Efficiency of the Chemical Amplification Technique for the Measurement and Speciation of Different Mixtures of Peroxy Radicals

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Thesis

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Abstract

Peroxy radicals $(HO_2 \text{ and } RO_2)$ are key intermediates of many tropospheric chemical processes and have a crucial impact in the ozone tropospheric chemistry and in particular in the formation of smog episodes.

Due to their high reactivity, this work was carried out to study the losses of HO_2 and CH_3O_2 radicals on the walls using Peroxy Radical Chemical Amplification (PeRCA), a technique used for measuring the sum of peroxy radicals indirectly. The analysis of the radical losses was characterized to improve the accuracy of the results obtained by this technique, and to propose a suitable method for radical speciation.

For this purpose a setup was designed to determine the radical losses on the walls of glass inlets with different diameters and lengths that have been attached prior to PeRCA reactor. A systematic series of measurements were performed to investigate the dependency of the wall losses, described by the wall loss rate coefficient k_w , on the radical diffusion to the inlet walls, as well as on the geometry of the inlet (length and diameter). Therefore, the radical diffusion coefficients (D_{HO_2} and $D_{CH_3O_2}$) were obtained experimentally and their values were used to calculate k_w for the different inlets.

The results of k_w calculations were compared with empirical values from the literature, and they agree reasonably with the previous studies. Furthermore, the analysis of the results indicates that no efficient speciation for the radicals can be achieved based on the differences of their wall loss rates with respect to the inlet length and diameter.

Table of Contents

Acknowledgementsiii				
Abstract iv				
Table of Contentsv				
List of Tables				
List of Figures				
. Introduction1				
1.1 Problem description				
1.1.1 Radical wall losses				
1.1.2 Radical Speciation4				
1.2 Objectives of this work				
2. Theoretical Background7				
2.1 Radicals in the troposphere				
2.2 Peroxy Radical measurement techniques10				
2.3 Principle of PeRCA				
2.3.1 General factors influencing <i>CL</i>				
3. Experimental21				
3.1 The radical source unit				
3.2 The radical reactor unit				
3.3 The detector unit				
3.4 The calibration procedures				
3.4.1 <i>NO</i> ₂ Calibration				
3.4.2 <i>HO</i> ₂ calibration/ <i>eCL</i> determination				
3.4.3 Determination of the mixing ratio of ozone:				
3.4.4. Determination of absorption cross section of oxygen33				
3.5 Experimental procedure for determining the wall losses				

4.	Results and discussion	37
	4.1 Measurements of the <i>eCL</i>	37
	4.1.1 NO ₂ calibrations	38
	4.1.2 HO ₂ /RO [*] ₂ Calibrations	42
	4.2 Analysis of the <i>eCL</i>	43
	4.2.1 Variation of the <i>eCL</i> with <i>RH</i> and with inlet length	49
	4.2.2 Variation of the <i>eCL</i> with the length of the inlet	57
	4.3 <i>D</i> and k_w calculations	60
	4.4 The effect of the inlet diameter on <i>eCL</i>	69
	4.5 Error Analysis	71
5.	Summary and conclusions	76
Bibliography		

List of Tables

Table 3.1: Main components of the radical source and their function			
Table 4.1: Calculation of NO_2 mixing ratio with respect to the deviations of the flow			
controllers			
Table 4.2: Relative errors of the water mixing ratios for different relative humidity			
and different inlet lengths during the experiments for 5 and 2.5 cm			
inlets53			
Table 4.3: The effect of the oxygen cross section on <i>eCL</i>			
Table 4.4: Ozone mixing ratios with respect to the PMT signal.			
Table 4.6: Calculation of k_w and the associated wall losses as a function of the inlet			
length with $4mm ID$, $D_{HO_2} = 0.02 \ cm^2/s$, and $D_{CH_3O_2} = 0.014 \ cm^2/s$			
Table 4.7: Comparison of k_w between this work and a previous study			

List of Figures

Figure 2.1 the amplification and background modes of the PeRCA system12				
Figure 2.2 some factors that influence the CL (Reichert et al., 2003; Clemitschaw et				
al., 1997; Kartal, 2009)20				
Figure 3.1 Schematic diagram of the set up used at IUP-UB for the present work.21				
Figure 3.2 A view of the humidifier for wetting the synthetic air24				
Figure 3.3 PeRCA radical source used at IUP-UB Bremen (Kartal, 2009)25				
Figure 3.4: The reactor unit where the chemistry is taking place. The reactor and its				
inlet are covered by an aluminum sheet to prevent the photolysis of NO_2 .				
Figure 3.5 the inner parts of the detector unit with an illustration of the air and				
luminol flows (Kartal, 2009)29				
Figure 3.6: Obtaining the effective chain length was obtained for different inlet				
lengths				
Figure 4.1: Schematic representation of the processes involved in the determination of				
the <i>eCL</i>				
Figure 4.2: Temporal response of NO_2 detector during a NO_2 calibration				
Figure 4.3: Linear relationship between NO_2 mixing ratios and the detector signal in				
volts				
Figure 4.4: A smoothed linear relationship between NO_2 mixing ratios and the				
detector signal in volts42				
Figure 4.5: Example of the HO_2 calibration. The slope corresponds to the value of the				
<i>eCL</i> 43				

Figure 4.6: Variation of eCL (for both HO_2 in blue and $HO_2 + CH_3O_2$ in red) versus
RH for an inlet with 4mm ID and 25 cm length44
Figure 4.7: Variation of eCL (for both HO_2 in blue and $HO_2 + CH_3O_2$ in red) versus
RH for an inlet with 4mm ID and 20 cm length45
Figure 4.8: Variation of eCL (for both HO_2 in blue and $HO_2 + CH_3O_2$ in red) versus
RH for an inlet with 4mm ID and 15 cm length45
Figure 4.9: Variation of eCL (for both HO_2 in blue and $HO_2 + CH_3O_2$ in red) versus
RH for an inlet with 4mm ID and 5 cm length46
Figure 4.10: Variation of eCL (for both HO_2 in blue and $HO_2 + CH_3O_2$ in red) versus
RH for an inlet with 4mm ID and 2.5 cm length46
Figure 4.11: Variation of eCL (for both HO_2 in blue and $HO_2 + CH_3O_2$ in red) versus
RH for an inlet with 1mm ID and 20 cm length47
Figure 4.12: Variation of eCL (for both HO_2 in blue and $HO_2 + CH_3O_2$ in red) versus
RH for an inlet with 1mm ID and 15 cm length48
Figure 4.13: Variation of eCL (for both HO_2 in blue and $HO_2 + CH_3O_2$ in red) versus
RH for an inlet with 1mm ID and 5 cm length48
Figure 4.14: Variation of eCL (for both HO_2 in blue and $HO_2 + CH_3O_2$ in red) versus
RH for an inlet with 1mm ID and 2.5 cm length49
Figure 4.15: Experimental calibrations for pure HO_2 using 4mm ID, showing the
variation of the eCL with the length of the inlet
Figure 4.16: Calibrations for the radical mixture using 4mm ID inlet, and how the
eCL is changing with different inlet lengths
Figure 4.17 the intensity measured by the photomultiplier (<i>PMT</i>) in volts and the NO_2
signal from the detector in volts when the shutter is on/off54

Figure 4.18: Calibrations for pure HO_2 (left side) and mixture (right side) using inlet			
with 1mm ID, and the change of eCL with different inlet lengths56			
Figure 4.19: Relation between eCL and inlet length at dry conditions (4% RH) for			
both pure HO_2 , and mixture (<i>Mix</i>) using two different internal diameters			
(4mm ID and 1mm ID) of the inlet			
Figure 4.20: Relation between eCL and inlet length at 20% <i>RH</i> for both pure HO_2 ,			
and mixture (Mix) using two different internal diameters (4mm ID and			
1mm ID) of the inlet			
Figure 4.21 Relation between eCL and inlet length at 40% RH for both pure HO_2 , and			
mixture (Mix) using two different internal diameters (4mm ID and			
1mm ID) of the inlet			
Figure 4.22 Relation between eCL and inlet length at 60% RH for both pure HO_2 , and			
mixture (Mix) using two different internal diameters (4mm ID and			
1mm ID) of the inlet			
Figure 4.23: Function used for obtaining the diffusion coefficient for pure HO_2 using			
different inlet lengths for both inlets with 4 mm ID and 1mm ID. The			
$slope = D^{2/3} = 0.0742$			
Figure 4.24: Function used for obtaining the diffusion coefficient for CH_3O_2 using			
different inlet lengths for both inlets with 4 mm ID and 1mm ID. The			
$slope = D^{2/3} = 0.0583$			
Figure 4.25: Relationship between the eCL and the square of the inlet radius70			

1. Introduction

Peroxy radicals are short lived trace gases playing a crucial role in the ozone tropospheric chemistry and in particular in the formation of smog episodes. The oxidizing capacity of the global Earth atmosphere is mainly controlled by these radicals that have a major impact on the concentration and distribution of greenhouse gases such as CH_4 , O_3 , H_2O ...etc. Thus, understanding the variability of these radicals is very important to evaluate human impacts on the atmosphere and climate (Wayne, 2000). The low concentration and short lifetime of the peroxy radicals require sensitive techniques to measure them. Several direct and indirect methods were developed since decades trying to determine the mixing ratios of several mixtures of peroxy radicals in the air.

The Peroxy Radical Chemical Amplification, (PeRCA), is an indirect technique for measuring peroxy radicals in either ground based or airborne measurements. The simplicity and low cost of this technique make it favorable to use, therefore several developments have been done to improve its efficiency (Cantrell et al., 1982; Reichert et al., 2003; Clemitshaw et al., 1997; Hastie et al., 1991). The Institute for Environmental Physics of the University of Bremen, (IUP-UB), is one of the leading institutes that deal with the development of PeRCA. In fact, several improvements of PeRCA have been achieved at this Institute through either airborne campaigns or laboratory experiments.

This work has been carried out at the IUP-UB for studying particular issue in PeRCA method regarding the radical losses on the walls, and the potentiality of this technique for the speciation of the radicals based on these losses. Several measurements were performed in the laboratory, and different analyses were carried out for this purpose. The structure of this work consists of the following chapters:

- 1. **Introduction**: A general description about the peroxy radicals, their wall losses and the state of art of the radical's speciation are presented in this chapter. Also the objectives of this work are introduced.
- 2. Theoretical back ground: In this chapter, the chemistry of the radicals, their role in the atmosphere and the state of art of their measurement techniques are discussed. In addition, the principle of PeRCA, the associated chemical reactions as well as the factors influencing its results are described in detail.
- 3. **Experimental**: In the experimental chapter, the setup of PeRCA used in this work is presented with the calibration procedures that have been done in the laboratory. In addition the experimental approach to achieve the objectives of the work is described.
- 4. Results and discussion: In chapter four, all the results of the calibrations of this work as well as the associated calculations are presented. Furthermore, observations and analyses of the data are discussed in detail. The error analysis of the results is provided as well.
- 5. **Summary and conclusions**: Finally the summary of the whole work is described in the last chapter with some recommendations for future work.

1.1 Problem description

The basic principle of PeRCA is the conversion of $RO_2^*(HO_2 + \sum RO_2)$ radicals into NO_2 , where R is an organic chain. As will be described in chapter 2, this conversion is achieved by a series of reactions that lead to NO_2 and CO_2 from the radicals, where the produced NO_2 molecules can be related to the concentration of the reacted radicals. Moreover, some termination reactions take place during this process leading to stopping the radical conversion.

One of these termination reactions is the loss of the radicals on the reactor walls of PeRCA instrument. The wall loss reaction plays a considerable role that affects the final radical conversion by this technique (Hastie et al., 1991). In this context, one of the objectives of this work is to determine the rate coefficient that describes these losses. In parallel, since PeRCA measures the sum of the peroxy radicals in the troposphere, determining the rate coefficients of the wall losses of different radicals could lead to a suitable method for achieving radical speciation as a second scope of this work.

