44±0.28
2015-03-05	C ₂ H ₄	2	3	4.01±0.48	2.87±0.05	1.40±0.17
2015-03-04	C ₂ H ₄	2	6	3.36±0.50	2.87±0.05	1.17±0.18
2015-11-23	CH ₃ CHO	1	3	3.63±0.26	2.35±0.02	1.55±0.11
2015-11-20	CH ₃ CHO	1	6	3.27±0.31	2.39±0.02	1.37±0.13
2015-11-19	CH ₃ CHO	1	9	3.24±0.27	2.40±0.02	1.35±0.11

Table 7: Ozone maximum and PMT maximum results

The maximum PMT signal corresponds to the Hg-lamp maximum emittance. The results of the PMT maximum intensity indicate that the lamp signal was very stable during November. The PMT max signal decreased roughly 0.5V from 04-03-2015 to 30-11-2015. The Hg-lamp has

limited working hours, which means that the maximum lamp intensity decreases over time. The errors from ozone maximum are considerably larger at higher *NO* mixing ratios; because the sensitivity of the *NO*₂ luminol detector is lower. The error propagates during the maximum ozone calculation.

 4.03 ± 0.05 PMT max signal was measured on 23-02-2015. At the beginning of the calibrations, the PMT signal had roughly 1V offset from a false configuration of the data acquisition programme (the problem was solved in later calibrations). According to the source calculation method mentioned in chapter 4.4.2 and chapter 4.4.3, the PMT signal offset does not play a role in the determination of eCL.

5.3. Determination of eCL for Amplification Agents: *CO*, *C*₂*H*₄, and *CH*₃*CHO*

As explained above, eCL calibrations were carried out for different amplification agents, and the calibrations with *CO* were used as the reference for the analysis of results. C_2H_4 and *CH*₃*CHO* will be discussed separately in this section, focusing on the performance at different *NO* mixing ratios (3ppm, 6ppm, 9ppm) and different sampling flow rates (11/min, 21/min).

5.3.1. Determination of eCL for *CO* and *C*₂*H*₄

Table 8 gathers the results of eCL calibrations using CO and C_2H_4 as amplification agents.

Date	Amplification	Sampling flow	NO mixing	eCL
	Agent	rate [l/min]	ratio [ppm]	
2015-11-28	СО	1	3	249 <u>±</u> 20
2015-11-30	СО	1	6	228±38
2015-11-27	СО	1	9	198±24
2015-02-23	СО	2	6	212±22
2015-11-24	C_2H_4	1	3	49±7
2015-11-25	C_2H_4	1	6	27±7
2015-11-26	C_2H_4	1	9	12±11
2015-03-05	C_2H_4	2	3	51±14
2015-03-04	C_2H_4	2	6	27±10

Table 8: eCL results using *CO* and C_2H_4 as amplification agent gas

Firstly, the results with 11/min sampling flow were compared. Figure 21 depicted eCL versus *NO* with *CO* and C_2H_4 acting as amplification agent.



Figure 21: eCL vs. NO mixing ratio, for CO and C_2H_4 as amplification gases with 11/min sampling flow rate.

eCL decreases for higher *NO* mixing ratios in both cases. The termination reactions for the amplification chain reaction are:

$$HO_2 + wall \rightarrow nonradical products$$
 (R5-1)

$$OH + wall \rightarrow nonradical products$$
 (R3-39)

$$HO_2 + HO_2 \to H_2O_2 + O_2$$
 (R3-28)

$$0H + HO_2 \rightarrow H_2O + O_2 \tag{R3-41}$$

$$OH + NO \xrightarrow{M} HONO$$
 (R3-21)

$$OH + NO_2 \xrightarrow{M} HNO_3 \tag{R3-31}$$

The dominating termination mechanisms of the chain reaction are (R5-1), (R3-21) and (R3-31). When *NO* increases, more *NO* react with *OH*, the terminating reactions are more dominant. The eCL therefore decreases.

The experimental eCL obtained for C_2H_4 calibrations in the present work is lower than for *CO*. The expected amplification reactions with C_2H_4 are shown in chapter 3.3 from (R3-47) to (R3-51). Reaction (R3-47) of C_2H_4 and *OH* is well studied by Atkinson et al., 1976, Chuong and Stevens, 2000, Cleary et al, 2005 and Golden, 2012. According to Mellouki et al., 2003 by analogy, the product from (R3-47) *CH*₂*CH*₂*OH* can react with *O*₂ through three chemical paths (R3-48), (R3-49), (R3-50). However, the yield from those reactions is not well defined in the literature.

A possible explanation for the low amplification results obtained is that reaction (R3-50) has the highest yield from the CH_2CH_2OH and O_2 reactions. The peroxy radical product $CH_2(OH)CH_2O_2$ from (R3-50) would introduce to additional termination reactions for the amplification chain with C_2H_4 :

$$CH_2(OH)CH_2O_2 + NO_2 \xrightarrow{M} CH_2(OH)CH_2O_2 \cdot NO_2$$
(R5-2)

$$CH_2(OH)CH_2O_2 + NO \xrightarrow{M} CH_2(OH)CH_2NO_3$$
(R5-3)

$$CH_2(OH)CH_2O_2 + HO_2 \rightarrow nonradical produts$$
 (R5-4)

$$CH_2(OH)CH_2O_2 + wall \rightarrow nonradical produts$$
 (R5-5)

$$CH_2CH_2OH + wall \rightarrow nonradical products$$
 (R5-6)

Since the mixing ratio for *NO* is 3 orders of magnitude higher than *NO*₂, reaction (R5-3) is possibly the most effective at terminating the amplification chain with C_2H_4 .

The effect of the sampling flow rate was also investigated for calibrations carried out for the same *NO* mixing ratio. The results for *CO* and C_2H_4 are listed in Table 9.

Table 9: eCL results with CO and	C_2H_4 as amplification agent	gas at the same NO mixing ra	tio condition
	- 2 I	8	

Date	Amplification	Sampling flow	NO mixing	eCL
	Agent	rate [l/min]	ratio [ppm]	
2015-11-30	CO	1	6	228±38
2015-02-23	СО	2	6	212±22
2015-11-25	C_2H_4	1	6	27±7
2015-03-04	C_2H_4	2	6	27±10

The sampling flow rate defines the retention time for the chemical reactions from the inlet to the NO_2 luminol detector. Within the error, there is no difference for eCL results between 11/min and 21/min sampling flow rate for both *CO* and C_2H_4 . That means that the reaction time has not been a limiting factor in the experiments.

5.3.2. Radical Interference in the usage of C_2H_4 as Amplification Agent

In addition to the low amplification factor obtained from C_2H_4 compared with *CO*, the amplification signal was found not to come exclusively from the radical amplification by C_2H_4 . The experiments showed that part of the amplification signal from the modulation did not originate from the amplification of the HO_2 generated at the source. Figure 22 shows two eCL determination calibrations that were performed in the same day with and without peroxy radicals in the sampling air. The plot on top is a standard eCL calibration, while the plot at the bottom is the result obtained when no HO_2 radicals were generated at the source. The PMT signal indicates different lamp intensities from the source, leading to the amplification and the background signal obtained at the different HO_2 generated from the source. Modulations are observed at the bottom plot, which means that part of the modulations from C_2H_4 was not coming from the amplification reaction of the HO_2 generated at the source but from other reactions.



Figure 22: 2 sets of eCL calibrations with C_2H_4 as amlification agent. The NO_2 and PMT signal are depicted for: a) standard eCL calibration with HO_2 generation in the source (top); b) eCL calibration without HO_2 generation in the source (bottom).

