Review of "A new technique for the direct detection of HO_2 radicals using bromide chemical ionization mass spectrometry (Br-CIMS): Initial characterization" by Sanchez et al.

This paper describes the initial characterization of a chemical ionization mass spectrometric technique for the measurement of tropospheric HO_2 radicals. The paper provides a small amount of justification for measurement of HO_2, and discusses other techniques that have been reported. It is argued that each of the other approaches have drawbacks that are partially or wholly due the indirect nature of the measurement. The technique and instrumentation employed for Br-CIMS are briefly described, including other methods of ionization that were evaluated before settling on bromide ion clustering. The results of laboratory studies including instrument calibrations are described. Finally, outcomes of a few days of ambient measurements are presented.

Accurate, precise, fast, and high-quality measurements of HO_2 (and other free radicals present in the troposphere) are important and desired as tests of tropospheric chemical mechanisms. This is particularly true in environments that are rich in biogenic VOCs since their oxidation chemistry is complex and may not be fully understood. Such instrument developments, including the present one, are definitely within the scope of AMT. This paper presents the development and initial characterization of a novel tool that could become valuable in tropospheric chemical studies. While the results presented are tantalizing, this reviewer would not characterize the conclusions as substantial. The scientific approach to the research included many valuable aspects, but also was lacking in procedures employed to arrive at some of the conclusions. This reviewer would like to see much more detail in the instrument description and in the laboratory characterizations, including calibrations. Thus, it is difficult to ascertain whether the interpretations and conclusions are supported by the results. More detail is needed in the development of the arguments related to the performance of the instrument as employed. This added detail will also allow the work to be reproduced by other scientists, which is not possible with the paper as it is currently written.

The discussion of previous methods for measurement of HO_2 is fairly complete, but each method is only briefly touched upon. A more detailed description of the most widely used methods is suggested. Also, while not all papers published with these various methods need be included in the references, this reviewer suggests including the most recent papers as well as those related to the initial development of these methods.

The title of the paper describes the features of the paper. This reviewer does take issue with the assertion that the method is direct, which is discussed below. The abstract accurately summarizes the paper concisely. With the paper expanded to include more detail on the instrument and the laboratory experiments, the abstract will need to include some of this additional information. Generally, the organization of the paper is well-structured, with a few exceptions that are described below. The language is mostly easy to read, precise, and grammatically correct. A few suggestions in this regard are presented below.

Equation 1 is a correct description of the amount of HO_2 produced in the photolysis of water vapor by 184.9 nm radiation. There is inconsistency with standard photochemical symbol usage. The symbol σ (sigma) is typically used for absorption cross sections (as used in this paper). Quantum yields, though, are usually represented by ϕ (phi). The photolysis time is usually represented by t (tee), while τ is usually reserved for lifetime, chemical or otherwise. The radiation flux is usually represented by I (eye)

or F (eff) rather than q (cue). Also, the equation should have delta values for [HO_2] and the photolysis time, since it describes the increase in HO_2 from the photolysis. If the HO_2 is below the detection limit in the absence of photolyzing radiation then the equation is correct without the deltas. Several selections for values were made without justification (e.g. the absorption cross section and the method for measurement of the lamp photon flux).

This reviewer does not believe there are substantial parts of the paper that should be eliminated. To the contrary, as discussed above, it should be expanded to include more detail. Such detail could be presented in the supplementary material, depending on its length.

The characterization of a new analytical method requires more than indication that it responds to the analyte of interest, that the calibration is linear, its behavior in the presence of possible interferences, and that ambient measurements look qualitatively correct. It requires careful characterization of the sources of background signals as well as those from addition of varying amounts of the analyte. It should also involve evaluation of response as functions of instrumental parameters, such as flows, pressures in the various chambers, temperature of ion source and ion-molecule reaction region, operating conditions for the quadrupoles and ion optics, pumping speeds, detector conditions, and so on. To give the reader a good understanding of the instrument behavior, plots of raw data collected in the laboratory and the field would be helpful. If any of the above parameters cause significant changes to instrument response, then such results should be presented as text with the possible inclusion of a graph or two. When describing the uncertainty of the measurement, the calculation involves more than the uncertainty of the calibration. For example, there are uncertainties in the signals that go into the calculation of HO_2 concentrations that should be included. It is important (via text and graphics) to describe how the various signals (analyte signal and background signal, and presumably, reagent ion signal) are used to calculated the abundance of HO_2 and how variations in the signals lead to uncertainties in the derived HO_2 amounts. The issue of stability should also be addressed: how much do the instrument sensitivity, background, and reagent ion levels vary over a period of hours, days, weeks and months?

