# A Comparison of the Enzyme Fluorometric and the Peroxyoxalate Chemiluminescence Methods for Measuring $H_2O_2$

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Abstract. During September 25 to October 28, 1985, the enzyme fluorometric (Lazrus *et al.*, 1985) and the peroxyoxalate chemiluminescence (Klockow and Jacob, 1986; Jaeschke, 1986) techniques for analyzing  $H_2O_2$  were compared in laboratory studies at the National Center for Atmospheric Research in Boulder, Colorado, U.S.A. and under field conditions at the Whiteface Mt. field station of the Atmospheric Sciences Research Center, Albany, New York, U.S.A. Both methods showed excellent agreement, with a maximum deviation of  $\pm 5\%$ . Only at unusually high concentrations of some potential atmospheric species could slight interferences be observed. During the experiments the detection limits were  $1.3 \times 10^{-8}$  mol/l (0.44 ppbm) of  $H_2O_2$  for the fluorometric instrument and  $4 \times 10^{-8}$  mol/l (1.36 ppbm) of  $H_2O_2$  for the chemiluminescence instrument. For the chemiluminescence technique, the response to methylhydroperoxide was approximately 80-fold less than that to an equivalent concentration of  $H_2O_2$ .

Key words. Enzyme fluorometry, peroxyoxalate chemiluminescence, hydrogen peroxide analysis, comparative study.

# 1. Introduction

Accurate measurements of  $H_2O_2$  in cloud and fog water are important because  $H_2O_2$  plays a dominant role as an oxidant in heterogeneous processes which lead to the formation of sulfuric or nitric acids in the atmosphere, particularly at high insolation and at pH-values below pH 5.

 $H_2O_2$  in precipitation and cloud water has been measured by several groups (Bufalini *et al.*, 1979; Kok, 1980; Roemer *et al.*, 1985) using a luminol chemiluminescence technique. However, there are some interferences in the technique (Ibusuki, 1983; Lazrus *et al.*, 1985) which brought its results into question and led to the development of other analytical techniques. One is the enzyme fluorometric technique (Lazrus *et al.*, 1985), which is applied by several groups in the United States for analyzing precipitation and cloud water samples (Richards et al., 1983; Kadlecek et al., 1983; McLaren et al., 1985; Kelly et al., 1985). Another technique is the peroxyoxalate chemiluminescence method (Klockow and Jacob, 1986), which is mainly used by different European groups with various modifications (Guebitz et al., 1985; Jaeschke, 1986; Neftel et al., 1984). A study comparing these two methods was conducted from September 25 to October 28, 1985, with laboratory tests at the National Center for Atmospheric Research (NCAR) at Boulder, Colorado and subsequent field measurements at the Whiteface Mt. (Atmospheric Sciences Research Center, Albany, New York).

#### 2. Laboratory Studies

#### 2.1. Experimental

The NCAR fluorometric method is based on the enzyme-catalyzed reaction of  $H_2O_2$  with *p*-hydroxyphenylacetic acid, which forms a fluorescent dimer (Lazrus *et al.*, 1985). The analytical chemical reaction responds both to  $H_2O_2$  and to organic hydroperoxides. With catalase as a discriminating agent for  $H_2O_2$ , and with a dual channel flow system, separate signals can be obtained for  $H_2O_2$  and the organic peroxides. For each analytical run in our study a 1.5-ml sample was used.

In the chemiluminescence method a reaction of  $H_2O_2$  with *bis*-trichloro phenyloxalate is used (Rauhut *et al.*, 1986). The high-energy dioxetanedione (Stauff and Jaeschke, 1972) that forms transmits its chemiluminescence to perylene as a fluororescent, which relaxes to its ground state with the emission of light (Jaeschke, 1972). Our analysis was performed in a batch process by injection of 0.5 ml of a sample into 1.1 ml of the reagent solution (Beltz, 1987).

In our study a common set of aqueous standards was used to calibrate both instruments daily. The samples to be tested for potential interferences were generated individually. Analyses were performed as quickly as possible after preparation to minimize the chances of reactions between the  $H_2O_2$  and a potential interferent. Analyses of the standards and the test samples (containing an unknown amount of  $H_2O_2$  and a variety of potential interferent compounds) were conducted simultaneously with both instruments.