As a matter of fact, C_2H_4 can react with O_3 from the source and generate radicals (Kan et al., 1981) which react with *NO*, and produce *NO*₂ which can be detected by the *NO*₂ luminol detector.

$$C_2H_4 + O_3 \rightarrow CH_2OOOCH_2 \tag{R5-7}$$

$$CH_2OOOCH_2 \rightarrow CH_2O + CH_2OO' \tag{R5-8}$$

 C_2H_4 reacts with O_3 , the production in (R5-7) will self-decompose into CH_2O and CH_2OO' (Criegee Intermediate). CH_2OO' will then go to complex pathways and create peroxy radicals which will be amplified by C_2H_4 in addition to the peroxy radicals generated at the radical source.

The complex C_2H_4 ozonolysis radical production is shown in Figure 23.



Figure 23: Schematic representation of C_2H_4 ozonolysis reaction system (Alam et al., 2011)

The ozonolysis of C_2H_4 had not been expected in the experiments carried out, as the ozone which is generated at the source is expected to be completely converted by *NO* into *NO*₂ at the reactor.

$$NO + O_3 \rightarrow NO_2 + O_2 \tag{R3-34}$$

The O_3 maximum generation at the source is 4ppb, the minimum NO mixing ratio at the reactor is 3ppm, O_3 should be completely converted into NO_2 by NO. The result from Figure 22 indicates that ozone from the source may not be fully converted into NO_2 . In order to check if the NO added at the reactor is sufficient to convert O_3 completely, a series of tests were performed by adding increasing NO mixing ratio at the reactor while keeping the maximum O_3 generation at the source. The ozone generation sensitivity obtained from the corresponding NO_2 detected at the luminol detector is plotted against NO mixing ratio at 11/min sampling flow rate for CO, and C_2H_4 in Figure 24.



Figure 24: Ozone generation sensitivity against NO mixing ratio at 11/min sampling flow rate

The O_3 generation sensitivity does not increase with the increase of *NO* mixing ratio in the system. This is an indication that O_3 can be converted completely, but *NO* and C_2H_4 are competing to react with O_3 at the reactor. In order to evaluate this, it is necessary to compare the reaction rate for the reactions involved.

The total reaction rate for O_3 according to Eq.(3-5):

2% of C_2H_4 is added into the reactor at 90ml/min at 11/min sampling flow, therefore, the mixing ratio of C_2H_4 at the reactor is 1800ppm. The calculations are made at the lowest *NO* mixing ratio 3ppm and the highest expected O_3 mixing ratio 4ppb, the results are shown in Table 10.

Table 10: Calculatd reaction rates at 298K for 3ppm NO and 2% C2H4 competing reactions with 4ppb O3

Reaction	Rate constant	Reaction rate,
	$k(298K), [cm^3 \cdot molec^{-1} \cdot s^{-1}]$	$[molec \cdot cm^{-3} \cdot s^{-1}]$
$\boldsymbol{0}_3 + \boldsymbol{N} \boldsymbol{0} \rightarrow \boldsymbol{N} \boldsymbol{0}_2 + \boldsymbol{0}_2$	1.9×10^{-14}	1.38×10^{11}
$C_2H_4 + O_3 \rightarrow product$	1.7×10^{-18}	7.43×10^{9}

According to the results of reaction rates, competition reaction between *NO* with O_3 and C_2H_4 with O_3 is possible. At the lowest *NO* mixing ratio, the reaction between O_3 and *NO* is favoured over the reaction between C_2H_4 and O_3 . So if the *NO* mixing ratio is increased, a higher reaction rate will be expected for the reaction between O_3 and *NO*. Therefore, less interference from the reaction between C_2H_4 and O_3 should be observed.

Now it is known that at the eCL calibrations, the NO₂ modulation signal consists of two parts:

- the real amplification signal from C_2H_4 amplification reactions;
- the interference amplification signal from C_2H_4 and O_3 reactions.

Therefore,

$$\Delta[NO_2]_{C_2H_4} = \Delta[NO_2]_{valid} + \Delta[NO_2]_{interference} \qquad \text{Eq.(5-2)}$$

$$eCL_{valid} = \frac{\Delta[NO_2]_{valid}}{\Delta[HO_2]} = \frac{\Delta[NO_2]_{C_2H_4} - \Delta[NO_2]_{interference}}{\Delta[HO_2]} \qquad \text{Eq.(5-3)}$$

$$eCL_{interference} = eCL_{total} - eCL_{valid}$$
 Eq.(5-4)

In order to determine the interference from C_2H_4 , it was proceeded as follows:

- Perform a calibration according to the eCL calibration procedure but without HO₂ generation in the source. From the corresponding NO₂ modulation, the Δ[NO₂]_{interference} is determined;
- Perform a standard eCL calibration which means HO₂ is generated in the source at the same conditions as in the former step. From the corresponding NO₂ modulation the Δ[NO₂]_{C₂H₄} is determined.

The results are shown in Table 11:

<i>NO</i> mixing	Date	Sampling	total eCL	eCL Interf.	eCL valid
ratio		flow rate			
3ppm	2015-11-24	1L/min	49±7	31±5	18±9
	2015-03-05	2L/min	51±14	33±12	18±18
6ppm	2015-11-25	1L/min	27±7	12±7	15±10
	2015-03-04	2L/min	27±10	8±11	19±15
9ppm	2015-11-26	1L/min	12±11	2±10	10±15

Table 11: Radical interference in the eCL determination using C_2H_4 as amplification agent

The interference and total eCL results obtained for different *NO* mixing ratios and sampling flows are plotted in Figure 25.



Figure 25: Total and interference eCL at 11/min and 21/min sampling flow rate with respect to NO mixing ratio

Summarizing, at 11/min sampling flow rate:

- The interference eCL is lowest at 9ppm *NO*. Because of the higher *NO* mixing ratio the reaction rate of *NO* and *O*³ is more effective. Therefore, less interference from reaction between *C*₂*H*₄ and *O*³ occurs, as expected. However, the eCL error is high due to the lower detector sensitivities at higher *NO* mixing ratios.
- The valid eCL is higher at 3ppm *NO*. The chain reaction for the peroxy radical amplification has the highest amplification at 3ppm *NO*. The same results were also observed when *CO* was used as the amplification agent.

At 21/min sampling flow rate:

- The inference eCL decreases with the increase of *NO* mixing ratio, similar with the results of 11/min sampling flow rate. Comparing with 11/min flow, the interference at 6ppm *NO* mixing ratio for 21/min sampling flow rate is lower. The higher sampling flow rate means lower retention time from the reactor to the *NO*₂ detector. Since the reaction rate for the reaction between O_3 and C_2H_4 is lower than that between O_3 and *NO*, higher retention times might favor interference reactions.
- The valid eCL results are very similar for 3ppm and 6ppm *NO*. Increasing *NO* mixing ratio leads to decreasing the rate of the amplifying reactions and to increasing efficiency of O_3 reaction with *NO*. Therefore, less interference is expected from the C_2H_4 ozonolysis. It is important to note that, due to the calculation procedure of the valid eCL proposed in this work, the propagation of errors of the individual eCL lead to high total uncertainties. Therefore, the effect of variations in the reaction rates of small variations in the *NO* mixing ratio might be within the error.

Comparing the sampling flow rate at the same NO mixing ratio conditions, the associated retention time differences do not affect the eCL determination for valid amplification within the error. As the sensitivity of the NO_2 luminol detector decreases with the increasing NO mixing ratio, the error of the eCL increases with increasing NO mixing ratio.

