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## Method for the Collection and HPLC Analysis of Hydrogen Peroxide and C<sub>1</sub> and C<sub>2</sub> Hydroperoxides in the Atmosphere

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### ABSTRACT

An HPLC (high-performance liquid chromatography) method was developed to quantify hydrogen peroxide, methyl hydroperoxide, hydroxymethyl hydroperoxide, ethyl hydroperoxide, and peroxyacetic acid in the atmosphere. Gas-phase hydroperoxides are collected in aqueous solution using a continuous-flow glass scrubbing coil and then analyzed by an HPLC postcolumn derivatization system. The detection system is based on fluorescence, produced by the product of the reaction of hydroperoxides with peroxidase and *p*-hydroxyphenylacetic acid. Reproducibilities are better than 3% for all hydroperoxides in aqueous concentrations of  $1 \times 10^{-7}$ – $6 \times 10^{-7}$  M. Detection limits in aqueous concentration are  $1.2 \times 10^{-9}$  M for hydrogen peroxide,  $1.5 \times 10^{-9}$  M for hydroxymethyl hydroperoxide,  $2.9 \times 10^{-9}$  M for methyl hydroperoxide,  $16 \times 10^{-9}$  M for peroxyacetic acid, and  $19 \times 10^{-9}$  M for ethyl hydroperoxide. Corresponding gas-phase detection limits are 5 pptv for hydrogen peroxide, 7 pptv for hydroxymethyl hydroperoxide, 13 pptv for methyl hydroperoxide, 72 pptv for peroxyacetic acid, and 84 pptv for ethyl hydroperoxide for an air sample flow rate of two standard liters per minute and collection solution flow rate of  $4 \times 10^{-4}$  L min<sup>-1</sup>. The gas-phase detection limits for the latter three hydroperoxides vary depending on temperature, pressure, air sample flow rate, and collection solution flow rate. This system was used for several airborne and ground measurements and showed reliable performance.

### 1. Introduction

Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) and organic hydroperoxides are indicators of the oxidative capacity of the atmosphere through their involvement in gas-phase chemistry including odd-oxygen, odd-hydrogen, and organic peroxy radicals (e.g., O<sub>3</sub>, HO<sub>2</sub>, CH<sub>3</sub>O<sub>2</sub>) (Logan et al. 1981; Kleinman 1986, 1991; Trainer et al. 1987; Jacob et al. 1995). The formation of hydroperoxides sequesters these radicals. Together with ozone and nitrogen trioxide, these radicals are the most important oxidizing species that control the fate of atmospheric trace gases, such as reactive hydrocarbons, nitrogen, and sulfur compounds (NAS 1984). The formation and loss of H<sub>2</sub>O<sub>2</sub> and organic hydroperoxides reduces the oxidizing capacity of the atmosphere. Hydrogen peroxide is known as a major oxidant-producing sulfuric acid in cloud water (Penkett 1979; Chameides and Davis 1982; Calvert et al. 1985), and organic hydroperoxides are also capable of oxidizing sulfur dioxide in clouds (Lind et al. 1987; Zhou and Lee 1992). Additionally, hydrogen peroxide and organic hydro-

peroxides can be phytotoxic and their suggested contribution to forest decline is in current debate (Gäb et al. 1985; Möller 1989; Ennis et al. 1990; Hewitt et al. 1990; Polle and Junkermann 1994a,b). Hydrogen peroxide in glacial deposits may record past atmospheric oxidation conditions (Laj et al. 1990). For example, Greenland ice cores show an increase in atmospheric H<sub>2</sub>O<sub>2</sub> concentrations over the past 200 years (Sigg and Neftel 1991). In the future, peroxide levels are expected to increase due to changes in atmospheric composition (Thompson et al. 1989; Thompson et al. 1991). The implications of this historical record and the extrapolations to future atmospheric oxidative conditions depend upon understanding present levels of H<sub>2</sub>O<sub>2</sub> and organic hydroperoxides.

Several techniques for measuring gaseous H<sub>2</sub>O<sub>2</sub> have been developed and include 1) a colorimetric method using Ti (IV) salts with 8-quinolinol (Bufalini et al. 1972; Kok et al. 1978b); 2) a chemiluminescence method using luminol and catalysts ( $\mu$ -peroxidase or a metal ion) (Kok et al. 1978a,b; Ames 1983; Dollard et al. 1989); 3) a chemiluminescence method using peroxyate (Jacob et al. 1990); 4) a dual-enzyme fluorescence method using peroxidase and catalase to differentiate H<sub>2</sub>O<sub>2</sub> and organic hydroperoxides (Lazrus et al. 1986); 5) an enzyme fluorescence method using MnO<sub>2</sub> to differentiate H<sub>2</sub>O<sub>2</sub> and organic hydroperoxides (Hwang and Dasgupta 1986); 6) a nonenzymatic fluorescence method using Fenton reagent and benzoic

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acid (Lee et al. 1990; Lee et al. 1994); 7) high performance liquid chromatography (HPLC) with enzyme fluorescence detection (Hellpointner and Gäb 1989; Hewitt and Kok 1991; Kurth et al. 1991; Fels and Junkermann 1994; Kok et al. 1995); and 8) tunable diode laser absorption spectroscopy (Slemr et al. 1986; Mackay et al. 1990). Except for the latter, all of these methods strip  $\text{H}_2\text{O}_2$  and organic hydroperoxides from the gas into aqueous solution using impingers (Kok et al. 1978a,b), diffusion scrubbers (Tanner et al. 1986; Dasgupta et al. 1990), scrubbing coils (Kok et al. 1978a; Lazrus et al. 1986; Lee et al. 1990; Heikes 1992), or cryogenic traps (Sakugawa and Kaplan 1987; Hellpointner and Gäb 1989; Jacob et al. 1990; Hewitt and Kok 1991; Fels and Junkermann 1994).

Several  $\text{H}_2\text{O}_2$  measurement datasets are available at the surface and at altitude using the above methodology. Measurements have been made under a variety of conditions and seasons: tropical (Jacob et al. 1990) to polar (de Serves 1994), desert (Farmer and Dawson 1982; Sakugawa and Kaplan 1989) to heavily forested (Lee et al. 1993), remote mountaintop (Heikes 1992) to urban (Mackay et al. 1990), and winter (Van Valin et al. 1987; Heikes et al. 1988; Barth et al. 1989) to summer (most of  $\text{H}_2\text{O}_2$  measurements). However, there are relatively few organic hydroperoxide data available. In some experiments using the dual-enzyme system (Lazrus et al. 1986), soluble organic hydroperoxide concentrations were reported (Heikes et al. 1987; Heikes 1992; Tremmel et al. 1994). Lee et al. (1993) have also reported organic hydroperoxide levels using a combination of the enzyme and Fenton chemistries.

