

The sensitivity of the radical amplifier to ambient water vapour

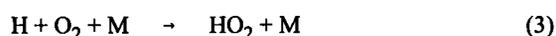
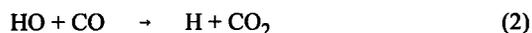
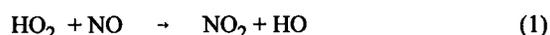
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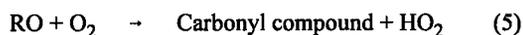
Abstract: The radical amplifier is an instrument used to measure radical concentrations in the troposphere. The critical parameter in determining the sensitivity is the chain length, which is shown to decrease with increasing water vapour in the reactor. When compared to measurements in dry air, this decrease is a factor 2 at a relative humidity of 40%. This suggests that field measurements using the radical amplifier may be underestimating the ambient radical concentration by a similar factor. One source of this deterioration in performance is an increase in the loss of radicals to the walls of the reactor, although there also appears to be a contribution from a water dependence on the gas phase chemistry.

Introduction

The radical amplifier is a technique used to determine total radical concentrations in the atmosphere (Cantrell and Stedman 1982, Hastie et al. 1991, Cantrell et al. 1993, Clemitshaw et al. 1997, Arias and Hastie 1996, Monks et al. 1996, Hu and Stedman 1994, and Mihelcic et al. 1993). This technique is indirect and relies on a series of chemical reactions which convert the radicals into a larger number of NO₂ molecules. It is the NO₂ that is measured and related to the radical concentration through a knowledge of the chemistry. In a typical instrument, ambient air is doped with high concentrations of NO and CO, with resulting concentrations of 2-6 ppmv and 4-10% respectively. Under these conditions atmospheric HO_x radicals enter into a chain reaction sequence as follows:



Organic radicals are largely converted to HO_x radicals through the reactions



and so also participate in the chain. Radicals are lost from this chain through gas phase termination reactions, or to the walls of the reactor such as:



The average number of times a radical cycles through the chain propagation reactions before being lost, which in typical systems is 100-150 times, is the chain length. Since one NO₂ molecule is produced each time a radical passes through the cycle, the radical concentration can be determined from the NO₂ concentration produced by this chemistry divided by the chain length. Thus the chain length is a critical parameter in determining the sensitivity of the radical amplifier.

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As with any indirect measurement, the quality of the radical amplifier measurements is only as good as the understanding of the technique. In this paper we report on the preliminary results of a laboratory study into the impact of ambient water concentrations on the performance of the radical amplifier, specifically the chain length. Given the high, and variable, concentrations of water in the atmosphere, any sensitivity would have a marked impact on the use of the technique in field studies.

Experimental

The radical amplifier used in this laboratory study is based on that of Arias and Hastie (1996). In the basic instrument, NO and CO are mixed with the sample air in a Teflon cross at the inlet to the Teflon tube reactor, to produce mixing ratios of 2 ppmv and 4% respectively. For the experiments reported here, an additional flow of air was introduced at the same point, to allow the addition of water vapour into the reactor. The luminol detector was operated in the linear regime by adding NO₂ from a permeation tube downstream of the reactor.

Tests were performed with HO₂ radical mixing ratios of 10 to 150 pptv generated from the photolysis of water in the presence of CO at atmospheric pressure (Schultz et al. 1995). These concentrations ensure the amplifier chemistry is operating in a linear regime (Hastie et al. 1991). To obtain the full range of water vapour concentrations it was necessary to vary the additional air flow to the reactor. As the total flow into the reactor is constant, the flow of air from the radical source, and thus the radical concentration, was not constant between experiments. Experiments in dry air showed the measured concentration of radicals agreed with that calculated from the dilution factor, showing there were no additional radical losses upon dilution. The change in chain length on the addition of water was obtained by measuring the NO₂ produced in the presence and absence of water in the additional air flow. The ratio of the NO₂ produced in the two experiments is the ratio of the chain lengths and, provided the experiments were performed in the linear region of the detector, is independent of the absolute concentration of the radicals and the sensitivity of the NO₂ detector.

