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# RESEARCH REPORT

EV-337

A COMPARISON OF INFRARED  
AND FLUOROMETRIC  
MEASUREMENTS OF GAS-PHASE  
HYDROGEN PEROXIDE

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April 28, 1989



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## Purpose

The most widely used techniques for measuring gas-phase hydrogen peroxide ( $H_2O_2$ ) in the troposphere are fluorometry and infrared spectroscopy. However, intercomparison studies on urban air show that results from the fluorometric method can be a factor of two or more higher than results from the infrared method. This disagreement may be caused by interferences in the fluorometric method, or it may be due to sample handling problems. Since we have been using the fluorometric method to measure  $H_2O_2$  yields from the reaction of ozone with ethylene, we initiated this project to verify that the fluorometric method gives accurate measurements of  $H_2O_2$  under laboratory conditions.

## Summary

Results from a fluorometric method as implemented at GMR and a Fourier transform infrared spectroscopic (FTIR) method for measuring  $H_2O_2$  were compared for thirteen air mixtures containing 0.1 to 1.0 ppm of  $H_2O_2$ . The mixtures were prepared by injecting small amounts of aqueous  $H_2O_2$  samples into an evacuated 104-L long-path White cell and then adding hydrocarbon-free air sufficient to increase the cell pressure to atmospheric pressure. The half-life of  $H_2O_2$  in the cell was only 25 - 30 minutes, due to wall losses and the presence of water in the cell. For each measurement of  $H_2O_2$  by the fluorometric method, about 5 L of the gas mixture was drawn through two impingers in series containing deionized water. The amount of  $H_2O_2$  collected in the impingers was then determined by adding p-hydroxyphenyl acetic acid (HPA) and horseradish peroxidase to the samples and fluorometrically measuring the yield of the fluorescent dimer of HPA. For each determination of  $H_2O_2$  by the FTIR method, several spectra of each gas mixture were measured using an FTIR spectrometer

interfaced to the long-path White cell. The concentrations of  $\text{H}_2\text{O}_2$  were determined by subtracting a calibrated reference spectrum from each measured spectrum. The FTIR measurement of  $\text{H}_2\text{O}_2$  at the time of the comparison with the fluorometric measurement was calculated from a least-squares fit of the FTIR measurements to time. A least-squares fit to the data for all of the comparisons showed that the results from the fluorometric method agreed with the FTIR method to within 13 %.

### Conclusions

The overall agreement between the fluorometric method and the FTIR method for determining  $\text{H}_2\text{O}_2$  concentrations under laboratory conditions was good; however, the comparisons had a large amount of scatter for concentrations below 0.35 ppm. All of this scatter could not be explained by the estimated uncertainties in the FTIR measurements. Part of the scatter was apparently due to sample handling or other problems in the fluorometric method; these problems may be even more important at the ppb concentration range found in the troposphere. The FTIR measurements showed that the absorption coefficients of  $\text{H}_2\text{O}_2$  reported in the literature by several research groups are not internally consistent nor are they consistent with the band intensities of  $\text{H}_2\text{O}_2$ . Thus, these absorption coefficients for  $\text{H}_2\text{O}_2$  should not be used to determine  $\text{H}_2\text{O}_2$  concentrations.

## Introduction

Hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) can play an important role in acid rain formation by efficiently oxidizing  $\text{SO}_2$  to sulfuric acid in aqueous solution [1-3]. To assess the importance of this process, accurate laboratory and atmospheric measurements of  $\text{H}_2\text{O}_2$  are needed. Two methods currently used for measuring atmospheric  $\text{H}_2\text{O}_2$  are: (1) various implementations of a fluorometric method, in which the fluorescent dimer formed in the peroxidase-catalyzed reaction of  $\text{H}_2\text{O}_2$  with p-hydroxyphenyl acetic acid (HPA) is detected by fluorometry [4,5]; and (2) infrared spectroscopic measurements of  $\text{H}_2\text{O}_2$  using tunable diode lasers [6].

Field intercomparisons [7,8] of these methods for determining  $\text{H}_2\text{O}_2$  are in poor agreement. An intercomparison study made in 1986 in Glendora, California, showed that concentrations measured with several variations of the fluorometric method were often a factor of two or more larger than the results of the infrared method [8]. Whether this disagreement was caused by the presence of organic peroxides, which may interfere with the fluorometric methods, or by other unidentified problems is not clear.