Several organic peroxides have been identified in air and precipitation samples (Hellpointner and Gäb 1989; Hewitt and Kok 1991; Fels and Junkermann 1994). Of these, hydroxymethyl hydroperoxide (HMHP) has recently drawn interest as a major hydroperoxide in the atmosphere (Gäb et al. 1985; Hewitt and Kok 1991; Fels and Junkermann 1994). In some rural areas, HMHP concentrations were reported to be higher than those of  $\text{H}_2\text{O}_2$  in summer (Hewitt and Kok 1991; Lee et al. 1993). Laboratory studies have shown that the formation of substantial quantities of several organic hydroperoxides is possible (Hanst and Gay 1983; Gäb et al. 1985; Hewitt and Kok 1991; Horie et al. 1994). However, the kinetics and formation mechanisms for most organic hydroperoxides remain to be determined (Calvert and Madronich 1987; Dodge 1989; Pierotti et al. 1990; Lightfoot et al. 1992; Horie et al. 1994). Ambient measurements remain scarce at the surface and there are even fewer at altitude.

This paper describes a method for measuring hydrogen peroxide and specific organic hydroperoxide species in the atmosphere using an HPLC analytical method with a glass scrubbing coil for collecting samples. All published measurements for hydroperoxides using an HPLC technique have employed cryogenic

sampling (Hellpointner and Gäb 1989; Hewitt and Kok 1991; Fels and Junkermann 1994). Cryogenic sampling requires collection times greater than 10 min and usually more than 30 min. Collection time is dependent upon the specific humidity of the air with short sampling times possible only in humid tropical regions (Jacob et al. 1990). In addition, cryogenic samples must undergo a phase change and need to be diluted before injection. Cryogenics and long sampling times pose logistical constraints to airborne measurement. The glass scrubbing coil was designed for continuous *in situ* measurements (Lazrus et al. 1986). The scrubbing coil collection system is also compact compared to cryogenic sampling systems and does not need intermediate processes between the collection and injection of samples, thereby reducing space and handling constraints for airborne measurements. Therefore, the scrubbing coil collection method has an advantage in airborne measurements. The HPLC analysis and coil sample collection described below can provide near-real-time airborne measurements of specific hydroperoxide species with sample temporal resolution limited only by elution time.

## 2. Experiment

### a. Instrumentation

The basic analytical scheme of Kok et al. (1995) was used to measure peroxides after sample collection. In this scheme, HPLC was used to separate the hydroperoxides prior to being quantified. The hydroperoxide analysis was based on the reaction of  $\text{H}_2\text{O}_2$  and organic hydroperoxides with *p*-hydroxyphenylacetic acid to produce a fluorescent dimer (6,6'-dihydroxy-3,3'-biphenyldiacetic acid) using peroxidase as an enzyme catalyst (Guilbault et al. 1968).

Figure 1 shows a schematic diagram of this system. A Dionex DXP-1 metal-free isocratic pump with a pulse damper was used for eluent delivery. The eluent was first degassed with electronic-grade He gas (Scott Specialty Gases) before use. The pump flow rate was  $0.6 \text{ mL min}^{-1}$ . Samples were injected using a Rheodyne 9010 metal-free injection valve and a  $20\text{-}\mu\text{L}$  PEEK (polyetheretherketone) sample loop. Hydroperoxides were separated on a  $5\text{-}\mu\text{m}$  Inertsil ODS-2 PEEK column ( $4.6 \text{ mm} \times 250 \text{ mm}$ , Metachem). A PEEK guard column with the same packing material was placed before the analytical column. The Metachem Inertsil column gave the best results for organic peroxides, but there was little variability in resolution and sensitivity for peroxides among columns.

The column effluent was mixed with a reagent to produce a fluorescent product. The fluorescence reagent was delivered at a flow rate of  $0.06 \text{ mL min}^{-1}$  by a multichannel peristaltic pump (G-07341-10, Ismatec). Coiled Teflon tubing [ $0.3 \text{ mm (i.d.)} \times 1.5 \text{ m}$ ] was used as a postcolumn reactor and yielded a 10-s reaction time. The pH of the column effluent was raised

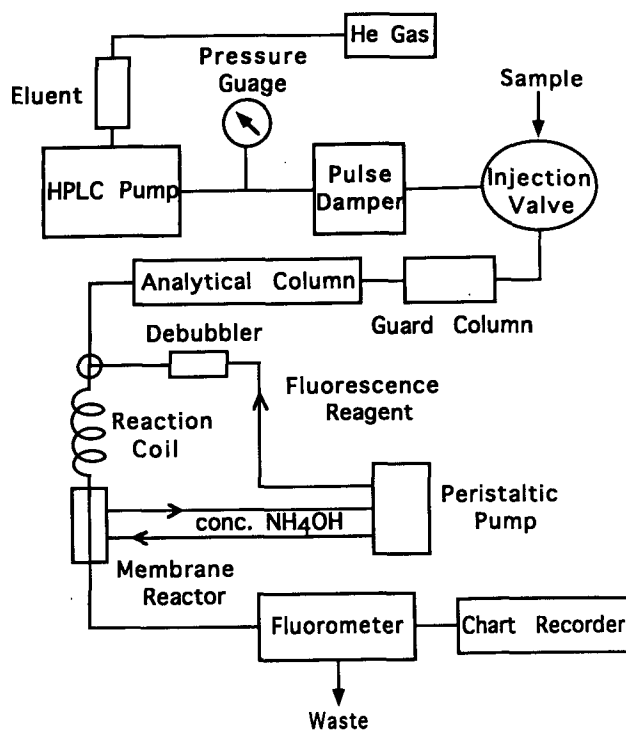


FIG. 1. Schematic diagram of the HPLC system.

to between 10 and 11 with a counterflow membrane reactor (Dasgupta 1984) to maximize the fluorescence signal. The column effluent flowed through the inside of the membrane tubing and  $\text{NH}_4\text{OH}$  (30%) flowed outside the membrane in the opposite direction. The membrane reactor was made with 2 cm of Nafion membrane tubing (811x, Perma Pure Products, Inc.).

A Milton-Roy fluoromonitor III was used for detection. It incorporated a cadmium lamp, a 326-nm excitation filter, and a 400–700-nm broadband emission filter. A simple strip-chart recorder was used to record the resulting fluorescence signal. Hydroperoxide concentrations were quantified by measuring peak heights.