1.1.1 Radical wall losses

In general, considering different radicals in an air flow entering a tube, different collisions will occur between the radicals themselves and also on the walls of the inner tube. As a result, these radicals will diffuse and be removed differently on the walls. This reaction with the wall can be controlled by several factors such as the velocity of the flow, the chemical nature and the reactivity of the radicals, the geometry of the tube, and the temperature and pressure.

The removal of radicals on the walls is a first-order reaction $(RO_2^* + walls = nonradical)$. The progress of this reaction is described by the wall loss rate coefficient (k_w) , where the following empirical equation (Eq. 1.1) can be used for calculating this coefficient (Hayman, 1997).

$$k_w = 1.85 * \left(\frac{v^{1/3}D^{2/3}}{d^{1/3}l^{1/3}}\right) * \frac{S}{V}$$
 Eq. 1.1

where k_w is the wall loss rate coefficient (s^{-1}) , v is the velocity of the air flow entering the inlet (cm/s), D is the diffusion coefficient of the radicals (cm^2/s) , d is the inner diameter of the inlet (cm), l is the inlet length (cm), and S/V is the surface to volume ratio of the inlet (cm).

As a consequence of the wall losses not all the radicals will be converted into NO_2 and they will destruct on the walls and give non radical products. Since the PeRCA technique measures the total radical mixture ($RO_2^* = HO_2 + \sum RO_2$), calculating the wall loss rate coefficient for each type of peroxy radicals is not straightforward.

1.1.2 Radical Speciation

As stated before, peroxy radicals have an essential contribution to the atmospheric chemistry especially to oxidation processes. Therefore, it is important to study the role of these radicals separately in their mixtures to have a clear picture about their contribution to the atmospheric processes and to precisely determine their sources.

Several studies tried to develop different techniques for the selective measurements of peroxy radicals. One of these studies used a laser-induced fluorescence instrument (LIF) for this goal (Fuchs, 2008). Two conversion modes are involved in this study. The first mode converts the atmospheric radical mixture $(RO_2 + RO + OH + HO_2)$ to HO_2 by adding *NO* and *CO* at reduced pressure which is then converted to *OH* through further reaction with *NO* and detected by LIF instrument. In the second mode, only *CO* is added to convert HO_2 and *OH* from the mixture into HO_2 and further detected following the same process. However, the sensitivity of this technique is dependent on the rate of the ambient air pollution, where in high polluted air, the interference of the RO_2 being converted into HO_2 during the HO_x mode, affected by the *NO* concentration

in the ambient air, would exceed 5% for equal amounts of HO_2 and RO_2 if the NO concentration is higher than 25 *ppbv* in the ambient air.

Another technique used for the quantification of peroxy radicals is the Peroxy Radical Chemical Ionization Mass Spectrometer (PerCIMS) (Edwards, 2003). In this study, peroxy radicals $(HO_2 + RO_2)$ are converted and amplified into an HSO_4^- ion by adding NO and SO_2 reagent gases. The quantification of the radicals is achieved using two modes, one for HO_2 only and the other for the radical mixture. These modes are controlled by changing the concentration of the reagent gases. Also this technique has limitations in the efficiency of RO_2 and HO_2 detection, where the interference of the converted RO_2 into HO_2 during the HO_2 mode depends on the NO concentration presented in the ambient air.

Furthermore, selective measurements of different peroxy radicals were investigated using PeRCA-LIF technique (Miyazaki, et al., 2010), where a pre-inlet filled with glass beads was used for the quantification of HO_2 and CH_3O_2 . As a result, a successful removal of 90 % of HO_2 was achieved while the loss of CH_3O_2 was only 15%. This technique provides promising improvement to the selective measurements of HO_2 and CH_3O_2 radicals, but it needs further developments in order to study the removal efficiency for other organic peroxy radicals.

1.2 Objectives of this work

The main objective of this work is to study all the parameters influencing the radical wall losses during the sampling, and the dependency of the wall loss rate k_w on these parameters. For this goal, pre-reactor inlets made of glass with different lengths and diameters have been attached to the reactor where the conversion of radicals take place and the net degree of radical conversion have been investigated.

Several measurements for pure HO_2 and a mixture of $50\% HO_2 + 50\% CH_3O_2$ have been done based on the inlet geometry changes and the results have been used to calculate experimentally the diffusion coefficients for both HO_2 and CH_3O_2 (D_{HO_2} and $D_{CH_3O_2}$). Using the obtained diffusion coefficients, k_w has been calculated for different lengths and diameters of the inlet.

A second objective of this work is to study the possibility of the radical speciation based on the differences of their wall losses. If there were significant differences of the loss rate between these radicals, it would be possible to define a suitable method for the radical speciation with a defined geometry of the inlet.

2. Theoretical Background

In this chapter, the importance of peroxy radicals and their role in the atmosphere are described and some of the techniques that are used for the measurements of peroxy radicals are presented. In addition, the principle of PeRCA technique is described, and the major factors and parameters that affect the process in this technique are clarified.

2.1 Radicals in the troposphere

The chemistry of the troposphere is highly dependent on the radicals such as peroxy radicals (hydroperoxyl HO_2 , and organylperoxyl RO_2). These short lived species have a special influence into the tropospheric chemistry with the involvement in some of the tropospheric processes such as hydrocarbons oxidation, acid formation, and especially through the participating in the production and loss mechanisms of ozone (O_3). The contribution to ozone production occurs by the reaction of peroxy radicals with nitrogen oxide (NO) producing nitrogen dioxide (NO_2) which is then the source of ozone in the troposphere through its photolysis.

$$HO_2 + NO \rightarrow OH + NO_2$$
 R. 2.1

$$RO_2 + NO \rightarrow RO + NO_2$$
 R. 2.2

$$NO_2 + hv (\lambda < 420mm) \rightarrow NO + O(^3P)$$
 R. 2.3

$$O({}^{3}P) + O_2 \to O_3$$
 R. 2.4

Reactions R. 2.1 to R. 2.4 predominate at high concentrations of $NO_x = NO + NO_2$ (in polluted areas). While when the NO_x concentration is low, peroxy radicals deplete ozone:

$$HO_2 + O_3 \rightarrow OH + 2O_2 \qquad \qquad \text{R. 2.5}$$

$$OH + O_3 \rightarrow HO_2 + O_2 \qquad \qquad \text{R. 2.6}$$

$$2O_3 \rightarrow 3O_2 \qquad \qquad \text{R. 2.7}$$

The major sources of peroxy radicals in the atmosphere are the oxidation reactions of CO, CH_4 or VOCs by OH. CO reacts with OH (R. 2.8) leading to HO_2 .

$$OH + CO + O_2 \rightarrow HO_2 + CO_2$$
 R. 2.8

Similarly, CH_4 is oxidized by OH by the following reactions (R. 2.9 to R. 2.14) to produce NO_2 .

$$CH_4 + OH \rightarrow CH_3 + H_2O$$
 R. 2.9

$$CH_3 + O_2 + M \rightarrow CH_3O_2 + M \qquad \text{R. 2.10}$$

$$CH_3O_2 + NO \rightarrow CH_3O + NO_2 \qquad \text{R. 2.11}$$

$$CH_3O_2 + O_2 \rightarrow HCHO + HO_2$$
 R. 2.12

$$HO_2 + NO \rightarrow OH + NO_2$$
 R. 2.13

$$2(NO_2 + hv (\lambda < 420mm) \rightarrow NO + O({}^{3}P))$$
 R. 2.3

$$2(O(^{3}P) + O_{2} \to O_{3})$$
 R. 2.4

Net:
$$CH_4 + 4O_2 + hv \rightarrow HCHO + 2O_3 + H_2O$$
 R. 2.14

The previous reactions are an example describing the formation of HO_2 , RO, RO_2 through the hydrocarbons (CH_4 in this example) oxidation by OH.

Moreover, there are some reactions that lead to the loss of peroxy radicals in the troposphere. For example, in clean air, the self-reactions of the peroxy radicals dominate as following:

$$HO_2 + HO_2 + M \to H_2O_2 + O_2$$
 R. 2.15

$$CH_3O_2 + HO_2 \to CH_3O_2H + O_2$$
 R. 2.16

$$CH_3O_2 + CH_3O_2 \rightarrow 2CH_3O + O_2$$
 R. 2.17

The washout of the resulted peroxides is a sink of peroxy radicals.

Clearly, the more accurate the understanding of the chemistry of the peroxy radicals is, the better the understanding of some tropospheric chemical cycles will be.

2.2 Peroxy Radical measurement techniques

Due to the importance of peroxy radicals for the chemistry of the troposphere, some studies were developed for peroxy radical measurements. In fact, these studies are few because of the difficulties of measuring the existing trace concentrations in the troposphere. Mainly there are two types of techniques used in radical measurements, direct and indirect techniques.

- The Matrix Isolation and Electron Spin Resonance (MIESR) is a direct technique that is used for ground base measurement of the radicals. In this technique, the radicals' concentrations are trapped in an ice matrix condensed at liquid nitrogen temperature. These trapped radicals are then analyzed in the laboratory using ESR. The measured spectra by the ESR are compared with a laboratory prepared spectra for different radicals to identify the radicals in the trapped matrix (Mihelcic et al., 1985; 1990).
- Another technique that uses an indirect method for detecting the radicals is the Proton Transfer Reaction Mass Spectrometry (PTR-MS). The principle of this method is a chemical ionization of the radicals using H_3O^+ ions to transfer a proton to the analyst, and to use mass spectrometric detection (Hansel et al., 1995).
- The Laser-Induced Fluorescence (LIF) is a technique that uses an indirect method for measuring *OH/HO*₂ radicals using a low pressure fluorescence detection cell. The principle of this method is converting *HO*₂ to *OH* by adding *NO* to the ambient air which is expanded through a nozzle into low pressure detection chamber. The converted *OH* is then excited using a laser beam at 308 *nm* and its fluorescence signal is measured (Hard et al., 1984; Kanaya et al., 2000).

Furthermore, an indirect technique which is being used in this work, created and developed by Cantrell and Stedman (Cantrell et al., 1982; 1984), is the peroxy radical chemical amplification technique (PeRCA). This technique is a simple method for measuring the total sum of peroxy radicals RO₂^{*} = HO₂ + ∑RO₂. Being a portable technique makes it applicable for ground based and airborne measurements. Moreover, PeRCA has been thoroughly characterized and calibrated through several studies such as (Hastie et al., 1991; Clemitshaw et al., 1997).

2.3 Principle of PeRCA

The main principle of PeRCA of converting RO_2^* radicals to a large number of NO_2 molecules using a chemical amplifier system is described by the following reactions for the conversion of HO_2 radicals :

$$HO_2 + NO \rightarrow OH + NO_2$$
 R. 2.1

$$OH + CO + O_2 \rightarrow HO_2 + CO_2$$
 R. 2.8

where *NO* is being oxidized to NO_2 and *CO* to CO_2 . The amplification factor that describes the yield of NO_2 molecules produced by this conversion is called chain length (*CL*).

In the case of RO_2 radicals, CH_3O_2 as an example, the following reactions take place by which CH_3O_2 is converted to HO_2 which leads to NO_2 .

$$CH_3O_2 + NO \rightarrow CH_3O + NO_2$$
 R. 2.11

$$CH_3O + O_2 \rightarrow CH_2O + HO_2$$
 R. 2.18

To achieve this conversion and the measurement of NO_2 , the measurement consists of three main levels: addition of reagent gases (*CO* and *NO*) conversion reactions in the reactor, and detection of NO_2 at the detector.

In order to discriminate the NO_2 that is coming from other sources than the conversion (such as the NO_2 that exists already in the air, or what comes from the reaction of O_3 in the ambient air with NO added in the reactor) from the yield NO_2 molecules from the radical conversion reactions, the reactor works in two modes as shown in the next figure (Figure 2.1), the amplification mode and the background mode.



