

Quantification of gas phase hydrogen peroxide and methyl peroxide in ambient air: Using atmospheric pressure chemical ionization mass spectrometry with O_2^- , and $O_2^-(CO_2)$ reagent ions



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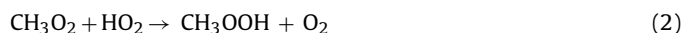
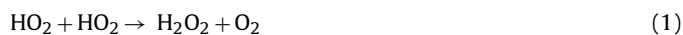
ABSTRACT

Instrumentation and ion chemistry are described for the measurement of hydrogen peroxide (H_2O_2) and methyl peroxide (CH_3OOH) in ambient air by chemical ionization mass spectrometry (CIMS). A CIMS, designed and certified for aircraft deployment, was used in this work. The reagent gas was ultra-pure air containing 400 ppm CO_2 . The resultant reagent ions, O_2^- and $O_2^-(CO_2)$, form cluster ions with CH_3OOH and H_2O_2 , respectively, and are monitored at 80 m/z [$O_2^-(CH_3OOH)$] and 110 m/z [$O_2^-(CO_2)(H_2O_2)$]. The CIMS instrument was periodically calibrated using gas-phase standards generated from aqueous solutions. A Carulite-200[®] catalyst was used to remove peroxides from ambient air to blank the system to account for variations in the ambient air matrix. H_2O_2 also forms a stable cluster ion with O_2^- though its calibration behavior was more complex than that for $O_2^-(CO_2)$ in ambient air. The instrument was deployed on the National Center for Atmospheric Research Gulfstream-V aircraft. Representative measurements from the May–June 2012 Deep Convective Clouds and Chemistry experiment spanning altitudes between 0 and 13 km over the south-central midwest and southeastern United States are shown. Laboratory experiments, airborne experiments and theoretical molecular modeling approaches were utilized to identify and select reagent ions and to understand the ion–molecule reactions for the formation of peroxide-ion clusters in the ambient air matrix under tropospheric conditions. The analytical viability of a particular ion–molecule adduct was supported by *ab-initio* molecular orbital calculations.

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1. Introduction

Hydrogen peroxide (H_2O_2), and methyl peroxide (CH_3OOH) are important atmospheric peroxide compounds [1,2]. The peroxides are predominantly formed in the atmosphere through gas phase radical reactions involving HO_2 radical through reactions (1) and (2).



Loss of H_2O_2 and CH_3OOH from the atmosphere occurs through wet and dry deposition [3], photolysis and reaction with OH radical.

The latter two processes generate additional HO_x radical species (OH and HO_2 radicals) which are very short lived, consequently the parent peroxides with longer lifetimes act as HO_x radical reservoirs [2].

Much of what is known about atmospheric peroxide chemistry was determined by partitioning the gas phase peroxides into an aqueous phase for quantitative analysis by colorimetric or fluorometric techniques [2]. Separation of H_2O_2 and organic peroxides by High Performance Liquid Chromatography (HPLC) and subsequent fluorescence detection has enabled quantification of individual peroxides. Using these techniques the distributions of the peroxides as a function of latitude and altitude over the oceans [4,5] and over the continental United States in multiple seasons has been determined [6,7]. Over the continental United States the median mixing ratio of H_2O_2 below 1 km and also in the middle troposphere was ~ 2 ppbv, reaching a maximum just above the boundary layer, and

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above 6 km the median concentration decreased to ~ 400 pptv. In the troposphere below 6 km the range of concentrations was from 12.5 pptv to 13 ppbv [6–9]. For CH_3OOH , the range of concentrations observed in the boundary layer was from 25 pptv to 2.1 ppbv, median mixing ratios decreased with altitude, ~ 630 pptv in the boundary layer, 600 pptv in the middle troposphere, and 200 pptv in the upper troposphere [7]. Since these peroxides act as reservoir species for OH radicals, transport from the lower troposphere to the upper troposphere, such as with deep convective clouds, can significantly impact the upper troposphere HO_x budget and tropospheric ozone formation [7–10].