$\text{H}_2\text{O}_2$  and organic hydroperoxides were stripped from the air into the collection solution using a continuous flow glass scrubbing coil (Lazrus et al. 1986). Collection solution and air flowed together through a glass coil (3 mm i.d., 30 turns, about 1.6-m length) and were separated using a cyclone separator of our own design (see Fig. 4). Air was sampled at 2 slpm (standard liters per minute,  $T_{std} = 0^\circ\text{C}$ ,  $P_{std} = 1\text{ atm}$ ). Collection solution was pumped into the coil at  $0.4\text{ mL min}^{-1}$  and removed from the separator using the same peristaltic pump described above. The aqueous flow rate was calibrated gravimetrically. Air sample flow rate was set by a mass flow controller, and the flow rate was calibrated using a Gilibrator (Gilian Instruments Corp.). The coil temperature was monitored by a thermistor (Deban Enterprises, Inc.) set in the cyclone separator, and pressure was measured using

an absolute pressure transducer (MKS Instruments). Gas flow rate, pressure, and coil temperature were monitored and recorded by computer since the collection efficiencies of organic hydroperoxides are dependent on temperature and volume flow rate. Organic hydroperoxide collection efficiencies will be discussed below.

#### b. Reagents and standards

The HPLC eluent was  $10^{-3}\text{ M H}_2\text{SO}_4$  solution with  $10^{-4}\text{ M EDTA}$  (ethylenediaminetetraacetic acid) (Table 1). EDTA was added to complex trace metals and prevented  $\text{H}_2\text{O}_2$  decomposition. The fluorescence reagent was  $2.2 \times 10^{-2}\text{ M p-hydroxyphenylacetic acid}$  (Fairfield Chemical) and  $8.3 \times 10^{-4}$  units per liter horseradish peroxidase (type II, Sigma Chemical) in  $0.42\text{ M}$  potassium hydrogen phthalate buffer. The pH of the fluorescence reagent was adjusted to 5.8 with NaOH. The collection solution was  $5 \times 10^{-3}\text{ M}$  sodium phthalate buffer adjusted to pH 3 or 6 with HCl and NaOH. All reagents and standard solutions were prepared with  $18\text{ M}\Omega\text{ cm}$  Milli-Q water.

$\text{H}_2\text{O}_2$  and peroxyacetic acid (PAA) were purchased from J. T. Baker and Aldrich Chemical, respectively. Methyl hydroperoxide (MHP) and ethyl hydroperoxide (EHP) were synthesized from  $\text{H}_2\text{O}_2$  and dimethyl sulfate or diethyl sulfate. The product vapors were collected in aqueous solution. Hydroxymethyl hydroperoxide (HMHP) and 1-hydroxyethyl hydroperoxide (1-HEHP) were synthesized from aqueous  $\text{H}_2\text{O}_2$  and formaldehyde or acetaldehyde. They were not purified and they contained residual  $\text{H}_2\text{O}_2$  and bis-hydroxyalkyl peroxide. The concentrations of stock  $\text{H}_2\text{O}_2$  and organic hydroperoxide standard solutions were determined using  $\text{KMnO}_4$  and  $\text{Na}_2\text{S}_2\text{O}_3/\text{KI}/\text{starch}$  (Johnson and Siddiqui 1970; Mair and Hall 1970). All aqueous standards were prepared by serial dilution of stock standards.  $\text{H}_2\text{O}_2$ , MHP, and EHP standards are stable, but the others are prone to decomposition. HMHP, bis-HMP, 1-HEHP, and PAA decompose at

TABLE 1. HPLC reagents.

Eluent ( $0.6\text{ mL min}^{-1}$ )
$10^{-3}\text{ M H}_2\text{SO}_4$
$10^{-4}\text{ M ethylenediaminetetraacetic acid (EDTA)}$
Fluorescence reagent ( $0.06\text{ mL min}^{-1}$ )
$2.2 \times 10^{-2}\text{ M p-hydroxyphenyl acetic acid (POHPAA)}$
$0.42\text{ M potassium hydrogen phthalate (KHP)}$
$8.3 \times 10^4$ units per liter peroxidase
adjusted to pH 5.8
Membrane reactor
30% $\text{NH}_4\text{OH}$
Collection solution
$5 \times 10^{-3}\text{ M KHP}$
adjusted to pH 3 or 6 with 1 N HCl and 1 N NaOH

TABLE 2. HPLC determination of hydroperoxides.

Peroxide	Formula	Abbreviation	Retention time (min)	Reproducibility <sup>a</sup> (%)	Detection limit <sup>b</sup> (nM)	Detection limit <sup>c</sup> (pptv)
Hydrogen peroxide	H <sub>2</sub> O <sub>2</sub>	H <sub>2</sub> O <sub>2</sub>	5.0	1.3	1.2	5
Hydroxymethyl hydroperoxide	HOCH <sub>2</sub> OOH	HMHP	5.6	1.0	1.5	7
bis-Hydroxymethyl peroxide	HOCH <sub>2</sub> OOCH <sub>2</sub> OH	bis-HMP	6.6	2.5	NA	NA
1-Hydroxyethyl hydroperoxide	CH <sub>3</sub> CH(OH)OOH	1-HEHP	7.2	NA	NA	NA
Methyl hydroperoxide	CH <sub>3</sub> OOH	MHP	7.5	1.2	2.9	13/CE
Peroxyacetic acid	CH <sub>3</sub> C(O)OOH	PAA	9.6	2.2	16	72/CE
Ethyl hydroperoxide	CH <sub>3</sub> CH <sub>2</sub> OOH	EHP	13.4	0.0	19	84/CE

<sup>a</sup> Relative precision of peak heights at the aqueous concentrations between 10<sup>-7</sup> and 6 × 10<sup>-7</sup> M. Relative precision equals standard deviation/mean, for five injections.

<sup>b</sup> Detection limit in aqueous concentration.

<sup>c</sup> Detection limit in gas-phase concentration with a gas flow rate of 2 slmp and aqueous flow rate of 0.4 mL min<sup>-1</sup>.

CE: collection efficiency.

NA: not available.

different rates upon dilution at pH > 5 but are stable over a couple of hours if prepared in low pH solution and refrigerated. Dilute standards of these hydroperoxides were prepared immediately before use with pH 3 water. Details about the synthesis and the standardization of hydroperoxides can be found in Lee (1995).

