Speciated Measurement of Peroxy Radicals Using the PerCIMS Technique

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ABSTRACT

The goal of the research was to improve the sensitivity and speciation of the Peroxy Chemical Ionization Mass Spectrometer (PerCIMS) technique used in measuring the concentration of hydroperoxy (HO₂) and organic peroxy (RO₂) radicals in the atmosphere. It is important to know the concentration of these radicals because it helps to give a better understanding of the atmospheric photochemistry particularly as it relates to the cleansing capacity of the troposphere and in estimating the net ozone budget.

The PerCIMS technique involves the conversion of peroxy radicals into ions using a combination of inlet and ion chemistry. Ions counts measured by this instrument were converted into concentration via a mathematical relationship developed from calibrating the instrument. A new dilution method was developed to try improving the PerCIMS instruments’ speciation of HO₂ and RO₂. This method is based on modifying the inlet chemistry of the instrument by altering the nitrogen oxide (NO): oxygen (O₂) ratio. It was observed that by adding more N₂, and thus decreasing the relative oxygen concentration in the inlet, HO₂ measurements were favored while detection of RO₂ radicals were favored by adding more oxygen to the inlet. Preliminary results of this new method looked favorable but some additional instrument modifications will be required to significantly improve the performance of the dilution method beyond that of the current technique. The success of this research will make available an improved way of measuring tropospheric peroxy radicals and thus improve our understanding of atmospheric photochemistry.

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SOARS® 2002, Olusegun Goyea, 1
INTRODUCTION

The earth’s atmosphere is made up of several distinct layers. Each layer contains many gases, which undergo different reactions at different times of the day. The bulk composition of the atmosphere is around 78% nitrogen and 21% oxygen while the remaining percentage constitutes noble gases, water vapor, carbon dioxide, carbon monoxide and other species. Sometimes, the way in which temperature changes with height is used to define various regions of the atmosphere. The lowest layer of the atmosphere closest to the earth surface is the troposphere. It contains gases such as N₂, O₂, CO₂ and trace gases such as NOₓ, hydrocarbons, peroxy radicals, etc. Predominant loss processes during the day are reaction involving the hydroxyl radical (OH) while the nitrate radical (NO₃) dominates its nighttime reactions [Wayne, 1991]. Above the troposphere is the stratosphere, which contains the ozone layer where about 90% of atmospheric ozone (O₃) is found. This layer protects the biosphere from harmful solar radiation. Other layers of the atmosphere include the mesosphere, thermosphere and exosphere in ascending order [Brimblecombe, 1986] as shown in diagram 1.

Diagram 1: Layers of the Atmosphere

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One of the most important species in the atmosphere are free radicals. The chemistry of free radicals in the atmosphere has been a subject of interest for several decades. They are species that have one or more unpaired electrons, which makes them very reactive and short lived. In addition, their lifetimes range from about half a second to five minutes which is a reason for their relatively low concentrations in the atmosphere. Examples of these radicals are hydroxyl radical (OH), peroxy radicals (HO$_2$ and RO$_2$), where R represents a hydrocarbon group, for example, methyl or butyl. There have been several recent missions embarked upon to measure the concentrations of atmospheric radicals or other trace gases using different platforms such as balloons, ships, aircrafts and satellites [e.g., Cantrell et al., 2002, Brune et al., 1999, Burkert et al., 2001].

This paper focuses on research into instrumentation for measuring the concentration of peroxy radicals, hydroperoxy (HO$_2$) and organic peroxy (RO$_2$) in the laboratory. HO$_2$ is a species of the HOX family, which is the summation of OH and HO$_2$ radicals. The summation of HO$_2$ and RO$_2$ make up the HO$_2$RO$_x$ family. The primary source of peroxy radicals, HO$_2$ and RO$_2$, is from the photolysis of ozone (O$_3$) to form molecular oxygen (O$_2$) and excited atomic oxygen (O($^1$D)) [1], followed by the reaction of O($^1$D) with water vapor to give hydroxyl radicals [2]. Subsequently, the hydroxyl radical can react with carbon monoxide in the presence of oxygen to form hydroperoxy radical and carbon dioxide [3]. In addition, the OH radical can also react with methane to form CH$_3$O$_2$ (an RO$_2$ compound) [4]. Other sources are from the photolysis of peroxides [3], formaldehyde (CH$_2$O) [4] and other carbonyl compounds (aldehydes and ketones).