It would have been good to have collected enough information in the ambient study to run a constrained photochemical model, which would then be compared with the observations. The HNO_4 equilibrium approach to estimating HO_2 is interesting, but it is not validated. This reviewer believes that such an approach has been compared with HO_2 observations by other methods with significant differences (unpublished). This means that there is really no other estimate (instrument, model or other) of HO_2 to compare with the observations presented. In the presentation of the HNO_4 method, the uncertainties of the components of the calculation (concentrations of HNO_4, NO_2, and the equilibrium coefficient) should be given, and the resulting uncertainty in HO_2 calculated. The uncertainties should then be shown in Figure 4.

To summarize this reviewer's general comments, much more rigor in the amount of detail in the characteristics of the instrument and its response to HO_2 and other possible interferences is needed to allow the reader to assess whether this new technique has reasonable promise for use in future atmospheric chemistry studies. Equations describing the calibration, calculation of radical levels, and calculation of uncertainties need to be given with clear descriptions and use of standard symbols. Examples of ambient data (signals, background and reagent ion signals) need to be given along with the average diurnal profiles as presented in the current version of the paper. Error bars should also be

included in most of the curves in most of the figures. The source of those error bars should be given (in the text and figure caption), whether it be overall uncertainty or bin standard deviations (e.g. to develop the diurnal averages).

Specific comments:

Title, abstract, and method description. Direct versus indirect measurements. This reviewer takes issue with the assertion that this method is direct. Indeed it can be argued that all chemical ionization mass spectroscopic methods are indirect. Direct ionization of analyte (though photoionization, electron impact or other) could perhaps be considered a direct method. The most direct methods do not rely on calibrations, but instead depend on fundamental spectroscopic and/or physical parameters. The statement in the abstract that "The indirect nature of current HO_2 measurements introduces challenges in accurately measuring HO_2…" is confounding and not justified. A method could be very indirect, but very accurate. It is recommended that the emphasis on the directness of this method be removed from the title, abstract, and body of the revised paper.

Body of paper, various locations. The term "diurnal" and "diurnals" are used as nouns. Diurnal is most definitely an adjective and should describe a noun such as "profile" or "behavior". Suggest changing throughout the paper.

Abstract and body. The discussion of the diurnal behavior of HO_2 being dictated (affected or determined?) by morning vehicle NO_x emissions is not consistent with the information shown in Figure 3. This may be due to the fact that the data is presented as a 4-day diurnal average, or a plotting error. At any rate, HO_2 increases with the UV flux, and the small delay in the increase (between about 8 and 10 AM) could be due to elevated NO levels, but there are likely contributions from low O_3 levels and perhaps other causes (clouds, winds, temperature profiles). Suggest rewording the discussion of this impact. The slow decay in the afternoon and evening is expected, but not to the degree shown by the observations. Indeed at sundown (2000 hours), the observed HO_2 is about half that at the midday peak. The slow decay is also not expected given the non-zero values of NO after sundown. This could imply non-photolytic sources of HO_2 rather than slow chemistry. The discussion should examine all possible causes. The timing of the peaks in UV flux compared to HO_2 is discussed on page 5 (line26). It states that there is a difference in the time of the peaks, but Figure 3 seems to show that the peaks coincide.

Page 1, line 28. suggest "…production of ozone via its reaction with NO."

Page 1, lines 29-30. This statement is worded in a confusing way. Suggest reworking to make the point clear

Page 1, line 33. The lifetime of HO_2 depends on a number of factors including the NO level. While it is true that the lifetime is less than one minute in urban atmospheres, it can be longer in remote environments.

Page 2, lines 11-12. It is stated that converting HO_2 to OH with NO introduces additional complexity. While this could be true, it is not necessarily so. Suggest rewording this sentence.

Page 2, lines 15-16. While most researchers use PERCA to measure HO_2+RO_2, there is no reason why techniques such as oxygen dilution could not be employed. This reviewer does not believe that the technique fundamentally precludes speciation. Someone has just not yet been successful in doing so. Suggest rewording.

Page 2, line 35. After description of previous techniques and their pitfalls, the Br-CIMS (and other ionization schemes) is briefly introduced. While not mentioned here or elsewhere, it is known that cluster-based ion techniques can suffer from issues such as variable cluster stability, which can depend on ambient conditions and water vapor concentrations. While this reviewer understands that the authors want to put their technique in the best light, it is also appropriate to recognize and discuss potential problems. Suggest adding such a discussion somewhere, probably on pages 3-4.