### 3. Result and discussion

#### a. HPLC performance

The postcolumn derivatization scheme employed requires a compromise between sensitivity and chromatographic resolution. The various hydroperoxides react at different rates with the fluorescence reagent, and long reaction times are desirable. However, the additional tubing required for this degrades chromatographic resolution. In batch-mode experiments, it was determined that a 10-s reaction time was sufficient to maximize signals for H<sub>2</sub>O<sub>2</sub>, MHP, PAA, and EHP with a minimum loss of chromatographic resolution. Reproducibilities obtained using a 10-s reaction time were also quite good, better than 3% for all species tested (Table 2). Frei et al. (1985) state reproducibility as the principal requirement in a postcolumn derivatization analytical method, and thus, reliable measurement of hydroperoxides could be achieved with a reaction time of 10 s.

Mechanical aspects affecting performance were also examined. An eight-roller peristaltic pump was found to introduce much less analytical noise than a six-roller pump. The membrane reactor used for pH adjustment greatly reduced the level of analytical noise compared to an earlier scheme in which NaOH was added to the postcolumn reagent stream via a peristaltic pump.

H<sub>2</sub>O<sub>2</sub> and six organic hydroperoxides have been measured with this HPLC system. A chromatogram from an injection of a synthetic mixture of seven hydroperoxides is shown in Fig. 2. Retention times and detection limits are listed in Table 2 for the same spe-

cies. The chromatographic baseline was stable. The minimum peak height resolution in our system was 0.5 mm on the chart. Species detection limits were determined by peak height resolution and defined as

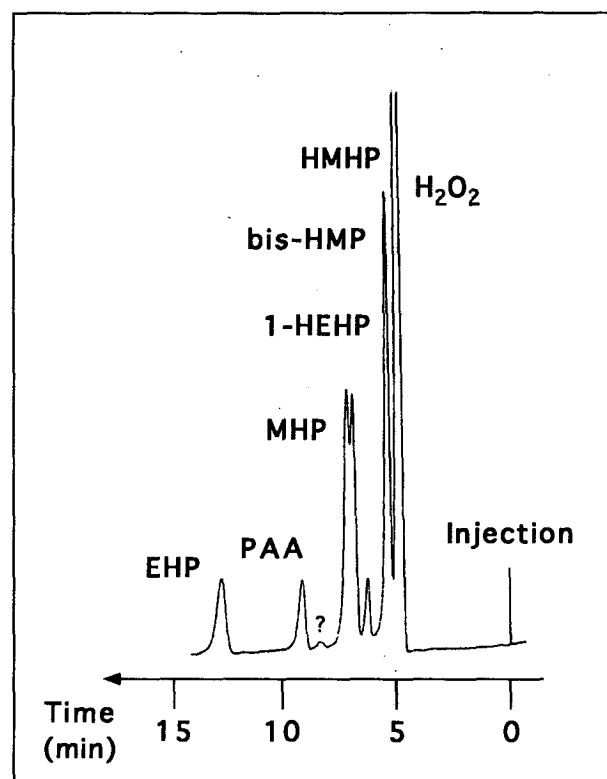


FIG. 2. Chromatogram from the injection of a synthetic mixture of hydroperoxides showing peak separation and elution time (at 10-mV scale). Here H<sub>2</sub>O<sub>2</sub> (6.6 × 10<sup>-7</sup> M), HMHP is hydroxymethyl hydroperoxide (3.2 × 10<sup>-7</sup> M), bis-HMP is bis-hydroxymethyl peroxide, 1-HEHP is 1-hydroxyethyl hydroperoxide, MHP is methyl hydroperoxide (3.0 × 10<sup>-7</sup> M), PAA is peroxyacetic acid (4.1 × 10<sup>-7</sup> M), and EHP is ethyl hydroperoxide (6.5 × 10<sup>-7</sup> M).

TABLE 3a. Collection efficiency of hydroperoxides.

Peroxide	CE <sup>a</sup> (%)	CE <sup>*b</sup> (%)
H <sub>2</sub> O <sub>2</sub>	99.9	98.7 ± 1.4
MHP	77.5	79.5 ± 0.6
PAA	90.4	91.7 ± 0.8
EHP	80.9	77.1 ± 0.2

<sup>a</sup> CE: theoretical collection efficiency with a gas flow rate of 2 slpm and collection solution flow rate of 0.4 mL min<sup>-1</sup>.  $CE = (V_a RT K_H) / (V_g + V_a RT K_H)$  at  $T = 10^\circ\text{C}$ ,  $P = 1$  atm.  $K_H$  for H<sub>2</sub>O<sub>2</sub>, MHP and PAA from Lind and Kok (1986, 1994) and for EHP from O'Sullivan et al. (1995).

<sup>b</sup> CE\*: Measured collection efficiency using two coils in series.  $CE^* = 1 - S_2/S_1$  at  $T = 10^\circ \pm 1^\circ\text{C}$ .

the concentration of each peroxide corresponding to 0.5 mm of peak height. The detection limits in aqueous concentration were  $1.2 \times 10^{-9}$  M for H<sub>2</sub>O<sub>2</sub>,  $1.5 \times 10^{-9}$  M for HMHP,  $2.9 \times 10^{-9}$  M for MHP,  $16 \times 10^{-9}$  M for PAA, and  $19 \times 10^{-9}$  M for EHP. Their corresponding gas-phase detection limits were 5 pptv for H<sub>2</sub>O<sub>2</sub>, 7 pptv for HMHP, 13 pptv for MHP, 72 pptv for PAA, and 84 pptv for EHP when air was sampled at a flow rate of 2 slpm and a collection solution flow rate of 0.4 mL min<sup>-1</sup>. System analytical blanks were determined by injecting collection solution directly, collection solution exposed to UHP zero air in the coil, and collection solution exposed to ambient air that had been passed through a Hopcalite (Mine Safety Appliance) filled trap. System blanks were important for H<sub>2</sub>O<sub>2</sub> alone. No response was observed for the organic hydroperoxides in these blanks. The H<sub>2</sub>O<sub>2</sub> detection limit, defined as  $3\sigma$  (standard deviation of these blanks), was less than 0.5-mm-chart resolution, and we have adopted the H<sub>2</sub>O<sub>2</sub> detection limits stated above as conservative measures of the H<sub>2</sub>O<sub>2</sub> detection limit.

HMHP and 1-HEHP peaks were not completely separated from those of H<sub>2</sub>O<sub>2</sub> and MHP at the baseline, and thus the detection limit of HMHP and 1-HEHP will be dependent on the relative concentrations of these four hydroperoxides in ambient samples. The detection limit for both HMHP and 1-HEHP in a sample would be significantly higher than the defined detection limits, 0.5-mm peak height, if H<sub>2</sub>O<sub>2</sub> and MHP concentrations were much higher than those of HMHP and 1-HEHP, and vice versa.