The relative interference signal for C_2H_4 amplification agent is defined as the NO_2 interference modulation signal (when the calibration is performed without HO_2 generation at the source) divided by the NO_2 total modulation signal (when the calibration is performed with HO_2 generation in the source):

Interference (%) =
$$\frac{[\Delta NO_2]_{interference}}{[\Delta NO_2]_{total}} \times 100\%$$
 Eq.(5-5)

For each *HO*² mixing ratios generation at the source:

$$Interference (\%) = \frac{\left(\frac{[\Delta NO_2]_{interference}}{[HO_2]}\right)}{\left(\frac{[\Delta NO_2]_{total}}{[HO_2]}\right)} \times 100\%$$
$$= \frac{eCL_{interference}}{eCL_{total}} \times 100\%$$

The detailed results for different HO₂ mixing ratios are shown in Table 12-14.

Conditions	HO2 generation (ppt)	eCLtotal	eCLinterference	Interference (%)	Conditions	HO2 generation (ppt)	eCL _{total}	eCLinterference	Interference (%)
	19	50±13	29 <u>±</u> 8	58		20	48±24	32±19	66
3nnm NO	54	48 <u>+</u> 7	31±6	65		29	51±16	30±9	58
11/min	86	49 <u>±</u> 5	32 <u>+</u> 4	65	3ppm NO	37	49 <u>+</u> 14	34±12	69
	114	50±4	32±3	63	21/min	54	52±9	34±10	66
	Average	49±7	31±5	63		72	53±9	36±8	67
						Average	51±14	33±12	65

Table 12: Interference calculations	at 3ppm NO
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Table 13: Interference calculations at 6ppm NO

Condition s	HO2 generatio n (ppt)	eCL _{total}	eCLinterfere nce	Interfere nce (%)	Condition s	HO2 generatio n (ppt)	eCL _{total}	eCLinterfere nce	Interferen ce (%)
	50	24 <u>±</u> 10	11±10	45	бррт <i>NO</i>	29	26±16	7 <u>±</u> 18	26
6ppm <i>NO</i>	80	27 <u>+</u> 7	12 <u>+</u> 7	44		42	26±12	7±13	28
11/min	98	28 <u>±</u> 6	12±5	43		54	28±10	9±11	33
	Average	27 <u>+</u> 7	12 <u>+</u> 7	44	21/min	78	28±7	9±8	32
						102	29±7	9±7	32
						Average	27±10	8±11	30

Conditions	HO ₂ generation (ppt)	eCL _{total}	eCLinterference	Interference (%)
	46	9±15	1±15	12
9ppm <i>NO</i>	72	14 <u>±</u> 10	2±10	17
11/min	98	14 <u>+</u> 7	3±7	24
	Average	12±11	2±10	18

 Table 14: Interference calculation at 9ppm NO

The interference for each selected HO_2 mixing ratio is similar. That means that at the same NO mixing ratio and sampling flow rate, the interferences from C_2H_4 and O_3 reactions are the same for the different O_3 mixing ratios generated at the source between 1 and 4ppb approximately.

The results in Table 12-14 show that the interference decreases with increasing *NO* mixing ratio as expected. Increasing the flow rate to 21/min seems to diminish the effect of the interference only at 6 ppm. It is likely to be the result of the combined effect of increasing *NO* which favors the amplification of the HO_2 generated at the source and decreasing retention time which might affect more effectively the slower and more complex reaction, i.e. the formation of peroxy radicals from the ozonolysis of C_2H_4 .

5.3.3. Determination of eCL for *CH₃CHO* as Amplification Agent

The eCL determination calibrations have been performed using CH_3CHO as the amplification agent. The plots of NO_2 signal and PMT signal during the eCL determination calibrations are shown in Figure 26-28. As described in chapter 4.1, the PMT signals correspond to different gas sampling illumination steps, achieved by the use of N_2O to attenuate the output of the Hglamp in the source, and therefore leading to a different generation of HO_2 . The NO_2 signal corresponds to the modulation detected by the NO_2 luminol detector for each HO_2 mixing ratio generated.



Figure 26: NO_2 and PMT signal vs. time for the eCL calibration performed on 23-11-2015, using CH_3CHO 0.5% and NO 3ppm. The sampling flow was kept at 11/min. The plot shows the modulation signal obtained for the 10, 40, and 70ppt HO_2 gererated at the source.



Figure 27: NO_2 and PMT signal vs. time for the eCL calibration performed on 20-11-2015, using CH_3CHO 0.5% and NO 6ppm. The sampling flow was kept at 11/min. The plot shows the modulation signal obtained for the 10, 30, and 50ppt HO_2 gererated at the source.



Figure 28: NO_2 and PMT signal vs. time for the eCL calibration performed on 19-11-2015, using CH_3CHO 0.5% and NO 9ppm. The sampling flow was kept at 11/min. The plot shows the modulation signal obtained for the 30, 50, and 70ppt HO_2 gererated at the source.

In Figure 26, 10ppt, 40ppt, and 70ppt HO_2 were generated at the radical source. NO_2 signal modulations below 0.1V which corresponds to 0.87 ppb NO_2 were observed. It is important to note that the modulations were negative, i.e. the background signal is higher than the amplification signal. The negative modulations were also observed for other mixing ratios as shown in Figure 27 and Figure 28. In Figure 27, the calibration was at 10ppt, 30ppt, and 50ppt HO_2 generation for 6ppm NO. Similarly, in Figure 28, the PMT signals for 30ppt, 50ppt, and 70ppt HO_2 generation and 9ppm are shown. The still negative modulations are in both cases hardly distinguishable as they remain below 0.02V which corresponds to roughly 0.31ppb and NO_2 detector sensitivity decreases at higher NO mixing ratios.

The chain results obtained are unexpected as the chemical chain reactions (R3-3, R3-5, R3-6, R3-57 to R3-61) presented in chapter 3.3. suggested a more effective chemical amplification leading to a potential sufficient eCL for ambient measurements. A possible reason for the observed values is that the terminating reactions are more dominant in the chain length as expected. Apart from the terminating reactions that are common with the amplification chain in the case of *CO*, i.e., *OH*, *HO*₂ radical loss (R3-21, R3-31, R3-32, R3-39), radical-radical reactions (R3-28, R3-40), and HO₂ radical wall reaction (R3-39, R5-1), when using *CH*₃*CHO*, other radical losses from the intermediate radical generation might play an important role in diminishing the overall eCL.

The radicals $CH_3CO \cdot O_2$ and CH_3O_2 from reaction (R3-58), (R3-5) may have lost through radical-radical reactions:

$$CH_3O_2 + HO_2 \rightarrow CH_3OOH + O_2 \tag{R5-9}$$

$$CH_3O_2 + CH_3CO \cdot O_2 \to CH_3COO + CH_3O + O_2$$
 (R5-10)

$$CH_3O_2 + CH_3CO \cdot O_2 \rightarrow CH_3COO + HCHO + O_2$$
(R5-11)

$$CH_3CO \cdot O_2 + HO_2 \rightarrow CH_3COOOH + O_2 \tag{R5-12}$$

$$CH_3CO \cdot O_2 + HO_2 \rightarrow CH_3COOH + O_3 \tag{R5-13}$$

$$2CH_3O_2 \rightarrow HCHO + CH_3OH + O_2 \tag{R5-14}$$

$$2CH_3CO \cdot O_2 \to 2CH_3COO + O_2$$
 (R5-15)

$$CH_3O_2 + OH \to CH_3OH + O_2 \tag{R5-16}$$

$$CH_3CO \cdot O_2 + OH \to CH_3COOH + O_2 \tag{R5-17}$$

And wall reactions:

$$CH_3O_2 + wall \rightarrow nonradical products$$
 (R5-18)

$$CH_3CO \cdot O_2 + wall \rightarrow nonradical products$$
 (R5-19)