Page 3, line 13. It is stated that "…only the integrated peak data is used in this paper…". This needs a bit of explanation, but this reviewer assumes you mean the integrated area of the peak. Also, the word data is plural, so it should be "…data are used…".

Page 3, lines 26-29. In the discussion of chloride and iodide ionization schemes, it is stated that the $Cl^-(HO_2)$ cluster was not observed. What is not stated is whether any ions where observed. In other words, were full mass scans conducted with the quadrupole CIMS?

Page 3, line 33. Suggest "…we observed that addition of NO_2…". Also, one needs to be careful that the mixture contains no NO. With a mixture in N_2, it is very likely that it does contain NO. It is better to employ mixtures of NO_2 in air or oxygen to minimize the amount of NO. Also, there are techniques for removing NO from a mixture of NO and NO_2.

Page 3, line 35. Suggest "… addition of NO_2 showed an increase…".

Page 3. The method of determining the instrument background is discussed on page 6, line 15, but it is probably better to include in this section (pages 3-4). Regarding the production of HO_x radicals in radioactive ion sources, this phenomenon is well known. Other CIMS researchers add reagents to the flow over the ion source to minimize this issue. It is suggested that experiments with reagents added to the ion source be conducted to determine whether the internal HO_2 can be eliminated, thus reducing the background and the impact of its variability. It may be that NO is not the best reagent in this case, but that is the obvious first choice.

Page 3, line 8. I was surprised that the ion source flow is the same as the sample flow, resulting in a 1:1 dilution of the sample. Also, N_2 was used as the main component of the ion source flow. Is this optimum, or does it not matter what is used. Perhaps a different configuration of the ion source could be optimum for this measurement.

Page 4, line 4. It is stated that there were no observed artifacts with the Br-CIMS approach. This disguises what was tested. Suggest testing every possible gas in the troposphere of reasonable concentration, and listing the gases tested here. Other factors should also be tested such as aerosol loading, and inlet temperature and pressure. Temperature is discussed later in the paper, but this reviewer suggest that this discussion be moved to this section.

Page 4, line 6. Suggest "…signals were observed."

Page 4, lines 16-20. In the introduction to the calibration procedure, it is stated that humidified and dry air were mixed together. How was the air humidified? If a bubbler was used, this could be problem. It is known that bubblers can produce small droplets that evaporate downstream and produce additional water vapor that is not accounted for. Also, it is stated that an AADCO air generator was used. Does this approach produce clean enough air for this important part of the instrument characterization? Since the photolysis of water produces OH, any hydrocarbons (in addition to CO discussed on line 30), particularly fast reacting ones, could influence the HO_2 amounts produced. Also, any NO_x present could cause additional problems. To overcome potential problems, suggest doing at least some experiments with very high purity air in cylinders with low hydrocarbon content. Various parameters of the calibration system should be given (e.g. total flow, range of dew points, impacts of using different slits, humidities, and flows on instrument performance).

Page 4, line25. It is stated that the Creasey et al. (2000) (reference not in the reference list) water vapor cross section was used, but it is not stated why. Also, why was the approach of photon flux measurement using a phototube employed rather than an actinometric method? Actually, it would be better to use multiple approaches.

Page 4, line 28. The discussion of measurement of flow velocity needs some more detail. Does the velocity profile match laminar or plug flow? Is the Reynolds number such that the flow in the photolysis section is turbulent or laminar? Is the entrance length sufficient that fully developed flow can be expected?

Page 4, line 31. Suggest saying specifically the range of HO_2 values employed in the calibrations (i.e. xx to yy pptv). Suggest rewording to "…were kept low so as to calibrate at atmospherically relevant levels…". It should be recognized that there are conditions where HO_2 can get above the 45 pptv shown in Figure 2.

Page 4, line 35. The issue of the intercept may be related to contaminants in the air (discussed above). For example, a carbonyl compound could be present that photolyzes at the mercury lamp wavelength. Suggest working (and describing that work) to minimize this "extra" HO_2 produced.

Page 5, Calibration section. One needs to include uncertainties in the signals (random fluctuations) used to derive the calibration to get an overall calibration uncertainty. Also, it is convention to give the uncertainty at the 95% confidence interval, although whatever confidence level or sigma value is used should be stated. It should also be stated how stable the calibration is with time.

Page 5, line 9. Suggest "…and can therefore be affected…", since it depends on wind direction.