Experiments were performed on three different reactors, using the same Teflon cross arrangement described above. No attempt was made to duplicate other inlet designs. The reactors used were: a 1/4" OD Teflon tubing reactor as used in the field by Arias and Hastie (1996); a 1/2" OD Teflon tube which has almost twice the volume to surface area ratio; and a 30 cm long, 3 cm OD glass reactor similar in size and shape to that used in some field studies (e.g. Cantrell et al. 1993).

Results and Discussion

Figure 1 shows the results of the room temperature experiments expressed as the fractional change in the chain length as a function of the relative humidity of the air in the reactor. The data show a significant decrease in the chain length with increasing relative humidity, dropping to almost half of the dry air value at 40% relative humidity. There is no significant difference in the response of the three reactors in spite of their different geometries and composition. In the context of field measurements this result

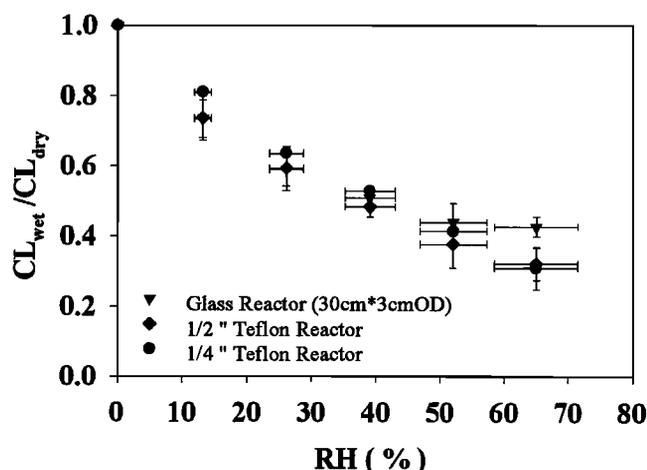


Figure 1. Change in the chain length of the radical amplifier with relative humidity in the reactor. Results for three different reactors are shown (see text).

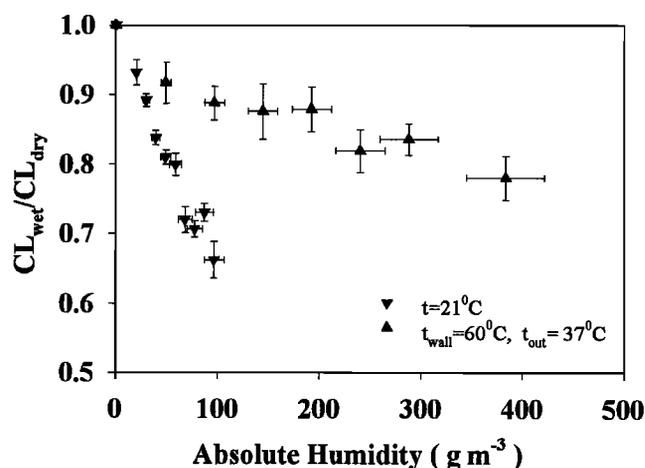


Figure 2. Change in the chain length of the radical amplifier with absolute humidity in the reactor for identical gas composition, but for different reactor wall temperatures.

implies that, if a radical detector is calibrated with dry air (as is usually the case) and the measurements are made at 40% relative humidity, the apparent radical concentration determined by the radical amplifier is only half of the actual radical concentration. Furthermore the chain length is very sensitive to changes in the relative humidity - at around 40% relative humidity it changes by 1% for every 1% change in relative humidity. Since field measurements are made at ambient humidity, and dry gases added to the reactor are at most 10% of the total, this observation suggests that measurements using this technique may underestimate the true radical concentration.