This disagreement between results from the fluorometric methods and the infrared method suggests that there are still problems with measuring  $\text{H}_2\text{O}_2$  accurately. The purpose of this work was to verify that the fluorometric method gives results for  $\text{H}_2\text{O}_2$  consistent with infrared methods under laboratory conditions. Here we report the results of a comparison of  $\text{H}_2\text{O}_2$  concentrations measured using the fluorometric method of Lazrus et al. [5] as modified by Ang and Groblicki [9] with  $\text{H}_2\text{O}_2$  concentrations measured in situ using Fourier transform infrared spectroscopy (FTIR).

## Experimental

The measurements were made on gaseous  $\text{H}_2\text{O}_2$ /air mixtures contained in a 104-L White cell. For each comparison, about 50  $\mu\text{L}$  of nominally 30% aqueous  $\text{H}_2\text{O}_2$  (J.T. Baker) was injected by syringe into the cell, and then the total pressure in the cell was increased to 760 torr by the addition of hydrocarbon-free air (Scott). This procedure resulted in about 1 - 2 ppm of  $\text{H}_2\text{O}_2$  and a few hundred ppm of  $\text{H}_2\text{O}$  in the cell. The cell contents were allowed to mix for 5 - 10 min before measurements were started. Infrared spectra were then measured periodically. When the infrared measurements showed that the  $\text{H}_2\text{O}_2$  had decayed to the concentration range desired for a comparison, a sample of the gas was drawn from the White cell through two impingers in series for analysis by the fluorometric method. An infrared spectrum was also measured during the collection of the fluorometric sample. Afterwards, spectra were again periodically measured until the detection limit for  $\text{H}_2\text{O}_2$  was neared.

The White cell is 2.6 m long, consisting of two 1.2 m pyrex glass tubes separated by a 0.2-m anodized-aluminum center section. The other interior surfaces of the cell are constructed of aluminum or brass. The mirrors are silver-coated pyrex with a protective overcoating of  $\text{MgF}_2$ .

Preliminary experiments showed that the half-life of gas-phase  $\text{H}_2\text{O}_2$  in the White cell was about 20 minutes. To decrease the reactivity of the surfaces, the two pyrex tubes of the White cell were lined with a cylindrical sleeve of teflon and all of the metal surfaces except the mirrors were coated with halocarbon wax (Halocarbon Products). This procedure increased the half-life of  $\text{H}_2\text{O}_2$  in the White cell to 25 - 30 min. Such a short half-life even after the surface modifications indicates that the gaseous  $\text{H}_2\text{O}_2$  was partially scavenged by the water present in the  $\text{H}_2\text{O}_2$ /air mixtures, as suggested by Junfeng et al. [10].

The infrared measurements were made with a Bomem DA 3.15 Fourier transform infrared spectrometer (FTIR) interfaced to the White cell. Spectra were measured at a resolution of  $1.0\text{ cm}^{-1}$  and a path length of 96 m. Concentrations of  $\text{H}_2\text{O}_2$  were determined from the infrared absorbance spectra by the subtraction of a calibrated reference spectrum of  $\text{H}_2\text{O}_2$ . The infrared detection limit was about  $0.05\text{ ppm H}_2\text{O}_2$  for 31 averaged scans. A band intensity of  $99.7\text{ km mol}^{-1}$  for the  $1266\text{ cm}^{-1}$  band of  $\text{H}_2\text{O}_2$  was used to calibrate the infrared reference spectrum. This value is the average of  $113 \pm 6\text{ km mol}^{-1}$  reported by Niki et al. [11] and  $86.3 \pm 0.2\text{ km mol}^{-1}$  reported by Valero et al. [12]. Since neither reported measurement of the band intensity has any obviously wrong experimental procedures, there was no justification for favoring one value over the other.

The water present in the aqueous  $\text{H}_2\text{O}_2$  samples injected into the White cell made it difficult to obtain background spectra of air in which the concentration of water matched the water concentration in the  $\text{H}_2\text{O}_2$ /air mixtures. Therefore, the background spectra were obtained by measuring a spectrum of the  $\text{H}_2\text{O}_2$ /air mixture after almost all of the  $\text{H}_2\text{O}_2$  had decomposed. For the comparisons in the  $0.1 - 0.3\text{ ppm H}_2\text{O}_2$  range, this background spectrum was measured after the concentration of  $\text{H}_2\text{O}_2$  was estimated to be less than  $0.01\text{ ppm}$ ; otherwise, a correction was made to account for the concentration of  $\text{H}_2\text{O}_2$  remaining at the time the background spectrum was measured.

