Optimized Operation and Calibration Procedures for Radical Amplifier-Type Detectors

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ABSTRACT

Laboratory experiments were conducted to improve the operation and calibration procedures for the ambient RO_x radical detectors ($RO_x = HO_2 + RO_2 + OH + RO$) based on chemical amplification. A new method for the experimental determination of the effective ratio between the absorption cross sections for water and molecular oxygen at 184.9 nm was developed and used to reduce the uncertainties associated with the peroxy radical source based on water photolysis. A novel peroxy radical source based on OClO was developed and employed to confirm the ambient humidity effect on the chain length of the radical detector. The humidity effect on the chain length can be reduced by heating the walls of the reactor and decreasing the residence time of the air sample in the reactor to avoid the possible interferences from thermolabile species.

1. Introduction

The tropospheric measurement of peroxy radicals by chemical amplification was first introduced by Cantrell and Stedman (1982) and has found application in a number of field studies over the last decade (Cantrell et al. 1992; Arias and Hastie 1996; Penkett et al. 1997). It overcomes the difficulties of low concentration and limited spectroscopic features by converting ambient radical concentrations into higher concentrations of the more easily measured NO_2, through reaction with high concentrations of CO (4%–10%) and NO (2–6 ppmv). For the odd hydrogen radicals ($HO_x = HO_2 + OH$) the amplifier chemistry is a straight chain reaction sequence that produces NO_2 and regenerates the radical:

$$HO_2 + NO \rightarrow OH + NO_2 \qquad (R1)$$

$$OH + CO \rightarrow H + CO_2 \qquad (R2)$$

$$H + O_2 + M \rightarrow HO_2 + M. \qquad (R3)$$

The length of the chain is limited by loss of radicals of which the wall reactions and HONO formation are the most significant (Hastie et al. 1991). Thus the chain length (CL), which is the number times the system cycles through reactions (R1)–(R3) or the number of NO_2 molecules produced for each radical that enters the system, is limited. By measuring the NO_2 produced by this chemistry and using the CL determined through calibrations, the ambient radical concentrations can be determined.

Organic radicals (RO_2 and RO) are also detected because, in the presence of NO in air, they are converted to HO_2 radicals, which are further amplified by reactions (R1)–(R3):

$$RO_2 + NO \rightarrow RO + NO_2 \qquad (R4)$$

$$RO + O_2 \rightarrow R'CHO + HO_2. \qquad (R5)$$

Therefore, the instrument generally measures the sum of radicals, usually defined as $RO_x = HO_2 + RO_2 + OH + RO$.

A typical radical detector samples air into a flow reactor where it is mixed with NO and CO and in which the chemistry takes place. The NO_2 produced is measured downstream of the reactor by a specific NO_2 detector, usually based on the chemiluminescent reaction with luminol (Wendel et al. 1983). To measure the radicals it is necessary to discriminate between the NO_2 produced by the chain reaction and that from other sources, for example, NO_2 in the ambient air sample and that produced by the titration of ambient ozone with the added NO. Discrimination against these background NO_2 sources is accomplished by modulating the signal. The chain chemistry is turned on and off by changing the time at which CO is added to the reactor. If the NO is added at the sample inlet but the CO is added further downstream, radicals are lost before encountering the CO, thus reaction (R2) does not occur and no radical amplifier chemistry occurs. However, the NO_2 from the

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background sources is still present. When CO is added simultaneously with NO at the ambient air inlet the chain chemistry is operative and the radicals are amplified. Thus, the NO_2 produced from the chain reaction is the difference between these two measurements.

One of the major difficulties in implementing this methodology was the development of calibration methods capable of quantitatively producing radicals at typical ambient concentrations. The most common calibration source uses the photolysis of water in air using a low-pressure mercury lamp to produce equal numbers of HO_2 and HO radicals. The ozone produced by the simultaneous photolysis of oxygen serves as an internal actinometer (Schultz et al. 1995). Therefore the total radical concentration $[HO_x]$ delivered by the source can be calculated using Eq. (I):

$$[\mathrm{HO}_x] = [\mathrm{O}_3]\frac{\sigma_{\mathrm{H_2O}}}{\sigma_{\mathrm{O_2}}}\frac{[\mathrm{H_2O}]}{[\mathrm{O_2}]}, \tag{I}$$