Given the magnitude of the effect of water and its sensitivity to variations in relative humidity, even the correction of data is likely to introduce significant errors into the measurements. Therefore the source of this change in sensitivity needs to be fully understood if the radical amplifier is to remain viable. The impact of the water could be via three mechanisms: an increase in reaction 7, the rate of radical loss to the walls of the reactor; an increase in the rate of the gas phase termination reactions such as reaction 6; or a decrease in the rate of the gas phase chain propagation reactions 1 or 2.

The impact of water on the nature of the reactor walls seems the most likely explanation. Radical loss to the walls of the reactor is the dominant loss mechanism in this radical detector and recent measurements of the rate coefficient for the loss of hydroperoxy radicals, in a 1/4"OD Teflon tubular reactor, show more than a factor of two increase for a relative humidity change from zero to 50% (Mihele et al., manuscript in preparation, 1998). If this is the most important factor, its impact could be reduced by heating the walls of the reactor to reduce the amount of adsorbed water.

Figure 2 shows the results of performing the experiment in the glass reactor with the walls held at two different temperatures. No attempt was made to equilibrate the gas temperature when the walls were heated. For a wall temperature of 60°C the gas temperature only reached a maximum of 37°C. The data are shown plotted against the absolute water concentration. There is much less impact of water at the wall higher temperature consistent with the lower water adsorption

If the sensitivity to water is due solely to variations in the wall termination reactions, the impact on the radical amplifier could be lowered by increasing the importance of the gas phase termination reactions. Additional experiments were performed at an NO mixing ratio of 12 ppmv. Under these conditions, reaction 6 is expected to remove 92% of the radicals compared with only 27% for the lower

NO concentration. The results obtained are compared with those of the original concentration of 2 ppm in Figure 3. They show that at higher NO concentrations the chain length has a reduced sensitivity to water. However given the expected dominance of the gas phase radical loss in the presence of higher NO concentrations, this improvement is not as large as would be expected. This suggests that the gas phase chemistry also has a dependence on water concentration.

The dominant radical in the reactor is the HO₂ radical. This radical is known to associate with water in the gas phase (Li et al. 1981, Sander and Peterson 1984) and while the adduct is known to increase the rates of self reaction (Kircher and Sander 1984) and reaction with NO₂ (Sander and Peterson 1984), it not known to undergo a radical termination reaction with NO. Since there are high concentrations of the adduct and NO in the reactor, even a minor channel to form nitric or pernitrous acid would have a large impact on the predicted chemistry. The adduct may also react more slowly with NO effectively reducing the rate of reaction 1. Both these effects would lower the observed chain length. To fully understand the source of the water dependence, additional kinetic data for reactions of radicals with NO_x species in the presence of water are required.

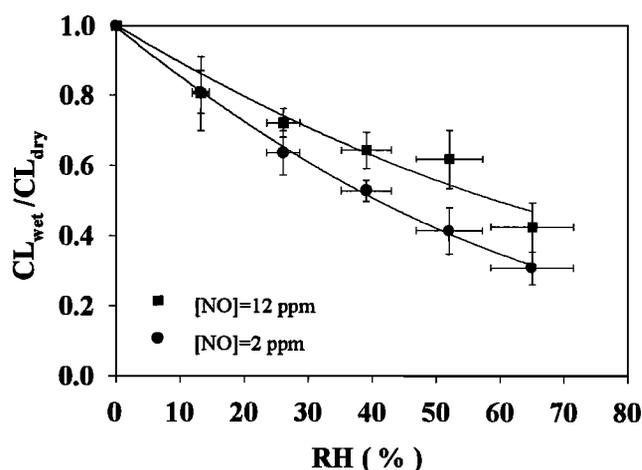


Figure 3. Measured chain lengths plotted against relative humidity for NO concentrations of 12 ppmv (squares) and 2 ppmv (circles).