Samples of the gas mixture to be analyzed by the fluorometric method were drawn from the White cell at a flow rate of  $0.6 - 1.5\text{ L min}^{-1}$  through a length of  $1/8\text{ in. o.d. Teflon tubing}$ , which extended about  $5\text{ cm}$  into the cell. About  $5\text{ L}$  of the gas mixture, as measured with a dry gas meter, was drawn through two standard  $25\text{ mL}$  impingers in series, each containing  $15\text{ mL}$  of deionized water. The contents of each impinger were then analyzed for  $\text{H}_2\text{O}_2$  by the fluorometric method of Lazrus et al. [5], as modified by Ang and Groblicki [9]. This method is based on the detection of a fluorescent dimer formed in the peroxidase-



catalyzed reaction between  $\text{H}_2\text{O}_2$  and p-hydroxyphenyl acetic acid (HPA). Fluorescence by the dimer is measured at 405 nm, using excitation light at 320 nm. The fluorescence signal from sample blanks, containing deionized water and HPA only, is also measured, and this fluorescence signal is subtracted from the total fluorescence signal. The concentration of  $\text{H}_2\text{O}_2$  in each impinger is then determined from fluorescence calibration curves, which are constructed by measuring the fluorescence from known dilutions of a standard  $\text{H}_2\text{O}_2$  solution. This standard solution had been assayed by  $\text{KMnO}_4$  titration. We summed the  $\text{H}_2\text{O}_2$  concentrations measured in each impinger to obtain the total  $\text{H}_2\text{O}_2$  concentration.

## Results

Examples of the temporal behavior of the  $\text{H}_2\text{O}_2$  in the White cell as measured by the FTIR method are shown in Figs. 1 and 2 for two measurements. Fig. 1 corresponds to the lowest concentration measured by the FTIR method, whereas Fig. 2 shows results of a more typical FTIR measurement.

For each comparison, the  $\text{H}_2\text{O}_2$  concentration determined by the FTIR method was obtained by fitting a least-squares line to the concentration vs. time data, such as that shown in Figs. 1 and 2. The concentration corresponding to the average collection time of the fluorometric sample was then computed from the least-squares line, and this concentration was used in the comparisons with the fluorometric method. Generally, the concentrations calculated in this manner agreed to within 3% with the concentration calculated directly from infrared spectra measured during the time interval over which the fluorometric sample was collected. For concentrations below about 0.35 ppm, however, the difference between calculated and measured concentrations occasionally varied randomly up to 9%. This variability probably arises because the subtractions of reference spectra are more difficult to do accurately at the lower concentrations. The

worst case is shown in Fig. 1, where the difference was 9%. Here, however, the calculated concentration of  $0.122 \pm 0.021$  ( $2\sigma$ ) ppm is only 2.5 times greater than the FTIR detection limit of 0.05 ppm. At these low concentrations, the least-squares fit provided a better measurement of the  $\text{H}_2\text{O}_2$  concentration, since the fit averaged out some of the uncertainties in the individual subtractions.

The  $\text{H}_2\text{O}_2$  concentrations determined by the FTIR method are compared to those determined by the fluorometric method in Table 1. The uncertainties listed for the FTIR measurements were calculated from the scatter about the least-squares lines. The results from duplicate analyses on three impinger samples are also included in Table 1. The ratio of the gas-phase concentration determined by the fluorometric method to that determined by the FTIR method for each comparison is also listed in Table 1. The mean of this ratio is  $0.9 \pm 0.5$  ( $2\sigma$ ), independent of the gas-phase  $\text{H}_2\text{O}_2$  concentration or sampling flow-rate used in the fluorometric method.

The concentration determined by the fluorometric method is plotted against the concentration determined by the FTIR method in Fig. 3. A least-squares fit to these data gave a line of slope  $0.89 \pm 0.08$  ( $2\sigma$ ) and an intercept of  $-0.02 \pm 0.05$  ( $2\sigma$ ) ppm. Since the intercept was zero within the calculated uncertainty, the data were refit with a least-squares line constrained to pass through the origin. This line had a slope of  $0.87 \pm 0.05$  ( $2\sigma$ ), and is included in Fig. 3.

## Discussion

The concentrations of  $\text{H}_2\text{O}_2$  measured by the fluorometric method were only 13% smaller than those measured by the FTIR method, as determined by the least-squares fit to all the comparisons; this is close to the expected 1:1 theoretical correspondence between the two methods.

Although we used an infrared band intensity of  $99.7 \text{ km mol}^{-1}$  for  $\text{H}_2\text{O}_2$  based on the average of the two literature values [11,12] for this band, perfect correspondence between the fluorometric method and the FTIR method could be obtained by using a band intensity of  $114 \text{ km mol}^{-1}$ . This is almost identical to one of the literature values: that of  $113 \pm 6 \text{ km mol}^{-1}$  reported by Niki et al. [11]. It is also close to the value of  $113 \text{ km mol}^{-1}$  calculated quantum mechanically by Rogers and Hillman [13], although the agreement is probably fortuitous since the accuracy of those calculations is probably no better than 50%.

