Proc. NIPR Symp. Polar Meteorol. Glaciol., 5, 113–119, 1992

DETERMINATION OF HYDROGEN PEROXIDE IN SNOW: PRELIMINARY RESULTS FOR SNOW SAMPLES IN THE INLAND REGION, ANTARCTICA

Kokichi KAMIYAMA[1] and Eiichiro NAKAYAMA[2]

[1]*Beppu Geophysical Research Laboratory, Faculty of Science,*
Kyoto University, Noguchibaru, Beppu 874
[2]*Research Center for Instrumental Analysis, Faculty of Science,*
Kyoto University, Kitashirakawa Oiwakecho, Sakyo-ku,
Kyoto 606–01

Abstract: Hydrogen peroxide (H_2O_2) in snow possibly marks annual layers of snow deposition as well as the atmospheric environments where it is created. Methods for the determination of H_2O_2 in snow and their suitability for field observation are discussed.

The vertical plate of a surface snow block obtained on the inland high plateau, Antarctica, (point γ-8) was analyzed to precisely determine H_2O_2 distribution. Relatively high concentrations of H_2O_2 were detected, suggesting seasonal fluctuation.

Laminated snow layers of glaciers record past depositional environments. Sufficiently fine sampling intervals of snow, both horizontally (geographically) and vertically, are important to make clear the depositional environments over the glaciers. The *in situ* measurements of some of the chemical constituents in snow will help us to determine the appropriate sampling intervals, as well as to avoid the possibility of contamination. The other analytical results, obtained later in the laboratory experiments, are increased in value by the fine sampling intervals.

1. Introduction

Hydrogen peroxide (H_2O_2) is one of the most important species in atmospheric chemistry. It is considered to be an important oxidizing agent in atmospheric liquid water, converting dissolved SO_2 into sulfuric acid, and contributing to the acidification of cloud water and precipitation (MÖLLER, 1980; RADOJEVIC, 1983). In natural environments, H_2O_2 is not so stable, but has been detected in air masses, rain water and surfaces of lakes and sea (KLOCKOW and JACOB, 1986). In the atmosphere, H_2O_2 is produced by photochemical processes and absorbed into water droplets. In the surfaces of lakes and the sea, it is photochemically generated from organic constituents present in the water (COOPER and ZIKA, 1983).

H_2O_2 is present in relatively large amounts in polar snow and ice samples (NEFTEL *et al.*, 1984), and strong seasonality is observed in the core at Siple Station, Antarctica (SIGG and NEFTEL, 1988). H_2O_2 is possibly preserved in snow and gives us information on the atmospheric conditions when the snow formed, as well as on the annual deposition of snow.

The determination of H_2O_2 needs relatively little time and small sample volume (SIGG and NEFTEL, 1988), which offers us the opportunity to obtain the results with high resolution.

Here we examine the methods for the determination of H_2O_2 in snow, as adapted for the samples in Antarctica, and discuss the suitability of the procedure for field observations.

2. Experimental

For the determination of H_2O_2 in natural water, two methods have been proposed: chemiluminescent and fluorometric methods. In the chemiluminescent method, the occurrence of metal ions, especially Fe, produces positive interference. On the other hand in the fluorometric method, PAN (peroxyacethy nitrate) also produces positive interference. In both cases, the interference can be confirmed by destroying H_2O_2 with catalase and H_2O_2 values are estimated undirectedly (LAZRUS *et al.*, 1985). In the sampling procedure, it will be difficult to avoid the possibility of contamination by metal ions. We determined here to use the fluorometric method after some trials.

2.1. *Apparatus*

The measuring system, with peristaltic pumps, mixing/delay coils and the fluorescence spectrometer, was constructed by Kimoto Electric Co. Ltd., as shown in Fig. 1. The system size is W33 × H29 × D50 cm and the weight is 20 kg with AC 100 V, *ca.* 420 VA in maximum. The system needs a voltmetric signal recorder, four storage bottles for three reagents and blank water.

2.2. *Analytical procedure*

The analytical method was modified from that reported by LAZRUS *et al.* (1985).