Figure 2.1: The amplification and background modes of the PeRCA technique.

The amplification mode introduces NO + CO in the first addition point in the top of the reactor, and N_2 in the second at the bottom of the reactor. Therefore, the conversion reactions take place and the NO_2 molecules are detected as a signal in volts (Figure 2.1). In the background mode, $NO + N_2$ enter the first addition point, and CO enters the second. In this case, there will be no conversion reaction and the NO_2 molecules that are detected are coming from the reaction of ozone with NO or NO_2 that exists in the ambient air or anything else which could produce NO_2 in the way inside the reactor, and give a signal in volts.

The chain reaction is terminated by some reactions, the so called terminating reactions, as following:

$$HO + NO + M \rightarrow HONO + M$$
 R. 2.19

$$HO + NO_2 + M \rightarrow HNO_3 + M$$
 R. 2.20

$$HO_2 + NO_2 + M \rightarrow HO_2NO_2 + M$$
 R. 2.21

$$HO_2 + HO_2 + M \to H_2O_2 + O_2$$
 R. 2.15

$$HO_2 + wall \rightarrow nonradical products$$
 R. 2.22

These reactions also exist in the alkylradicals, and in the case of CH_3O_2 , that leads to a 0.85 factor of the chain length of HO_2 . This is because of the fact that *RO* radicals (such as CH_3O that comes from R. 2.11) have a high possibility of reacting with *NO* and producing stable alkyl nitrate instead of undergoing conversion reaction into HO_2 (R. 2.23):

$$RO + NO + M \rightarrow RONO + M$$
 R. 2.23

Or for CH_3O :

$$CH_3O + NO + M \rightarrow CH_3ONO + M$$
 R. 2.24

2.3.1 General factors influencing CL

The chain length (*CL*) of the chain reaction amplifying RO_2^* radicals to NO_2 molecules can be defined as:

$$CL = \frac{\Delta[NO_2]}{[HO_2] + \sum[RO_2]}$$
Eq. 2.1

where $\Delta[NO_2]$ is the difference in the NO_2 concentration due to the amplification process, and $[HO_2] + \sum [RO_2]$ is the sum of peroxy radical concentrations entering the reactor of PeRCA instrument.

Some parameters influence the chain length such as the concentration of the reagent gases (*NO* and *CO*), the reaction time in the reactor, temperature, pressure, relative humidity, and any radical removal processes. The factor which is being studied in this work is the geometry of the inlet of the reactor and thus the wall losses and diffusion coefficients associated with its change.

• Radical wall losses and diffusion coefficients

The *CL* decreases with the increase of the radical losses on the walls of the PeRCA instrument. These losses are influenced by several factors such as: the material and shape of the reactor, the surface to volume ratio, and as a result the velocity and retention time of the gas flow as shown in Eq. 1.1. The removal of the radicals on the

walls is described by the wall loss reaction rate coefficient k_w which is expressed using the following exponential equation for a first order reaction (Eq. 2.2):

$$[RO_2^*(t)] = [RO_2^*(0)] \times \exp(-k_w t)$$
 Eq. 2.2

where the radical mixing ratio $[RO_2^*(t)]$ after a time t can be calculated from the initial radical mixing ratio entering the reactor $[RO_2^*(0)]$ if k_w is known.

Moreover, the radical wall losses depend on the composition, i.e. nature of the peroxy radicals that are measured and also on the geometry of the reactor. If there is an inlet attached to the reactor, then the losses will depend on its geometry, i.e. length and diameter. Therefore, it is important to characterize the radical wall losses for different geometries of the inlet and also for different mixtures of peroxy radicals.

The effect of changing the length of the inlet should be the result of changing the velocity and the residence time of the radicals in the inlet. This can be seen from the following equations:

$$v = \frac{F}{A}$$
Eq. 2.3
$$t = \frac{l}{v}$$
Eq. 2.4
$$t = \frac{lA}{F}$$
Eq. 2.5

where F is the air flow through the inlet (l/min), v is the velocity of the air (cm/s), t is the retention time of the flow (s), l is the inlet length (cm), A is the internal area of the inlet (cm^2) .

Moreover, k_w is proportional to the surface to volume ratio of the tube (*S*/*V*) and given by the following relationship (Eq. 2.6):

$$k_w = c \frac{S}{V}$$
 Eq. 2.6

The constant c is proportional to the diameter of the flow tube d and the diffusion coefficient D through Sherwood number Sh:

$$c = Sh \frac{D}{d}$$
 Eq. 2.7

And the Sherwood number could be described by Reynolds and Schmidt numbers, *Re* and *Sc* respectively:

$$Re = \frac{\rho v d}{\eta}$$
Eq. 2.8
$$Sc = \frac{\eta}{\rho D}$$
Eq. 2.9

Where ρ the gas density, v is the gas velocity, and η is the gas viscosity. From the previous relations (Eq. 2.6 \rightarrow Eq. 2.9) results the Eq. 1.1:

$$k_w = 1.85 \times \frac{v^{\frac{1}{3}} D^{\frac{2}{3}}}{l^{\frac{1}{3}} d^{\frac{1}{3}}} \times \frac{S}{V}$$
 Eq. 1.1

The diffusion coefficient *D* describes the collision and the destruction of the radicals on the walls. As this destruction is described by a first order reaction (Eq. 2.2), then there must be a relation between the wall loss rate coefficient and the diffusion coefficient of the radical. In fact, several studies have been done to estimate the diffusivities in gaseous systems (Gilliland, 1934; Arnold, 1930; Wilke et al., 1955) based on a general expression starting with the Stefan-Maxwell hard sphere model derived from the kinetic theory of the gases (Sutherland, 1894).

Arnold (Arnold, 1930) suggested equation Eq. 2.10 as a reference for estimating the diffusion coefficient from the boiling temperature of the substances and their molecular volumes:

$$D = \frac{0.00837\sqrt{\frac{1}{M_1} + \frac{1}{M_2}}}{(V_1^{\frac{1}{3}} + V_2^{\frac{1}{3}})^2} (\frac{T^{\frac{5}{2}}}{(T+C)})$$
 Eq. 2.10

where;

C is Sutherland constant,

 V_1 , V_2 are the molecular volumes for the constituents 1 and 2,

T is the boiling temperature,

 M_1 , M_2 are the molecular weight of the molecules 1 and 2.

Also, in another study, Gilliland (Gilliland, 1934) developed an empirical equation assuming that the collision diameters are proportional to the cube roots of the molar volumes at normal boiling temperature T.

In addition, a study by Fuller et al, (Fuller et al., 1966) showed a high correlation between the methods used for the estimation of the diffusion coefficient and suggested a new empirical method based on the previous studies. The following formula (Eq. 2.11) is suggested to be simple, wide applicable, and has a higher accuracy:

$$D = \frac{1.00 \times 10^{-3} T^{1.75} \sqrt{\frac{1}{M_A} + \frac{1}{M_B}}}{(V_A^{\frac{1}{3}} + V_B^{\frac{1}{3}})^2 P}$$
Eq. 2.11

where the constant 1.00×10^{-3} was derived empirically.

• The effect of some other factors on CL

The effect of changing *CO* or *NO* concentrations on *CL* is significant and has been studied in detail (Ashbourn et al., 1998; Clemitshaw et al., 1997). It has been observed that at *CO* constant, the *CL* increases with *NO* mixing ratio until it reaches a maximum at 5 - 6 ppm NO. This occurs due to the fact that the increase of *NO* favors the reaction (R. 2.1) and gives higher *CL*. After that, R. 2.19 dominates which leads to the decrease of *CL*.

On the other hand, an increase in *CL* is observed with *CO* as the termination reaction (R. 2.19) dominates for low *CO* mixing ratios. Then, the increase of [*CO*] favors R. 2.8 relative to reaction R. 2.19 having more of the peroxy radicals and higher *CL* as a result. After that, having more HO_2 radicals will favor reactions R. 2.1 and R. 2.21, and R. 2.15 (loss reaction) more than the reaction R. 2.8 and the loss reaction R. 2.19. Further increase of *CO* mixing ratio higher than $\sim 7 - 9\%$ is not advisable because it is explosive above 10 %.

Furthermore, it has been shown (Hastie et al., 1991) that the reaction time has a significant effect on chain length at very short retention times in the reactor. An increase

of *CL* has been observed up to a reaction time $\sim 1 \ s$. After that, the increase of the reaction time in the reactor has almost no further effect on the chain length.

Moreover, the chemical nature of the peroxy radical plays a crucial role in the determination of the *CL*. Before reacting in the chemical reactor, the destruction of HO_2 radicals on the walls is expected to be higher than the same reaction in case of RO_2 . This is because of the higher polarity and reactivity of HO_2 radicals. This affect the resulting *CL* (see *eCL* in chapter 3) of the corresponding radical differently depending on the shape and nature of the inlet of the reactor used.

Another important factor affecting the *CL* significantly is the relative humidity (*RH*). It has been observed that the *CL* decreases with increasing *RH*. This behaviour is still not fully explained but some reactions involving $HO_2 - nH_2O$ dimers and *CO* or *NO* might be a reason for this tendency (Mihele et al., 1998; Reichert et al., 2003), where some non-radical products are produced (e.g. HNO_3) (R. 2.20, R. 2.21, R. 2.22).

The following figure (Figure 2.2) describes how the different parameters have an influence on the CL as they have been explained in this chapter.



Figure 2.2: Factors affecting *CL* (Reichert et al., 2003; Clemitshaw et al., 1997; Kartal, 2009).

3. Experimental

The study of the efficiency of the conversion of peroxy radicals and the calculation of the chain length in the laboratory require producing a known concentration of peroxy radicals to be converted into NO_2 . The Figure 3.1 illustrates the general scheme of the set up used at IUP-UB for carrying out the present work. Peroxy radicals are produced at the radical source from the photolysis of water as explained below.



Figure 3.1 Schematic diagram of the set up used at IUP-UB for the present work.

According to Figure 3.1, the operation of PeRCA in general starts by humidifying a certain synthetic air flow which enters the humidifier in parallel with *CO* or CH_4 . In the radical source, the photolysis of water occurs and the peroxy radicals are produced (see R. 3.1, R. 3.2, R. 2.8, R. 2.9, and R. 2.10). By sucking 2 *l/min* of the air using an

exhaust flow controller, the xRO_2^* radicals produced from the source enter the glass inlet before the reactor, where they collide, diffuse, and destruct on the walls of the inlet.

Then, the yields radicals $x - nRO_2^*$ enter the reaction zone where they react with *NO* and *CO* molecules which enter the reactor continuously via reactions (R. 2.1, R. 2.8, and R. 3.1). The *NO*₂ molecules that are produced will be then added to a certain offset of *NO*₂ and be detected, and finally the effective chain length (*eCL*) is determined. *eCL* is the measured chain length that combines the chain length in the reactor (*CL*) and the losses in the inlet. Moreover, a specific system is used for the data acquisition and the control of the process.

In this work, the concentrations of the reagent gases are kept constant and also the material and shape of the reactor. Therefore, CL in the zone where the chemistry is taking place is considered to be the same (Figure 3.1) and the change in the effective chain length (*eCL*) which is measured is considered to be only because of changing the geometry of the inlet before the radicals enter the reactor.

The units that contribute together to the amplification process of PeRCA which are illustrated in Figure 3.1 are described in detail in this chapter. The starting point is the production of the radicals, and then the reactions are taken place in the reactor to produce NO_2 molecules that are detected to obtain the *eCL*. In addition, this chapter describes the calibrations that have been done for obtaining the effective chain length for the different mixtures of peroxy radicals.