There was considerable scatter about the least-squares line for the comparisons of  $\text{H}_2\text{O}_2$  concentrations below about 0.35 ppm, as seen in Fig. 3. Many of the comparisons for this region, such as  $0.122 \pm 0.021$  ppm measured by the FTIR vs. 0.205 ppm measured by the fluorometric method, do not agree to within the estimated uncertainties of the FTIR method. The cause of this scatter at the lower  $\text{H}_2\text{O}_2$  concentrations is not clear, but may be due to sampling losses or sample handling problems with the fluorometric method or due to the FTIR technique being used near its detection limit of 0.05 ppm. Some of the possible reasons for the scatter are considered below.

The reproducibility of the results from the fluorometric method was examined by repeating the analyses of the fluorometric samples for three of the comparisons. In one case, replicate analyses gave similar results of 0.218 and 0.206 ppm  $\text{H}_2\text{O}_2$ ; however, in the other two cases, the results were not as consistent; namely, 0.308 vs. 0.340 ppm and 0.208 vs. 0.277 ppm. This last case corresponds to a 33% difference between the two replicated analyses and indicates that sample handling or measurement repeatability may have been a problem in the fluorometric method.

Another potential problem with the fluorometric method is whether the absorption efficiency of the impingers for  $H_2O_2$  is actually 100%. Ang and Groblicki [9] measured a 98% absorption efficiency; however, a recent study by Hartkamp and Bachhausen [14] showed that, despite the high solubility of  $H_2O_2$  in water, impingers have poor absorption efficiencies for  $H_2O_2$ . We used two impingers in series so that any break-through of  $H_2O_2$  past the first impinger, which might be expected for higher concentrations of  $H_2O_2$  or faster gas flow rates, would be collected in the second impinger. Overall, the average concentration of  $H_2O_2$  in the backup impinger expressed as a percent of the total  $H_2O_2$  concentration in both impingers varied from 0% up to 16% with a mean of  $8 \pm 11$  (2 $\sigma$ )%. However, there was no apparent correlation of the concentration of  $H_2O_2$  in the backup impinger with the concentration in the first impinger or with flow rate. Furthermore, the percent of  $H_2O_2$  in the backup impinger even varied for the three replicated fluorometric measurements. In one case, replicate analyses of the backup impinger were in agreement; in the second case, the percent of  $H_2O_2$  in the backup impinger changed from 12% to 16%; and in the third case, the percent of  $H_2O_2$  in the backup impinger changed from 0% to 12%. This apparent variation in the amount of  $H_2O_2$  contained in the backup impinger suggests that sample handling or measurement repeatability was a problem.

One other possible cause for error in the fluorometric  $H_2O_2$  measurements may have been the purity of the water used in the impingers. We used deionized water, but other investigators have used distillation as well as deionization to purify the water used in their experiments. Water purity is important in the fluorometric method because any bacteria present may destroy  $H_2O_2$ . It is conceivable that the bacterial concentrations in the water we used could have varied. In this case, variable results would have been obtained with the fluorometric method.

A potentially serious problem with the FTIR method involves the spectrophotometric accuracy of intensity measurements made on gas mixtures at atmospheric pressure. At the  $1.0 \text{ cm}^{-1}$  resolution commonly used for FTIR measurements, the apparent band intensities are less than their true values because the molecular line widths are much smaller than  $1.0 \text{ cm}^{-1}$ , and the band intensities may even be nonlinear with concentration. This can lead to inaccuracies in the concentrations calculated from these intensities. However, linear and accurate plots of integrated intensity vs. concentration are obtained if the spectra are measured at  $0.1 \text{ cm}^{-1}$  resolution. Therefore, we computed reference spectra both at  $0.1 \text{ cm}^{-1}$  and  $1.0 \text{ cm}^{-1}$  resolution from each measured interferogram. The concentration of  $\text{H}_2\text{O}_2$  for each  $1.0 \text{ cm}^{-1}$  resolution spectrum was calculated using the absorption intensities measured in the corresponding  $0.1 \text{ cm}^{-1}$  resolution spectrum. This procedure avoided the problem of using absolute band intensities strictly valid only at high resolution to determine concentrations for  $\text{H}_2\text{O}_2$  directly from spectra measured at  $1.0 \text{ cm}^{-1}$  resolution. Indeed, we found the absorption intensity of the  $1266 \text{ cm}^{-1}$  band of  $\text{H}_2\text{O}_2$  measured at  $1.0 \text{ cm}^{-1}$  resolution to be only  $94 \pm 1 \%$  of the intensity measured at  $0.1 \text{ cm}^{-1}$  resolution. Our approach has general applicability to the quantitative measurements of other gases, some of which have infrared spectra even more sensitive to resolution.