#### 2.2. Results and Discussion

The results of these interference studies are compiled in Table I. These studies were conducted in the presence of  $H_2O_2$  and a variety of organic and inorganic compounds, typically in concentrations of  $1 \times 10^{-4}$  mol/l. This is much higher than would be seen in ambient precipitation or cloud water samples; however, it provides a rigorous check on the techniques. The test did not include common compounds, such as sulfate, nitrate, or heavy metals, because their role had

already been examined individually in the home laboratories for each technique and could be neglected (Lazrus *et al.*, 1985; Beltz, 1987). A solution containing a mixture of common anions and cations was used which provided a surrogate of ambient precipitation (Kok *et al.*, 1986). Analysis of the synthetic rain mixture gave an excellent agreement between the two techniques.

The reproducibility of the techniques can be seen from the analysis of eight individually prepared standards  $(2.15 \times 10^{-7} \text{ mol/l } H_2O_2)$  incorporated into this series of samples. The fluorometric technique gave  $2.31 \pm 0.06 \text{ mol/l}$  and

Matrix	[H <sub>2</sub> O <sub>2</sub> ] 10 <sup>-7</sup> mol/l				
	Fl	%	Cl	%	
$\overline{x}$ for H <sub>2</sub> O (8 samples)	2.31		2.09		
$s_{n-1}$	0.06		0.25		
Synth. rain, pH 4.0	2.26	-1.7	2.24	+7.2	
Synth. rain, $10^{-4}$ mol/l CO <sub>3</sub> <sup>=</sup> , pH					
5.6	2.35	+2.2	2.79	+33.5	
Synth. rain, pH 2.7 ( $H_2SO_4$ )	2.35	+2.2	0.00	·	
$Ca^{2+} 10^{-4} mol/l, pH 6.5$	2.35	+2.2	3.06	+46.4	
HCOO <sup>-</sup> 10 <sup>-4</sup> mol/l, pH 4.7	2.44	+6.1	2.41	+15.3	
Cl- 10-3 mol/l	2.35	+2.2	2.38	+13.8	
$C_2 H_5 OH 0.2 \text{ mol/l}$	2.32	+0.9	3.09	+47.9	
$C_2 H_5 OH 0.2 \text{ mol/l}$	2.32	+0.9	3.09	+47.9	
MeNH <sub>3</sub> Cl 10 <sup>-4</sup> mol/l, pH 5.7	2.18	-5.2	ь		
$MeNH_3Cl \ 10^{-5} mol/l$	2.26	-1.7	b		
$MeNH_3Cl 10^{-5} mol/l$	2.24	-2.4	ь		
MeNH <sub>3</sub> Cl 10 <sup>-6</sup> mol/l	2.29	-0.4	2.29	+8.1	
$NH_4Cl 10^{-4} mol/l$	2.26	-1.7	b		
NH <sub>4</sub> Cl 10 <sup>-5</sup> mol/1	2.24	-2.4	1.65	-21.1	
$NH_4C1 \ 10^{-6} \ mol/l$	2.24	-2.4	2.09	0.0	
$C_6 H_5 NH_3 Cl \ 10^{-5} mol/l$	1.94	-15.7	2.18	+4.3	
NH <sub>2</sub> OH 10 <sup>-4</sup> mol/l, pH 4.6	а		1.44	-31.1	
HCHO 10 <sup>-4</sup> mol/l	2.35	+2.2	2.18	+4.3	
Catalase + H <sub>2</sub> O	с		b		
Catalase + synth. rain	с		b		

Table Ia. Interference studies.

The samples were prepared freshly to contain  $2.15\times 10^{-7}$  mol/l  $H_2O_2$  for each analytical cycle.

Fl = fluorescent instrument, Cl = chemiluminescent instrument

% = percentage deviation from x

a = peak shape distorted, no quantitation possible

b = same value as the blank water (Milli-Q)

c = below baseline of blank water.