(1) Standard solution

Standard solutions could be obtained by the dilution of a 30% of H_2O_2 solution obtained in a commercial base for atomic absorption spectrometry, which was used

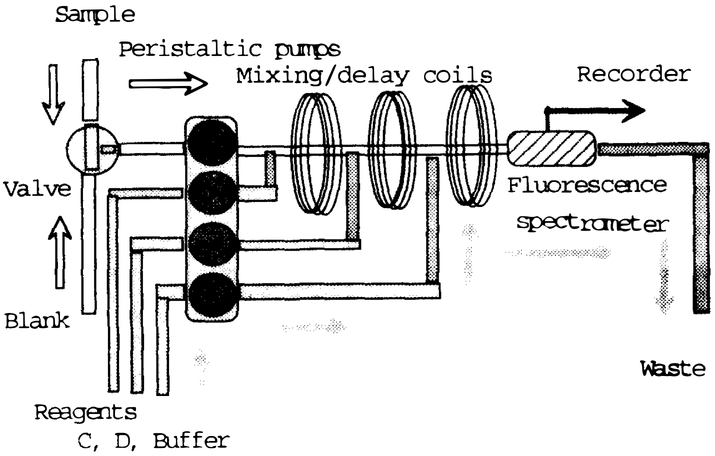

Fig. 1. Measuring system of hydrogen peroxide in snow samples.

as the stock solution, more stable than the diluted standards. The stock solution has to be calibrated by titration with $KMnO_4$.

(2) Reagents

Peroxidase from horseradish (HRP) was used as the enzyme to build the dimers of *p*-hydroxyphenylacetic acid (POPHA). Potassium hydroxide was used as the buffer solution. The buffer solution at higher pH brought higher H_2O_2 signals, but needed more reacting time. We used here the buffer solution at high pH, requiring high and stable signals, in spite of the need for increased length of delay coils. The reagents are listed in Table 1.

(3) Analysis

The reagents for used and blank water were set up in the system lines as shown in Fig. 1. The excitation and the emission wavelengths of the fluorescence spectrometer were set at 320 and 400 nm, respectively. The sampling tube was moved from sample to sample while the peristaltic pumps were running. The sampling time was about 2 min, requiring about 4 m*l* of each sample. While the tube was moved, an air segment was inserted automatically between two sample segments, which divided each sample and signal to the recorder. The connection could be switched from the sampling line to a blank line with the valve. About ten samples were measured in one series between two blanks. After some series of the measurements, the system was calibrated with the standard solutions. Measuring 100 samples took about 5 hours. The calibration was carried out by $10^{-8} \sim 10^{-4}$ mol/*l* (0.4–4000 ppb) of H_2O_2; good linearity was obtained with the detection limit about 0.2×10^{-8} mol/*l*. Standardization at one point, corresponding to sample concentration, 10^{-6} or 10^{-5} mol/*l*, was sufficient for practical use. The decay of the output signals relative to the initial values for the standard solutions are listed in Table 2. It was difficult to preserve the standard solution in low concentration. A better way is to store the standard at low temperature. The contamination by metal ions, especially Fe, did not cause interference but had the advantage of destroying H_2O_2 in the solutions. H_2O_2 in 10^{-6} mol/*l*, with 10^{-8} mol/*l* of Fe, decreased in concentration by a factor of 0.98 after 2 hours. The

Table 1. Reagents used in the measuring system.

Stock solutions	Procedure
A (0.8 M POPHA)	3.043 g fill up to 25 m*l* with ethanol
B (HRP 2 mg/m*l*)	0.100 g fill up to 50 m*l* with distilled water

Reagents for practical use	Procedure
Reagent-C	4 m*l* of A fill up to 400 m*l* with distilled water
Reagent-D	8 m*l* of B fill up to 400 m*l* with distilled water
Buffer solution	2N-KOH

Table 2. Decay of output signals relative to initial values for standard solutions of H_2O_2.

Concentration	Initial	After 4 hours	After 24 hours	Remarks
10^{-8} mol/*l*	1.00	ND	ND	Room temperature
10^{-6} mol/*l*	1.00	0.98	0.77	Room temperature
10^{-6} mol/*l*	1.00	1.00	0.99	Stored at 5°C

decreasing rate became faster and stronger in higher contamination of Fe. For the samples where a higher level of metal ions is expected, it is advisable that analytical procedures be carried out as fast as possible.

3. Results and Discussion

We discuss here the practical usage of the H_2O_2 measuring system, taking the actual level of H_2O_2 in snow into consideration.

Table 3. Concentration of H_2O_2 in precipitation (rain and ice core samples) in natural environments, reported previously.