One final point concerning the FTIR method involves the use of infrared absorption coefficients measured at  $1.0 \text{ cm}^{-1}$  resolution to calibrate reference spectra of  $\text{H}_2\text{O}_2$ . We found that most of the absorption coefficients reported in the literature are inconsistent with both the experimental [11,12] and the theoretical [13] band intensities of  $\text{H}_2\text{O}_2$ . The problem is illustrated in Table 2, in which absorption coefficients reported by several groups [15-18] for  $\text{H}_2\text{O}_2$  are compared with the results of our calibrations using band intensities of  $\text{H}_2\text{O}_2$ . Our absorption coefficient of  $2.44 \pm 0.02 \text{ cm}^{-1} \text{ atm}^{-1}$  at  $1265.38 \text{ cm}^{-1}$  is

38% smaller than the value reported by Tuazon et al. [16], and 48% smaller than the value reported by Su et al. [15]. Furthermore, our absorption coefficients of  $2.58 \pm 0.05 \text{ cm}^{-1} \text{ atm}^{-1}$  at  $1250.98 \text{ cm}^{-1}$  and  $0.725 \pm 0.016 \text{ cm}^{-1} \text{ atm}^{-1}$  measured from  $1251.76 \text{ cm}^{-1}$  to  $1252.60 \text{ cm}^{-1}$  are 33% and 60% smaller, respectively, than the values reported by Tuazon et al. in a later study [17]. However, better agreement is found between our absorption coefficient of  $3.60 \pm 0.02 \text{ cm}^{-1} \text{ atm}^{-1}$  at  $1250.83 \text{ cm}^{-1}$  and that of  $3.91 \text{ cm}^{-1} \text{ atm}^{-1}$  reported by Hanst et al. [18] at a higher resolution of  $0.25 \text{ cm}^{-1}$ . Part of the reason for the disagreement may be that the absorption coefficients at some frequencies (such as  $1250.98 \text{ cm}^{-1}$ ) are not linear with  $\text{H}_2\text{O}_2$  concentration.

The problems encountered in this laboratory comparison of the fluorometric method with the FTIR method do not necessarily explain why field measurements of  $\text{H}_2\text{O}_2$  using fluorometric methods and infrared methods sometimes disagree. In fact, the concentrations of  $\text{H}_2\text{O}_2$  measured here using the fluorometric method were generally quite close to those measured using the FTIR method. However, the replicated fluorometric measurements and the scatter in the comparisons below 0.35 ppm suggest that sample handling or measurement repeatability can be a problem in the fluorometric method. These are probably even more important at atmospheric  $\text{H}_2\text{O}_2$  concentrations, which are a factor of fifty or so lower than the lowest concentration of  $\text{H}_2\text{O}_2$  compared here. Other factors in addition to those discussed above could also be significant in the measurement of such very low concentrations of  $\text{H}_2\text{O}_2$ .

#### Acknowledgment

The assistance of C. A. Ang in performing the analyses of the impinger samples is gratefully acknowledged.

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Table 1. Hydrogen Peroxide Comparisons Using FTIR and the Fluorometric Method

Measured Concentration (ppm) <sup>a</sup>		Ratio
<u>FTIR</u>	<u>Fluorometric</u> <sup>b</sup>	<u>(Fluorometric/FTIR)</u>
1.35 ± 0.07	1.22	0.905
1.12 ± 0.05	0.963	0.858
0.91 ± 0.05	0.815	0.893
0.66 ± 0.05	0.600	0.912
0.177 ± 0.013	0.227	1.282
0.169 ± 0.027	0.148	0.876
0.122 ± 0.021	0.205	1.680
0.356 ± 0.022	0.325 <sup>c</sup>	0.913
0.302 ± 0.010	{ 0.218 <sup>c,d</sup>	0.722
	{ 0.206 <sup>c,d</sup>	0.682
0.280 ± 0.022	0.187 <sup>c</sup>	0.668
0.383 ± 0.021	{ 0.308 <sup>d,e</sup>	0.804
	{ 0.340 <sup>d,e</sup>	0.888
0.350 ± 0.024	{ 0.208 <sup>d,e</sup>	0.594
	{ 0.277 <sup>d,e</sup>	0.791
0.302 ± 0.007	0.204 <sup>e</sup>	0.675

<sup>a</sup>Uncertainties listed for the FTIR method are based on the scatter about the least squares lines; uncertainties for the fluorometric method are probably ± 10 %, based on the average of three duplicated analyses.

<sup>b</sup>Flow rate 1.0 L/min, unless otherwise noted.