Matrix + $[H_2O_2]$	[org.] 10 <sup>-6</sup> mol/1	[H <sub>2</sub> O <sub>2</sub> ] 10 <sup>-6</sup> mol/	1
mol/l	Fl	Fl Ci	
HMSA $1.0 \times 10^{-4}$ ,			
HCHO $9.0 \times 10^{-3} + 4.29 \times 10^{-6}$		4.41	4.47
TBHP $5.3 \times 10^{-6}$ –	0	0.07	0.17
TBHP $5.3 \times 10^{-6} + 4.29 \times 10^{-6}$	0	4.50	4.29
PAA $6.6 \times 10^{-6}$ –	6.44	0	0.37
PAA $6.6 \times 10^{-6} + 2.15 \times 10^{-6}$	6.44	2.38	2.14

Table Ib. Interference studies.

HMSA = Hydroxymethanesulfonic acid

TBHP = t-butylhydroperoxide

PAA = peroxyacetic acid

[org.] = concentration of organic peroxide (analyzed with the fluorometric instrument).

the chemiluminescence instrument  $2.09 \pm 0.25$  mol/l of  $H_2O_2$ . These values include the variation in the sample preparation, and the variation in analysis is less than that.

Table Ia shows a positive interference in the presence of  $CO_3^=$ ,  $Ca^{++}$ , and ethanol in the chemiluminescence technique, but not interference in the fluorometric instrument. In the case of the extremely acidified synthetic rain (pH 2.7), the chemiluminescence signal was destroyed since the buffer capacity of the system was exceeded. This is a recognized problem in the chemiluminescence system; therefore, most of the samples are diluted before analysis.

Table Ia lists detailed studies on amine compounds and some organic acids. At the  $1 \times 10^{-4}$ -mol/l level the chemiluminescence technique had a negative interference from methylamine, hydroxylamine, and ammonia. Only hydroxylamine gave an interference in the fluorescence technique. These negative interferences were still observed at  $10^{-5}$  mol/l. At the  $10^{-6}$ -mol/l level no interferences were seen for either technique. Formaldehyde at a concentration of  $10^{-4}$  mol/l did not effect either instrument.

Included in these series (Table Ib) was a sample containing  $4.3 \times 10^{-6}$  mol/l (146 ppbm) of H<sub>2</sub>O<sub>2</sub>, which was analyzed in the presence of  $1 \times 10^{-4}$  mol/l of hydroxymethanesulfonate (HMSA) and of  $1 \times 10^{-3}$  mol/l of formaldehyde. No interference was noted in either technique. Samples containing *t*-butyl-hydroperoxide (TBHP) and peroxyacetic acid (PAA) were also examined. The chemiluminescence technique does not see TBHP or PAA. The fluorometric method responds only to PAA.

The detection limits for the techniques are not directly comparable. The fluorometric instrument uses a continuous-flow system referenced against a base line. In contrast, the chemiluminescence instrument analyzes each sample individually in a batch process, and there is a contributing signal from the background chemiluminescence. Deriving a detection limit for the fluorometric technique based on three times the signal-to-noise yields a value of  $1.3 \times 10^{-8}$  mol/l (0.44 ppbm). Using three times the standard deviation of the blank as detection limit criteria for the chemiluminescence instrument a value of  $4 \times 10^{-8}$  mol/l (1.36 ppbm) is obtained.

The precision of the analytical techniques can be examined by considering the standard deviation in the analysis of a sample containing  $H_2O_2$ . At an  $H_2O_2$ concentration of  $4.3 \times 10^{-8}$  mol/l (1.46 ppbm), the fluorometric technique has a standard deviation of  $0.06 \times 10^{-8}$  mol/l (0.02 ppbm). For the chemiluminescence technique the standard deviation is  $0.3 \times 10^{-8}$  mol/l (0.10 ppbm). Both of these measurements are based on three analysis.