Page 5, line 10. The length of the inlet is given, but the reaction time (derived from length, diameter and flow) should also be given. Also suggest using "minimize" rather than "avoid".

Page 5, line 11. It is stated that 4 ppm NO is added to determine the background. What is the concentration in the inlet resulting from such additions? Has the amount been optimized though systematic studies and/or calculations? Such experiments should be performed and described. Also, it would be helpful to be given information on the size of the background compared to ambient signals

Page 5, lines 14-15. It is stated that the m/z 112 signal is normalized for reagent ion signal at m/z 79. Is it clear that the detector and associated electronics are fast enough to measure count rates in the 10^6 range? Experiments conducted to verify this should be described.

Page 5, line 26. It says that there is a difference in time between the peak UV flux and peak HO_2 concentrations in Figure 3, but this reviewer does not see this. Perhaps it is a problem with the time scales in the figure. Please investigate this. Also, the statement that an HO_2 peak mixing ratio of 7 pptv is comparable to other studies in urban areas is misleading. Peak HO_2 values depend on many factors and the range of peak mixing ratios seen in urban environments varies over a very large range. This statement does not lend credence to the ability of this technique to quantitatively measure ambient HO_2.

Page 5, lines 31-34. Suggest indicating that the sources of HO_2 from biogenic VOCs after sundown is due to non-photolytic processes. This is obvious, but suggest being explicit. It is also not clear how a change in the boundary layer height would affect the decay of HO_2 after dark.

Page 5, lines 35-36. Suggest stating that the calculation of HO_2 from observations of HNO_4 and NO_2 depends on the temperature dependent equilibrium coefficient. Give the value used. Show the equation for calculating HO_2 using this approach. Do some calculations to indicate the time scale for approach to equilibrium at the conditions of the study (range of temperatures and concentrations).

Page 6, line 3. A positive bias in the HNO_4 measurement is mentioned. This should be discussed a bit more, giving indications of how large the bias appears to be (based on measurement-model comparisons in previous studies, for example), and its possible causes.

Page 6, line 7. Here the laboratory studies on temperature effects on sensitivity are described. Suggest moving this back to the laboratory studies section.

Page 6, line 13. It is stated that the measured diurnal profile of HO_2 agrees with expectations. This is vague enough to be not of much use. Especially since the diurnal profiles shown in Figure 4 differ significantly. The scaled profiles are within about 20% at the peak, but differ by a factor of 2-3 at midnight.

Page 6, line 17. A "metal wood scrubber" was used to remove HO_2 to compare with the NO addition method of background determination. Did you verify that there was enough contact time to remove all the HO_2? For example, double or triple the amount of contact to see if it makes a difference.

Page 6,line 25. The discussion of the iodide-CIMS seems a bit out of place here. Perhaps this should be moved to the discussion of the investigation of various ionization schemes. Suggest hypothesizing why this approach doesn't work. Is it purely a resolution issue or some other problem?

Page 7, line 6. Suggest "… charge exchange ionization is not feasible…".

Page 7, line 12. It is stated that observations at lower m/z decreases the likelihood of interferences. This statement needs explanation because it is not obvious that is true.

Page 7, line 16. Work on reagent addition to the source, may eliminate the issue of source-produced HO_2, making increased performance using higher activity sources possible. One can encounter space charge issues as the activity is increased, with the result of no improved sensitivity.

Page 7, references. In the future, suggest listing the reference as hanging paragraphs, so the first author's last name can easily be found.

Page 11. Suggest "Figure 1. Schematic diagram of the…". Suggest giving information on the roles of the various ion guiding components (quadrupoles, ion optics) and how they are configured. Indicate whether or not the inlet region is dark, or transparent to solar radiation.

Page 12. Suggest adding the word "laboratory" to indicate the calibration studies are not done in the field. Suggest indicating the variability of the calibration results (error bars and/or multiple calibration curves).

Page 13. Suggest indicated that these are "average" diurnal profiles for the time period indicated. Suggest changing the tic marks on the x-axis to every 4 or 6 hours, so that noon and midnight re clearly indicated. In the text and/or the caption, indicate the wavelength range and instrument for the UV flux measurement.

Page 15. The signal levels for the bromide ion CIMS are much higher than shown in the calibrations in Figure 2. This significantly changes the relative levels of background, signal and the interference at m/z 112.0127 at ambient HO_2 levels. Suggest either showing a spectrum at realistic ambient levels or discussing the relative amounts of background, signal, and interference at ambient levels.