<sup>c</sup>Flow rate 1.5 L/min

<sup>d</sup>Analysis of impinger samples replicated.

<sup>e</sup>Flow rate 0.6 L/min

Table 2. Infrared Absorption Coefficients for Hydrogen Peroxide

<u>Frequency (cm<sup>-1</sup>)<sup>a</sup></u>	<u>Abs. Coeff. (cm<sup>-1</sup> atm<sup>-1</sup>, base 10)</u>	<u>Resolution (cm<sup>-1</sup>)</u>
1265.38	4.71 [15]	1.0
	3.91 [16]	
	2.44 ± 0.02 This Work	
1250.98	3.82 [17]	1.0
	2.56 ± 0.05 <sup>b</sup> This Work	
1251.76 - 1252.60 <sup>c</sup>	1.82 [17]	1.0
	0.725 ± 0.016 This Work	
1250.83	3.91 [18]	0.25
	3.60 ± 0.02 This Work	

<sup>a</sup>Peak-to-baseline measurements, unless otherwise noted.

<sup>b</sup>Absorbances above 0.3 show curvature with concentration.

<sup>c</sup>Peak-to-valley measurement.

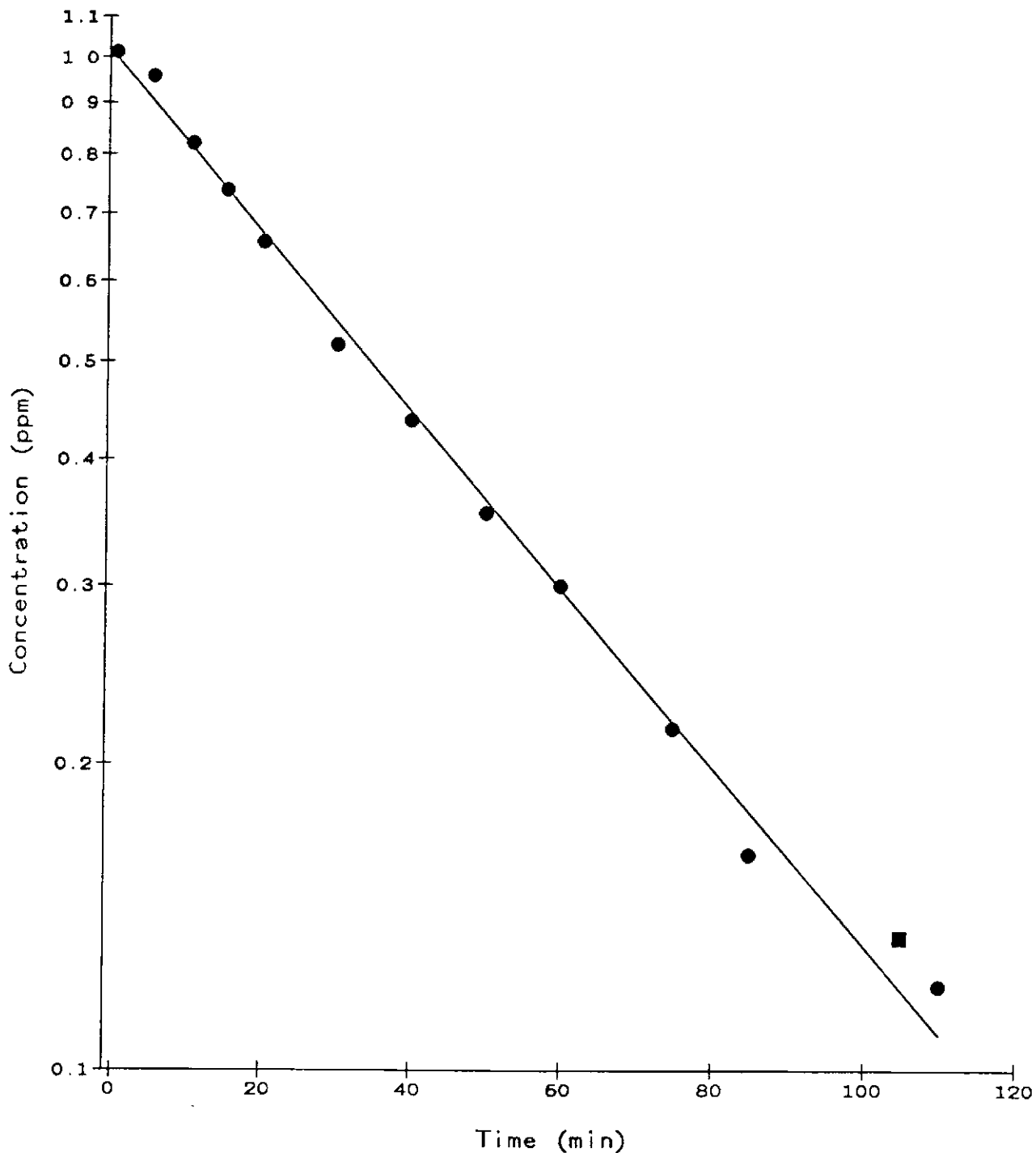