3.1 The radical source unit

The calibration/source unit is used for producing peroxy radicals. The radicals are produced by the photolysis of water at wavelength 184.9 nm in the presence of the oxygen (Schultz et al., 1995). As it is shown by reactions R. 3.1, R. 3.2, R. 2.8, the

hydrogen *H* and hydroxyl *OH* atoms that are produced from the photolysis will react with O_2 and *CO* respectively to produce HO_2 .

$$H_20 + hv(\lambda = 184.9 \text{ nm}) \rightarrow H + H0$$
 R. 3.1

$$H + O_2 + M \rightarrow HO_2 + M \qquad R. 3.2$$

$$CO + OH \xrightarrow{O_2} HO_2 + CO_2$$
 R. 2.8

Adding methane (CH_4) instead of *CO* will give a radical mixture consisting of 50% HO_2 +50% CH_3O_2 where the hydroxyl atoms *OH* will react with CH_4 to produce the methyl peroxide molecules CH_3O_2 .

$$CH_4 + OH \rightarrow CH_3O + H_2O$$
 R. 2.9

$$CH_3O + O_2 + M \to CH_3O_2 + M$$
 R. 2.10

The radical source consists of a cell made of quartz where the water and the calibrated air are mixed by pumping water into the air flow using a peristaltic pump, and therefore the synthetic air gets wet (Figure 3.2).



Figure 3.2 A view of the humidifier for wetting the synthetic air.

For *RH* below 10%, the relative humidity of the wetted air is controlled by the velocity of peristaltic pump and measured with a dew point sensor (Vaisala DMP 248). For higher *RH*, a mixed flow of the dry and wet air is controlled using a liquid pump and a humidifier. The consequent humidified air goes to the photolysis zone, and there the radicals will be produced.

Figure 3.3 describes the internal parts of the radical source that is used in the laboratory.



Figure 3.3 PeRCA radical source used at IUP-UB Bremen (Kartal, 2009).

The radical source consists of the components described in the following table (Table 3.1) associated with their function:

Table 3.1: Main components of the radical source and their function.

Component	Function
Hg-lamp	This lamp is used for the photolysis of water at 184.9 <i>nm</i> emission wavelength of the mercury vapor. It is installed in a block that is kept at constant temperature (by warming up the lamp using a heater before starting the experiment) to avoid variations in the lamp profile as the lamp spectrum is sensitive to the operation conditions of the lamp. A shutter permits or blocks the light coming from the lamp.
Cylindrical lens	It is used to parallelize the light beam coming from the lamp.
Absorption cell	This cell is between the lamp and the photolysis area and confined by quartz glass windows. To generate different concentrations of peroxy radicals, the intensity of the light at the absorption cell has to be changed while adding a constant mixing ratio of water in the synthetic air. This is achieved by the injection of a gas mixture of $N_2O + N_2$ through the absorption cell and this gas filter leads to the reduction of the intensity leading to different mixing ratios of the radicals. Nitrous oxide N_2O is an inert gas that can reduce the intensity to 90% (Cantrell et al., 1997).
Photolysis zone	This zone is a part of a cylindrical quartz tube (20 <i>cm</i> length and 16 <i>mm</i> inner diameter) under the influence of the light emitted by the lamp where H_2O , synthetic air and <i>CO</i> enter and the photolysis reactions take place.
Interference filter	This filter lets the wavelength of interest at 184.9 nm to transmit
	through and blocks the rest.
Photomultiplier	A photomultiplier Hamamatsu 1259 with MgF_2 window and spectral response between $115 - 195 nm$ is used for the detection of the attenuated intensity.

Before the humidified air enters the photolysis zone, *CO* (or *CH*₄) is added to mix with the air so as to react with *OH* that will be produced from the photolysis reaction of water and give the peroxy radicals instead of getting lost on the walls. At the same time, ozone molecules are produced from the photolysis of oxygen at the same wavelength $(\lambda = 184.9 \text{ nm})$ (R. 3.3 and R. 3.4):
$$O_2 + hv \ (\lambda = 184.9 \ nm) \rightarrow O(^3P) + O(^3P)$$
 R. 3.3

$$O(^{3}P) + O_{2} \to O_{3}$$
 R. 3.4

The mixing ratio of the yield peroxy radicals $[HO_2]$ or $[RO_2]$ is calculated using Eq. 3.1:

$$[HO_2] = \frac{\sigma_{H_2O}^{184.9nm} * [H_2O]}{\sigma_{O_2}^{184.9nm} * [O_2]} * [O_3]$$
Eq. 3.1

where:

 $\sigma_{H_2O}^{184.9nm}$ is the water absorption cross section at 184.9 nm that is used as $7.14 * 10^{-20} cm^2 molecule^{-1}$ (Cantrell et al., 1997; Hofzumahaus et al., 1997), $[H_2O]$ is the water mixing ratio calculated from a dew point sensor measurements, $[O_2]$ is the mixing ratio of the oxygen that is known from the synthetic air cylinder, $\sigma_{O_2}^{184.9nm}$ is the oxygen absorption cross section at 184.9 nm, and $[O_3]$ is the mixing ratio of ozone. Both $\sigma_{O_2}^{184.9nm}$ and $[O_3]$ are calculated experimentally.

Eq. 3.1 is derived from the integration of the change of the concentration of HO_2 and O_3 as following (Kartal, 2009):

$$\frac{\partial HO_2}{\partial t} = 2 * \Theta^{184.9nm} * \sigma^{184.9nm}_{H_2O} * [H_2O]$$
 Eq. 3.2

$$\frac{\partial O_3}{\partial t} = 2 * \Theta^{184.9nm} * \sigma_{O_2}^{184.9nm} * [O_2]$$
 Eq. 3.3

Where $\Theta^{184.9nm}$ is the photon flux which is the same for both HO_2 and O_3 .

3.2 The radical reactor unit

In this unit (Figure 3.4) the reactions of the radicals with *NO*, and *CO* take place. The standard reactor is made of glass and has an inlet of 2.5*cm* length and 4*mm* inner diameter (*ID*).



Figure 3.4: Reactor unit where the chemistry is taking place. The reactor and its inlet are covered by an aluminum sheet to prevent the photolysis of NO_2 .

The synthetic air enters through the inlet and mix with the mixture of NO, and CO or NO, and N_2 entering through the first addition point. For this, there are 3-way magnet valves that operate the addition of N_2 and CO entering the first and second addition points alternatively for controlling the amplification and background modes (see chapter 2). In addition, there is a NO scrubber which is filled with $FeSO_4$. $7H_2 O$ (Ferrous sulphate hepthahydrate). This scrubber removes NO_2 traces from the NO flow which is mixed then with N_2 or CO and added to the reactor. In the laboratory, the reactor, magnet valves

and the scrubber are installed on a plate and connected to the other units (NO_2 detector, flow controllers...).

3.3 The detector unit

The NO_2 molecules which are produced into the reactor flow with the air to the detector unit as shown in the following figure by the blue arrows (Figure 3.5):



Figure 3.5: Inner parts of the detector unit with an illustration of the air and luminol flows (Kartal, 2009).

The detector has a Whattman fiber filter paper, and a photodiode (Hamamatsu Si-1248). There is a quartz glass which separates the photodiode from the filter paper. In the detector, there is a continue flow of $5 \times 10^{-4} M$ luminol solution ($C_8 H_7 N_3 O_2$) by a peristaltic pump shown in red arrows (Kartal et al., 2010; Wendel et al., 1983).

The detection process is done as following:

- 1. The NO_2 molecules that enter the detector react with the luminol solution on the surface of the filter paper by a chemiluminescence reaction.
- 2. As a result of this reaction, NO_2 molecules emit photons at wavelength 400 500 nm.
- 3. The photons are detected by the photodiode. The resulting signal is amplified, converted to a voltage and digitized, and finally stored in a data acquisition system.

3.4 The calibration procedures

There are two factors defining the sensitivity of the PeRCA instrument. The first factor is the efficiency of converting the radicals into NO_2 , quantified by the *eCL*, and the second is the NO_2 detector performance, quantified by the NO_2 calibrations. Therefore, regular calibrations have to be done for NO_2 response and *eCL* before starting the experiments. These calibrations have to be done under specific conditions of the reactor and the addition gases. Thus, it has been noticed in previous studies that the NO_2 sensitivity becomes nonlinear below 25 *ppb* NO_2 offset in the presence of 3 *ppm* NO (Clemitshaw et al., 1997). Besides that, adding 4-5 ppm NO gives a maximum value of *eCL* as explained in chapter 2 (factors influencing the *CL*). On the other hand, adding *CO* up to 10% does not affect the response of the NO_2 detector. Moreover, adding the same amount of *CO* and N_2 is to avoid pressure variations and as a result keep the mixing ratio the same in the detector. During this work 180 *ml CO*, 180 *ml N*₂, and 10 *ml NO* have

been added and a total of 2 l/min has been sucked through the reactor. The acquisition of the data and the calculations in PeRCA lab has been done using Matlab and Excel.

3.4.1 NO₂ Calibration

 NO_2 calibrations are done to examine the detector response and sensitivity by adding various NO_2 -air mixtures from calibrated air. The response of the NO_2 detector is determined by applying different concentrations of NO_2 and changing the mixing ratio of NO_2 each time (between 45 ppb and 61 ppb), where a volume of NO_2 from its gas cylinder is mixed with a volume of synthetic air. During this work, 50 NO_2 calibrations were done in the laboratory and an example of the results is described in detail in chapter 4.

3.4.2 HO₂ calibration/eCL determination

 HO_2 calibrations are carried out for the determination of the *eCL*, and they consist of the following steps:

- Synthetic air is humidified by pumping water into the air flow (7 *l/min*) inside the source unit (4% *RH*) or mixing wet and dry air for higher *RH* as described previously in section 3.1.
- 2. The humidified air enters the photolysis zone in the source unit. In this area the UV photolysis of water-air mixture is taking place (Error! Reference source not found.) as described in section 3.1. In addition, various N_2O/N_2 mixtures are added in the absorption cell for attenuating the intensity of the Hg-lamp.
- 3. HO_2 radicals are produced according to (R. 3.2)
- 4. *OH* molecules produced from R. 2.1 react with *CO* that is being added continuously (10 *ml* pure *CO*) to produce HO_2 (R. 2.8). Both steps (3 and

4) are enough to convert all the products from the photolysis of H_2O into HO_2 .

Moreover, CH_4 can be added instead of CO to the photolysis zone to get CH_3O_2 that has the same mixing ratios as HO_2 (Error! Reference source not found. and Error! Reference source not found.).

5. The HO_2 radicals generated react with *NO* and *CO* in the reactor to produce NO_2 which signal is detected in the detector.

The mixing ratio of HO_2 can be calculated from (Eq. 3.1) that has been described in section 3.1. During this work, 50 HO_2 calibrations and 50 mixture calibrations were performed in the laboratory and an example of the results are described in chapter 4.

3.4.3 Determination of the mixing ratio of ozone:

During the HO_2 calibration, ozone is produced by the photolysis of oxygen at the same wavelength (184.9 *nm*) in the photolysis area and gives a background signal which has to be determined accurately (R. 3.3 and R. 3.4).

The accurate determination of the mixing ratio of the ozone produced contributes essentially to the accuracy of the ΔNO_2 that defines the *eCL*. Therefore, it is important to have direct measurements of the small O_3 variations between single points of the HO_2 calibration.

The experiment is done in by adding dry synthetic air, emitting the light by the Hg-lamp through the photolysis zone, and measuring the attenuated intensity due to the absorption of light by ozone. This attenuated intensity is detected by a photomultiplier. As a result, the amount of O_3 produced can be calculated and the maximum of ozone

mixing ratio can be determined by detecting the light intensity at the maximum production of ozone.

The results of three ozone calibrations that have been done in the lab with respect to their photomultiplier (*PMT*) values are described in detail in chapter 4.