\[
\begin{align*}
O_3 + h\nu & \rightarrow O_2 + O(^1D) \quad [1] \\
O(^1D) + H_2O & \rightarrow 2OH \quad [2] \\
OH + CO + O_2 & \rightarrow HO_2 + CO_2 \quad [3] \\
CH_4 + OH + O_2 & \rightarrow CH_3O_2 + H_2O \quad [4] \\
H_2O_2 + h\nu & \rightarrow 2HO_2 \quad [5] \\
CH_3O + h\nu + O_2 & \rightarrow HO_2 + CHO \quad [6]
\end{align*}
\]

However, there are reactions that interconvert radicals from one form to the other and also remove them from the atmosphere. These include reactions with NO, CO, O$_3$, methane and hydrocarbons, for example CO reacts with OH to produce HO$_2$ while HO$_2$ can then react with CO to give CO$_2$ and OH.

\[
\begin{align*}
CO + OH + O_2 & \rightarrow HO2 + CO_2 \quad [7] \\
CO + HO2 & \rightarrow OH + CO_2 \quad [8]
\end{align*}
\]

The study of peroxy radicals is important because it helps give us a better understanding the details of the chemistry of the atmosphere. Atmospheric cleansing is an aspect of atmospheric chemistry in which these species are key intermediates. Knowing the concentrations of these radicals, we can estimate the level at which the atmosphere can cleaning itself: the greater the concentration of peroxy radicals, generally, the greater the cleaning capacity of the atmosphere.

Furthermore, peroxy radicals take part in reactions that lead to the production and loss of ozone. These reactions are shown below:

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\[ O_3 + OH \rightarrow HO_2 + O_2 \] [9]
\[ O_3 + HO_2 \rightarrow OH + 2O_2 \] [10]
\[ HO_2 (RO_2) + NO \rightarrow OH (RO) + NO_2 \] [11]

However, the primary source of ozone is from the photolysis of NO\(_2\) to give NO and an O(\(^3\)P) atom. The O atom reacts with O\(_2\) to give O\(_3\) [Pitts & Pitts, 1999]. Therefore, knowing the concentrations of peroxy radicals, this will help in determining net ozone budget.

The method used in this study in measuring the concentrations of peroxy radicals is Peroxy Radical Chemical Ionization Mass Spectrometer (PerCIMS) Technique. The technique involves the conversion of the radicals, through chemical reactions, into ions. These ions are then filtered based on their different atomic masses. The detector is located at the rear of the mass spectrometer where filtration takes place. Ion counts measured using the instrument are converted into concentration using a mathematical relationship. A program called LabVIEW is used to control the operation of the PerCIMS instrument.

One of the main goals of the research is to improve the sensitivity and speciation of peroxy radicals, HO\(_2\) and the RO\(_2\) family of compounds, using the PerCIMS instrument. Speciation, in relation to this research, refers to measuring the concentration of each radical on its own. However, the two instrument measurement modes are HO\(_2\) only and HO\(_x\)RO\(_x\), with RO\(_2\) being the difference of both measurement modes. A potential to the PerCIMS instrument may be \textit{via} a new inlet chemistry dilution scheme. This dilution method involves the addition of oxygen or nitrogen to the inlet to control its chemistry. Introducing more oxygen at the inlet may enhance the conversion of RO\(_2\) into HO\(_2\). On the other hand, adding more nitrogen may prevent this conversion. This is the ultimate task of this research is to assess the feasibility of this method.

The success of this research would give us an improved PerCIMS instrument which could then be mounted on the NSF/C-130 or other aircraft and deployed in future ground-based campaigns to take \textit{in situ} measurement of these radicals, in the process giving us more information on the atmospheric chemistry, distribution and budget of peroxy radicals.
METHODOLOGY

Instrument Description

The PerCIMS instrument consists of a pinhole inlet, a reaction tube, an ion drift tube, a mass spectrometer chamber, injection valves, pressure pumps, lenses, and mass flow controllers. Ambient air enters into the instrument through the inlet pinhole, which is approximately 100 micrometers in diameter. The pinhole leads into a teflon reaction tube where inlet chemistry occurs. In the inlet, NO and SO$_2$ are injected into the airflow where they react with peroxo radicals to form OH (reaction 12) which then reacts with SO$_2$ in the presence of water vapor within the air to form H$_2$SO$_4$ (reaction 13).

\[
\text{HO$_2$/RO$_2$ + NO \rightarrow OH + NO$_2$} \quad [12]
\]
\[
\text{SO$_2$ + OH \rightarrow H$_2$SO$_4$} \quad [13]
\]