where $[O_3]$ is the ozone concentration produced by the source, and σ_{H_2O} and σ_{O_2} are the absorption cross sections for water and molecular oxygen at the wavelength of the lamp, 184.9 nm. This method has also been used to generate organic peroxy radicals by subsequently reacting the HO with hydrocarbons. This then gives equal concentrations of HO_2 and RO_2 radicals (where R is an organic group whose structure depends on the hydrocarbon being reacted). More recently, this calibration method has been shown to have some problems, most notably the effective absorption cross sections in a practical system are not those given in the literature; in fact, they are lamp and system dependent (Lanzendorf et al. 1997; Cantrell et al. 1997). Furthermore, this method cannot produce a "clean" source of organic radicals, without equal numbers of HO_2 radicals. Thus, even though this method has enabled the widespread use of the radical amplifier, it is not without problems and complementary calibration methods are desirable.

A further problem has recently been reported—the chain length of the radical detector has been shown to be extremely sensitive to ambient water vapor, primarily due to surface effects (Mihele and Hastie 1998; Mihele et al. 1999). Therefore, there is a need to redesign the radical amplifier to reduce this effect and to develop calibration sources that, unlike water vapor photolysis, can be used in ambient air. The present paper focuses on (i) a novel method to more readily overcome the problems around the absorption cross sections of water and oxygen; (ii) development of a novel, nonphotolytic peroxy radical calibration source; (iii) verifying the published water vapor dependence of the radical detector using this source; and (iv) redesigning the instrument to reduce the water vapor dependence while also limiting the interference from the decomposition of thermolabile species.

2. Results and discussion

a. Determination of the $\sigma_{H_2O}/\sigma_{EF,O_2}$ ratio for the water photolysis radical source

The radical source based on water photolysis relies on Eq. (I) to calculate the radical concentrations delivered by this source. Given the widespread use of this method the absorption cross sections for water and molecular oxygen at 184.9 nm have been investigated recently. Both values have been shown to be in error, although for different reasons.

The absorption cross section for water vapor (σ_{H_2O}) at 184.9 nm has been recently remeasured by two groups. The values obtained were similar: $7.14 \pm 0.20 \times 10^{-20}$ cm^2 (Cantrell et al. 1997) and $7.10 \pm 0.10 \times 10^{-20}$ cm^2 (Hofzumahaus et al. 1997), about 30% higher than the earlier value recommended by Baulch et al. (1982).

A potentially much more important problem has been identified in the effective absorption cross section for molecular oxygen. At 184.9 nm the oxygen absorption cross section is a very strong function of wavelength. The low-pressure mercury lamp commonly used for the photolysis is not a line source, the emission has a finite line width, and the center wavelength suffers from line reversal. The linewidth and the extent of the reversal depends on the individual lamp and its operating conditions (Lanzendorf et al. 1997). Thus the effective absorption cross section for molecular oxygen (σ_{EF,O_2}) must be determined for each calibration source and used in Eq. (I). A high-resolution spectrum of the lamp can be taken and used with the known cross sections to calculate σ_{EF,O_2} over the lamp spectrum (Hofzumahaus et al. 1997).

A somewhat simpler method can be used to experimentally measure the $\sigma_{H_2O}/\sigma_{EF,O_2}$ ratio for a particular experimental system. In the photolysis region of the calibration source, the photochemistry is dominated by the following reactions:

$$\mathrm{H_2O} + h\nu \rightarrow \mathrm{OH} + \mathrm{H} \tag{R6}$$

$$\mathrm{O_2} + h\nu \rightarrow 2\mathrm{O} \tag{R7}$$

$$\mathrm{O} + \mathrm{O_2} + M \rightarrow \mathrm{O_3} + M \tag{R8}$$

$$\mathrm{H} + \mathrm{O_2} + M \rightarrow \mathrm{HO_2} + M. \tag{R9}$$

By neglecting the loss reactions for the radicals the continuity equations for the above processes are

$$\frac{d[\mathrm{O_3}]}{dt} = \Phi_{184.9}\sigma_{\mathrm{EF,O_2}}\eta_{\mathrm{O_3}}[\mathrm{O_2}] \tag{II}$$

$$\frac{d[\mathrm{HO_2}]}{dt} = \Phi_{184.9}\sigma_{\mathrm{H_2O}}\eta_{\mathrm{HO_2}}[\mathrm{H_2O}], \tag{III}$$