3.4.4. Determination of absorption cross section of oxygen

It is important to determine the effective absorption cross section of the oxygen in the photolysis zone of each calibration source because the O_2 absorption spectrum in the Schumann-Runge bands is located near 184.9 nm (Yoshino et al., 1983) and the Hglamp that is used in the calibration has an emission spectrum which is therefore a function of O_2 column. For this reason and in order to reduce the O_2 present, the space between the lamp and the photolysis area is flushed continuously during the calibration with N_2 . The effective absorption cross section of O_2 for the setup has been determined for the setup used at the beginning and during the experiments and this process should be repeated to monitor any changes in the lamp as a consequence of ageing and whenever a change in the setup is applied. The determination of the effective cross section is done by adding different oxygen columns by using mixtures of N_2 -synthetic air entering the photolysis zone. Using this method, the attenuated intensity can be determined and then the apparent absorption cross section can be calculated using the Beer-Lambert law (Eq. 3.4) (Creasey et al., 2000):

$$\sigma_{O2,app}(x) = \left(\frac{1}{x}\right) * \ln(\frac{I_0}{I(x)})$$
 Eq. 3.4

where:

x is the oxygen column, I_0 is the incident light intensity if there is only N_2 in the photolysis zone, and I(x) is the attenuated intensity measured after the oxygen column has been added and interacted with the incident light.

The apparent absorption cross section is derived from the integration of the effective cross section through an oxygen column x (Creasey et al., 2000), and the relation between both apparent and effective absorption cross sections can be expressed by the following equation (Eq. 3.5):

$$\sigma_{02,eff}(x) = \sigma_{02,app}(x) + \frac{d[\sigma_{02,app}(x)]}{dx} * x$$
 Eq. 3.5

Following this procedure, values of the oxygen effective cross section were determined and are described in chapter 4..

3.5 Experimental procedure for determining the wall losses

As discussed in chapter 1, the approach followed in this work is studying the diffusion of HO_2 and CH_3O_2 using inlets with different lengths and diameters and calculating the corresponding wall loss rate according to Eq. 1.1. Therefore, the calibrations, described previously in this chapter, were firstly done using a glass reactor with a 4mm ID and 25cm length inlet. After obtaining the eCL, the length of the inlet was gradually reduced by cutting about 5cm of its length and the calibrations were repeated to obtain the eCL associated with each inlet length. This procedure is clarified in the Figure 3.6.



Figure 3.6: Obtaining the *eCL* for different inlet lengths.

As shown in Figure 3.6, changing the length of the inlet leads to different eCL from the same initial radical concentration xRO_2^* , as the CL inside the reactor is supposed to remain constant.

In the next step the whole procedure was repeated using an inlet with a different diameter (1mm ID) which length was reduced and the *eCL* for each length was determined. Changing the diameter of the inlet gives information about the effect of changing the surface to volume area of the inlet on the wall losses.

These calibrations using different diameters and lengths were performed for different relative humidities (4%, 20%, 40%, and 60%) and the diffusion coefficient was derived as a function of the *eCL* and the geometry of the inlet. Finally the k_w is calculated using the obtained value of the diffusion coefficient for both HO_2 and CH_3O_2 based on Eq. 1.1.

Furthermore, the variation of the eCL with the diameter of the inlet was investigated more in detail by additionally using other two different inlets with 8mm ID and 5cm length, and with 0.4mm ID and 5cm length. Both of them were used to obtain the eCL in dry conditions (4% *RH*).

Furthermore, the reproducibility of the experiments in this work was studied by repeating calibrations of some lengths and diameters of the measurements that was obtained as well. The results of these experiments and the corresponding error analysis will be described in detail in the following chapter.

4. Results and discussion

In this chapter the results obtained from the experiments are presented and analyzed. Different observations are discussed regarding the variation of the *eCL* respect to the change of several parameters and conditions such as the diameter and length of the inlet. Based on these observations, a method is used for deriving the diffusion coefficient for HO_2 and CH_3O_2 . Additionally, an experimental wall loss rate coefficient k_w is calculated using Eq.1.1 (see chapter 1) based on the derived diffusion coefficient values.

Finally, the error analysis of the experiments is discussed to describe the different sources of data uncertainties, as well as to estimate the total accuracy of this method.

4.1 Measurements of the eCL

As discussed in the previous chapter, the eCL was measured for different lengths and diameters of the inlet. The general approach for obtaining eCL is based on the following process as shown in Figure 3.1, here repeated for clarification (Figure 4.1):



Figure 4.1: Schematic representation of the processes involved in the determination of the *eCL* (from Figure 3.1 in chapter 3).

In this figure, the initial concentration of the radicals that enters the inlet ($[RO_2^*]_0$) is subject to losses on the walls ($[RO_2^*]_{loss}$). Thus the yielded concentration after a

residence time (t) in the inlet ($[RO_2^*]_t$) enters the reactor and the corresponding radicals are amplified and converted into NO_2 according to the reactor chain length (CL) (Eq. 4.1).

$$[RO_2^*]_{loss} = [RO_2^*]_0 - [RO_2^*]_t$$
 Eq. 4.1

The actual chain length (*CL* in the reactor) is unknown since the loss on the wall is undetermined and therefore also the exact radical concentration that enters the reactor. Thus, the measured chain length at the end of the calibration is an effective chain length (*eCL*) that results from $[RO_2^*]_0$.

As discussed in the calibration procedures (see chapter 3), the *eCL* is obtained from both NO_2 and HO_2 calibrations. The results of the calibrations carried out during this work are shown in the next sections.

4.1.1 NO₂ calibrations

A NO_2 calibration is shown exemplary in the next figure (Figure 4.2).



Figure 4.2: Variation of the signal of the NO_2 detector during a NO_2 calibration.

The calibration is obtained by applying different concentrations of NO_2 and changing the mixing ratio of NO_2 every 8 minutes. The zero of the calibration corresponds to 45 ppb NO_2 offset (for the linearity of the detector) at the beginning and at the end of the calibration. The mixing ratios of NO_2 in *ppb* are plotted as a function of the detector signal in volts (Figure 4.3). The NO_2 mixing ratios are calculated from the following formula (Eq. 4.2):

$$MR of NO_2 (ppb) = \frac{MR of NO_2 in the gas cylinder * NO_2 FC}{NO_2 FC_t} \quad Eq. 4.2$$

where, the mixing ratio (MR) of the NO_2 in the gas cylinder during this study is 10.11 *ppm*, $(NO_2 FC)$ is the voltage of NO_2 flow controller, $(NO_2 FC_t)$ is the sum of the voltages taken from both the NO_2 flow controller and the exhaust flow controller.



Figure 4.3: Linear relationship between NO_2 mixing ratios and the detector signal in volts.

This linear relationship is fitted by y = ax + b using linear regression analysis where S = 1/a represents the sensitivity of the detector for different NO_2 concentrations.

The next mathematical analysis was done to demonstrate the cause of the deviations of the calculated NO_2 mixing ratios around the regression line. Based on Eq. 4.2, the governing variables for calculating the NO_2 mixing ratio are the measured voltages of the NO_2 flow controller ($NO_2 FC$) and the exhaust flow controller.

By taking one cluster of the NO_2 mixing ratios from the calibration above (e.g. 45 *ppb*), the averages and the standard deviations of both flow controllers were calculated for some minutes. Thus, the corresponding NO_2 mixing ratios, using the averages of the flow controllers \pm the standard deviation, were calculated as shown in the following table.

Minutes	NO ₂ FC (volts)		Exhaust FC $(\frac{l}{m})$		NO₂ mixing ratio (ppb)		NO₂ mixing ratio (ppb)	
	mean	std	mean	std	using NO ₂ FC (mean+std)	using $NO_2 FC$ (mean-std)	using Exhaust FC (mean+std)	using Exhaust FC (mean-std)
1 st	0.902	0.008	1.990	0.029	46.074	45.180	44.971	46.302
2 nd	0.899	0.008	1.994	0.027	45.781	44.998	44.783	46.012
3 rd	0.899	0.008	1.995	0.035	45.812	44.940	44.604	46.175
4 th	0.903	0.009	2.000	0.049	45.899	44.994	44.358	46.589
5 th	0.900	0.009	1.990	0.038	46.069	45.127	44.739	46.491

Table 4.1: Calculation of NO₂ mixing ratio with respect to the deviations of the flow controllers.

From this table, it can be seen that the deviation of each flow controller causes a variation of ± 1 ppb of the NO_2 mixing ratio. As a result, 92% to 95% of the points have variances around ± 2 ppb from the mean value which are caused by the variation of the FC signal but do not correspond to a real variation in the flow and consequently do not affect the accuracy of the determination of the NO_2 sensitivity.

Therefore, a smoothing average filter was applied on the points as shown in the following figure where the outliers in the calibration can be better identified (Figure 4.4).



Figure 4.4: Smoothed linear relationship between NO_2 mixing ratios and the detector signal in volts.

Based on the linear regression in this figure $([NO_2] = a * V + b)$, the sensitivity (1/a) of the detector is determined to be 0.13 ± 0.02 volts/ppb, where the relative error is calculated in detail in the error analysis section.

4.1.2 HO₂/RO^{*}₂ Calibrations

Once determined the detector sensitivity, each NO_2 calibration was followed by both the HO_2 and RO_2^* calibrations that are needed for obtaining the *eCL*. Figure 4.5 describes the linear relationship from one example of the HO_2 calibration that have been done in this work.



Figure 4.5: Example of the HO_2 calibration. The slope corresponds to the value of the *eCL*.

Using different mixing ratios of HO_2 as described in chapter 3, a linear NO_2 concentration response is observed with the increase of HO_2 mixing ratio. In the previous figure (Figure 4.5), the eCL value is determined using the linear regression analysis (where R^2 is the correlation coefficient). This value is represented by the slope of the regression line using Eq.2.1, and it is $\approx 181.5 \pm 19$ in this calibration (the error analysis of the *eCL* is explained later in this chapter).

4.2 Analysis of the eCL

In this section, the obtained eCL for different inlet lengths and diameters are analyzed using two different inlet diameters (4mm ID and 1mm ID), different inlet lengths between 2.5cm and 25cm, and different RH between 4% and 60%. As discussed in chapter 2, the chain length is expected to decrease with the increase of the relative humidity (*RH*) (Reichert et al., 2003). This is clearly shown in Figure 4.6 that describes the relation between *eCL* and *RH* for both HO_2 and a (50% HO_2 +50% CH_3O_2) mixture obtained experimentally within this work.



Figure 4.6: Variation of eCL (for both HO_2 in blue and $HO_2 + CH_3O_2$ in red) versus RH for an inlet with 4mm ID and 25 cm length.

As can be seen in the plot (Figure 4.6), the *eCL* from HO_2 slightly differs from the *eCL* of the radical mixture. This is also noticed when changing the length of the inlet, as shown in the following figures (Figure 4.7, Figure 4.8, Figure 4.9, and Figure 4.10).



Figure 4.7: Variation of eCL (for both HO_2 in blue and $HO_2 + CH_3O_2$ in red) versus RH for an inlet with 4mm ID and 20 cm length.



Figure 4.8: Variation of eCL (for both HO_2 in blue and $HO_2 + CH_3O_2$ in red) versus RH for an inlet with 4mm ID and 15 cm length.



Figure 4.9: Variation of eCL (for both HO_2 in blue and $HO_2 + CH_3O_2$ in red) versus RH for an inlet with 4mm ID and 5 cm length.



Figure 4.10: Variation of eCL (for both HO_2 in blue and $HO_2 + CH_3O_2$ in red) versus RH for an inlet with 4mm ID and 2.5 cm length.

These plots show a slight variation of the eCL between the HO_2 and the mixture which is within the experimental error, except for the dry conditions (4% *RH*) where the difference is distinguishable, especially when the length of the inlet is shortened. The variances of the obtained eCL shown in the plots will be discussed in details in the error analysis section.

The slight difference of the eCL from HO_2 and mixture conversions is also seen when using 1mm ID inlet and different inlet lengths as shown in the next figures (Figure 4.11, Figure 4.12, Figure 4.13, and Figure 4.14).