### b. Collection efficiency of organic hydroperoxides

The performance of the collection system is dependent upon the aqueous solubility of the hydroperoxides, temperature, and volume flow rate. In an airborne application with variable altitudes, temperatures, and pressures, the coil temperature may vary by as much as 20°C and the volume flow rate may vary from 2 to 10 L min<sup>-1</sup> for a constant mass flow rate of 2 slpm. The collection efficiency (CE) of the coil sampling system for hydroperoxide is described by the following

equation, which assumes the gas and aqueous phases are at equilibrium:

$$CE = \frac{V_a K_H RT}{V_g + V_a K_H RT} \quad (1)$$

where  $V_g$  (L min<sup>-1</sup>) is the gas sample flow rate at a given temperature and pressure,  $V_a$  (L min<sup>-1</sup>), the aqueous flow rate,  $R$  the ideal gas constant,  $T$  (K) the temperature, and  $K_H$  Henry's law constant at a given temperature  $T$ .

The constant  $K_H$  for H<sub>2</sub>O<sub>2</sub> and HMHP is quite large and for our conditions their collection efficiencies are greater than 99%;  $K_H$  for other hydroperoxides are smaller than those of H<sub>2</sub>O<sub>2</sub> or HMHP and their collection efficiencies will vary depending on  $T$  and  $V_g$ .

Collection efficiency can be experimentally determined by connecting two coils in series. Then the collection efficiency is given by

$$CE = 1 - \frac{S_2}{S_1} \quad (2)$$

where  $S_1$  is the signal in the first coil and  $S_2$  is the signal in the second coil.

Measured CEs for H<sub>2</sub>O<sub>2</sub>, MHP, PAA, and EHP and theoretical CEs from (1) using  $K_H$  values from Lind and Kok (1986, 1994) and O'Sullivan et al. (1995) are listed in Table 3a. Considering the uncertainty in Henry's law constants, the theoretical CE and the empirical CE were in excellent agreement.

Additionally, if a standard solution is used in place of the normal collection solution and zero air is sampled, then CE can be measured as the ratio of the signal through the coil to that directly injected. The CE of MHP was determined using this method in several field experiments. The theoretical and empirical CEs during TRACE-A (Transport and Atmospheric Chemistry near the Equator-Atlantic) are given in Table 3b, and the difference between the two is less than 7%. We have concluded that the thermodynamic equilibrium assumption is valid for the coil collector and in practice

TABLE 3b. Collection efficiency of MHP.

TRACE-A flight	CE <sup>a</sup> (%)	CE <sup>*b</sup> (%)
10	64	64
12	58	62
14	69	70
14	54	53
15	59	56
17	57	59
19	62	63

<sup>a</sup> CE: theoretical collection efficiency at variable temperatures and pressures  $CE = (V_a RT K_H) / (V_g + V_a RT K_H)$ .

<sup>b</sup> CE\*: Measured collection efficiency during the flight by standard addition to one coil.

have used (1) to estimate CE for the different hydroperoxides.

### c. SO<sub>2</sub> interference

H<sub>2</sub>O<sub>2</sub> and organic hydroperoxides can react with SO<sub>2</sub> in the collection solution and cause a negative artifact in the determination of H<sub>2</sub>O<sub>2</sub> and organic hydroperoxides (Heikes et al. 1982; Lazrus et al. 1986). The SO<sub>2</sub> interference was reduced to a 0.5% loss of H<sub>2</sub>O<sub>2</sub> at 10-ppbv SO<sub>2</sub> in the method of Lazrus et al. (1986) by using a pH 6 buffered collection solution and  $5 \times 10^{-3}$  M CH<sub>2</sub>O reagent. Zhou and Lee (1992) recommended a collection solution pH of 3 to collect HMHP because of its decomposition at pH > 6. The reaction of SO<sub>2</sub> with hydroperoxide is strongly dependent on the pH of the solution as well as on the temperature. The reaction rate increases with increasing H<sup>+</sup> ion concentration (Lind et al. 1987). On the other hand, the reactive form of SO<sub>2</sub> decreases in concentration with increasing H<sup>+</sup> ion concentration (Penkett et al. 1979). Therefore, it was important to reassess the level of SO<sub>2</sub> artifact in sampling hydroperoxides at different pHs.

The SO<sub>2</sub> experiments were done with 23- and 1-ppbv gas-phase SO<sub>2</sub>, generated by SO<sub>2</sub> permeation wafers (Dynacal, VICI Metronics). Gas-phase peroxide standards were generated by equilibrating an airstream with aqueous standards at room temperature. The concentrations of gas-phase standards produced were approximately 4 and 2 ppbv for H<sub>2</sub>O<sub>2</sub> and 2 ppbv for MHP. Peroxide vapor was mixed with SO<sub>2</sub> gas before it entered the collection coil. Here pH 3 and pH 6 collection solutions were tested with and without CH<sub>2</sub>O being added. The results are summarized in Table 4.

The addition of 23-ppbv SO<sub>2</sub> caused 100% of the H<sub>2</sub>O<sub>2</sub> to be lost and nearly 100% loss of MHP, when

a pH 3 collection solution was used (case A in Table 4). The loss of both H<sub>2</sub>O<sub>2</sub> and MHP was less than 10% for a pH 6 collection solution with 23 ppbv SO<sub>2</sub> added (case B). There was no detectable loss of H<sub>2</sub>O<sub>2</sub> or MHP when pH 6 collection solutions were used with the addition of 1 ppbv SO<sub>2</sub> (case D). At pH 3 and 1 ppbv of SO<sub>2</sub>, a stoichiometric loss of H<sub>2</sub>O<sub>2</sub> was noted (case C).

The addition of CH<sub>2</sub>O ( $5 \times 10^{-3}$  M) to the collection solution prevented H<sub>2</sub>O<sub>2</sub> from being lost by reaction with SO<sub>2</sub>. However, CH<sub>2</sub>O addition caused HMHP to be produced when pH 6 collection solutions were used (cases G and H). Approximately 30% of the H<sub>2</sub>O<sub>2</sub> was converted to HMHP regardless of whether SO<sub>2</sub> was or was not added. The conditions of case G are the same as those of case B except for CH<sub>2</sub>O addition. When CH<sub>2</sub>O was added (case G) to pH 6 solution with SO<sub>2</sub> the concentration of H<sub>2</sub>O<sub>2</sub> was lower but the sum of H<sub>2</sub>O<sub>2</sub> and HMHP was higher than that of H<sub>2</sub>O<sub>2</sub> when CH<sub>2</sub>O was not added (case B). In pH 3 collection solutions, the addition of CH<sub>2</sub>O was of no consequence (cases E and F), and all H<sub>2</sub>O<sub>2</sub> was lost when SO<sub>2</sub> was added (case E).