Behind the reaction tube is a radioactive metal (Americium 241, $^{241}$Am). There is an ion drift tube located between the radioactive metal and the mass spectrometer inlet, which is the region where ion chemistry occurs. In this region, the Americium metal ionizes HNO$_3$ gas injected into the system to form NO$_3^-$ ions (reaction 14), which subsequently reacts with the H$_2$SO$_4$ gas to form HNO$_3$ and HSO$_4^-$ ions (reaction 15).

\[
\text{HNO$_3$ + $^{241}$Am \rightarrow NO$_3^-$} \quad [14]
\]
\[
\text{NO$_3^-$ + H$_2$SO$_4$ \rightarrow HSO$_4^-$} \quad [15]
\]

At this point, ions are the predominant constituents in the instrument. These ions are drawn into a vacuum chamber containing the mass spectrometer.

In the mass spectrometer, the speciation and detection of ions takes place. It houses a quadrupole ion filter, detector and a multiple of ion lenses. The quadrupole mass filter allows certain atomic masses to go through based on high frequency and direct current signals sent to it from the main program. For example, if NO$_3^-$ ions (atomic mass 62) are to be measured, the mass filter is tuned to allow only ions with this mass to get through to the detector. Positively charged lenses situated inside the vacuum chamber propel and focus the ions into the mass spectrometer. The detector is located at the rear of the quadrupole filter, which converts ion abundance into electrical signals. This is the device used to detect the ratio of HSO$_4^-$: NO$_3^-$ ions in the instrument.

Other components of the instrument are injection valves, pressure pumps and flow controllers. Two injection valves are attached at two points at the inlet of the instrument. They transport gases from their sources through the mass flow controllers to where they are needed. There are two sets of pumps. First are the diaphragm pumps which help to pump down the system and hold the inlet at 150 torr while the second set are the turbo pumps that help keep the pressure in the mass spectrometer quadrupole chamber at about 1x$10^{-5}$ torr.

The operations of the instrument are controlled through a LabVIEW program written in-house. Signals are sent from the program to any part of the instrument through electronic control boards.
Instrument Operation

The measurement experiments were carried out in two modes. These are the *signal mode* and *background mode*.

In the signal mode of operation, inlet chemistry allows the conversion of peroxy radicals to H$_2$SO$_4$ gas, which is converted by ion chemistry to HSO$_4^-$ ions as shown in reactions [12], [13], [14], [15]. Below is a schematic diagram of this mode.

Diagram 2: Signal Mode

![Signal Mode Diagram]

Diagram 3: Background Mode

![Background Mode Diagram]
In this mode as shown in diagram 1, NO and SO$_2$ are injected into the inlet through the front injection valve which allows reactions [12] and [13] to occur while reactions [14] and [15] occur in the ion drift tube. Ion counts from the signal mode corresponds to the sum of counts from peroxy radical, noise and ambient HSO$_4^-$ ions.

In the background mode of measurement, NO is injected through the front injection valve and SO$_2$ in the rear injection valve of the inlet as shown in diagram 2. As illustrated above, the NO gas reacts with HO$_2$ to form OH and NO$_2$. OH is a very reactive radical that rapidly reacts with NO to form HONO and RONO in RO$_2$ case before it gets to the SO$_2$ region. Both HONO and RONO are “interlocking compounds” when formed cannot be broken down within the instrument or photolysed due to of UV absence. The formation of these compounds causes the lost of peroxy radicals within the instrument therefore, [12] occurs insignificantly. However, reactions [14] and [15] occurs as normal. Ion counts from this mode is the sum of ambient HSO$_4^-$ and noise. In order to obtain the actual ion count rate, it is necessary to subtract the background from the signal mode.

True Signal = Signal mode – Background mode

Measurement Mode

Measurements are carried out within the PerCIMS instrument in two sub-modes under the signal and background modes. First is the HO$_2$ only mode in which counts detected are from conversion of HO$_2$ radicals to HSO$_4^-$ ions. In this mode, high concentrations of NO and SO$_2$ gases were used to inhibit the conversion of RO$_2$ to HO$_2$. NO concentrations are key factor in this mode because it converts RO$_2$ radicals to RONO in order to detect prevent RO$_2$ detection. Second is the HO$_2$RO$_2$ mode in which diluted NO and SO$_2$ gases are used to measure the concentration of HO$_2$ and RO$_2$ radicals. Using diluted NO reduces the formation of RONO in the inlet. Initially, RO$_2$ radicals are converted to HO$_2$ and afterward converted to HSO$_4^-$ ions; therefore the count detected in this mode is a sum of HO$_2$ and RO$_2$ concentrations.