Figure 4.11: Variation of eCL (for both HO_2 in blue and $HO_2 + CH_3O_2$ in red) versus RH for an inlet with 1mm ID and 20 cm length.



Figure 4.12: Variation of eCL (for both HO_2 in blue and $HO_2 + CH_3O_2$ in red) versus RH for an inlet with 1mm ID and 15 cm length.



Figure 4.13: Variation of eCL (for both HO_2 in blue and $HO_2 + CH_3O_2$ in red) versus RH for an inlet with 1mm ID and 5 cm length.



Figure 4.14: Variation of eCL (for both HO_2 in blue and $HO_2 + CH_3O_2$ in red) versus RH for an inlet with 1mm ID and 2.5 cm length.

From Figure 4.7 to Figure 4.14 the *eCL* seems to be slightly higher for pure HO_2 than for the mixture in dry conditions (4%*RH*), but for higher *RH* (higher than 20% *RH*) no significant difference can be observed.

After finishing the experiments using different sets of parameters, a proper way for analyzing the data in a simplified method is by studying the effect resulted from the change of these parameters. This will help us to characterize the role of each parameter in the process and its associated effect.

4.2.1 Variation of the eCL with RH and with inlet length

For more clarity, the relation between eCL and RH is plotted in Figure 4.15 for the pure HO_2 using 4mm ID inlet, where the inlet was cut 5cm gradually. It can be seen that the eCL increases each time when the length of the inlet is shortened although this increase seems to be close to the experimental error. Small cutting steps do not lead to big differences in the eCL as it was expected, and they are only noticeable when bigger steps are considered like between the lengths 5cm and 25cm of the inlet.



Figure 4.15: Experimental calibrations for pure HO_2 using 4mm ID, showing the variation of the *eCL* with the length of the inlet.

The next figure (Figure 4.16) shows a similar variation for the *eCL* with the length of the inlet for the radical mixture $(50\% HO_2+50\% CH_2O_2)$.



Figure 4.16: Calibrations for the radical mixture using 4mm ID inlet, with the variation of the *eCL* for different inlet lengths.

The *eCL* for 2.5*cm* inlet length resulted unexpectedly to be smaller than for 5*cm* in contrast with the tendency shown by the other inlet lengths. This led to necessarily repeating the experiment again for the inlet with 2.5*cm* length to assure that the calibration was done accurately. As it is shown in the previous figures (Figure 4.15, Figure 4.16), the repeated measurement reproduced the first observation. Therefore, it is necessary to investigate the reason for such result.

Recalling Eq. 2.1, a possible cause for the different behavior could be from either the NO_2 calibration or the HO_2 calibration. Therefore, possible changes in both calibrations between the eCL determinations at 5cm and at 2.5cm inlet length were analyzed in detail.

First, the NO_2 calibration was checked and no significant change in the calibration (for instance in the linearity and noise) was observed.

Concerning the HO_2 calibration, the initial mixing ratio of HO_2 is calculated from the recalled Eq.3.1 (see chapter 3)

$$[HO_2] = \frac{\sigma_{H_2O}^{184.9nm} * [H_2O]}{\sigma_{O_2}^{184.9nm} * [O_2]} * [O_3]$$
Eq.3.1

In this equation, the absorption cross section of the $H_2O(\sigma_{H_2O}^{184,9nm})$ is taken from the literature (Cantrell et al., 1993). Also, the stability of the water mixing ratio ([H_2O]) during the *eCL* determination was checked for both inlet lengths. [H_2O] is calculated based on the dew point temperature that is measured during the calibration. The associated relative errors of the water mixing ratios in Table 4.2 show no unexpected uncertainties.

Table 4.2: Relative	errors of the water	mixing ratios	s for different re	lative humidi	ty and
differen	nt inlet lengths du	ring the exper	iments for 5 and	1 2.5 cm inlet	s.

<i>RH</i> (%)	[<i>H</i> ₂ <i>0</i>] relative error (%)				
	l = 5cm	l = 2.5cm	l = 2.5cm (repeated)		
4	0.7	0.9	0.5		
20	0.2	0.4	0.4		
40	0.07	1	1		
60	1	0.4	1		
Average error	0.5	0.7	0.8		

As described in chapter 3, the effective oxygen cross section $(\sigma_{O_2}^{184.9nm})$ of the setup could change as a consequence of the aging of the lamp (Hofzumahaus et al., 1997). Two calibrations were performed for determining the oxygen cross section in March and September. The first calibration gave a cross section = $1.34 * 10^{-20} \pm 5.5 * 10^{-22}$, while the second calibration gave a cross section = $1.3 * 10^{-20} \pm 3.76 * 10^{-22}$.

These values were used to check the effect of the slight change in the cross section on the resulted *eCL* as shown in Table 4.3.

Table 4.3: The effect of the oxygen cross section on *eCL*.

$\sigma_{0_2}^{184.9nm}(cm^2molecule^{-1})$	eCL (HO ₂)		
	l = 5cm	l = 2.5 cm	
$1.34 * 10^{-20} \pm 5.5 * 10^{-22}$	$212\pm12\%$	202 <u>+</u> 20%	
$1.3 * 10^{-20} \pm 3.76 * 10^{-22}$	$206\pm12\%$	196 <u>+</u> 20%	

Small difference in the *eCL* was observed but this difference cannot explain the difference observed in the results of both inlet lengths.

Finally, another potential cause for the difference observed can be an unexpected change in the intensity of the lamp as a result of ageing. This can have an effect in the O_3 calibration. The ozone calibration is done as shown in Figure 4.17 that describe the transmittance of light by the photomultiplier (shutter on/off) and the response of the NO_2 detector at the same time.



Figure 4.17 the intensity measured by the photomultiplier (PMT) in volts and the NO_2 signal from the detector in volts when the shutter is on/off.

The *PMT* signal is due to the absorption of light by ozone, and there is no signal for *PMT* where there is no light. The signal of NO_2 is due to the production of NO_2 from the reaction of O_3 produced with the *NO* added into the inlet. Therefore, from the

difference of NO_2 signal in presence and absence of light (the signal from ozone absorption-the background signal without absorption), the mixing ratio of ozone that is produced during the measurements can be calculated.

During this work, several calibrations for determining the relationship between the photomultiplier signal (*PMT*) and the ozone mixing ratio were performed as shown in Table 4.4.

date	[0 ₃] (ppb)	PMT (volts)	Max	Min	Max	Min
			eCL _{5cm}	eCL _{5cm}	eCL _{2.5cm}	eCL _{2.5cm}
11.02.2013	3.64 ± 0.06	4.2 <u>+</u> 0.09	263.46	244.22	244.3	226.45
06.03.2013	3.80 <u>+</u> 0.08	4.1 ± 0.007	242.73	231.92	225.07	215.06
24.06.2013	3.33 ± 0.20	3.6 ± 0.05	256.38	221.1	237.73	205.02
24.09.2013	3.40 <u>+</u> 0.20	3.2 <u>+</u> 0.03	221.92	193.59	205.78	179.51

Table 4.4: Ozone mixing ratios with respect to the *PMT* signal.

The variation of $[O_3]$ was between $3.33 \pm 0.2 \, ppb$ for $PMT = 3.6 \pm 0.05 \, volts$ and $3.8 \pm 0.08 \, ppb$ for $PMT = 4.1 \pm 0.007 \, volts$.

It should be stated that the *eCL* for both inlet lengths (2.5cm and 5cm) was obtained using the $[O_3]$ and PMT values in 24.06.2013 (in red). In the previous table, the maximum and minimum *eCL* were obtained (*Max* and *Min* respectively) with respect to the variations of both *PMT* and $[O_3]$. It can be seen that these variations have significant effect on the yielded *eCL* and might partially explain the unexpected behavior for having *eCL* for the 5*cm* inlet length higher than the *eCL* for 2.5*cm* length.

Furthermore, the same observation associated with the inlet with 2.5cm and 5cm lengths can be seen using an inlet with (1mm ID) as shown in Figure 4.18.



Figure 4.18: Calibrations for pure HO_2 (left side) and mixture (right side) using inlet with 1mm ID, and the change of *eCL* with different inlet lengths.

The reproducibility of the 2.5*cm* inlet length is worse than the one for the inlet with 4*mm ID*, and the measurements using long inlets have higher errors in the detector signals that give the fluctuations seen in Figure 4.18. Although the differences in the *eCL* are more noticeable in dry conditions than at higher *RH*, the fluctuations do not lead to any clear conclusion regarding the wall loss associated with different inlet lengths. These results were thought to be caused by turbulences in the flow within the 1*mm ID* inlet, due to the high air velocity through the inlet. The value of the Reynolds number (\approx 266.46) shows that the flow is still laminar (*Re* < 2300).

4.2.2 Variation of the eCL with the length of the inlet

The effect of different inlet lengths on the eCL in dry conditions (4% *RH*) for both diameters was studied more in detail as shown in Figure 4.19.



Figure 4.19: Relation between eCL and inlet length at dry conditions (4% *RH*) for both pure HO_2 , and mixture (*Mix*) using two different internal diameters (4mm *ID* and 1mm *ID*) of the inlet.

Interesting results are shown here, where for 4mm ID inlet the *eCL* decreases for both pure HO_2 (in blue) and mixture (in red) linearly with the increase in the inlet length. As discussed earlier in Figure 4.15, it is expected that more radicals are lost when the inlet length increases. But the crucial difference is clearly shown with the results of the inlet with 1mm ID. The *eCL* increases when increasing the inlet length for both HO_2 and mixture (in black and green respectively). This increment emphasizes that when the inlet diameter decreases, there is likely other factor that plays a role in the process and their effect exceeds the effect caused by the wall loss.

The next figures (Figure 4.20, Figure 4.21, and Figure 4.22) show the variations of the *eCL* with the inlet length for higher relative humidity.



Figure 4.20: Relation between eCL and inlet length at 20% RH for both pure HO_2 , and mixture (*Mix*) using two different internal diameters (4mm ID and 1mm ID) of the inlet



Figure 4.21 Relation between eCL and inlet length at 40% RH for both pure HO_2 , and mixture (*Mix*) using two different internal diameters (4mm ID and 1mm ID) of the inlet



Figure 4.22 Relation between *eCL* and inlet length at 60% *RH* for both pure HO_2 , and mixture (*Mix*) using two different internal diameters (4*mm* ID and 1*mm* ID) of the inlet.

It can be seen that the variation of eCL with respect to the inlet length is smaller with the increase of *RH*, while the experimental errors generally increase. Therefore, the dry conditions (4%*RH*) were selected to be the best for the calculation of *D* and *kw*.

4.3 D and k_w calculations

In this part, the wall loss rate coefficient is calculated based on the results of the experiment and the observations of the previous sections.

The Eq. 1.1 for k_w can be simplifies as follows:

$$k_w^3 = (1.85)^3 * \left(\frac{vD^2}{dl}\right) * \left(\frac{S}{V}\right)^3$$
 Eq. 4.3

where; v is the velocity of the air flow entering the inlet (cm/s), D is the diffusion coefficient of the radicals (cm^2/s) , d is the inner diameter of the inlet (cm), l is the inlet length (cm), and S/V is the surface to volume ratio of the inlet (cm^{-1}) . Or it can be written:

$$k_w^{3} = (1.85)^3 * \left(\frac{8FD^2}{2\pi r^2 r^3 rl}\right)$$
 Eq. 4.4

where;

$$\frac{S}{V} = \frac{2\pi r l}{\pi r^2 l} = \frac{2}{r}$$
 Eq. 4.5

and

$$F = \frac{V}{t} = \frac{Al}{t} \rightarrow v = \frac{F}{\pi r^2}$$
 Eq. 4.6

where *F* is the flow of the air through the inlet $(2 l/min = 33.33 cm^3/s)$, *A* is the internal area of the inlet (cm^2) , and *r* is the radius of the inlet (cm). This yields:

$$k_w^3 = (1.85)^3 * \left(\frac{4FD^2}{\pi r^6 l}\right)$$
 Eq. 4.7

and

$$k_w = 2 * \left(\frac{F^{1/3}D^{2/3}}{r^2 l^{1/3}}\right)$$
 Eq. 4.8

and finally this could be written as follows:

$$k_w = 6.66 * \left(\frac{D^{2/3}}{r^2 l^{1/3}}\right)$$
 Eq. 4.9

Eq. 4.9 shows that the main parameters that affect the k_w are D, l, and r.