The theoretical loss of H<sub>2</sub>O<sub>2</sub> can be estimated from experimental conditions (Maahs 1982; Kelly et al. 1985). These are listed in Table 4. There is general agreement between the theoretical losses and experimentally determined losses.

These tests indicated that SO<sub>2</sub> interference was dependent on the pH of the collection solution; thus, an acidic collection solution, pH 3, could not be used if SO<sub>2</sub> was present. The experiment of Lee et al. (1993) used pH 3 collection solutions, and they have since gone to pH 6 (Lee et al. 1994). The addition of CH<sub>2</sub>O eliminated much of the SO<sub>2</sub> artifact in pH 6 solutions, but millimolar concentrations of CH<sub>2</sub>O produced HMHP, which reduced H<sub>2</sub>O<sub>2</sub> concentrations in the

TABLE 4. SO<sub>2</sub> interference in collection of hydroperoxides.

	Control	Case A	Case B	Case C	Case D	Case E	Case F	Case G	Case H
H <sub>2</sub> O <sub>2</sub> (ppbv)	2, 4	4	4	2	2	4	4	4	4
pH	3, 6	3	6	3	6	3	3	6	6
SO <sub>2</sub> (ppbv)	0	23	23	1	1	23	0	23	0
CH <sub>2</sub> O (mM)	0	0	0	0	0	5	5	5	5
E-loss (%) <sup>a</sup>	0	100	7-11 <sup>b</sup>	41-48	0	100	0	0 <sup>c</sup>	0
E-loss (%) <sup>d</sup>	0					0	0	30	25
T-loss (%) <sup>e</sup>	0	100	13	40	1				
MHP (ppbv)	2	2	2	2	2				
pH	3, 6	3	6	3	6				
SO <sub>2</sub> (ppbv)	0	23	23	1	1				
CH <sub>2</sub> O (mm)	0	0	0	0	0				
E-loss (%) <sup>a</sup>	0	99	7	NA	0				
T-loss (%) <sup>e</sup>	0	87	2	9	0				

<sup>a</sup> H<sub>2</sub>O<sub>2</sub> (MHP) loss by SO<sub>2</sub> measured from the experiment.

<sup>b</sup> One extreme value of 31 has been removed.

<sup>c</sup> It was assumed to be zero by comparing the concentration of the sum of H<sub>2</sub>O<sub>2</sub> and HMHP in case G with that of H<sub>2</sub>O<sub>2</sub> in the control.

<sup>d</sup> H<sub>2</sub>O<sub>2</sub> loss by the production of HMHP measured from the experiment.

<sup>e</sup> H<sub>2</sub>O<sub>2</sub> (MHP) theoretical loss calculated based on 10-min sample collection time.

NA: not available.



samples and caused an HMHP sampling artifact. This effect would not have been observable by Lazrus et al. (1986). In a pH 3 solution,  $\text{CH}_2\text{O}$  addition had no effect. In remote regions and at altitudes,  $\text{SO}_2$  concentrations are often less than 100 pptv (Bandy et al. 1992). For  $\text{SO}_2$  less than 100 pptv, the lifetime of  $\text{H}_2\text{O}_2$  is over 1.5 h in a pH 3 solution and the  $\text{SO}_2$  artifact is not important in collecting hydroperoxides in the remote atmosphere. We recommend the use of a pH 3 collection solution when low  $\text{SO}_2$  is expected and preservation of HMHP, PAA, and 1-HEHP is required. Otherwise use pH 6 with  $5 \times 10^{-4}$  M  $\text{CH}_2\text{O}$ .

#### d. $\text{O}_3$ interference

It is known that ozone ( $\text{O}_3$ ) in the sampled air produces  $\text{H}_2\text{O}_2$  in aqueous traps and this causes a positive artifact in measurements of gas-phase  $\text{H}_2\text{O}_2$  (Heikes 1982; Lazrus et al. 1986). A maximum possible interference could be assessed from data obtained during several field experiments when stratospheric air was sampled. The maximum  $\text{H}_2\text{O}_2$  artifact caused by  $\text{O}_3$  is estimated to be less than 0.03 ppbv per 100 ppbv of  $\text{O}_3$ , which is in agreement with Lazrus et al. (1986).

#### e. Decomposition of hydroxyalkyl hydroperoxides

HMHP, 1-HEHP, and PAA are unstable and prone to decomposition. Their decomposition kinetics are dependent on both pH and temperature. They are more stable at low pH and temperature. Zhou and Lee (1992) give the HMHP half-life as  $1.9 \times 10^9 [\text{H}^+]$  s at  $22^\circ\text{C}$ , and it is  $1.9 \times 10^3$  and  $1.9 \times 10^6$  s at pH 6 and 3, respectively. The pH dependent decomposition rate of 1-HEHP was evaluated in this study, yielded a half-life of  $6 \times 10^7 [\text{H}^+]$  s at  $17^\circ\text{C}$ , and it is 60 and  $6 \times 10^4$  s at pH 6 and 3, respectively. The decomposition of 1-HEHP is much faster than that of HMHP. Therefore, the matrix of the standard solution and collection solution for these hydroperoxides must be acidic; otherwise, artifacts may arise in the determination of  $\text{H}_2\text{O}_2$  and hydroxyalkyl hydroperoxides. It is also possible for HMHP and 1-HEHP to interfere with the measurement of  $\text{H}_2\text{O}_2$  and MHP, and vice versa, if HMHP and 1-HEHP peaks are not completely separated from those of  $\text{H}_2\text{O}_2$  and MHP. Particularly, the resolution of 1-HEHP and MHP is poor. However, in real atmospheric samples, this interference is thought to be insignificant. Figure 3 shows chromatograms of air samples that show the most number of organic hydroperoxides with the highest concentrations of our measurements to date. These were atypical tropospheric samples. Figure 3a depicts a sample taken using a cryogenic trap at the University of Rhode Island (URI) Bay Campus, Fig. 3b shows samples taken using a coil collector during the same time interval as the cryogenic trap shown in Fig. 3a, and Fig. 3c illustrates samples taken using a coil in biomass fire plumes during