*NO*₂ and *CH*₃*CHO* can react with $CH_3CO \cdot O_2$ (Moortgat et al., 1989), both reactions compete with the amplifying reaction (R3-59) and may lead to a chain reaction termination:

$$CH_3CO \cdot O_2 + NO_2 \xrightarrow{M} CH_3CO \cdot O_2 \cdot NO_2$$
(R5-20)

$$CH_3CO \cdot O_2 + CH_3CHO \rightarrow CH_3COOOH + CH_3CO$$
(R5-21)

$$CH_3CO \cdot O_2 + NO \to NO_2 + CH_3 \cdot CO_2 \tag{R3-59}$$

In order to evaluate the competition between these reactions, related rate constants must be taken into account (see Table 15) at 1 atmosphere pressure and 25 degrees Celsius temperature. *NO*₂ comes from the *NO* oxidation by the peroxy radicals and ozone from the source, the mixing ratio of *NO*₂ should be therefore 4 ppb (9.84 × 10¹⁰ $\left[\frac{molec}{cm^3}\right]$) at maximum. 0.5% *CH*₃*CHO* is added in to 11/min flow at 90ml/min, *CH*₃*CHO* mixing ratio is 450ppm (1.11 × $10^{16} \left[\frac{molec}{cm^3}\right]$). At 3ppm (7.38 × $10^{13} \left[\frac{molec}{cm^3}\right]$) *NO* and maximum ozone generation at the source, the reaction rate for (R5-20), (R5-21), and (R3-59) are:

$$\begin{array}{ll} CH_{3}CO \cdot O_{2} + NO_{2} &: \qquad k_{(R5-20)} \cdot [NO_{2}] \\ &= 8.6 \times 10^{-12} \left[\frac{cm^{3}}{molec \cdot s} \right] \cdot 9.84 \\ &\times 10^{10} \left[\frac{molec}{cm^{3}} \right] \approx 8.46 \times 10^{-1} [s^{-1}] \end{array}$$

$$CH_{3}CO \cdot O_{2} + CH_{3}CHO &: \qquad k_{(R5-21)} \cdot [CH_{3}CHO] \\ &= 5.7 \times 10^{-17} [\frac{cm^{3}}{molec \cdot s}] \cdot 1.11 \\ &\times 10^{16} \left[\frac{molec}{cm^{3}} \right] \approx 6.33 \times 10^{-1} [s^{-1}] \end{array}$$

$$\begin{array}{ll} CH_3CO \cdot O_2 + NO: & k_{(R3-59)} \cdot [NO] \\ & = 2 \times 10^{-11} \left[\frac{cm^3}{molec \cdot s} \right] \cdot 7.38 \\ & \times 10^{13} \left[\frac{molec}{cm^3} \right] \approx \mathbf{1.48} \times \mathbf{10^3} [s^{-1}] \end{array}$$

Table 15: Chemical reactions and rate constants used for the analyse of CH_3CHO reaction competition. Rate constants for termolecular reactions are calculated using Eq.(3-9)(3-10)(3-11)(3-12). Termolecular rate constants are calculated for 1bar and 298K.

Reaction	Reaction mechanism		Source
number	$([M], 1bar = 2.45 \times 10^{17} [cm^3])$	Unit: $\left[\frac{cm^3}{molec \cdot s}\right]$	
(R3-21)	$CH_3CO \cdot O_2 + CH_3CHO \rightarrow CH_3COOOH + CH_3CO$	5.7×10^{-17}	Moortgat et al., 1989
(R3-59)	$CH_3CO \cdot O_2 + NO \rightarrow NO_2 + CH_3 \cdot CO_2$	2×10^{-11}	JPL, 2011
(R3-61)	$CH_3O + O_2 \rightarrow HO_2 + HCHO$	1.9×10^{-15}	JPL, 2011
(R3-62)	$CH_3O + CH_3CHO \rightarrow CH_3OH + CH_3CO$	2.7×10^{-14}	Kelly and Keicklen,
			1978
(R5-9)	$CH_3O_2 + HO_2 \rightarrow CH_3OOH + O_2$	4.1×10^{-13}	JPL, 2011
(R5-10)	$CH_3O_2 + CH_3CO \cdot O_2 \rightarrow CH_3COO + CH_3O + O_2$	5.5×10^{-12}	Moortgat et al., 1989a
(R5-11)	$CH_3O_2 + CH_3CO \cdot O_2 \rightarrow CH_3COO + HCHO + O_2$	5.5×10^{-12}	Moortgat et al., 1989a
(R5-12)	$CH_3CO \cdot O_2 + HO_2 \rightarrow CH_3COOOH + O_2$	4.5×10^{-12}	Moortgat et al., 1989
(R5-13)	$CH_3CO \cdot O_2 + HO_2 \rightarrow CH_3COOH + O_3$	1.5×10^{-12}	Moortgat et al., 1989
(R5-14)	$2CH_3O_2 \rightarrow HCHO + CH_3OH + O_2$	6.1×10^{-13}	Moortgat et al., 1989a
(R5-15)	$2CH_3CO \cdot O_2 \rightarrow 2CH_3COO + O_2$	1.6×10^{-11}	Moortgat et al., 1989a
(R5-16)	$CH_3O_2 + OH \rightarrow CH_3OH + O_2$	8.6×10^{-12}	JPL, 2011
(R5-20)	$CH_3CO \cdot O_2 + NO_2 \xrightarrow{M} CH_3CO \cdot O_2 \cdot NO_2$	8.95×10^{-12}	JPL, 2011
(R5-22)	$CH_3O + NO \xrightarrow{M} CH_3ONO$	2.87×10^{-11}	JPL, 2011
(R5-23)	$CH_3O + NO_2 \xrightarrow{M} CH_3ONO_2$	1.67×10^{-11}	JPL, 2011

The rate from both reactions (R5-20, R5-21) is three orders of magnitude lower than the amplification reaction (R3-59). Therefore, these terminations do not play a role.

Other termination channels could be through the reactions of CH_3O with NO, NO_2 , and CH_3CHO (Moortgat et al., 1989), which compete with the amplifying reaction (R3-61):

$$CH_3O + NO \xrightarrow{M} CH_3ONO$$
 (R5-22)

$$CH_3O + NO_2 \xrightarrow{M} CH_3ONO_2 \tag{R5-23}$$

$$CH_3O + CH_3CHO \rightarrow CH_3OH + CH_3CO$$
 (R3-62)

$$CH_3O + O_2 \to HO_2 + HCHO \tag{R3-61}$$

Roughly 808ml/min synthetic air consist with 20.5% O_2 is sampled at the inlet when *NO* is 3ppm $(7.38 \times 10^{13} \left[\frac{molec}{cm^3}\right])$, so that O_2 mixing ratio is about 1.66×10^5 ppm $(4.08 \times 10^{18} \left[\frac{molec}{cm^3}\right])$. Similarly, the maximum *NO*₂ mixing ratio is 4ppb $(9.84 \times 10^{10} \left[\frac{molec}{cm^3}\right])$, *CH*₃*CHO* is 450ppm $(1.11 \times 10^{16} \left[\frac{molec}{cm^3}\right])$. The reaction rates for the competition between the terminating reactions (R5-22), (R5-23), (R3-62) and the corresponding amplifying reaction (R3-61) are:

$$\begin{array}{ll} CH_{3}O + NO: & k_{(R5-22)} \cdot [NO] = 2.87 \times 10^{-11} [\frac{cm^{3}}{molec \cdot s}] \cdot 7.38 \times 10^{13} \left[\frac{molec}{cm^{3}}\right] \\ & \approx 2.12 \times 10^{3} [s^{-1}] \\ CH_{3}O + NO_{2}: & k_{(R5-23)} \cdot [NO_{2}] = 1.67 \times 10^{-11} [\frac{cm^{3}}{molec \cdot s}] \cdot 9.84 \times 10^{10} \left[\frac{molec}{cm^{3}}\right] \\ & \approx 1.64 [s^{-1}] \\ CH_{3}O + CH_{3}CHO: & k_{(R3-62)} \cdot [CH_{3}CHO] \\ & = 2.7 \times 10^{-14} \left[\frac{cm^{3}}{molec \cdot s}\right] \cdot 1.11 \times 10^{16} \left[\frac{molec}{cm^{3}}\right] \\ & \approx 3.00 \times 10^{2} [s^{-1}] \\ CH_{3}O + O_{2}: & k_{(R3-61)} \cdot [O_{2}] = 1.9 \times 10^{-15} \left[\frac{cm^{3}}{molec \cdot s}\right] \cdot 4.08 \times 10^{18} \left[\frac{molec}{cm^{3}}\right] \end{array}$$

The reaction rate of the reaction (R5-23) is four order of magnitude lower than this of the amplifying reaction (R3-61), therefore, it does not play role in these competition reactions. The reaction rate of (R3-62) is also lower than amplifying reaction rate (R3-61), however, the *CH*₃*O* production from (R3-62) will react with
$$O_2$$
 and produce $CH_3CO \cdot O_2$ (R3-58) which continues the chain reaction through (R3-59). Therefore, these two reactions do not effectively terminate the amplification chain reaction.

 $\approx 7.76 \times 10^{3} [s^{-1}]$

The rates of reaction (R5-22) and (R3-61) are similar. Therefore, the reaction between CH_3O and NO can effectively compete with the amplifying reaction and suppress the eCL. The reaction rate will increase with increasing NO mixing ratio. This might explain the lower modulations observed with higher NO mixing ratios.

Based on the chemical reactions expected to take place and described above, a potential explanation for the negative modulations observed during the eCL calibrations is can be the reaction between $CH_3CO \cdot O_2$ with NO_2 (R5-20) in the reactor. The $CH_3CO \cdot O_2 \cdot NO_2$ (PAN) produced is a stable compound at the laboratory temperature and pressure. $CH_3CO \cdot O_2$ is produced from the amplification reactions when adding CH_3CHO in to the reactor at the "amplifying" mode. As mentioned before NO_2 is generated in the inlet from the NO oxidation of O_3 from the source and can reach a maximum of 4ppb. Due to the low amplification efficiency from CH_3CHO , the generation of NO_2 from the amplification reactions is less than the NO_2 consumption from the reaction with $CH_3CO \cdot O_2$. As $CH_3CO \cdot O_2$ is not generated at the reactor at the "background" mode, and NO_2 is not consumed through the PAN generation reaction (R5-18), for any radical generation at the source during a radical calibration, the observed modulations are negative.

5.4. Error Analysis

The uncertainties from the calibration results are related to the uncertainties of each measurable values. The detail calculations are explained for each calibration.

The eCL is determined from *NO*₂ and *HO*₂ mixing ratio measurements, the error of the eCL is calculated as:

$$\frac{\sigma_{eCL}}{eCL} = \sqrt{\left(\frac{\sigma_{[\Delta NO_2]}}{[\Delta NO_2]}\right)^2 + \left(\frac{\sigma_{[\Delta HO_2]}}{[\Delta HO_2]}\right)^2} \qquad \text{Eq.(5-7)}$$

According to Eq.(4-6), NO_2 mixing ratio is related to the detection signal from the NO_2 detector and the slope value determined from the NO_2 detector sensitivity calibration which is:

$$[\Delta NO_2] = a \cdot V_{amplification} + b - (a \cdot V_{background} + b)$$

= $a \cdot \Delta V$ Eq.(5-8)

So that the uncertainty from $[\Delta NO_2]$ is determined as:

$$\frac{\sigma_{[\Delta NO_2]}}{[\Delta NO_2]} = \sqrt{\left(\frac{\sigma_{\Delta V}}{\Delta V}\right)^2 + \left(\frac{\sigma_a}{a}\right)^2} \qquad \text{Eq.(5-9)}$$

So for the *NO*² signals, the error is calculated by:

$$\sigma_{\Delta V} = \sqrt{\left(\sigma_{V_{amplification}}\right)^2 + \left(\sigma_{V_{background}}\right)^2} \qquad \qquad \text{Eq.(5-10)}$$

Where $\sigma_{V_{amplification}}$ and $\sigma_{V_{background}}$ are the standard deviations from the *NO*₂ signal (in voltage) statistics. σ_a is determined in the *NO*₂ luminol detector sensitivity calibration with the least square fit method, the error of the slope *a* is 2%~5%. It depends on the uncertainties from *NO*₂ flow controller which controls the *NO*₂ mixing ratio at the detector sensitivity calibration, the uncertainty from the sampling flow controller, the uncertainty from the *NO*₂ detector response, and the error of *NO*₂ mixing ratio from the *NO*₂ cylinder.

According to the $[\Delta HO_2]$ calculation Eq.(4-3), the uncertainty from HO_2 mixing ratio is determined as:

$$\frac{\sigma_{[\Delta HO_2]}}{[\Delta HO_2]} = \sqrt{\left(\frac{\sigma_{\sigma_{H_2O}^{184.9nm}}}{\sigma_{H_2O}^{184.9nm}}\right)^2 + \left(\frac{\sigma_{[H_2O]}}{[H_2O]}\right)^2 + \left(\frac{\sigma_{\sigma_{O_2}^{184.9nm}}}{\sigma_{O_2}^{184.9nm}}\right)^2 + \left(\frac{\sigma_{[O_3]}}{[O_3]}\right)^2} \qquad \text{Eq.(5-11)}$$

Where the uncertainty for water absorption cross section is taken from the literature as 1.4% (Cantrell et al., 1993), water mixing ratio uncertainty is depending on the dew point sensor, the calculated result is $0.2\%\sim0.9\%$. The error for oxygen cross section is used from previous calibrations as 3.5%.

The O₃ uncertainty is determined according to Eq.(4-6) and Eq.(4-9) as:

$$\frac{\sigma_{[O_3]}}{[O_3]} = \sqrt{\left(\frac{\sigma_a}{a}\right)^2 + \left(\frac{\sigma_{I_{ozone\,max}}}{I_{ozone\,max}}\right)^2 + \left(\frac{\sigma_{I_{detected}}}{I_{detected}}\right)^2 + \left(\frac{\sigma_{\Delta V_{ozone\,max}}}{\Delta V_{ozone\,max}}\right)^2} \qquad \text{Eq.(5-12)}$$

Where $\Delta V_{ozone\ max}$ is the NO₂ signal difference at the O₃ mixing ratio maximum determination; the error for $I_{detected}$ is the standard deviation of the PMT signal at eCL calibration; the error for $I_{ozone\ max}$ is the standard deviation of the PMT signal at O₃ mixing ratio maximum determination. The overall O₃ error is 6%~19%, because the stability of the Hg-lamp is not stable as previous performance. Then it gives the HO₂ mixing ratio error at 7%~20%.