where $\Phi_{184.9}$ is the actinic flux at 184.9 nm. Integrating the above equations, knowing the formation yields for ozone ($\eta_{O_3} = 2$) and HO_2 radicals ($\eta_{HO_2} = 1$), and recognizing that τ is the time interval that the air parcel flows through the illuminated region, which can be related to the air flow and the volume of the illuminated region by $\tau = V/F_{\mathrm{air}}$, the following relations are obtained:

$$[\mathrm{O_3}] = 2\Phi_{184.9}\sigma_{\mathrm{EF,O_2}}[\mathrm{O_2}]\frac{1}{\tau}$$

$$= 2\Phi_{184.9}\sigma_{\mathrm{EF,O_2}}[\mathrm{O_2}]\frac{V}{F_{\mathrm{air}}} \qquad \text{(IV)}$$

$$[\mathrm{HO_2}] = \Phi_{184.9}\sigma_{\mathrm{H_2O}}[\mathrm{H_2O}]\frac{1}{\tau}$$

$$= \Phi_{184.9}\sigma_{\mathrm{H_2O}}[\mathrm{H_2O}]\frac{V}{F_{\mathrm{air}}}. \qquad \text{(V)}$$

Therefore, it follows that, if the $[\mathrm{O_3}]$ and $[\mathrm{HO_2}]$ are measured for different air flows, but with constant and known concentrations of water and oxygen, plots of $[\mathrm{O_3}]$ and $[\mathrm{HO_2}]$ versus $1/F_{\mathrm{air}}$ should be linear, and the slopes of the plots would be

$$m_{\mathrm{O_3}} = 2\Phi_{184.9}\sigma_{\mathrm{EF,O_2}}[\mathrm{O_2}]V \qquad \text{(VI)}$$

$$m_{\mathrm{HO_2}} = \Phi_{184.9}\sigma_{\mathrm{H_2O}}[\mathrm{H_2O}]V. \qquad \text{(VII)}$$

While the absorption cross sections could be computed from these equations, $\Phi_{184.9}$ and V are difficult to determine, and since it is the ratio of the absorption cross sections that appears in Eq. (I), $\sigma_{\mathrm{H_2O}}/\sigma_{\mathrm{EF,O_2}}$ can be calculated as

$$\frac{\sigma_{\mathrm{H_2O}}}{\sigma_{\mathrm{EF,O_2}}} = 2\frac{[\mathrm{O_2}]}{[\mathrm{H_2O}]}\frac{m_{\mathrm{HO_2}}}{m_{\mathrm{O_3}}}. \qquad \text{(VIII)}$$

Alternatively, plotting $[\mathrm{HO_2}]$ against $[\mathrm{O_3}]$ would generate a slope $m_{\mathrm{HO_2/O_3}}$, which is then used to calculate $\sigma_{\mathrm{H_2O}}/\sigma_{\mathrm{EF,O_2}}$:

$$\frac{\sigma_{\mathrm{H_2O}}}{\sigma_{\mathrm{EF,O_2}}} = 2\frac{[\mathrm{O_2}]}{[\mathrm{H_2O}]}m_{\mathrm{HO_2/O_3}}. \qquad \text{(IX)}$$

This novel method is relatively easy to perform using the apparatus used for the calibration itself. Moreover, since fluctuations in the mercury lamp have a disproportionately large effect on the ozone production, monitoring the ozone concentration can provide a simple check on the performance of the calibration system.

The major constraint is that the $\mathrm{HO_2}$ radical losses between the photolysis and sampling regions, in the time Δt, should be minimized. The main loss for $\mathrm{HO_2}$ in this case is the reaction with OH:

$$\mathrm{OH} + \mathrm{HO_2} \rightarrow \mathrm{H_2O} + \mathrm{O_2}. \qquad \text{(R10)}$$

Based on the rate coefficient for (R10) (Atkinson et al. 1997), the $\mathrm{HO_2}$ losses are less than 3% for $[\mathrm{HO_2}] = 0.4$ ppbv and $\Delta t < 28$ ms.