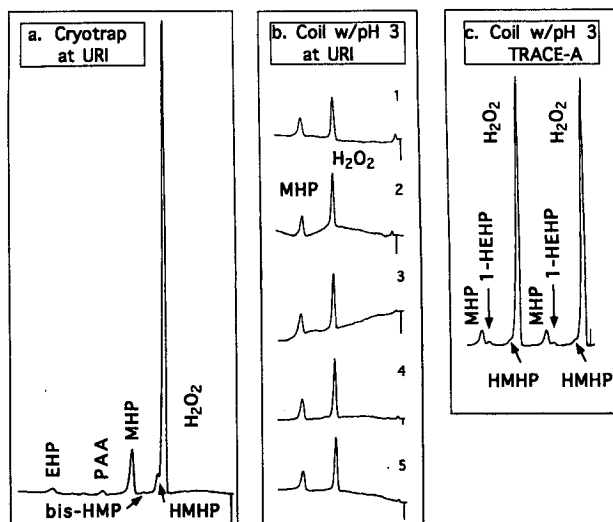


FIG. 3. Sample chromatograms: (a) sample taken using cryotrap at the URI Bay Campus (1140–1340 EDT 23 July 1993) (at 20-mV scale), (b) samples taken using coil collector with a pH 3 solution over the same time interval as a cryotrap sample (at 10-mV scale), and (c) samples taken in biomass burning plumes during TRACE-A using coil collector with a pH 3 solution (at 20-mV scale).

TRACE-A. For coil samples, a pH 3 collection solution was used to preserve HMHP and 1-HEHP. Nonetheless, HMHP and 1-HEHP concentrations were very low compared to those of  $\text{H}_2\text{O}_2$  and MHP. On the other hand, if the sampled air contains considerable amounts of these hydroxyalkyl hydroperoxides and the collection solution is near-neutral pH, then the positive artifact in  $\text{H}_2\text{O}_2$  would be more significant due to their fast decomposition, particularly 1-HEHP at pH  $>$  6. At pH 6, the lifetime of 1-HEHP is 1 min. Simonaitis et al. (1991) reported complete decomposition of 1-HEHP during analysis with a pH 5.85 collection solution.

#### f. Aircraft installation

The airborne implementation of the collection and HPLC analysis system was direct. Variable cabin pressures and temperatures onboard the National Aeronautics and Space Administration (NASA) DC-8 did not affect analytical performance as determined by a lack of variation in either system blanks or sensitivity. Several tests were conducted in-flight: 1) with a Hopcalite trap or UHP zero air (Aircro grade 0.1) to check for variability in analytical blanks, 2) with aqueous standards of  $\text{H}_2\text{O}_2$ , MHP, and HMHP to check for changes in sensitivity, 3) with UHP zero air and aqueous  $\text{H}_2\text{O}_2$  and MHP standards or gas standards of  $\text{H}_2\text{O}_2$  and MHP to check collection efficiency, sensitivity, and inlet artifacts, and 4) with gas-phase standard additions to check for interferences and inlet artifacts. No degradation in performance was noted beyond what was described in sections 3b–e. Figure 4 shows a sche-

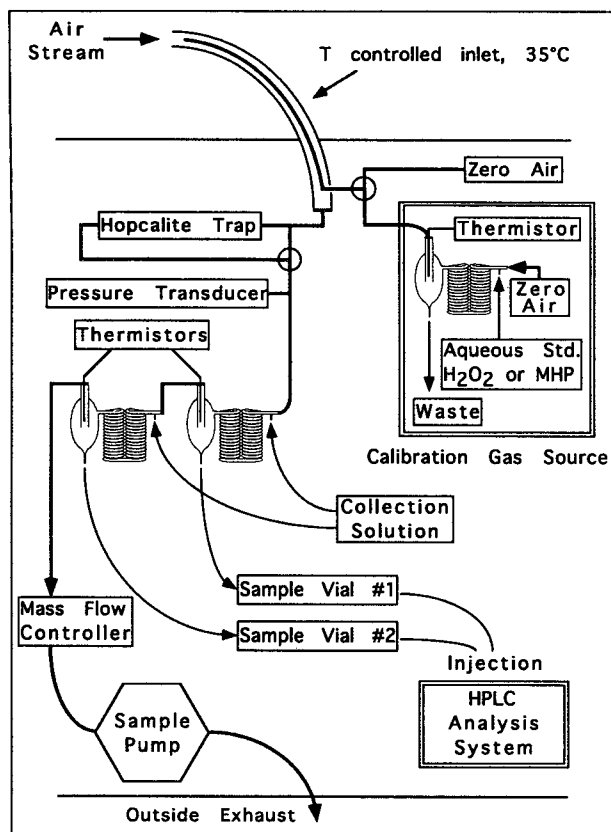


FIG. 4. Schematic diagram showing the gas collection and through-the-inlet calibration system used onboard the NASA DC-8 for PEM-West (B).

matic diagram of the instrument installation onboard the NASA DC-8. The gas-phase calibration system is described in detail in O'Sullivan et al. (1995). A scrubbing coil is used to saturate an airstream with the hydroperoxide of choice. The gas-phase hydroperoxide pressure depends on aqueous source concentration and coil temperature.

#### g. Ambient air measurement

The HPLC system was used aboard the NASA DC-8 aircraft during PEM-West (A) (Pacific Exploratory Mission—West) in the fall of 1991, PEM-West (B) in the winter of 1994, and TRACE-A (Transport and Atmospheric Chemistry near the Equator—Atlantic) in the fall of 1992, and was used for ground measurements at the Harvard Forest in the summer and fall of 1992, at the URI Bay Campus in the summer of 1993, and at Mauna Loa Observatory, Hawaii, during the fall of 1991 to the summer of 1992.

In PEM-West (A), the HPLC system had two significant differences from that described above. An Alltech Adsorbosphere HS column (5  $\mu\text{m}$ , 4.5 mm  $\times$  250 mm) was used and, instead of the membrane reactor,

a NaOH solution was added to the postreactor effluent to increase its pH. Both resulted in decreased performance as estimated by chemical noise and sensitivity measured by peak height. The pH 6 collection solution was used. MHP was the only organic hydroperoxide detected. This was also the case at Mauna Loa Observatory. The detection limits for  $\text{H}_2\text{O}_2$  and MHP were 30 and 50 pptv, respectively.  $\text{H}_2\text{O}_2$  and MHP were observed up to 6 and 2.5 ppbv, respectively (see Heikes et al. 1995).