There are two ways to deal with the water sensitivity. The first is by performing radical calibrations as a function of relative humidity and collecting ambient humidity data in conjunction with the radical measurements. The second is to redesign the radical amplifier to minimise the impact of ambient water vapour. In cases where the termination is dominated by the loss of radicals to the walls, the problem can be minimised by lowering the relative humidity. The reactor could be heated, but this would increase the rate of radical production from stable species such as PAN, and so would compromise the radical measurements in many environments. The reactor could be operated at low pressure, but this would also decrease the rates of all reactions and force a re-evaluation of the technique. The removal of water using membrane tubing or cooling the gas, as in other applications, seems unrealistic given the reactivity of the target radicals. Thus there does not appear to be a universal, simple method to overcome the water sensitivity identified here.

Conclusion

The radical amplifier as it is currently deployed has been shown to be adversely affected by ambient levels of water vapour that could make measurements severely underestimate the actual concentrations. The effect is at least partly due to an increased rate of radical loss to the walls of the reactor in the presence of water, but there also appears to be a contribution by the gas phase chemistry. Additional kinetic data on the reactions of radicals and NO_x in the presence of water are needed. Calibration of this instrument at varying relative humidities appears to be the only method to overcome this problem as no viable method for modifying the instrument is suggested.

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References

- Arias M. C., and D. R. Hastie, Radical chemistry at the SONTOS site in rural Ontario. *Atmospheric Environment* 30, 2167-2175, 1996.
- Cantrell, C. A., and D. H. Stedman, A possible technique for the measurement of atmospheric peroxy radicals *Geophys. Res. Lett.*, 9, 846-849, 1982
- Cantrell C. A., R. E. Shetter, J. A. Lind, A. H. McDaniel, and J. G. Calvert, An improved chemical amplifier technique for Peroxy Radical measurements *J. Geophys. Res.* 98, 2897-2909 1993.
- Clemittshaw K. C., L. J. Carpenter, S. A. Penkett, and M. E. Jenkin., A calibrated peroxy radical chemical amplifier for ground-based tropospheric measurements. *J. Geophys. Res.* 102, 25,405-25,416, 1997.
- Hastie, D. R., M. Weissenmayer, J. P. Burrows, and G. W. Harris, A calibrated chemical amplifier for atmospheric RO_2 measurements. *Anal. Chem.*, 63, 2048-2057, 1991.
- Hu J., and D. H. Stedman Free radical detector for tropospheric measurements using chemical amplification. *Anal. Chem.* 66, 3384-3393 1994.
- Kircher C. C., and S. P. Sander Kinetics and mechanism of HO_2 and O_2 disproportionation *J. Phys. Chem.* 88, 2082-2091, 1984.
- Li R-R, M. C. Sauer Jr., and G. Sheffield Temperature dependence of the gas phase self-reaction of HO_2 in the presence of H_2O *J. Phys. Chem.* 85, 2833-2834, 1981.
- Mihelcic D., D. Klemp, P. Mütgen, H. W. Pätz, and A. Volz-Thomas, Simultaneous measurements of peroxy and nitrate radicals at Schauinsland. *J. Atmos. Chem.* 16, 313-335, 1993.
- Monks P. S., L. J. Carpenter, S. A. Penkett, and G. P. Ayers, Night-time peroxy radical chemistry in the remote marine boundary layer over the Southern Ocean. *Geophys. Res. Lett.* 97, 535-538, 1996.
- Sander S. P. and M. E. Peterson, Kinetics of the reaction $\text{HO}_2 + \text{NO}_2 + \text{M} \rightarrow \text{HO}_2\text{NO}_2 + \text{M}$ Kinetics and mechanism of HO_2 and O_2 disproportionation *J. Phys. Chem.* 88, 1571-1575, 1984.
- Schultz M., M. Heitlinger, D. Mihelcic, and A. Volz-Thomas, Calibration source for peroxy radicals with built-in actinometry using H_2O and O_2 photolysis at 185 nm. *J. Geophys. Res.* 100, 18,811-18,816, 1995

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Correction to “ The sensitivity of the radical amplifier to ambient water vapour” by C. M. Mihele and D. R. Hastie

In the paper, “ The sensitivity of the radical amplifier to ambient water vapour” by C. M. Mihele and D. R. Hastie (*Geophysical Research Letters*, 25 [11], 1911-1913), there is an error in Figure 2. The corrected figure is shown correctly below:

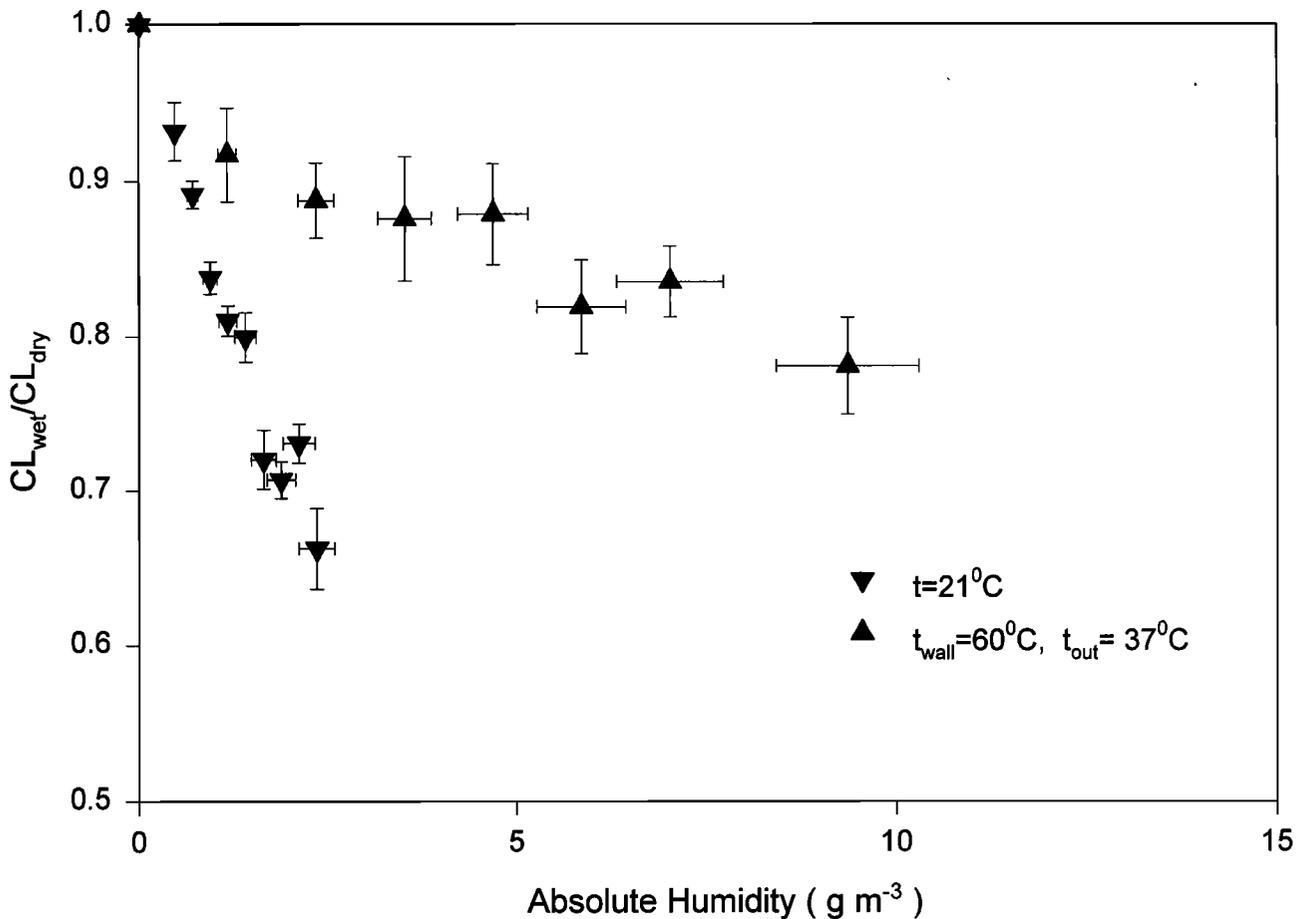


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