Figure 1. Concentration of  $\text{H}_2\text{O}_2$  determined by FTIR vs. time. The point denoted by a square near  $t = 105$  min. corresponds to the concentration determined by the FTIR method during the collection of the fluorometric sample. The concentration was calculated from the least-squares line to be  $0.122 \pm 0.021$  ( $2\sigma$ ) ppm at the time of the fluorometric measurement.

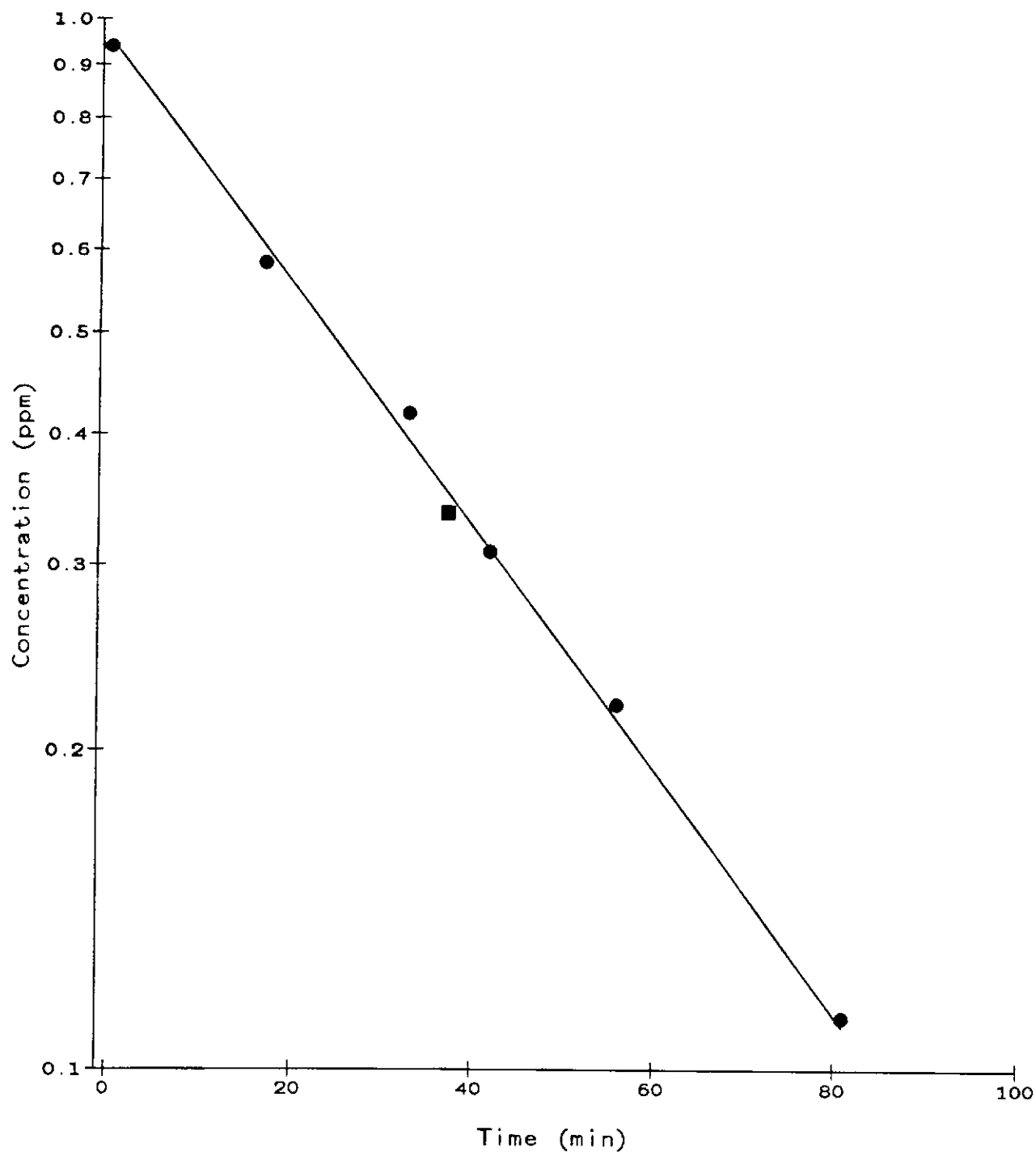


Figure 2. Concentration of  $\text{H}_2\text{O}_2$  determined by FTIR vs. time. The point denoted by a square near  $t = 35$  min. corresponds to the concentration determined by the FTIR method during the collection of the fluorometric sample. The concentration was calculated from the least-squares line to be  $0.350 \pm 0.024$  ( $2\sigma$ ) ppm at the time of the fluorometric measurement.