The scales of horizontal and vertical changes in peroxide concentrations coupled to the speed of an aircraft (e.g., turboprop $\sim 100 \text{ m s}^{-1}$; jet $\sim 200 \text{ m s}^{-1}$) require rapid sample time resolution for in situ atmospheric measurements. The wet chemical analysis time is on the order of 10^2 s , and does not allow for sufficient temporal-spatial resolution to examine faster chemical-transport processes involving the peroxides (of order $\leq 1 \text{ s}$ or $\leq 100 \text{ m}$ for convective cloud scale) from an aircraft. To elucidate these processes, techniques to quantify the peroxides on sub-second time scales and at 15–25 ppt (ppt, mole mixing ratio times one trillion) are needed.

Prior laboratory and field work has shown the detection of peroxides by CIMS with both positive and negative reagent ions can achieve the needed detection limits and time resolution. Španěl et al. [11] investigated whether H_3O^+ , NO^+ and O_2^+ could be used to quantify H_2O_2 and $\text{CH}_3\text{C}(\text{O})\text{OOH}$ (peroxyacetic acid, PAA) in humid air and found NO^+ and O_2^+ could be used for H_2O_2 and $\text{CH}_3\text{C}(\text{O})\text{OOH}$, respectively. Proton-transfer reaction mass spectrometry was used to detect isoprenehydroxy-hydroperoxides at a mass-to-charge ratio (m/z) of 101 over a tropical rain forest [12]. Although, proton-transfer reactions have been unsuccessful for the determination of H_2O_2 due to the proton affinity of H_2O (691 kJ mol^{-1}), H_2O essentially out competes H_2O_2 , and in practice eliminates the formation of $\text{H}^+(\text{H}_2\text{O}_2)$ adducts in humid air streams [13]. Several negative ion reagents have been used to quantify peroxides. Fluoride anion (F^-) has been shown to form a cluster with H_2O_2 and CH_3OOH in laboratory studies [14]. The $\text{CO}_3^-(\text{H}_2\text{O}_2)$ cluster was observed in airborne observations over Germany during a 1991 field campaign aboard the DLR Falcon [15] and was used to quantify H_2O_2 . A negative ion CIMS technique using the cluster chemistry of CF_3O^- for the sensitive and selective airborne measurements of H_2O_2 and $\text{CH}_3\text{C}(\text{O})\text{OOH}$ has been successful [16]. CF_3O^- has proven to be a versatile reagent ion, and is the basis for a number of CIMS techniques [16–19]. However, CF_3O^- was not a viable reagent ion for CH_3OOH for a single quadrupole CIMS due to the presence of an interfering isobaric compound. Quantification of CH_3OOH required a triple quadrupole mass spectrometer to first select for the $\text{CF}_3\text{O}^-(\text{CH}_3\text{OOH})$ adduct mass and then used fragmentation to isolate CH_3OOH and determine its atmospheric concentration [20]. Chen et al. [21] have demonstrated the vapor phase detection and quantification of H_2O_2 in laboratory air at the sub-ppb level using O_2^- as a reagent ion. Last, Treadaway [22] and Treadaway et al. [23] using a mixed reagent ion system for formic acid and acetic acid also observed H_2O_2 and CH_3OOH using I^- chemistry although their sensitivities were fair and poor, respectively.

The focus of this study is the development and application of multi-reagent chemical ionization mass spectrometry (CIMS) for the sensitive, specific, and quantitative detection of both H_2O_2 and CH_3OOH using a single quadrupole. An additional goal was the development of an instrument that could be Federal Aviation Administration (FAA) certified to deploy on the National Science Foundation's National Center for Atmospheric Research (NSF/NCAR) Gulfstream-V High-performance Instrumented Airborne Platform for Environmental Research (GV-HIAPER) for *in situ* measurements. The development of a fast response instrument for the *in situ* measurement of peroxides meeting the GV-HIAPER

certification would provide a new tool to address a number of unresolved scientific questions surrounding the atmospheric chemistry of peroxide compounds in the upper troposphere.