The fluorometric method is known to respond to organic hydroperoxides. The dual-channel flow system employs catalase as a discriminating agent to determine both  $H_2O_2$  and organic hydroperoxides. To examine the response of the chemiluminescence technique to organic hydroperoxides detailed tests were employed. Table II gives the response of the chemiluminescence instru-

Matrix	$[H_2O_2]$ 10 <sup>-6</sup> mol	$[H_2O_2]$ $10^{-6} mol/l$		
	Fl	Cla	СІЬ	
MHP $4.57 \times 10^{-7}$ mol/l	1.09	0.09	0.69	5
MHP $1.37 \times 10^{-6}$ mol/l	0.96	0.23	0.72	6
MHP $4.57 \times 10^{-6}$ mol/l	0.98	0.12	0.75	38
MHP $1.37 \times 10^{-5}$ mol/l	-	0.19	0.87	72
MHP $4.57 \times 10^{-5}$ mol/l	-	0.69	1.21	66
MHP $1.37 \times 10^{-4}$ mol/l	-	1.96	2.41	70
MHP $4.57 \times 10^{-4}$ mol/l	-	7.15	9.06	64

Table II. Chemiluminescent response to methylhydroperoxide

All samples contained a fixed amount of  $0.86 \times 10^{-6}$  mol/l H<sub>2</sub>O<sub>2</sub>. With no added MHP the fluorometric instrument gave  $0.8 \times 10^{-6}$  mol/l and the chemiluminescence instrument  $0.68 \times 10^{-6}$  mol/l.

Cla = Cl signal for MHP alone with no added  $H_2O_2$ 

Clb = Cl signal for samples containing MHP and  $0.86 \times 10^{-6}$  mol/l H<sub>2</sub>O<sub>2</sub>

Response ratio = MHP-concentration/ $H_2O_2$  response Cla.

ment, at a fixed H<sub>2</sub>O<sub>2</sub> concentration of  $8.59 \times 10^{-7}$  mol/l (29.2 ppbm), to the presence of methylhydroperoxide (MHP) in the range from  $4.57 \times 10^{-4}$ mol/l to  $4.57 \times 10^{-4}$  mol/l and to MHP alone in water (in the same range). These data show an additive response due to the added MHP. At high MHP concentrations (>10<sup>-5</sup> mol/l) the response was approximately 60- to 80-fold less than for H<sub>2</sub>O<sub>2</sub> in the same molar concentration. At low concentrations of MHP there was a small elevated signal due to the organic hydroperoxide. An exact quantitation is not possible. The signal caused by the added MHP was in the same range as the response of the blank water for this analytical run (0.14 ±  $0.06 \times 10^{-6}$  mol/l). The samples were also analyzed by the fluorometric instrument up to a MHP concentration of  $4.57 \times 10^{-6}$  mol/l, which was the upper limit in the dynamic range of the instrument configured for these studies.

In Table III the results from a series of samples containing a fixed concentration  $(4.57 \times 10^{-5} \text{ mol/l})$  of MHP and varying concentrations of  $H_2O_2$  are given. This MHP concentration was above the operational range of the fluorometric technique as implemented, and duplicate samples of  $H_2O_2$  without the MHP were prepared for analysis as a check on the sample preparation. With the chemiluminescence instrument the response to the added MHP was independent of the concentration of  $H_2O_2$ . In all cases the average response of the chemiluminescence instrument to MHP was 80-fold less than that of an equivalent  $H_2O_2$  concentration.

There are no accurate measurements of MHP or other organic hydroperoxides in atmospheric liquid samples. Some limited measurements of peroxides

Matrix						
[H <sub>2</sub> O <sub>2</sub> ] 10 <sup>-6</sup> mol/1	[org.] 10 <sup>-5</sup> mol/l	$[H_2O_2]$ 10 <sup>-6</sup> mol/l			Response ratio	
		Fl	Cl	Cla	•	
4.29	_	4.56	4.15	0.64	71	
4.29	4.57		4.79			
3.32	-	3.4	2.79	0.87	53	
3.32	4.57		3.66			
2.15	-	2.29	1.89	0.55	83	
2.15	4.57		2.44			
1.29	_	1.38	1.22	0.4	114	
1.29	4.57		1.62			
0.43	-	0.43	0.38	0.49	93	
43	4.57		0.87			
H <sub>2</sub> O	-		0.04	70		
H <sub>2</sub> O	4.57		0.69			

Table III. Chemiluminescent response to MHP

Cla = Cl signal with MHP minus Cl signal without MHP Response ratio = MHP concentration/ $H_2O_2$  response Cla Mean value of response ratio =  $80 \pm 21$ .

in precipitation and fog samples indicate that the residual signal which can be attributed to the organic hydroperoxides is about 10%. The results of the chemiluminescence instruments indicate an influence due to organic peroxides only for low  $H_2O_2$  concentrations (i.e.  $10 \times ^{-6}$  mol/l) and relatively high MHP concentrations ( $10 \times ^{-5}$  mol/l). It is highly unlikely that these conditions would occur in ambient samples.