6. SUMMARY and CONCLUSION

The thesis work has focused on investigating and characterizing the performance of C_2H_4 and CH_3CHO , as amplification gases for airborne peroxy radical measurement using chemical

amplification techniques. The calibrating results for the alternatives selected have been compared with the standard amplification gas *CO*.

The *NO* mixing ratio in the system affects the *NO*₂ luminol detector sensitivity, while the sampling flow rate can affect the retention time for the reactions. Therefore, the influence of these variables at selected conditions was investigated and series of calibrations were carried out 3ppm, 6ppm, or 9ppm *NO* mixing ratio, and l/min and 2l/min sampling flow rates.

For the NO_2 luminol detector sensitivity, the calibration results for C_2H_4 were similar as those of the standard amplification gas CO. The sensitivity decreases with increasing NO mixing ratios. For constant NO mixing ratios, the sensitivities were higher at higher sampling flow rates for CO and C_2H_4 . The distribution of NO_2 on the filter is likely more homogeneous at higher sampling flow rates, and the chemiluminescence reaction between NO_2 and luminol can consequently become more effective.

In the case of CH_3CHO , instabilities during the NO_2 detector calibrations were observed. These might be the result of the reaction of CH_3CHO with KOH in the luminol solution, as according to literature the chemiluminescence emission from the reaction lies at the detection range of the photodiode used. Additionally, the CH_3CHO photolysis by the daylight might have introduced additional instabilities during the experiments.

Concerning the eCL determination, the results for C_2H_4 were significantly low compared with *CO*. At 11/min sampling flow rate, the eCL for C_2H_4 at 3ppm, 6ppm, 9ppm *NO* mixing ratio are 49 ± 7 , 27 ± 7 , 12 ± 11 respectively. The eCL for *CO* at the same *NO* mixing ratios are 249 ± 20 , 228 ± 38 , 198 ± 24 respectively. The lower eCL results from C_2H_4 might be explained by additional terminating reactions associated to $CH_2(OH)CH_2O_2$. If this radical has the highest yield of the amplifying reactions can lead to the radical loss by radical wall reaction, radical-radical reaction, and possibly the most efficient lost reaction with *NO*. The overall terminating reactions would therefore be more efficient than in the amplification chain with *CO*.

Furthermore, interference modulations from the C_2H_4 ozonolysis were observed during the radical calibrations. Although, it was not anticipated that O_3 is not fully converted by NO when C_2H_4 is added into the reactor at the amplification mode, the competition reaction between O_3 with NO and C_2H_4 with O_3 , the latter reaction generating a Criegee intermediate happens to be significant under the conditions investigated. Then the Criegee intermediate leads to generation of a series of peroxy radicals which interfere in the eCL determination. The interference has *University of Bremen Postgraduate Programme ENVIRONMENTAL PHYSICS (PEP) 2015* 59

been calibrated experimentally for C_2H_4 . The calculated interference eCL were 31 ± 5 , 12 ± 7 , 2 ± 10 for 11/min sampling flow and 3ppm, 6ppm, 9ppm NO mixing ratio respectively. Similarly, for 21/min sampling flow and 3ppm, 6ppm NO mixing ratio, the interference eCL obtained were 33 ± 12 , 8 ± 11 respectively. The interference from the C₂H₄ ozonolysis decreases with increasing the NO mixing ratio as expected. Higher NO mixing ratios increase the reaction rate for NO and O_3 , therefore the interference reaction for O_3 and C_2H_4 becomes less effective. Variations in the sampling flow rate for constant NO mixing ratios do not have any significant influence in the observed interference. The relative interferences were very similar for different O_3 generated at the source for the same sampling flow and NO mixing ratio. The relative interference varied with the sampling flow rates and the NO mixing ratios. In conclusion, C_2H_4 showed limited amplification potential at the selected laboratory conditions. It is important to note that in real airborne measurements, higher and more variable ambient O_3 mixing ratio than under the laboratory conditions are to be expected. In addition, the pressure for the measurements will be lower, which may affect the balance between amplification and termination reactions involved. Therefore, further investigation is required to determine more accurately the potential of C_2H_4 as amplification agent for airborne measurements.

In the case of CH_3CHO , the modulations were within the noise of NO_2 signal with the exception of 3ppm NO; and all the modulations are negatively observed.

Two reasons are proposed to explain the experimental results obtained:

1. additional termination reactions such as radical-radical reactions and wall reactions from peroxy radical intermediates of the amplifying chain reactions of *CH3CHO* suppress effectively the chain reaction;

2. the *CH*₃*O* generated in an intermediate reaction can efficiently react with *NO* leading to a non-radical product *CH*₃*ONO* which significantly compete with the amplifying reaction.

The "negative modulation" is interpreted to be caused by the generation of $CH_3CO \cdot O_2 \cdot NO_2$ (PAN) from $CH_3CO \cdot O_2$ reacting with NO_2 . $CH_3CO \cdot O_2$ is only generated at the amplification mode of the system, and at low chain lengths, the consumption of NO_2 during amplification can lead to a signal smaller than in the background mode.

It can therefore be concluded that the usage of CH_3CHO as amplifying agent is problematic and therefore, CH_3CHO it is not a suitable alternative to CO for the measurement of peroxy radicals with PeRCA.

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8. ANNEX

8.1. Table of Chemical Reactions and Rate Constants

REACTION	REACTION MECHANISM	RATE	SOURCE
NO.		CONSTANT	
(R3-1)	$OH + CO \xrightarrow{M} H + CO_2$	3.5 × 10 ⁶	JPL, 2011
(R3-2)	$H + O_2 \xrightarrow{M} HO_2$	9.5×10^{-13}	JPL, 2011
(R3-3)	$HO_2 + NO \rightarrow OH + NO_2$	8×10^{-12}	JPL, 2011
(R3-4)	$OH + CH_4 \to CH_3 + H_2O$	6.3×10^{-15}	JPL, 2011
(R3-5)	$CH_3 + O_2 \xrightarrow{M} CH_3O_2$	8.1 × 10 ⁻¹³	JPL, 2011
(R3-6)	$CH_3O_2 + NO \rightarrow CH_3O + NO_2$	7.7×10^{-12}	JPL, 2011
(R3-7)	$CH_3O + O_2 \rightarrow HCHO + HO_2$	1.9×10^{-15}	JPL, 2011
(R3-8)	$HO_2 + CH_3O_2 \rightarrow CH_3OOH + O_2$	5.2×10^{-12}	JPL, 2011
(R3-9)	$CH_3OOH \xrightarrow{hv} CH_3 O + OH$		
(R3-10)	$CH_3OOH + OH \rightarrow CH_3O_2 + H_2O$	7.4×10^{-12}	JPL, 2011
(R3-11)	$RH + OH \rightarrow R + H_2O$		
(R3-12)	$R + O_2 \xrightarrow{M} RO_2$		
(R3-131)	$RO_2 + NO \rightarrow RO + NO_2$		
(R3-14)	$RO + O_2 \xrightarrow{M} R'CHO + HO_2$		
(R3-15)	$O_3 \xrightarrow{hv(\lambda < 320nm)} O({}^1D) + O_2$		
(R3-16)	$O_3 \xrightarrow{hv(\lambda < 1180nm)} O({}^3P) + O_2$		
(R3-17)	$O\left({}^{3}P\right) + O_2 \xrightarrow{M} O_3$	1.5×10^{-14}	JPL, 2011
(R3-18)	$O({}^{1}D) \xrightarrow{M} O({}^{3}P)$		
(R3-19)	$O(^{1}D) + H_2O \to 2OH$	2.0×10^{-10}	JPL, 2011
(R3-20)	$HONO \xrightarrow{h\nu(\lambda < 390nm)} OH + NO$		
(R3-21)	$OH + NO \xrightarrow{M} HONO$	7.3×10^{-12}	JPL, 2011
(R3-22)	$NO_3 + HO_2 \rightarrow OH + NO_2 + O_2$	3.5×10^{-12}	JPL, 2011
(R3-23)	$NO_2 + O_3 \rightarrow NO_3 + O_2$	3.2×10^{-17}	JPL, 2011
(R3-24)	$HCHO \xrightarrow{hv(\lambda < 360nm)} H_2 + CO$		
(R3-25)	$HCHO \xrightarrow{h\nu(\lambda < 335nm)} H + HCO$		
(R3-26)	$HCHO + OH \rightarrow HCO + H_2O$		

All of the rate constants are considered at 298K and 1bar condition.