Sampling site (Rain or ice core)	Sampling periods	Concentration (ppb) (Analytical method)	References
Claremont, California (Rain)	Summer in 1979	200–1600 (A)	KOK (1980)
Claremont, California (Rain)	Winter in 1979	40–100 (A)	KOK (1980)
Miami, Florida (Rain)	Feb-May	300–2000 (B)	ZIKA *et al.* (1982)
Dortmund, F.R.G. (Rain)	Daytime	2–2200 (A)	KLOCKOW and JACOB (1986)
Dortmund, F.R.G. (Rain)	Night	0–440 (A)	KLOCKOW and JACOB (1986)
Dortmund, F.R.G. (Rain)	Winter	0–290 (A)	KLOCKOW and JACOB (1986)
Dortmund, F.R.G. (Rain)	Summer	25–2200 (A)	KLOCKOW and JACOB (1986)
Tokyo, Japan (Rain)	Summer	10–1000 (A)	YOSHIZUMI *et al.* (1984)
Tokyo, Japan (Rain)	Winter	10–100 (A)	YOSHIZUMI *et al.* (1984)
Dye 3 (Ice core)	30–25000 years BP	100–≤0.5 (A)	NEFTEL *et al.* (1984)
Dye 3 (Ice core)	0–75000 years BP	400–0.3 (A)	NEFTEL *et al.* (1986)
Dye 3 (Ice core)	1976–1986	10–300 (B)	SIGG and NEFTEL (1988)
Camp Century (Ice core)	0–40000 years BP	0.3–150 (A)	NEFTEL *et al.* (1986)
Central Greenland (Ice core)	1783–1942	10–122 (A)	LAJ *et al.* (1990)
North Central (Ice core)	650 years BP	149 (A)	NEFTEL *et al.* (1984)
Byrd (Ice core)	1300, 22000 years BP	8, 2.8 (A)	NEFTEL *et al.* (1984)
Byrd (Ice core)	0–52000 years BP	40–0.3 (A)	NEFTEL *et al.* (1986)
South Pole (Ice core)	650, 1600, 20000 years BP	17, 12, 17 (A)	NEFTEL *et al.* (1984)
Siple Station (Ice core)	1980–1900	10–120 (B)	SIGG and NEFTEL (1988)

A: chemiluminescent method, B: fluorometric method.

3.1. H_2O_2 level in snow on the inland high plateau, Antarctica

The concentration of H_2O_2 in the precipitation in natural environments varies widely. The reported values in rains and ice cores are compiled in Table 3. H_2O_2 in air is produced by the UV in sunlight. Significantly higher concentrations are believed to occur as a result of the oxidation of reactive hydrocarbons in an urban or polluted atmosphere (BUFALINI *et al.*, 1972). H_2O_2 is caught in rain water and reaches the ground surface. Therefore, H_2O_2 in rain water varies widely, depending on atmospheric conditions, as shown in Table 3. H_2O_2 content in rain is higher in summer than in winter. The highest levels occur in urban environments in summer. H_2O_2 content in ice cores is higher in the Arctic region than in Antarctica.

The surface snow blocks (*ca.* 50×28×34 cm) had been obtained by JARE-26 at point γ-8 in the central region of the inland plateau, East Queen Maud Land, Antarctica, and have been preserved frozen at −20°C. The point γ-8 is *ca.* 700 km distant from the sea and *ca.* 3650 m a. s. l. (76°00′S, 31°23′E). For the samples taken continuously from one of the vertical planes of the block, we repeated the analytical procedures. After melting at room temperature, the samples were introduced to the measuring system. The almost constant signals were detected during 30 min after melting. The vertical profile of H_2O_2 at γ-8 is shown in Fig. 2. In spite of the short length of the vertical snow plate, the results suggested to us the possibility of seasonal cyclic distribution of H_2O_2. Among some reports in Antarctica listed in Table 3, though few results were available, relatively high level of H_2O_2 was observed at γ-8. It is possibly considered that H_2O_2 levels in an ice core do not keep their original values at the time of deposition. The maximum values and range of seasonal fluctuations, obtained by SIGG and NEFTEL (1988), seem to decrease with depth. The concentrations at deeper points of the cores seem to be depressed more than those at shallower points. In spite of doubt regarding the occurrence of diffusion and reaction processes, H_2O_2 in the core samples presents useful information on past atmospheric conditions. It has been reported that SO_2 is oxidized into SO_4 by H_2O_2; strong inverse