In this paper we describe a developed multi-reagent ion chemical ionization mass spectroscopic technique, which was used to quantify atmospheric concentrations of CH_3OOH and H_2O_2 during the Deep Convective Clouds and Chemistry (DC3) field campaign. *Ab-initio* molecular orbital calculations were used to identify thermodynamically favorable ion-molecule adducts which were confirmed by experiment. These calculations and experiments suggest $\text{O}_2^-(\text{CO}_2)$ as the species clustering with H_2O_2 to form the analytical adduct ion, rather than a CO_4^- ion. Last, CIMS observations of the peroxides from GV-HIAPER performed in the DC3 field program (an assessment of the importance of the photochemistry, transport, microphysical processes, and multiphase chemistry that control ozone and water vapor levels in the upper troposphere over the mid-western and southeastern United States [24]) are presented, which illustrate the viability of the technique.

2. Methods

2.1. Instrumentation

CIMS has been shown to be a versatile and fast measurement technique for a wide variety of atmospheric trace gases [17]. Chemical ionization typically allows for much greater specificity in the detection of neutral species. The choice of a particular reagent ion for adduct formation with the primary analyte of interest often limits the detection other species of interest and the matrix within which the reagent ion scheme will be successful. Due to the reactivity of the reagent ion with the analyte of interest and with other gases that may be present (e.g. H_2O , CH_4 , O_3 , NO , etc), interferences may arise through the formation of adducts with the same mass (within the mass resolution of the spectrometer used) as the analyte of interest but with a different chemical composition. The goal of this work was the development of a single instrument enabling the quantification of H_2O_2 and CH_3OOH at ambient levels in the atmosphere.

A diagram of the peroxide chemical ionization mass spectrometry (PCIMS) instrument is shown in Fig. 1. PCIMS is based upon a CIMS hardware configuration, originally described by Slusher et al. [25], and is comprised of a ^{210}Po alpha emitter ionization source (NRD LLC, static eliminator), a drift tube, a collision dissociation cell, an octopole ion guide and a quadrupole mass filter (THS Instruments, Atlanta, GA). It is a differentially pumped system, using two molecular turbo-pumps, a hybrid turbo-drag pump and a scroll pump. The drift tube is kept at a constant pressure of 22.4 hPa by using a critical orifice on the sample inlet, a second critical orifice on the reaction cell outlet, and varying a supplemental ultrapure N_2 flow with a mass flow controller. Reagent ions were generated by passing 400 ppm CO_2 in ultrapure air through the ^{210}Po source at 80 sccm.

For *in situ* measurements from the GV-HIAPER aircraft, ambient air was sampled through a heated $\sim 8 \text{ ft}$ ($\sim 2.4 \text{ m}$) length of $\frac{1}{2}$ ($\sim 1.27 \text{ cm}$) O.D. PFA Teflon tubing connected to a heated NCAR GV-HIAPER Modular Inlet held at 30°C and mounted on the topside of the GV-HIAPER aircraft. During laboratory characterization experiments, ambient laboratory air or zero air was sampled through an $\sim 8 \text{ in}$ ($\sim 20.3 \text{ cm}$) length of $\frac{1}{2}$ ($\sim 1.27 \text{ cm}$) O.D. PFA Teflon tubing at room temperature. The total sample air flow through the inlet line was 10.0 slpm. For both inlet configurations, sample air passes through a 0.51 mm diameter critical orifice to enter the PCIMS instrument reaction chamber. The high pressure side is the ambient inlet atmospheric pressure and the low pressure side is fixed at 22.4 mbar by a pressure controlled mass flow of ultrapure

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