REACTION NO.	REACTION MECHANISM	RATE CONSTANT	SOURCE
(R3-27)	$HCO + O_2 \rightarrow HO_2 + CO$		
(R3-28)	$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	1.4×10^{-12}	JPL, 2011
(R3-29)	$HO_2 + RO_2 \rightarrow ROOH + O_2$		
(R3-30)	$RO_2 + RO_2 \rightarrow products$		
(R3-31)	$OH + NO_2 \xrightarrow{M} HNO_3$	1.1×10^{-11}	JPL, 2011
(R3-32)	$HO_2 + NO \xrightarrow{M} HNO_3$	6.0×10^{-13}	JPL, 2011
(R3-33)	$NO_2 \xrightarrow{h\nu(\lambda < 420nm)} NO + O({}^{3}P)$		
(R3-34)	$NO + O_3 \rightarrow NO_2 + O_2$	1.9×10^{-14}	JPL, 2011
(R3-35)	$HO_2 + O_3 \rightarrow OH + 2O_2$	1.9×10^{-15}	JPL, 2011
(R3-36)	$RO_2 + O_3 \rightarrow RO + 2O_2$		
(R3-37)	$OH + O_3 \rightarrow HO_2 + O_2$	7.3×10^{-14}	JPL, 2011
(R3-38)	$RO_2 + wall \rightarrow nonradical products$		
(R3-39)	$OH + wall \rightarrow nonradical products$		
(R3-40)	$HO_2 + NO_2 \xrightarrow{M} HO_2NO_2$	1.1×10^{-12}	JPL, 2011
(R3-41)	$OH + HO_2 \to H_2O + O_2$	1.1×10^{-10}	JPL, 2011
(R3-42)	$CO + CH_3O \rightarrow CO_2 + CH_3$		
(R3-43)	$H_2 O \xrightarrow{h\nu(\lambda = 184.9nm)} H + OH$		
(R3-44)	$O_2 \xrightarrow{hv(\lambda=184.9nm)} 2O({}^1D)$		
(R3-45)	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		
(R3-46)	$\begin{bmatrix} NH_2 & 0 \\ 0 & -0H \\ 0 & 0H \end{bmatrix}^* \longrightarrow \begin{array}{c} hv \\ 425 \text{ nm} \\ \end{array}$		
(R3-47)	$C_2H_4 + OH \xrightarrow{M} CH_2CH_2OH$	7.0×10^{-12}	
(R3-48)	$CH_2CH_2OH + O_2 \rightarrow CH_2CHOH + HO_2$		
(R3-49)	$CH_2CH_2OH + O_2 \rightarrow CH_2CH_2O + HO_2$		
(R3-50)	$CH_2CH_2OH + O_2 \xrightarrow{M} CH_2(OH)CH_2O_2$		
(R3-51)	$CH_2(OH)CH_2O_2 + NO \rightarrow CH_2(OH)CH_2O + NO_2$		
(R3-52)	$C_2H_4 + CH_3O \xrightarrow{M} CH_2CH_2OCH_3$		
(R3-53)	$CH_2CH_2OCH_3 + O_2 \rightarrow CH_2CHOCH_3 + HO_2$		
(R3-54)	$CH_2CH_2OCH_3 + O_2 \rightarrow CH_2CHCH_3O + HO_2$		

REACTION NO.	REACTION MECHANISM	RATE CONSTANT	SOURCE
(R3-55)	$CH_2CH_2OCH_3 + O_2 \xrightarrow{M} CH_2(OCH_3)CH_2O_2$		
(R3-56)	$CH_2(OCH_3)CH_2O_2 + NO \rightarrow CH_2(OCH_3)CH_2O + NO_2$		
(R3-57)	$CH_3CHO + OH \rightarrow CH_3CO + H_2O$	1.5×10^{-11}	JPL, 2011
(R3-58)	$CH_3CO + O_2 \xrightarrow{M} CH_3CO \cdot O_2$	2.0×10^{-12}	Moortgat et al., 1989
(R3-59)	$CH_3CO \cdot O_2 + NO \rightarrow NO_2 + CH_3 \cdot CO_2$	2.0×10^{-11}	JPL, 2011
(R3-60)	$CH_3 \cdot CO_2 \to CH_3 + CO_2$	2.2×10^{10}	Moortgat et al., 1989
(R3-61)	$CH_3O + O_2 \rightarrow HO_2 + HCHO$	2.2×10^{-12}	Moortgat et al., 1989
(R3-62)	$CH_3CHO + CH_3O \rightarrow CH_3CO + CH_3OH$	2.8×10^{-11}	Moortgat et al., 1989a
(R5-1)	$HO_2 + wall \rightarrow nonradical products$		
(R5-2)	$CH_2(OH)CH_2O_2 + NO_2 \xrightarrow{M} CH_2(OH)CH_2O_2 \cdot NO_2$	2.8×10^{-11}	JPL, 2011
(R5-3)	$CH_2(OH)CH_2O_2 + NO \xrightarrow{M} CH_2(OH)CH_2NO_3$		
(R5-4)	$CH_2(OH)CH_2O_2 + HO_2 \rightarrow nonradical produts$		
(R5-5)	$CH_2(OH)CH_2O_2 + wall \rightarrow nonradical produts$		
(R5-6)	$CH_2CH_2OH + wall \rightarrow nonradical products$		
(R5-7)	$C_2H_4 + O_3 \rightarrow CH_2OOOCH_2$	1.7×10^{-18}	JPL, 2011
(R5-8)	$CH_2OOOCH_2 \rightarrow CH_2O + CH_2OO'$		
(R5-9)	$CH_3O_2 + HO_2 \rightarrow CH_3OOH + O_2$		
(R5-10)	$CH_3O_2 + CH_3CO \cdot O_2 \rightarrow CH_3COO + CH_3O + O_2$		
(R5-11)	$CH_3O_2 + CH_3CO \cdot O_2 \rightarrow CH_3COO + HCHO + O_2$		
(R5-12)	$CH_3CO \cdot O_2 + HO_2 \rightarrow CH_3COOOH + O_2$	4.5×10^{-12}	Moortgat et al., 1989
(R5-13)	$CH_3CO \cdot O_2 + HO_2 \rightarrow CH_3COOH + O_3$	1.5×10^{-12}	Moortgat et al., 1989
(R5-14)	$2CH_3O_2 \rightarrow HCHO + CH_3OH + O_2$		
(R5-15)	$2CH_3CO \cdot O_2 \rightarrow 2CH_3COO + O_2$		
(R5-16)	$CH_3O_2 + OH \rightarrow CH_3OH + O_2$		
(R5-17)	$CH_3CO \cdot O_2 + OH \rightarrow CH_3COOH + O_2$		
(R5-18)	$CH_3O_2 + wall \rightarrow nonradical products$		
(R5-19)	$CH_3CO \cdot O_2 + wall \rightarrow nonradical products$		
(R5-20)	$CH_3CO \cdot O_2 + NO_2 \xrightarrow{M} CH_3CO \cdot O_2 \cdot NO_2$	8.6×10^{-12}	JPL, 2011
(R5-21)	$CH_3CO \cdot O_2 + CH_3CHO \rightarrow CH_3COOOH + CH_3CO$	5.7×10^{-17}	Moortgat et al., 1989
(R5-22)	$CH_3O + NO \xrightarrow{M} CH_3ONO$	2.9×10^{-11}	JPL, 2011
(R5-23)	$CH_3O + NO_2 \xrightarrow{M} CH_3ONO_2$	1.7×10^{-11}	JPL, 2011