The calculation of k_w requires the diffusion coefficient to be determined. One of the objectives of the present work is to calculate empirically the diffusion coefficient and compare it with literature values (Fuller et al., 1966).

Based on (Eq. 2.1), and by considering the calibration of pure HO_2 , the *eCL* at any specific length *x* could be written as follows:

$$eCL_{(at x cm)} = \frac{\Delta NO_{2(at x cm)}}{[HO_2]_0}$$
 Eq. 4.10

If the ratios between the *eCL* for each specific inlet length and for a standard length (5*cm*) are taken, where the initial concentrations $[HO_2]_0$ for all lengths are identical, this yields:

$$\frac{eCL_{(at \ x \ cm)}}{eCL_{(at \ 5 \ cm)}} = \frac{\Delta NO_{2(at \ x \ cm)}}{\Delta NO_{2(at \ 5 \ cm)}}$$
Eq. 4.11

Writing the same ratios for the *CL* in the reactor:

$$\frac{CL_{(at \ x \ cm)}}{CL_{(at \ 5 \ cm)}} = \frac{\frac{\Delta NO_{2(at \ x \ cm)}}{[HO_2]_{t(at \ x \ cm)}}}{\frac{\Delta NO_{2(at \ x \ cm)}}{[HO_2]_{t(at \ 5 \ cm)}}}$$
Eq. 4.12

and

$$\frac{CL_{(at \ x \ cm)}}{CL_{(at \ 5 \ cm)}} = \frac{\Delta NO_{2(at \ x \ cm)}}{[HO_2]_{t(at \ x \ cm)}} * \frac{[HO_2]_{t(at \ 5 \ cm)}}{\Delta NO_{2(at \ 5 \ cm)}}$$
Eq. 4.13

Provided that the CL is constant in the reactor, the change of the eCL is a consequence of the losses on the walls, or in other words, of the change of the inlet length. Therefore, the Eq. 4.13 can be written as follows:

$$1 = \frac{\Delta NO_{2(at \ x \ cm)}}{\Delta NO_{2(at \ 5 \ cm)}} * \frac{[HO_2]_{t(at \ 5 \ cm)}}{[HO_2]_{t(at \ x \ cm)}}$$
Eq. 4.14

By using Eq. 4.11,
$$\frac{eCL_{(at \ x \ cm)}}{eCL_{(at \ 5 \ cm)}} = \frac{[HO_2]_{t(at \ x \ cm)}}{[HO_2]_{t(at \ 5 \ cm)}}$$
Eq. 4.15

Taking into account that the wall loss reaction is a first order reaction, then it can be written as:

$$\frac{eCL_{1(at \ x \ cm)}}{eCL_{2(at \ 5 \ cm)}} = \frac{[HO_2]_0 * e^{-k_{w1}t_{1(at \ x \ cm)}}}{[HO_2]_0 * e^{-k_{w2}t_{2(at \ 5 \ cm)}}}$$
Eq. 4.16

By simplifying it:

$$\frac{eCL_{1(at \ x \ cm)}}{eCL_{2(at \ 5 \ cm)}} = e^{-k_{w1}t_1 + k_{w2}t_2}$$
Eq. 4.17

and

$$\ln\left(\frac{eCL_{(at \ x \ cm)}}{eCL_{(at \ 5 \ cm)}}\right) = -k_{w1}t_1 + k_{w2}t_2 \qquad \text{Eq. 4.18}$$

Replacing k_w with Eq. 4.9 yields:

$$\ln\left(\frac{eCL_{1(at\ x\ cm)}}{eCL_{2(at\ 5\ cm)}}\right) = -\left(6.66 * \frac{D^{\frac{2}{3}}t_1}{r^2 l_1^{\frac{1}{3}}}\right) + \left(6.66 * \frac{D^{\frac{2}{3}}t_2}{r^2 l_2^{\frac{1}{3}}}\right) \qquad \text{Eq. 4.19}$$

and finally:

$$-\ln\left(\frac{eCL_{1(at\ x\ cm)}}{eCL_{2(at\ 5\ cm)}}\right) = \frac{6.66}{r^2} \left(\frac{l_2^{\frac{1}{3}}t_1 - l_1^{\frac{1}{3}}t_2}{l_2^{\frac{1}{3}}l_1^{\frac{1}{3}}}\right) D^{\frac{2}{3}}$$
 Eq. 4.20

This equation shows the relation between the ratio of eCL with different parameters (D, r, t, l). In order to determine the diffusion coefficient for $HO_2(D_{HO_2})$, the previous equation (Eq. 4.20) can be written in the following linear formula:

$$y = D^{2/3}x$$
 Eq. 4.21

where

$$y = -\ln\left(\frac{eCL_{1(at \ x \ cm)}}{eCL_{2(at \ 5 \ cm)}}\right)$$
Eq. 4.22
$$x = \frac{6.66}{r^2} \left(\frac{l_2^{\frac{1}{3}}t_1 - l_1^{\frac{1}{3}}t_2}{l_2^{\frac{1}{3}}l_1^{\frac{1}{3}}}\right)$$
Eq. 4.23

Figure 4.23 shows the plot of the Eq. 4.21, where a linear regression was taken.



Figure 4.23: Function used for obtaining the diffusion coefficient for pure HO_2 using different inlet lengths for both inlets with 4 mm ID and 1mm ID. The slope $= D^{2/3} = 0.0742$

In the plot, different behaviors are associated with different diameters of the inlet. A positive slope occurs when the 4mm ID inlet was used, while a negative slope associated with the inlet with 1mm ID. The positive slope $D_{HO_2}^{2/3}$, leads to a value of $D_{HO_2} = 0.02 \pm 0.001 \ cm^2/s$ for the inlet with 4mm ID, where the error analysis of the diffusion coefficient is discussed in detail in the error analysis section.

Regarding the narrower inlet, a negative diffusion coefficient does not seem to have any physical behavior. Therefore, it seems that the experimental results are not accurate enough for the empirical calculation of the diffusion coefficient as indicated by the non-systematical variations observed in the Figure 4.18. However, the diffusion coefficient should be the same for both inlets as it is independent of the inlet diameter (see chapter 2). Therefore, the same value that is taken for the inlet with 4 mm ID will be considered also for the inlet with 1mm ID. This unexpected behavior in the inlet with 1mm ID, described by the negative slope in the plot, requires however further investigation in the future.

The calculation of the diffusion coefficient $D_{CH_3O_2}$ follows the same approach used for determining (D_{HO_2}) as shown in Figure 4.24.



Figure 4.24: Function used for obtaining the diffusion coefficient for CH_3O_2 using different inlet lengths for both inlets with 4 mm ID and 1mm ID. The slope $= D^{2/3} = 0.0583$

The *eCL* for CH_3O_2 is calculated from Eq. 4.24:

$$eCL_{MIX} = 50\% eCL_{HO_2} + 50\% eCL_{CH_3O_2}$$
 Eq. 4.24

therefore,

$$eCL_{CH_3O_2} = \frac{eCL_{MIX} - 0.5eCL_{HO_2}}{0.5}$$
 Eq. 4.25

Based on Figure 4.24 and Eq. 4.25, $D_{CH_3O_2}$ was determined to be $D_{CH_3O_2} = 0.014 \pm 0.0007 \ cm^2/s$, where the relative error is calculated in details in the error analysis section.

If the values for the diffusion coefficients obtained within this work are compared to the values calculated from the theoretical equation (Eq.2.11), a factor of 10 difference is seen:

$$D = \frac{1.00 \times 10^{-3} T^{1.75} \sqrt{\frac{1}{M_A} + \frac{1}{M_B}}}{(V_A^{\frac{1}{3}} + V_B^{\frac{1}{3}})^2 P}$$
Eq.2.11

as the $D_{HO_2} = 0.21 \ cm^2/s$ and $D_{CH_3O_2} = 0.14 \ cm^2/s$, when calculated from the molecular weight of the air and the radicals and their molecular volumes at the normal pressure and temperature.

Using D_{HO_2} and $D_{CH_3O_2}$ obtained experimentally in this work, the k_w and $[RO_2]_{loss}$ for different lengths of the inlet with 4mm ID were calculated as shown in the Table 4.5.

l (cm)	$k_{w(HO_2)}(s^{-1})$	$k_{w(CH_3O_2)}(s^{-1})$	$[HO_2]_{loss}(\%)$	$[CH_3O_2]_{loss}(\%)$
25	4.23±0.17	1.16 ± 0.05	33	10
20	4.55±0.14	1.25 ± 0.04	29	9
15	5.01±0.3	1.37 ± 0.08	25	8

Table 4.5: Calculation of k_w and the associated wall losses as a function of the inlet length with 4mm ID, $D_{HO_2} = 0.02 \ cm^2/s$, and $D_{CH_3O_2} = 0.014 \ cm^2/s$

The values for $[HO_2]_{loss}$ and $[CH_3O_2]_{loss}$ were calculated using Eq. 4.1, and the table shows that more HO_2 radicals are lost in the inlet than CH_3O_2 , where the diffusion coefficient has major effect on the k_w .

On the other hand, the inlet length slightly decreases the wall loss rate, and thus, the difference is too small to achieve a real effective speciation of radicals by just changing the length of the inlet.

The obtained values have been compared with other existing values in the literature. There were some attempts to estimate the value of k_w in PeRCA reactor. For example, a study by Hastie (Hastie et al., 1991) observed this first order reaction for HO_2 radicals in a flow tube of 0.25 *inch* inner diameter. In this study, for low concentration experimental data $k_w = 2.5 s^{-1}$ was considered as a best fit for both laboratory system and the ambient monitor. This value was taken as a constant for all the radicals in the measured mixture and independent of the concentrations of *CO* and *NO*.

Another studies by (Mozurkewich, 1987) using a PYREX tube, and by (Ql et al., 2006) using a quartz tube determined $k_w = 0.175 \, s^{-1}$ and $k_w = 2 \, s^{-1}$ respectively.

The next table shows the comparison of the k_w values obtained in this work with the previous studies taking into account different geometries.

	d(cm)	$S/V(cm^{-1})$	F(l/min)	$k_w(s^{-1})$
This work	0.4	10	2	≈ 4.5
Hastie et al., 1991	4.3	≈ 1	2.4	2.5
Mozurkewich et al. 1987	7.5	≈ 0.27	2	0.175
Qi et al., 2006	2.6	≈ 0.77	2	2

Table 4.6: Comparison of k_w between this work and a previous study.

As the S/V values are less in the other studies and the k_w is proportional to this ratio, it looks reasonable that they get less value of k_w .

4.4 The effect of the inlet diameter on eCL

Following (Eq. 4.9), the losses are expected to decrease inversely to the square of the inlet radius and as a result *eCL* is expected to be higher with increasing r^2 . Two additional calibrations to study the effect of changing the inlet diameter on the *eCL* were done. The first calibration was done using an inlet with 8*mm ID* and 5*cm* length. The second one used an inlet with 0.4*mm ID* and 5*cm* length.

The Figure 4.25 shows the comparison of the *eCL* with different inlet squared radius (r^2) for both HO_2 and CH_3O_2 .



Figure 4.25: Relationship between the *eCL* and the square of the inlet radius.