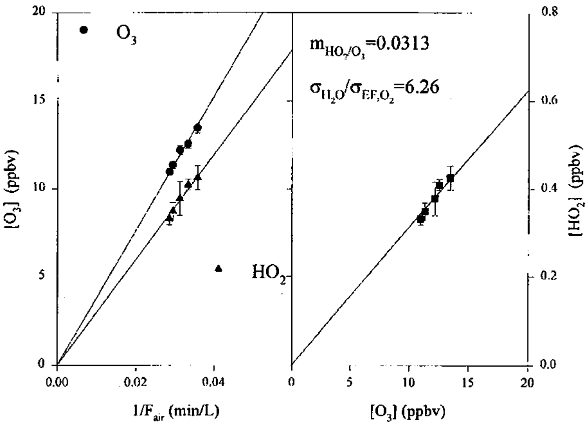

FIG. 1. Determination of the $\sigma_{\mathrm{H_2O}}/\sigma_{\mathrm{EF,O_2}}$ ratio for $[\mathrm{H_2O}] = 2100$ ppmv using the 33-mm ID photolysis cell; the error bars indicate the 95% confidence limits for 10 measurements and the regression lines were forced through zero.

Experiments were performed to test this methodology. A standard water photolysis system was used (Schultz et al. 1995). Ozone and $\mathrm{HO_2}$ radicals were converted to $\mathrm{NO_2}$ by reaction with NO [(R11) and (R12)] and the $\mathrm{NO_2}$ measured with an LMA-3 detector. In the absence of hydrocarbons and CO the HO radicals are lost to HONO (R13):

$$\mathrm{O_3} + \mathrm{NO} \rightarrow \mathrm{NO_2} + \mathrm{O_2} \qquad \text{(R11)}$$

$$\mathrm{HO_2} + \mathrm{NO} \rightarrow \mathrm{NO_2} + \mathrm{OH} \qquad \text{(R12)}$$

$$\mathrm{OH} + \mathrm{NO} + M \rightarrow \mathrm{HONO} + M. \qquad \text{(R13)}$$

The experiments for $\sigma_{\mathrm{H_2O}}/\sigma_{\mathrm{EF,O_2}}$ determination were conducted as follows.

1) A flow of zero air (Matheson, Research purity grade) was passed through the photolysis cell (not illuminated). A fraction of this air was sampled into a reactor where it was mixed with NO to give a mixing ratio of 3 ppmv and sampled by a linearized luminol detector.
2) After turning on the mercury lamp, the ozone produced was converted to $\mathrm{NO_2}$ by reaction with NO in the reactor and measured as $\mathrm{NO_2}$ by the luminol detector. A range of air flows, between 30 and 40 L $\mathrm{min^{-1}}$, were used to change the residence time in the photolysis region and consequently produce a range of ozone concentrations.
3) A set of identical experiments to (2) were performed where up to 8% of the air was saturated with water vapor by passing through a series of constant-temperature, distilled water bubblers. In this case both ozone and $\mathrm{HO_2}$ radicals are formed and converted to $\mathrm{NO_2}$, which is quantified by the luminol detector. Subtracting the signal from (2) gives the $\mathrm{HO_2}$ concentration.

The results of a typical $\sigma_{\mathrm{H_2O}}/\sigma_{\mathrm{EF,O_2}}$ determination are shown in Fig. 1. The experiments were performed three times for two photolysis cells of different geometry. The overall results for to $\sigma_{\mathrm{H_2O}}/\sigma_{\mathrm{EF,O_2}}$ determination are presented in Table 1. Our radical sources are similar in

TABLE 1. Determination of $\sigma_{H_2O}/\sigma_{EF,O_2}$ at 184.9 nm.

33-mm ID photolysis cell		15-mm ID photolysis cell	
$[H_2O]$ ppmv	$\sigma_{H_2O}/\sigma_{EF,O_2}$	$[H_2O]$ ppmv	$\sigma_{H_2O}/\sigma_{EF,O_2}$
2100	6.26	1300	6.49
2040	6.09	1500	6.08
1920	6.32	1600	6.17
	Avg: 6.2		Avg: 6.2

design to those developed and used by various groups involved in RO_x radical measurements. Recent experiments were conducted to determine σ_{EF,O_2} for these systems (Hofzumahaus et al. 1997). Combining the obtained range of values for σ_{EF,O_2} ($1.1–1.5 \times 10^{-20}$ cm^2) with the absorption cross section for water as measured by Cantrell et al. (1997) $\sigma_{H_2O} = 7.14 \pm 0.20 \times 10^{-20}$ cm^2, leads to a range of values for the ratio $\sigma_{H_2O}/\sigma_{EF,O_2}$ ranging from 4.8 to 6.5. Our $\sigma_{H_2O}/\sigma_{EF,O_2}$ measurements are consistent with the above range.