During TRACE-A, the system described in this paper was used and the detection limits were much better than those in PEM-West (A): 5 pptv for  $\text{H}_2\text{O}_2$  and 15 pptv for MHP.  $\text{H}_2\text{O}_2$  and MHP concentrations were observed up to 10 and 2.5 ppbv, respectively. Other organic hydroperoxides were detected in and near fire plumes (Fig. 3c). HMHP peaks appeared on the shoulder of the  $\text{H}_2\text{O}_2$  peaks in most samples collected in and near fire plumes. The 1-HEHP peaks were almost always resolved from MHP at the baseline. PAA was also observed in many samples. Standards for these organic hydroperoxides were not brought to the field but they can be possibly identified based upon their retention times. The concentrations of HMHP, PAA, and 1-HEHP could be also estimated using calibration curves obtained in the laboratory because  $\text{H}_2\text{O}_2$  and MHP sensitivities varied by less than 10% (2% for  $\text{H}_2\text{O}_2$  and 7% for MHP) over the course of the field experiment (2 months) and with pre-postlaboratory determinations. In most cases, their concentrations were much lower than those of  $\text{H}_2\text{O}_2$  and MHP. In TRACE-A, a pH 3 collection solution was used to enhance preservation of HMHP, 1-HEHP, and PAA. Here  $\text{SO}_2$  interference was believed to be negligible because  $\text{SO}_2$  concentrations were expected to be low in this research area (Bandy et al. 1993; Ferek and Hegg 1993; Thornton et al. 1993) and the average sample collection time was 4.5 min. In this case, the loss of  $\text{H}_2\text{O}_2$  would be less than 5%.

All HPLC methods that have observed high HMHP concentrations, employed a cryogenic trap for air sampling and sampled in a forested area (Hellpointner and Gäb 1989; Hewitt and Kok 1991; Fels and Junkermann 1994). We made measurements in the Harvard Forest in the summer and fall of 1992 with the same HPLC system used in TRACE-A. No HMHP was detected in the forest. To ensure the coil collects and preserves HMHP and other hydroperoxides, ambient air samples were collected using both a cryogenic trap and a glass coil at the URI Bay Campus in the summer of 1993. The detailed procedure for cryogenic sampling followed Sakugawa and Kaplan (1987) and Staffelbach and Kok (1993). The cryogenic cooling agent was a mixture of dry ice and acetone and the average sampling time was about 1 h. HMHP, bis-HMP, PAA, and EHP were detected in cryotrap samples, but their concentrations were much lower than those of  $\text{H}_2\text{O}_2$ . Concentrations of PAA and EHP were higher than those of HMHP

TABLE 5. Measurement of organic peroxides (pptv).

Date/time (EDT)	Collector	MHP	HMHP	bis-HMP	PAA	EHP
23 July 1993 1140-1340	coil cryotrap (1)	362 138	— 34	— ++	— 75	— 102
30 July 1993 1111-1200	coil cryotrap (1)	74 —	— 5	— —	— —	— —
3 August 1993 1054-1204	coil cryotrap (1)	126 —	++ ++	++ —	— —	167 —
3 August 1993 1419-1601	coil	467	++	—	143	418
11 August 1993 1333-1458	coil cryotrap (2)	306 147	— —	— —	— 10	167 54
11 August 1993 1530-1630	coil cryotrap (3)	387 184	— ++	— ++	— 19	— 56
12 August 1993 1558-1648	coil cryotrap (3)	479 93	— ++	— ++	— 21	— 35
14 September 1993* 1546-1654	coil cryotrap (4)	1286 1392	— 11	— ++	— 51	— 119
14 September 1993* 1604-1706	coil cryotrap (4)	1315 1385	— 10	— ++	— 43	— 134

Measurements at URI Bay Campus: ++: bis-HMP or HMHP detected but not quantifiable; —: not detected; MHP < 10, HMHP < 10, PAA < 70, EHP < 80 pptv; \*MHP standard addition to the ambient air (1.25 ppbv).

Cryotrap: (1) Ace glass cylinder; (2) U-shape cylinder; (3) Aldrich glass flask with three necks; (4) Horibe trap borrowed from G. Kok (NCAR).

(Table 5). We were able to detect but not quantify these organic hydroperoxides in some coil samples. It can be seen from Table 5 that the concentrations of HMHP, PAA, and EHP detected with the cryotrap were usually much lower than the detection limits of the coil. It was observed that the H<sub>2</sub>O<sub>2</sub> concentration increased slightly as the time increased between dilution and injection of cryogenic samples, consistent with the decomposition of small amounts of HMHP, 1-HEHP, or PAA. The coil method is sufficiently sensitive for HMHP, H<sub>2</sub>O<sub>2</sub>, and MHP. The fact that we failed to observe high levels of HMHP is not due to the use of the coil but to other unknown factors.

#### 4. Conclusions

An HPLC method was developed to measure hydrogen peroxide and C<sub>1</sub> and C<sub>2</sub> hydroperoxides in the atmosphere. Air samples were taken using a glass scrubbing coil. This system was installed in the NASA DC-8 aircraft for several airborne measurements and was used on the ground. The results from the field experiments as well as the lab experiments showed that this HPLC system can provide reliable measurements with a relatively short sampling resolution of a few minutes. The detection limits for H<sub>2</sub>O<sub>2</sub>, HMHP, MHP, PAA, and EHP were 5, 7, 13, 72, and 84 pptv, respectively, with 2-slm air sample flow rate and 0.4 mL min<sup>-1</sup> collection solution flow rate. The collection ef-

iciency of organic hydroperoxides was determined. There was good agreement among the collection efficiencies derived from thermodynamic equilibrium, determined using two coils in series, and determined by standard addition to one coil. For H<sub>2</sub>O<sub>2</sub>, the collection efficiency was greater than 98% at temperatures up to 30°C. For the other hydroperoxides, the collection efficiency was dependent on the temperature of the coil as well as the volume flow rate. The positive artifact of O<sub>3</sub> in H<sub>2</sub>O<sub>2</sub> measurement is estimated to be about 0.03 ppbv per 100 ppbv of ozone. The SO<sub>2</sub> artifact in H<sub>2</sub>O<sub>2</sub> and MHP determination was assessed for different collection solution pHs. In pH 6 collection solutions, the loss of H<sub>2</sub>O<sub>2</sub> was less than 10%. The addition of 5 × 10<sup>-3</sup> M CH<sub>2</sub>O caused HMHP to be produced. The H<sub>2</sub>O<sub>2</sub> loss by SO<sub>2</sub> was considerably greater in pH 3 collection solutions. However, HMHP and 1-HEHP are stable only in acidic solution, and the pH of the collection solution must be acidic to collect and preserve them for analysis. The pH-dependent lifetime of 1-HEHP was evaluated and it was 6 × 10<sup>7</sup>[H<sup>+</sup>] s at 17°C. The half-life of 1-HEHP at pH 6 is 1 min and it can cause a positive artifact in H<sub>2</sub>O<sub>2</sub> measurement with collection solution pH > 6.

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