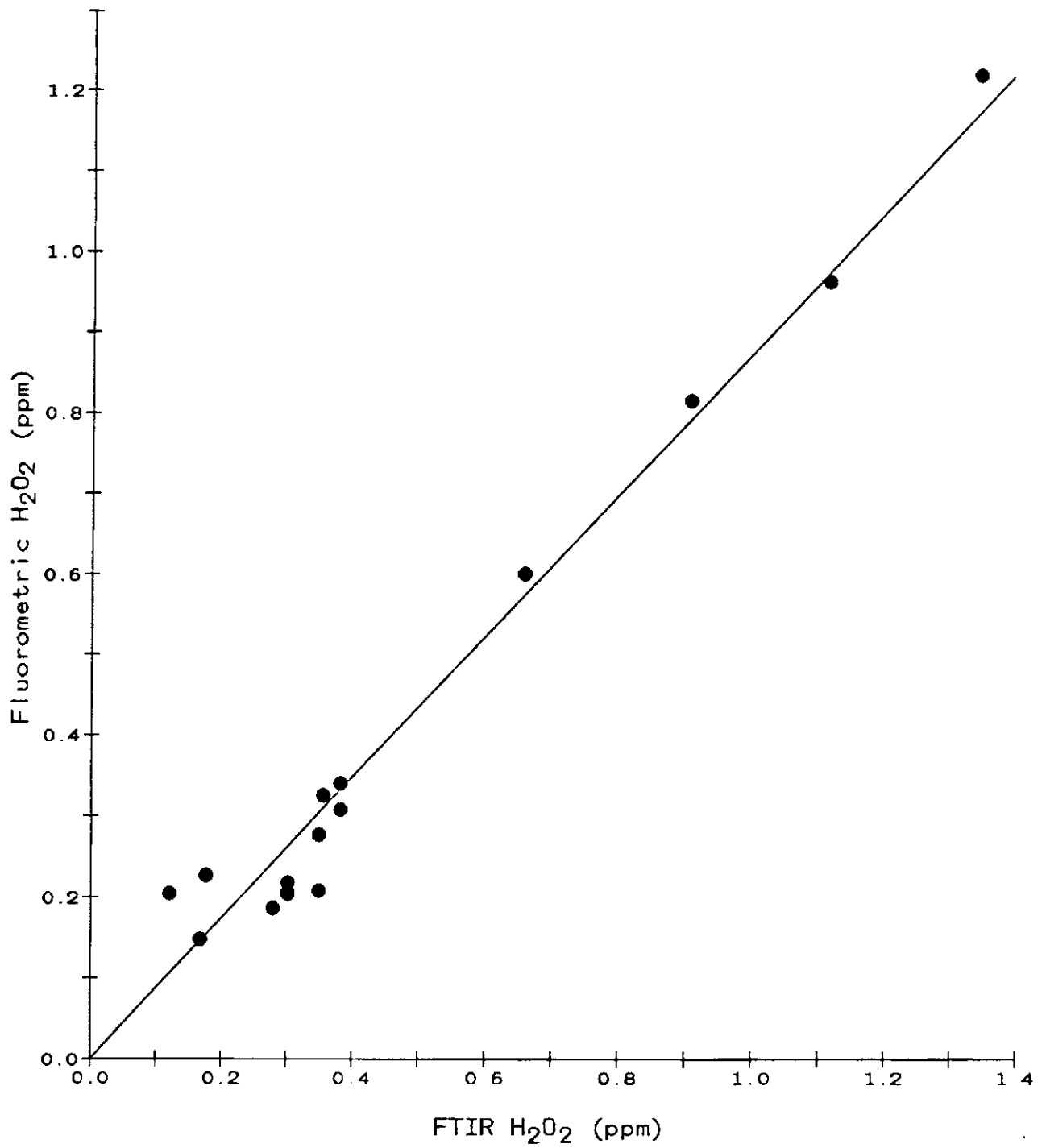


Figure 3. Comparison of concentrations of H<sub>2</sub>O<sub>2</sub> determined by the fluorometric method vs. concentrations of H<sub>2</sub>O<sub>2</sub> determined by FTIR. The line is the least-squares fit to the comparisons.



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