It should be stated that the ozone calibration for the inlet with 8mm ID and 5cm length, gave a value of $3.67 \pm 0.05 \ ppb$ for $PMT = 3.8 \pm 0.05$, while the obtained value for both 1mm ID inlet and 4mm ID inlet with the same length gave a value of $3.33 \pm 0.2 \ ppb$ with $PMT = 3.6 \pm 0.05$. Therefore, it can be seen from the previous figure that eCL of the inlet with 8mm ID is slightly less than the one with 4mm ID. This unexpected behavior could be the result of differences in the ozone calibration values as the distribution of O_3 and HO_2 in the cross section of the calibration tube is not homogeneous (Stöbener, 1999) and as a consequence the 8mm ID inlet might sample a different O_3 average than the 4mm ID inlet. For this reason a O_3 calibration was performed for the 8mm ID inlet. However, as can be seen in Figure 4.25, the small change of the ozone mixing ratio affects only slightly the obtained eCL, and thus, more investigation should be done in the future to explain the curvature observed in Figure 4.25.

The comparison of inlets with different diameter are subject to an additional inaccuracy which is difficult to be taken into account associated with the fact that

different inlets are attached to different reactors and they are slightly different and the geometry of the junction between the inlet and the reactor can also imply a different additional radical loss. This can affect the shape of the relation obtained for different diameters.

On the other hand, when performing the calibrations using an inlet with 0.4 mm ID, the exhaust flow controller was not able to reach 2 l/min because the 5cm inlet with this narrow was offering to much resistance to the flow. For this reason, it was only reaching 1 l/min. This required a decrease of the reagent gases in parallel to keep the mixing ratios in the reactor constant and therefore the chemistry inside. Then, the NO_2 calibration was done for this inlet diameter and to confirm that the sensitivity was adequate. But performing the calibrations for eCL determination, based on the NO_2 calibration, showed no modulation at all. The possible reason for this result is that all the radicals are lost on the walls and therefore no radical conversion is possible.

4.5 Error Analysis

In this section, the uncertainties of the data, represented by the error bars in the previous plots, are explained in detail to give an indication of the significance of the involved factors affecting the accuracy of the measured and calculated values.

The effective chain length resulted in the measurement, which was calculated from Eq.2.1, $(eCL = \frac{[\Delta NO_2]}{[RO_2]_0})$, is dependent on the sensitivity of the NO_2 detector, as well as on the initial concentration of RO_2^* . Thus the uncertainty of eCL is calculated as follows:

$$\frac{\Delta eCL}{eCL} = \sqrt{\left(\frac{\Delta[\Delta NO_2]}{[\Delta NO_2]}\right)^2 + \left(\frac{\Delta[RO_2]}{[RO_2]}\right)^2} \qquad \text{Eq. 4.26}$$

The ΔNO_2 is calculated as follows:

$$[\Delta NO_2] = a * V_{sg} + b - a * V_{bg} - b = a * \Delta V$$
 Eq. 4.27

where the parameters *a* and *b* are known from the ΔNO_2 calibration and represent the slope and intercept of the linear relationship respectively (Figure 4.3). The source of uncertainty for it comes from the difference between signal-background modes (ΔV) as well as from the sensitivity of the detector ($\Delta(\frac{1}{a})$). Therefore:

$$\frac{\Delta[\Delta NO_2]}{[\Delta NO_2]} = \sqrt{\left(\frac{\Delta[\Delta V]}{[\Delta V]}\right)^2 + \left(\frac{\Delta a}{a}\right)^2} \qquad \text{Eq. 4.28}$$

The standard deviation of the detector response $(\frac{\Delta[\Delta V]}{[\Delta V]})$ (section 4.1.1) was calculated to be around 3% to 4% where $\Delta[\Delta V]$ is calculated from:

$$\Delta[\Delta V] = \sqrt{(\Delta V_{sg})^2 + (\Delta V_{bg})^2} \qquad \text{Eq. 4.29}$$

On the other hand, Δa was determined in the NO_2 calibration, which depends on the detector response (volts), the error of the NO_2 concentration of the gas cylinder, and the error of the flow controllers that are used for producing different NO_2 mixing ratios.

In this calibration the NO_2 concentration is calculated from Eq. 4.2. From this equation, the governing variables are the measured voltages of NO_2 flow controller and

the flow measured by the exhaust flow controller (2 l/min). Accordingly, the error of the NO_2 concentrations that are associated with their values is calculated to be $\pm 2 ppb$. As a result, Δa is calculated to be 2 - 5% and therefore the relative error of $[\Delta NO_2]$ from Eq. 4.28 is in the range between 2-6%.

In the next step the term $\frac{\Delta[RO_2^*]}{[RO_2^*]}$ was calculated based on Eq. 3.1 (see chapter 3). From this equation we could the uncertainty of the initial concentration $[RO_2^*]$ is determined as follows:

$$\frac{\Delta[\mathrm{R}O_2^*]}{[\mathrm{R}O_2^*]} = \sqrt{\left(\frac{\Delta\sigma_{O_2}^{184.9nm}}{\sigma_{O_2}^{184.9nm}}\right)^2 + \left(\frac{\Delta\sigma_{H_2O}^{184.9nm}}{\sigma_{H_2O}^{184.9nm}}\right)^2 + \left(\frac{\Delta[H_2O]}{[H_2O]}\right)^2 + \left(\frac{\Delta[O_3]}{[O_3]}\right)^2} \quad \text{Eq. 4.30}$$

The error of the water mixing ratio is around 0.5 - 0.8% (Table 4.2), and it depends on the dew point sensor accuracy. The error of the determination of the ozone mixing ratios is around 2 - 6% (Table 4.4), and the error of the absorption cross section of the oxygen is around 3 - 4% calculated from their calibrations (Table 4.3). In addition, the error of the absorption cross section of the H_2O taken from the literature is around 1.4% (Cantrell et al., 1993). This yields that $\frac{\Delta[RO_2^*]}{[RO_2^*]}$ error is between 4 - 8%.

Based on Eq. 4.26, where $\frac{\Delta[\Delta NO_2]}{[\Delta NO_2]} = 2 - 6\%$ and $\frac{\Delta[RO_2^*]}{[RO_2^*]} = 4 - 8\%$, this yields that

the relative error of eCL is between 5 - 10%.

The last error calculation is made for the calculated diffusion coefficient and k_w using the following equations:

$$\Delta D^{2/3} = \left[\frac{r^2 l_2^{\frac{1}{3}} l_1^{\frac{1}{3}}}{6.66 \left(l_2^{\frac{1}{3}} t_1 - l_1^{\frac{1}{3}} t_2\right)} * \Delta \left(-\ln\left(\frac{eCL_{(at\ x\ cm)}}{eCL_{(at\ 5\ cm)}}\right)\right)\right] \quad \text{Eq. 4.31}$$

and,

$$\Delta\left(-\ln\left(\frac{eCL_{1(at\ x\ cm)}}{eCL_{2(at\ 5\ cm)}}\right)\right) = -\frac{\Delta\left(\frac{eCL_{1(at\ x\ cm)}}{eCL_{2(at\ 5\ cm)}}\right)}{\frac{eCL_{1(at\ x\ cm)}}{eCL_{2(at\ 5\ cm)}}}$$
Eq. 4.32

this yields:

$$= -\frac{\frac{eCL_{1(at \ x \ cm)}}{eCL_{2(at \ 5 \ cm)}} * \sqrt{(\frac{\Delta eCL_{1(at \ x \ cm)}}{eCL_{1(at \ x \ cm)}})^{2} + (\frac{\Delta eCL_{2(at \ 5 \ cm)}}{eCL_{2(at \ 5 \ cm)}})^{2}}{\frac{eCL_{1(at \ x \ cm)}}{eCL_{2(at \ 5 \ cm)}}}$$
Eq. 4.33

thus,

$$\Delta\left(\ln\left(\frac{eCL_{1(at\ x\ cm)}}{eCL_{2(at\ 5\ cm)}}\right)\right) = \sqrt{\left(\frac{\Delta eCL_{1(at\ x\ cm)}}{eCL_{1(at\ x\ cm)}}\right)^{2} + \left(\frac{\Delta eCL_{2(at\ 5\ cm)}}{eCL_{2(at\ 5\ cm)}}\right)^{2}} \qquad \text{Eq. 4.34}$$

Combining Eq. 4.31 and Eq. 4.34 yields:

$$\Delta D^{2/3} = \left[-\frac{r^2 l_2^{\frac{1}{3}} l_1^{\frac{1}{3}}}{6.66 \left(l_2^{\frac{1}{3}} t_1 - l_1^{\frac{1}{3}} t_2 \right)} * \sqrt{\left(\frac{\Delta e C L_{1(at \ x \ cm)}}{e C L_{1(at \ x \ cm)}} \right)^2 + \left(\frac{\Delta e C L_{2(at \ 5 \ cm)}}{e C L_{2(at \ 5 \ cm)}} \right)^2} \right)} \right]$$
 Eq. 4.35

thus

$$\frac{\Delta D}{D} = \frac{3}{2} * \frac{\Delta D^{2/3}}{D^{2/3}}$$
 Eq. 4.36

and for k_w

$$\Delta k_w = \frac{6.66}{r^2 l^{\frac{1}{3}}} * \Delta D^{2/3}$$
 Eq. 4.37

From Eq. 4.35, Eq. 4.36 and Eq. 4.37 the relative error of the diffusion coefficient is ≈ 5 % and for k_w is $\approx 3 - 6$ %.

5. Summary and conclusions

This work aimed at the study in detail of the radical wall losses previous to their conversion into NO_2 in the reactor of a PeRCA instrument used at the IUP-UB. For this purpose different glass inlets were attached to the reactor, and series of calibrations were performed to obtain *eCL*.

To achieve this goal, several inlets with different lengths and diameters were used, and the *eCL* for both pure HO_2 and a mixture of 50% HO_2 +50% CH_3O_2 was measured for each inlet geometry. In addition some of these measurements were repeated to have a cross check on the results and to see the reproducibility of the experiment.

Based on the measured *eCL* and the inlet length, the diffusion coefficients for both HO_2 and CH_3O_2 were determined experimentally. The calculated diffusion coefficients ($D_{HO_2} = 0.020 \ cm^2/s$ and $D_{CH_3O_2} = 0.014 \ cm^2/s$) are a factor 10 smaller than the theoretical values that are calculated based on an empirical equation suggested by Fuller et al. However, the corresponding values for the wall loss rate coefficient based on these diffusion coefficients and on an empirical equation that describes the relation between k_w and these parameters agree reasonably with the available literature values. Thus, the calculated wall loss rate coefficients were then between 4.23±0.17 and 5.01±0.3 for HO_2 and between 1.16±0.05 and 1.37±0.08 for CH_3O_2 , using the obtained diffusion coefficient values, and different inlet geometry.

Experiments performed with a 1mm ID inlet were associated with higher detector noise and seemed not to be accurate enough for an empirical determination of the *D*.

A second objective of this work was to use these results to analyze the potential of the differences in the wall losses for developing a method for the speciation of radicals, at least of HO_2 and CH_3O_2 which are the most frequent in the troposphere. Although the observations indicate that HO_2 is lost more effectively than CH_3O_2 as a consequence of the differences in the wall losses, changing length and diameter do not seem to be effective enough to deploy such a method for speciation in the field.

In order to get experimental values like D and k_w , all the parameters playing a role in the inaccuracies of the *eCL* must be very well controlled. Therefore, during this work a careful analysis of the factors involved was made, and results in the following recommendations for future work:

- Regular ozone calibrations should be done especially each time a change in the setup is made in order to get more accurate results for the ozone mixing ratios and *PMT* signals since their variations slightly affect the obtained *eCL*.
- Regular calibrations for determining the oxygen effective cross section is important once a month to evaluate the efficiency of the lamp.
- 3) Controlling the position of the inlet in the radical source to determine if the ratio of O_3/HO_2 that enters the inlet remains constant.
- 4) Controlling very carefully the stability of the H_2O mixing ratio during the calibration especially at high *RH* (e.g. heating the source).

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