Calibrations

Prior to carrying out experimental procedures, the instrument had to be calibrated. The purpose of this was to derive functions relating parameters that would be used for subsequent calculations. The calibration process involved two experiments: water photolysis and chemical actinometry.

Chemical Actinometry Experiment

This experiment was carried out using a low-pressure mercury lamp which emits light at 184.9nm wavelength to photolysed N$_2$O molecules into NO and NO$_2$. The nitrogen oxide products were detected using a commercial NO$_x$ analyzer (TECO 42, Thermo Electron Instrument Inc.). Below is a diagram of the experiment.
The purpose of the experiment was to develop a relationship between the lamp flux intensity ($I^*t$) and UV output signals of the light source measured using a phototube detector during the experiment. From the chemical actinometry, it can be shown that the flux intensity is given by:

$$I^*t = \frac{k_{(O_2 + O^1D)} + k_{(O^1D + N_2)} + k_3[N_2O]}{2 \cdot k_3 \cdot \sigma_{(N_2O)} \cdot \phi_{(N_2O)} \cdot [N_2O]}$$

The reaction of $O(^1D) + N_2O$ can proceed via two pathways:

$$O(^1D) + N_2O \rightarrow O_2 + N_2 \quad [16]$$
$$O(^1D) + N_2O \rightarrow 2NO \quad [17]$$

In (I) above, $K_3$ is the composite rate coefficient of [16] + [17].
Figure 1: Chemical Actinometry Experiment

\[ y = 2 \times 10^{9}x^2 - 7 \times 10^9x + 7 \times 10^{11} \]
\[ R^2 = 0.9998 \]

Figure 1, shows sample data illustrating the relationship between \( I^t \) and UV. As shown in Figure 1, there exists a polymeric relationship between \( I^t \) and UV whose equation is also described.

**Water Photolysis Experiment**

This experiment is an absolute instrument calibration. The experiment involved the photolysis of water molecules, using the same mercury lamp used in the actinometry experiments presence of oxygen, \( \text{H}_2\text{O} \) is photolysed to ultimately form \( \text{HO}_2 \) radicals. This reaction is shown below:

\[
\text{H}_2\text{O} + \nu + \text{O}_2 \rightarrow \text{HO}_2 + \text{O} \quad [18]
\]

During this experiment, fixed and known concentrations of \( \text{HO}_2 \) species were prepared at different lamp distances and their corresponding ultraviolet (UV) signals were noted as illustrated by the diagram 4.
From the above water photolysis experiments, it can be shown that

\[ [\text{HO}_2] = \sigma \cdot \phi \cdot [\text{H}_2\text{O}] \cdot (I^* t) \]  

(iii)

where, \( \sigma \) - absorption cross-section of water molecules, \( \phi \) - the quantum yield, \([\text{H}_2\text{O}]\) - water vapor concentration and \((I^* t)\) - lamp flux intensity.

There exists a parabolic relationship between the \( \text{HO}_2 \) concentration and resulting ion count ratio (figure 2).
During this experiment, for every fixed concentration of HO₂ prepared, there was a corresponding count ratio of HSO₄⁻ / NO₃⁻. Therefore, by substituting both quantities into the relation shown below, a calibration factor, (F) was obtained.

\[
[\text{HO}_2] = \text{Calibration Factor (F)} \times \text{Count ratio}
\] (iv)

Subsequently, the above relationship was used to calculate HO₂ concentrations for any count ratio measured using the instrument.

**Dilution Method**

As described earlier, the main goal of this research was to improve the sensitivity and speciation of the PerCIMS instrument via a new inlet chemical scheme. This new method has two aspects namely, nitrogen dilution (N₂) and oxygen dilution (O₂). Both methods are used to control the chemistry in the inlet. This current approach is meant to improve the inlet chemical
HO$_2$ and RO$_2$ speciation and as a side benefit, it avoids use of concentrated NO and SO$_2$ gases that are hazardous to human health when exposed to the atmosphere.

To improve the HO$_2$ only mode, N$_2$ is added to the inlet to reduce oxygen in order prevents the conversion of RO$_2$ to HO$_2$ thereby allowing only the detection of HO$_2$ concentrations. RO$_2$ in this case reacts with dilute NO, to form RONO. This scheme has been employed with success in similar instruments [Hanke et al., 2002]. Below is a schematic of the inlet chemistry of the N$_2$ method.