8.2. Result plots



8.2.1. *NO*₂ Luminol detector sensitivity calibration

Figure 29: NO₂ luminol detector sensitivity calibration NO₂ signal vs. time on 2015-11-28. Amplification agent: CO, 11/min sampling flow, 3ppm NO mixing ratio



Figure 30: NO₂ luminol detector sensitivity calibration NO₂ mixing ratio vs. signal on 2015-11-28. Amplification agent: CO, 11/min sampling flow, 3ppm NO mixing ratio



Figure 31: NO₂ luminol detector sensitivity calibration NO₂ signal vs. time on 2015-11-30. Amplification agent: CO, 11/min sampling flow, 6ppm NO mixing ratio



Figure 32: NO₂ luminol detector sensitivity calibration NO₂ mixing ratio vs. signal on 2015-11-30.

Amplification agent: CO, 11/min sampling flow, 6ppm NO mixing ratio



Figure 33: NO₂ luminol detector sensitivity calibration NO₂ signal vs. time on 2015-11-27. Amplification agent: CO, 11/min sampling flow, 9ppm NO mixing ratio

1.3

12:14

12:21

12:28

12:36



Figure 34: NO₂ luminol detector sensitivity calibration NO₂ mixing ratio vs. signal on 2015-11-27.



Amplification agent: CO, 11/min sampling flow, 9ppm NO mixing ratio

Figure 35: NO₂ luminol detector sensitivity calibration NO₂ signal vs. time on 2015-02-23. Amplification agent: CO, 21/min sampling flow, 6ppm NO mixing ratio

time

12:43

12:50

12:57

13:04

13:12

13:19



Figure 36: NO₂ luminol detector sensitivity calibration NO₂ mixing ratio vs. signal on 2015-02-23. Amplification agent: CO, 2l/min sampling flow, 6ppm NO mixing ratio



Figure 37: NO₂ luminol detector sensitivity calibration NO₂ signal vs. time on 2015-11-24. Amplification agent: C₂H₄, 11/min sampling flow, 3ppm NO mixing ratio







Figure 39: NO₂ luminol detector sensitivity calibration NO₂ signal vs. time on 2015-11-25. Amplification agent: C_2H_4 , 11/min sampling flow, 6ppm NO mixing ratio



Figure 40: NO₂ luminol detector sensitivity calibration NO₂ mixing ratio vs. signal on 2015-11-25. Amplification agent: C₂H₄, 11/min sampling flow, 6ppm NO mixing ratio



Figure 41: NO₂ luminol detector sensitivity calibration NO₂ signal vs. time on 2015-11-26. Amplification agent: C₂H₄, 11/min sampling flow, 9ppm NO mixing ratio



Figure 42: NO₂ luminol detector sensitivity calibration NO₂ mixing ratio vs. signal on 2015-11-26.

Amplification agent: C2H4, 11/min sampling flow, 9ppm NO mixing ratio



Figure 43: NO₂ luminol detector sensitivity calibration NO₂ signal vs. time on 2015-03-05. Amplification agent: C_2H_4 , 2l/min sampling flow, 3ppm NO mixing ratio



Figure 44: NO₂ luminol detector sensitivity calibration NO₂ mixing ratio vs. signal on 2015-03-05. Amplification agent: C₂H₄, 2l/min sampling flow, 3ppm NO mixing ratio



Figure 45: NO₂ luminol detector sensitivity calibration NO₂ signal vs. time on 2015-03-04. Amplification agent: C_2H_4 , 2l/min sampling flow, 6ppm NO mixing ratio



Figure 46: NO₂ luminol detector sensitivity calibration NO₂ mixing ratio vs. signal on 2015-03-04.



Amplification agent: C₂H₄, 21/min sampling flow, 6ppm NO mixing ratio

Figure 47: NO₂ luminol detector sensitivity calibration NO₂ signal vs. time on 2015-11-23. Amplification agent: CH₃CHO, 11/min sampling flow, 3ppm NO mixing ratio



Figure 48: NO₂ luminol detector sensitivity calibration NO₂ mixing ratio vs. signal on 2015-11-23.

Amplification agent: CH3CHO, 11/min sampling flow, 3ppm NO mixing ratio



Figure 49: NO₂ luminol detector sensitivity calibration NO₂ signal vs. time on 2015-11-20. Amplification agent: CH₃CHO, 11/min sampling flow, 6ppm NO mixing ratio



Figure 50: NO₂ luminol detector sensitivity calibration NO₂ mixing ratio vs. signal on 2015-11-20. Amplification agent: CH₃CHO, 11/min sampling flow, 6ppm NO mixing ratio



Figure 51: NO₂ luminol detector sensitivity calibration NO₂ signal vs. time on 2015-11-19. Amplification agent: CH₃CHO, 11/min sampling flow, 9ppm NO mixing ratio



Figure 52: NO₂ luminol detector sensitivity calibration NO₂ mixing ratio vs. signal on 2015-11-19. Amplification agent: CH₃CHO, 11/min sampling flow, 9ppm NO mixing ratio

8.2.2. Ozone and PMT signal maximum determination



Figure 53: PMT signal and NO₂ signal at ozone calibration on 2015-11-28. Amplification agent: CO, 11/min sampling flow, 3ppm NO mixing ratio



Figure 54: PMT signal and NO₂ signal at ozone calibration on 2015-11-30. Amplification agent: CO, 11/min sampling flow, 6ppm NO mixing ratio







Figure 56: PMT signal and NO₂ signal at ozone calibration on 2015-02-23. Amplification agent: CO, 2l/min sampling flow, 6ppm NO mixing ratio



Figure 57: PMT signal and NO₂ signal at ozone calibration on 2015-11-24. Amplification agent: C₂H₄, 11/min sampling flow, 3ppm NO mixing ratio



Figure 58: PMT signal and NO₂ signal at ozone calibration on 2015-11-25. Amplification agent: C₂H₄, 11/min sampling flow, 6ppm NO mixing ratio



Figure 59: PMT signal and NO₂ signal at ozone calibration on 2015-11-26. Amplification agent: C₂H₄, 11/min sampling flow, 9ppm NO mixing ratio



Figure 60: PMT signal and NO₂ signal at ozone calibration on 2015-03-05. Amplification agent: C₂H₄, 2l/min sampling flow, 3ppm NO mixing ratio



Figure 61: PMT signal and NO₂ signal at ozone calibration on 2015-11-23. Amplification agent: CH₃CHO, 11/min sampling flow, 3ppm NO mixing ratio



Figure 62: PMT signal and NO₂ signal at ozone calibration on 2015-11-20. Amplification agent: CH₃CHO, 11/min sampling flow, 6ppm NO mixing ratio



Figure 63: PMT signal and NO₂ signal at ozone calibration on 2015-11-19. Amplification agent: CH₃CHO, 11/min sampling flow, 9ppm NO mixing ratio