b. A nonphotolytic peroxy radical calibration source

Chlorine dioxide (OClO) was proposed as a dark source for chlorine radicals (Molina et al. 1980; Margitan 1983). The principle of the peroxy radical source presented here is that, in the presence of NO and a hydrocarbon, OClO can be quantitatively converted to organic peroxy radicals by the following reactions (shown with ethane as the hydrocarbon):

$$OClO + NO \rightarrow ClO + NO_2 \qquad (R14)$$

$$ClO + NO \rightarrow Cl + NO_2 \qquad (R15)$$

$$Cl + C_2H_6 \rightarrow HCl + C_2H_5 \qquad (R16)$$

$$O_2 + C_2H_5 + M \rightarrow C_2H_5OO + M. \qquad (R17)$$

These organic peroxy radicals can then be used for calibration, provided a method of quantifying the OClO is available.

Gas phase chlorine dioxide, from a permeation device, is added to the air stream entering the radical detector and the only modification necessary to use this calibration is to add a hydrocarbon to initiate reaction (R16). The major advantage of this calibration method is that the chlorine dioxide can be added to ambient air or any synthetic air mixture, as there is no need to photolyse the reagents. In addition, any desired peroxy radical to be produced by judicious selection of the hydrocarbon.

The standard radical detector has sufficient NO ([NO] = 2–6 ppmv) for reactions (R14) and (R15) to dominate the chlorine chemistry and therefore any other secondary reactions [e.g., (R18), (R19)] are negligible:

$$ClO + NO_2 + M \rightarrow ClONO_2 + M \qquad (R18)$$

$$ClO + ClO + M \rightarrow (ClO)_2 + M. \qquad (R19)$$

We have tested this method by modifying a radical detector and developing an OClO permeation source. The OClO was prepared by adding a dilute H_2SO_4 solution to a saturated solution of sodium chlorite ($NaClO_2$), similar to Wellington et al. (1965, pp. 116–119):

$$5NaClO_2 + 4H^+ \rightarrow 4OClO + 5Na^+ + Cl^- + 2H_2O. \qquad (R20)$$

The OClO was flushed from this solution by a flow of air that then passed through two bubblers containing saturated $NaClO_2$ to ensure the removal of Cl_2 impurities (Kieffer and Gordon 1968), which affect the quantification of OClO after conversion to HCl (see below). The resulting purified OClO was dissolved in distilled water. A permeation source was built by immersing a porous tube (Imperial Eastman Poly Filo 22 P 1/8″) into a further diluted OClO solution, kept in the dark at constant temperature in an ice bath. As a small flow of zero air (50 cm^3 min^{-1}) passed through this tube, OClO molecules permeated through the walls into the zero air flow.

The gas phase OClO concentration was quantified by titration with NO [reactions (R14), (R15)]. Two NO_2 molecules are produced for each OClO molecule, and the NO_2 produced can be measured with the luminol detector. A second method reacted the OClO with NO and CH_3CH_3 where reactions (R14)–(R16) produce HCl. The HCl was dissolved in distilled water and quantified by ion chromatography (IC). A comparison between the two calibration methods was undertaken for a gaseous OClO mixing ratio of 6.8 ppbv, and the agreement was within 10%. The good agreement between the two methods gave confidence in our ability to measure standards of gaseous OClO. In practice we used the first method to quantify the OClO concentration. Our experience is that concentrated solutions of OClO can be kept in the refrigerator for several weeks, and the permeation rate for a dilute solution is stable for over 8 h.

The suitability of this method as a calibration source was tested by modifying the radical detector to allow the addition of a small flow of ethane into the reactor, and the results of a calibration using OClO as a radical source are shown in Fig. 2. The NO_2 produced by the amplification chemistry is plotted against the added OClO concentration calculated from the dilution of the output from the permeation device. The chain length obtained (110) was within error of the chain lengths obtained using the radical source based on water photolysis. In principle the chain length should be 7% lower due to the loss of ethyl peroxy radicals to ethyl nitrite, but as several groups (Ashborne et al. 1998) have found the response of the radical detector to be less sensitive to the nature of the radical than expected, no correction has been applied.

