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With ACP funding, we have designed a three-channel continuous peroxide analyzer, similar to the Kok and Lazrus design, that uses a combination of fluorescence reagents to speciate H_2O_2 , methyl hydroperoxide (MHP) and hydroxymethyl hydroperoxide (HMHP). We have fabricated two instruments, one for ground and one for aircraft measurements. Figure 1 shows a schematic diagram, illustrating the different stripping solutions, fluorescence reagents and fluorescence enhancing reagents utilized. Hydrogen peroxide, HMHP and MHP are stable under low pH scrubbing conditions. MHP and H_2O_2 are stable in alkaline solution, but HMHP hydrolyzes rapidly to form H_2O_2

Figure 1: Schematic diagram of the three-channel peroxide analyzer

Thus channels 1 and 2 contain only H_2O_2 and MHP when they meet the fluorescence reagent. The pOHPAA/HRP reagent in channel 1 responds to all peroxides, although individual peroxides will be scrubbed with different efficiencies. Channels 2 and 3 use Fenton chemistry to convert H_2O_2 to a fluorescent product:

In the presence of O_2 and dissolved iron, the cyclohexadienyl radical formed in the second step produces fluorescent hydroxybenzoic acid isomers (OHBA). Fluorescence intensity is enhanced

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by adding Al(III) acetate or citrate buffer to the OHBA product stream. Unlike pOHPAA/HRP, FeBA reagent is specific for H_2O_2 , because the reaction between Fe(II) and CH_3OOH is slow, and does not generate OH radical. We have developed an HPLC separation scheme for the OHBA and OCH_3BA products expected from the reaction of FeBA with a mixture of H_2O_2 and CH_3OOH , and have demonstrated that OHBA is in fact the only product of this reaction. Thus, the difference between channels 1 and 2 gives the MHP concentration and the difference between channels 2 and 3 gives the HMHP concentration. The ground-based instrument incorporates an "inletless" sampler, deployed outdoors, to avoid line losses that may compromise measurements in dirty humid air. Both instruments include now include temperature control to regulate reaction time for the Fenton chemistry channels.

These instruments have been deployed in several field programs during the past six years (see Table 1). Principal findings of the peroxide measurements include (i) observation of substantial contribution of organic peroxides to total peroxide in summer air, particularly in southern latitudes; (ii) agreement in measured total peroxide, in a field intercomparison with NOAA in Nashville, but significant disagreement in speciation; (iii) observation of a peroxide "reservoir" above the nocturnal boundary layer that can be transported for many days; (iv) depletion of "background" peroxide in urban plumes by deposition, reaction with OH and photolysis.

These peroxide measurements were incorporated into a number of observation-based modeling studies to evaluate ozone production efficiency (SOS Metter '92; NARE Nova Scotia '93; SOS Nashville '95, NARSTO NE '96). In these models, instantaneous ozone production rates are calculated from measured values of the concentration of trace gases, CO, NO_x , VOC, H_2O_2 , ROOH, and HCHO. In some cases, the sensitivity of ozone production to changes in NO_x and HC emissions have been assessed. Sillman has incorporated our measurements into a somewhat different observation-based model to compute values of indicator species believed to predict whether ozone formation is NO_x or VOC limited. The ratio of H_2O_2 to HNO_3 appears to be the most reliable of these indicator species. These approaches have shown that ozone formation is VOC limited in urban plumes, and approaches NO_x limitation as the plume travels downwind.

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Table 1 Summary of H₂O₂ and Organic Peroxide Field Measurements

PEROXIDE	H ₂ O ₂		MHP		HMHP		DATES	# OF DAYS or FLIGHTS
	MEDIAN CONC. ppbv ²	HIGH CONC. ppbv ²	MEDIAN CONC. ppbv ²	HIGH CONC. ppbv ²	MEDIAN CONC. ppbv ²	HIGH CONC. ppbv ²		
Metter, GA (SOS)	1.5	5.5	0.3	2.5	0.3	1.3	06/92	22 days
Atlanta, GA (SOS)	1.0	2.0	(⁵)	(⁵)	1.2	3.0	07/92-08/92	5 days ⁴
Long Island, NY	0.2	1.5	0.2	1.5	0.2	0.8	11/92-10/94	18 days
Yarmouth, NS (NARE)	0.5	2.8	0.3	2.2	0.2	1.4	08/93-09/93	19 days ⁴
Halifax, NS ¹ (NARE)	2.5	11.4	0.3	1.2	(³)	(³)	08/93	13 flights
Dallas, TX ^{1,6}	1.0	1.0	0.6	0.6	(³)	(³)	02/95	3 flights
Nashville, TN ¹ (SOS)	2.3	4.5	1.6	4.0	0.9	2.3	06/95-07/95	15 flights
Nashville, TN ¹ (SOS)	1.9 ⁷	4.9 ⁷	1.5 ⁷	3.5 ⁷	1.0 ⁷	3.9 ⁷		
Long Island, NY ^{1,7} (NARSTO NE)	1.1	4.7	0.9	3.2	0.4	1.0	7/96	15 flights
Long Island, NY (NARSTO NE)								
Fall '97 intensive	0.8	1.9	0.03	1.1	0.2	0.5	08/97-09/97	14 days ⁴
Spring '98 intensive	0.9	2.5	(⁵)	(⁵)	0.1	0.8	03/98-04/98	14 days ⁴
Fall '98 intensive	(⁸)	(⁸)	(⁸)	(⁸)	(⁸)	(⁸)	9/98	14 days ⁴
Phoenix, AZ	(⁸)	(⁸)	(⁸)	(⁸)	(⁸)	(⁸)	05/98-06/98	23 flights
Aircraft ¹	(⁸)	(⁸)	(⁸)	(⁸)	(⁸)	(⁸)	05/98-06/98	8 days ⁴
Ground								

¹ Aircraft data

² One minute averages for ground data, ten second averages for aircraft data, except where noted

³ HMHP was not measured, H₂O₂ is actually the sum of H₂O₂ and HMHP

⁴ Nighttime data included

⁵ Not detected

⁶ Study conducted for Sonoma Technology Inc., 15-second average

⁷ Boundary layer, mid-day subset only

⁸ Results not yet available