In summary, both the fluorometric and the chemiluminescence techniques for analyzing  $H_2O_2$  were subjected to a wide variety of potentially interfering species. A few minor interferences have been observed; however, none of these species would be expected in ambient water samples at concentrations near the levels which were used in these studies. Direct comparison of the two methods demonstrates excellent agreement. Both techniques performed satisfactorily during the studies. An advantage of the fluorometric method is the possibility to detect both  $H_2O_2$  and organic peroxides. The chemiluminescence technique has the capability to process samples at a faster rate than the fluorometric technique (about 35 samples per hour for the chemiluminescent instrument and 10–12 samples per hour for the fluormetric).

## 3. Field Measurements

#### 3.1. Experimental

Additional comparisons were conducted under field conditions at the Whiteface Mt. field station of the Atmospheric Sciences Research Center (ASRC), State University New York at Albany. ASRC used its own analytical instrument based on the NCAR fluorometric technology in comparison with the chemiluminescence technique.

The field studies consisted of the common analysis with both instruments of 27 cloud water samples collected at the summit of Whiteface Mt. from October 10 to 28. One sample of snow from Boulder, Colorado, was also included.

The samples were collected by the ASRC string collector mounted above the roof of the observatory at the summit of Whiteface Mt. (Falconer and Falconer, 1980). Cloud water flows from the collector through a Teflon tube to a bottle inside the laboratory. All samples were analyzed immediately after the end of a collection cycle (20-60 minutes). At the measuring site both instruments were calibrated with the same standards, and the analyses of each sample were carried out simultaneously. Some of the samples were used for standard addition procedures or dilution tests.

# 3.2. Results and Discussion

Table IV shows the results of the analysis of ambient cloud water samples.

Sample	$[H_2O_2]$ $10^{-6}$ mol	/1	Sample	[H <sub>2</sub> O <sub>2</sub> ] 10 <sup>-6</sup> mol/1	
Date/Time	Fl	Cl	Date/Time	Fl	Cl
10/10/85			10/14/85		
14:00	а	а	12:00	20.21	22.21
14:25	a	а	12:30	15.62	15.32
14:45	а	0.21	13:00	10.76	10.53
15:22	а	0.21	13:30	7.74	8.12
15:45	а	0.21	14:05	5.91	7.00
10/13/85			14:30	4.59	5.50
11:15	а	а	15:00	4.32	4.76
12:00	а	0.18	10/24/85		
13:00	а	0.18	14:30	2.18	2.26
14:00	а	0.21	15:30	0.68	0.65
15:00	1.00	1.29	16:30	0.29	0.24
16:00	3.38	3.44	17:30	0.21	0.15
16:55	1.79	1.94	18:30	0.15	0.06
			19:30	0.47	0,41
			20:30	0.29	0.29
			21:30	1.53	1.32

Table IV. Intercomparison of cloud water samples

Time is the end time of a collection cycle.

a = below detection limit (Fl =  $0.15 \times 10^{-6}$  mol/l, Cl =  $0.06 \times 10^{-6}$  mol/l).

The samples gathered between October 10 and 13 contained very low amounts of  $H_2O_2$ , amounts only slightly above the detection limit of the chemiluminescence instrument. At this low concentration the fluorometric instrument showed no signals above the background noise, which was unusually high because HF radiation was present. This interference is an artifact of radio transmitters present at the site. At higher concentrations the data showed good agreement between the two instruments. All data of Table IV are plotted in Figure 1 for regression analysis. The coefficient of  $r = \pm 0.997$  is obtained, and the regression curve is given by the following equation:

Fluorometric  $[H_2O_2] = 0.944$  Chemiluminescent  $[H_2O_2] + 0.024$ .

All the measured values fit in the 1:1 line with a deviation of  $\pm 5\%$  to 10%.