In addition to the ease of handling, a major advantage of the nonphotolytic radical source is that the OClO can be added to any of the gases as the radicals are generated

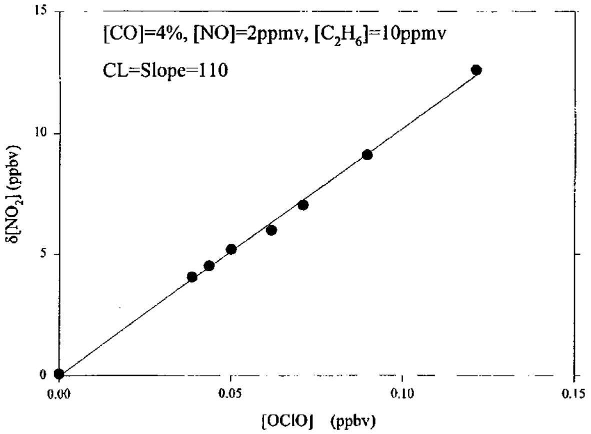

FIG. 2. Calibration curve for the RO_x radical detector using the OClO source.

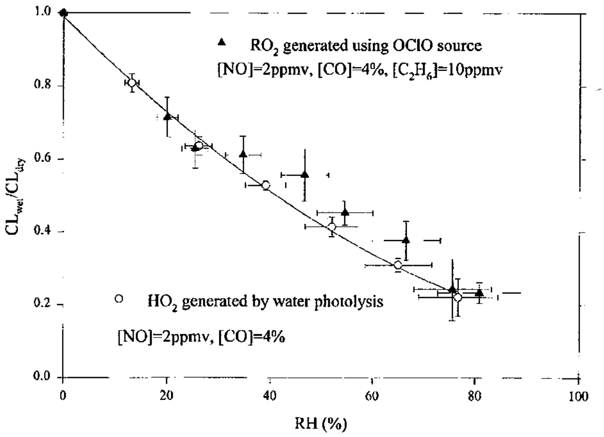

FIG. 3. Relative humidity effect on the chain length of the RO_x radical detector tested using two different radical sources.

inside the instrument. This greatly simplifies laboratory studies on the effect of added reagents on the radical detector response. As an example we used this radical source to confirm the water vapor dependence first described in Mihele and Hastie (1998).

In an experimental arrangement similar to Mihele et al. (1999), OClO was added to a synthetic air flow in which the relative humidity could be varied. The results, along with those for the water photolysis source, are shown in Fig. 3. The identical water vapor dependence is found for both calibration sources.

The addition of OClO as a calibration provides the opportunity for a standard addition radical calibrations in ambient air. This is a significant improvement over the calibrations in zero air followed by a correction of the measurement data using measured relative humidity. Even so, given the sensitivity of this humidity correction, at 40% relative humidity a 1% change in relative humidity gives a 1% change in chain length, a preferable approach would be to reduce the water effect through instrument design.

c. *Reduction of the ambient water vapor effect on the radical detector*

The water vapor dependence on the radical detector has been shown to be a function of the relative humidity rather than the absolute humidity (Mihele and Hastie 1998). Therefore, the most obvious way to reduce this effect is to heat the walls of the reactor. The consequence of this is that thermolabile species, such as PAN, would generate an interference through the production of radicals in the reactor. Any attempt to overcome the water effect by heating the reactor must also address this class of interference.

The radical detector has two cycles: in the absence of CO, the radicals are removed to give a baseline signal; in the presence of CO, the radicals are measured. The decomposition of species to give radicals poses an interference if it takes place in the time before the second addition of CO. The chemistry involved in these cycles have very different timescales. Modeling studies (e.g., Hastie et al. 1991) have shown that, in the absence of CO, the radicals are removed by reaction with NO and wall losses with a time constant of about 0.03 s, whereas the amplification process requires 0.8–1.0 s to run to completion. The optimum instrument design is to minimize the reaction time used to generate the background signal, the time between the addition of the NO (usually at the inlet), and the downstream addition of CO, consistent with the 0.03-s time constant. The amplification chemistry can then take place in a heated section of the flow reactor after the second CO addition point. This ensures that a true background is measured, the interferences are minimized, and the sensitivity of the detector toward humidity is significantly reduced.