**Diagram 5: Inlet chemistry of N$_2$ Dilution**

\[
 RO_2 + NO \rightarrow RO + N_2
\]

\[
 \downarrow \text{NO}
\]

RONO

RO$_2$’s lost:

Measure HO$_2$ only

Conversely, the oxygen dilution method is used to improve the HO$_x$RO$_x$ mode. In this mode, RO$_2$ is first converted to HO$_2$, which is eventually converted to HSO$_4^-$ ions and the sum of both radicals are measured. In this method, the concentration of oxygen is increased at the inlet to amplify the conversion efficiency of RO$_2$ to HO$_2$ and reduce RONO formation. Shown below is a chemical scheme of the O$_2$ dilution at the inlet.

**Diagram 6: Inlet Chemistry of O$_2$ Dilution**

\[
 RO_2 + NO \rightarrow RO + \text{Added } O_2 \rightarrow HO_2
\]

\[
 \downarrow \text{NO}
\]

OH

\[
 \downarrow \text{SO}_2
\]

↓

HSO$_4^-$

Measure HO$_2$ + RO$_2$

SOARS® 2002, Olusegun Goyea, 12
RESULTS AND DISCUSSION

Figure 3 illustrates a graphical representation of one of the N₂ dilution method.

As shown (figure 3), as the flow of N₂ was increased in the PerCIMS instrument’s inlet, the average concentration of RO₂ observed simultaneously decreased. This implies that there exists inverse relationship between these two concentrations and in addition this figure demonstrates that the N₂ dilution method has a potential of being successful. The decrease in signal is desired for the HO₂ only mode where an increase in N₂ should favor HO₂ only measurement.

Figure 4 shows a result of using the O₂ dilution method. The graph is a plot of O₂ concentration against average RO₂ concentration detected as shown below.
Figure 4: RO$_2$ Dilution Using O$_2$

\[ y = -2 \times 10^{-6} x^2 + 0.0127x + 14.029 \]
\[ R^2 = 0.9732 \]

Figure 5: O$_2$ Dilution Time series

O$_2$ increased to 1000 sccm

No oxygen added

O$_2$ increased to 500
From Figure 4, it is shown that as more O$_2$ was added to the inlet, greater concentrations of RO$_2$ radicals were measured. This suggests that the oxygen method looks favorable and be further exploited improve the RO$_2$ detection technique of the instrument as described by the chemical schematic shown above (O$_2$ dilution). The oxygen method would be used to increase the conversion efficiency of RO$_2$ to HO$_2$ in the HO$_2$RO$_2$ mode.

To further examine this method, a time plot series was also considered. This is a graphical representation of the behavior within the inlet as different concentrations of gas were added. This is illustrated in figure 5.

From the graph, it is shown that initially, the average concentration of RO$_2$ detected was about 19 pptv due to high NO and low O$_2$ concentrations. Subsequently, oxygen concentration was increased within the inlet by increasing the flow rate to 500sccm, as a result, RO$_2$ detected picked up to about 25 pptv (figure 5). O$_2$ flow was further increased to 1000 sccm to further investigate its effects and as shown on the graph, RO$_2$ detected increased to about 45 pptv. This further rein enforces the potential future success of O$_2$ dilution.

**CONCLUSIONS AND FUTURE WORK**

Initial results have proved the success of the new dilution method. This method has the potential to improve the speciation and specificity of measuring HO$_2$ and RO$_2$ radicals and also to prevent the use of concentrated NO and SO$_2$ gases, which are harmful to humans. Further experiments as well as modifications are required to fully ascertain if the N$_2$ / O$_2$ dilution method is better than the original inlet chemical scheme. Further refinements to the inlet dilution method include: (1) reducing the inlet pinhole diameter and (2) using a pre-inlet mixing chamber. A smaller pinhole will reduce the airflow into the inlet thus allowing a greater range of dilution without over pressurizing the inlet. A pre-inlet mixing chamber will allow a greater dilution and thus increasing the inlet flow. The increased flexibility of the mixing chamber allows more control on the mixing parameters. This is an ongoing project in the Atmospheric Radical Group (ARS) at NCAR. The success of this research will make available an improved PerCIMS technique that will be used in campaigns to measure tropospheric peroxy radicals and thus improve our understanding of atmospheric photochemistry.
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