The results of the standard addition procedures are compiled in Table V. In a first run each sample was analyzed in the normal manner. Then three aliquots of 20 ml of each sample were taken and 20  $\mu$ l, 40  $\mu$ l, or 60  $\mu$ l of a 2.94 × 10<sup>-4</sup>mol/l (10000 ppbm) H<sub>2</sub>O<sub>2</sub> standard were added before the subsequent analysis. In the case of the snow sample analyzed at NCAR other amounts of added H<sub>2</sub>O<sub>2</sub> were used. Again both instruments showed good agreement, even when the added H<sub>2</sub>O<sub>2</sub> obviously reacted with reduced compounds in the sample (two samples from October 13).



Fig. 1. Intercomparison between the fluorometric and the chemiluminescent techniques on cloud water samples collected at Whiteface Mt., New York. The straight line represents least-squares fit; the 1:1-line represents perfect agreement and the dashed lines are  $\pm 5\%$  deviation from this line.

In order to examine the effects of diluting samples, in two experimental runs 1 and 2 ml of sample were added to 10 ml of deionized water. The results of these experiments are presented in Table VI. The results of analysis and the calculated value are in a reasonably good agreement.

# 4. Summary

Both instruments worked well in laboratory tests and under field conditions. Analytical results show good agreement over a wide range of  $H_2O_2$  concentration. Both methods are also applicable in standard addition and dilution procedures. The result of this comparison underlines the capability of both methods

Sample	$[H_2O_2]$ 10 <sup>-6</sup> mol/1	$[H_2O_2]$ 10 <sup>-6</sup> mol/l			
Date/Time	added	Fl		Cl	
		total	diff.	total	diff.
9/29/85		2.26		2.29	
b	0.85	3.18	2.33	2.94	2.09
	1.71	4.00	2.29	3.82	2.11
	2.15	4.44	2.29	4.44	2.29
	2.59	4.82	2.23	4.79	2.20
10/13/85					
13:00		а		0.18	
c	2.94	1.68	-1.26	1.97	-0.97
	5.88	4.56	-1.32	4.85	-1.03
	8.82	7.85	-0.97	8.21	-0.61
14:00		а	•	0.21	
c	2.94	1.94	-1.00	2.21	-0.70
	5.88	5.12	-0.76	5.53	-0.35
	8.82	7.85	-0.97	8.20	-0.62
15:00		1.00		1.29	
с	2.94	4.00	1.06	3.94	1.00
	5.88	7.29	1.41	6.79	0.91
	8.82	10.32	1.50	10.06	1.24
10/24/85					
16:30		0.29		0.23	
с	2.94	3.24	0.29	3.24	0.29
	5.88	6.18	0.29	6.00	0.12
	8.82	8.82	0	9.11	0.29
19:30		0.47		0.42	
с	2.94	3.53	0.59	3.09	0.15
	5.88	6.47	0.59	6.00	0.12
	8.82	8.47	-0.35	9.29	0.47

Table V. Standard addition on cloud water samples

a = below detection limit.

b = snow sample collected in Boulder, Colorado.

c = cloud water samples collected at Whiteface Mt., New York.

for accurate measurements of  $H_2O_2$  in ambient precipitation, cloud, and fog water samples.

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The Atmospheric Sciences Research Center's Whiteface Mountain participa-

Date/Time	dil. factor	[H <sub>2</sub> O <sub>2</sub> ] 10 <sup>-6</sup> mol/l				
		Fl		Cl		
		а	b	а	b	
10/14/85						
12:00		20.21		22.21		
	1:6	3.06	18.35	3.38	20.29	
	1:11	1.79	19.74	2.21	24.26	
12:30		15.62		15.44		
	1:6	2.62	15.71	2.85	17.12	
	1:11	1.29	14.24	1.44	15.85	
13:00		10.76		10.53		
	1:6	1.62	9.71	1.82	10.94	
	1:11	0.88	9.71	0.88	9.71	

Table VI. Dilution tests on cloud water samples

 $a = measured [H_2 O_2].$ 

 $b = calculated initial [H_2O_2].$ 

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#### References

Beltz, N., 1987, PhD Thesis, University of Frankfurt.