This modified geometry was applied to the existing instrument by reducing the residence time in the reactor from 1 to 0.3 s. Experiments were performed with the reactor walls held at 21°, 60°, or 80°C. The results of experiments on the humidity effect in the new detector are presented in Fig. 4. Clearly the humidity effect is less pronounced if the reactor walls are heated, which is consistent with previous results (Mihele and Hastie 1998).

The same configuration was used to test for interferences using PAN, the most common radical generating species at ground level. Solutions of PAN in dodecane were prepared as in Nielsen et al. (1982), and constant concentrations of gaseous PAN were obtained by bubbling a small flow of nitrogen through diluted PAN solutions. Gaseous PAN was quantified by measuring the amount of NO_2 produced from the PAN thermal decomposition at 200°C in the presence of 3 ppmv of NO, knowing that four NO_2 molecules are produced for each molecule of PAN. Gaseous PAN, in the 0–500 pptv range, was admitted to the radical detector, with the reactor walls again maintained at 21°, 60°, or 80°C,

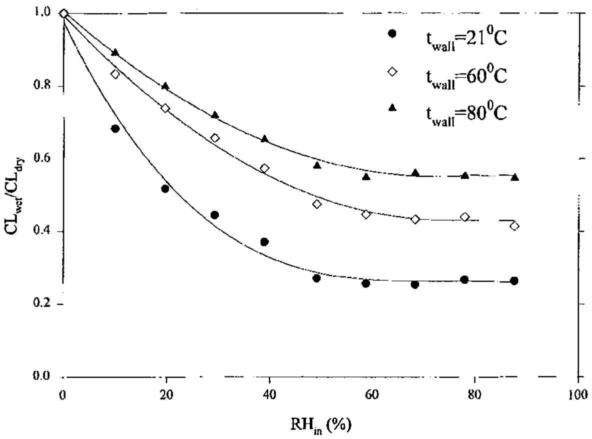

FIG. 4. Humidity effect on the chain of the RO_x radical detector equipped with a 0.3-s residence time reactor and the walls heated at various temperatures.

respectively. Note that the optimal operation would require that the 0.3 s of reaction time be in an unheated reactor, but this was not practical for these initial tests. The results for PAN interference on the radical detector are shown in Fig. 5, where the radical signal from the radical detector is plotted against added PAN concentration. These laboratory experiments showed the PAN interference, expressed as the radical signal measured as a fraction of the PAN concentration is 0.1% ± 0.1% for t_{wall} = 21°C, 0.6% ± 0.1% for t_{wall} = 60°C, and 0.8% ± 0.1% for t_{wall} = 80°C. As expected the interference becomes more pronounced at higher temperatures, but it is still below 1% even at the highest temperature used. While this shortening of the time for background determination does not overcome the interference, the reduction in water sensitivity comes at the price of a small PAN interference. Comparing the PAN and radical concentrations in a number of studies suggests this trade-off would be reasonable.

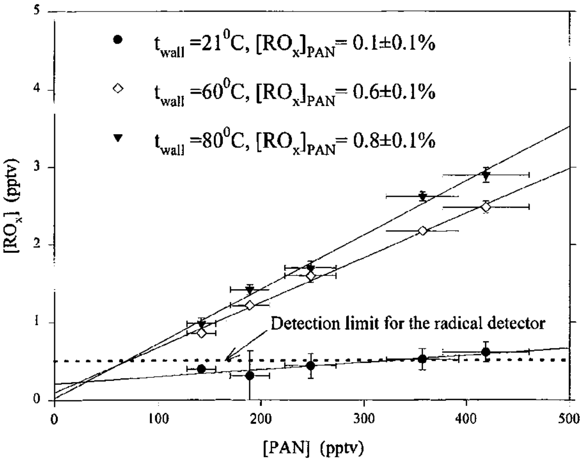

FIG. 5. PAN interference for the new configuration of the RO_x radical detector.

3. Conclusions

A method for the determination of the effective ratio between the absorption cross section for water and molecular oxygen in a particular experimental system has been developed and tested. This will reduce the uncertainties for the radical source based on water photolysis at 184.9 nm.

A new nonphotolytic peroxy radical source based on the reaction of OClO with NO and a hydrocarbon has been developed. This source was used to test the humidity effect on the chain length of the radical detector. The results bring additional proof that ambient humidity levels severely degrade instrument performance.

A modified radical amplifier that reduces the water vapor effect on the chain length and controls interferences from thermolabile species, such as PAN, has been developed and tested.

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