- Bufalini, J. J., Lancaster, H. T., Namie, G. R., and Gay, B. W. Jr., 1979, Hydrogen peroxide formation from the photooxidation of formaldehyde and its presence in rainwater, J. Environ. Sci. Health Part A 14, 135-141.
- Falconer, R. E. and Falconer, P. D., 1980, Determination of cloud water acidity at a Mountain observatory in the Adirondack Mountains of New York State, J. Geophys. Res. 7465-7470.
- Guebitz, G., Van Zoonen, P., Gooijer, C., Velthorst, N. H., Frei, R. W., 1985, Immobilized fluorophores in dynamic chemiluminescence detection of hydrogen peroxide, *Anal. Chem.* 57, 2071-2074.

Ibusuki, T., 1983, Influence of trace metal ions on the determination of hydrogen peroxide in rainwater by using a chemiluminescent technique, Atmos. Environ. 17, 393-396.

- Jaeschke, W., 1972, Zur Chemilumineszenz des sogenannten Dioxetandions, PhD thesis, J. W. Goethe-Universität, Frankfurt am Main.
- Jaeschke, W., 1986, Multiphase atmospheric chemistry, in W. Jaeschke (ed.), *Chemistry of Multiphase Atmospheric Systems*, Springer Verlag, Heidelberg, 1986, Proc. of a NATO ASI, held in Corfu, Greece, Oct. 1983.
- Kadlecek, J. A., McLaren, S., Mohnen, V., Mossl, B., Kadlecek, A., and Camarota, N., 1983, Wintertime cloudwater chemistry studies, ASRC Publ. No. 1008.
- Kelly, T. J., Daum, P. H., and Schwartz, S. E., 1985, Measurements of peroxides in cloudwater and rain, J. Geophys. Res. 7861-7871.

- Klockow, D., Jacob, P., 1986, The peroxyoxalate chemiluminescence and its application to the determination of hydrogen peroxide in precipitation, in W. Jaeschke (ed.), *Chemistry of Multiphase Atmospheric Systems*, Springer Verlag, Heidelberg, Proc. of a NATO ASI held in Corfu, Greece, 1983.
- Kok, G. L., 1980, Measurements of hydrogen peroxide in rain water, Atmos. Environ. 14, 653-656.
- Kok, G. L., Thompson, K., Lazrus, A. L., and McLaren, S. E., 1986, Derivatization technique for the determination of peroxides in precipitation, *Anal. Chem.* 58, 1192–1194.
- Lazrus, A. L., Kok, G. L., Gitlin, S. N., Lind, J. A., and McLaren, S., 1985, Automated fluorometric method for hydrogen peroxide in atmospheric precipitation, *Anal. Chem.* 57, 917–922.
- McLaren, S. E., Kadlecek, J. A., and Mohnen, V. A., 1985, SO<sub>2</sub> oxidation in summertime cloud water at Whiteface Mountain, in D. D. Adams and W. P. Page (eds.), *Acid Deposition*, Plenum Press, New York, London.
- Neftel, A., Jacob, P., and Klockow, D., 1984, Measurements of hydrogen peroxide in polar ice samples, *Nature* 311, 43-45.
- Rauhut, M. M., Bollyky, L. J., Roberts, B. G., Loy, M., Whitman, R. H., Lannotta, A. V., Seusel, A. M., Clarke, R. A., 1967, Chemiluminescence from reactions of electronegatively substituted aryl oxalates with hydrogen peroxide and fluorescent compounds, J. Am. Chem. Soc. 89: 25, 6615-6625.
- Richards, L. W., Anderson, J. A., Blumenthal, D. L., McDonald, J. A., Kok, G. L., and Lazrus, A. L., 1983, Hydrogen peroxide and sulfur (IV) in Los Angeles cloudwater, Atmos. Environ. 17, 911-914.
- Roemer, F. G., Viljier, J. W., van den Beld, L., Slangeval, H. J., Veldkamp, A. A., and Reijnders, H. F. R., 1985, The chemical composition of cloud and rainwater. Results of preliminary measurements from an aircraft, *Atmos. Environ.* 19, 1847–1858.
- Stauff, J. and Jaeschke, W., 1972, Chemilumineszenz des 'Dioxetandions', Z. Naturforsch. 27b, 1434-1435.