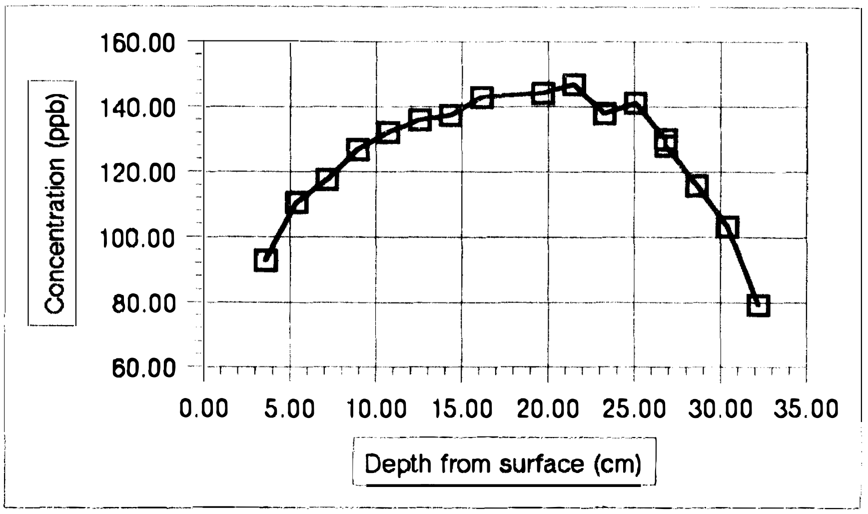

Fig. 2. Vertical profile of H_2O_2 at γ-8 in the inland high plateau, East Queen Maud Land. Antarctica.

correlation between SO_4 and H_2O_2 was observed in cloud waters (DAUM *et al.*, 1984). The inverse correlations were also observed in ice core vertical profiles, and sulphur conversion rates and chemical life times in the atmosphere were proposed for some volcanic events (LAJ *et al.*, 1990).

Further investigations are needed on H_2O_2 in deposition processes from the atmosphere and physical and/or chemical processes in snow and ice, taking atmospheric and glaciological conditions into consideration.

3.2. *Application of the system for the, in situ, measurement*

This system does not need much space nor a complicated analytical procedure, which makes it suitable for field operations. The fluctuations of the sample temperature between 5–25°C does not influence the analytical results. In cold conditions, as in Antarctica, it is better to keep the mixing/delay coils and bottles of reagents and water blank in a warm bath, which keeps the flow analytical system into unfrozen and stable conditions.

The data obtained *in situ* will give us the opportunity of reconfirming the results immediately and reconsidering the sampling procedures, both horizontally (geographically) and vertically. After the laboratory experiments on snow samples, taking their depositional environments into consideration in advance, we will obtain more precise chemical information on the snow and, furthermore, on the atmospheric environments in their depositional periods. The direct measurement of NO_3 in snow was carried out *in situ* by ZELLER *et al.* (1986), by ultraviolet spectrophotometry. The NO_3 detection system can be easily installed into the H_2O_2 detection system. These systems will give us results rapidly and provide high resolution information on the snow layers. Furthermore, after the measurement of acidity and NO_3 in the field, the samples can be kept at low pH with the addition of HNO_3 in the liquid phase. Such treatments offer us suitable conditions for measuring other components later, especially metal ions.

4. Conclusions

The methods for determination of H_2O_2 were discussed for the purpose of direct measurement in the field. The results will give us, immediately in the field, the opportunity for determining the sampling intervals both geographically (horizontally) and vertically. The samples, obtained at adequate intervals, give us a great advantage in judging the depositional environments from laboratory experiments later.

We determined H_2O_2 levels of the snow on the inland high plateau, Antarctica. Relatively high concentrations of H_2O_2 were observed compared to the values reported previously, and the seasonal variation was suggested in spite of insufficient length of the vertical snow layer. Further measurements of H_2O_2 in snow layers have been carried out, taking glaciological information into consideration. Such an investigation will help us to determine the annual layers of snow deposition and transformation processes of H_2O_2 in snow layers, as well as atmospheric conditions.

References

Bufalini, J. J., Gay, B. W. and Brubaker, K. L. (1972): Hydrogen peroxide formation from formaldehyde photoxidation and its presence in urban atmospheres. Environ. Sci. Tech., **6**, 816–821.

Cooper, W. J. and Zika, R. G. (1983): Photochemical formation of hydrogen peroxide in surface and ground waters exposed to sunlight. Science, **220**, 711–712.

Daum, P. H., Kelly, T. J., Schwartz, S. E. and Newman, L. (1984): Measurements of the chemical composition of stratiform clouds. Atmos. Environ., **18**, 2671–2684.

Klockow, D. and Jacob, P. (1986): The peroxyoxalate chemiluminescence and its application to the determination of hydrogen peroxide in precipitation. Chemistry of Multiphase Atmospheric Systems, ed. by W. Jaeschke. Berlin, Springer, 117–128.

Kok, G. L. (1980): Measurements of hydrogen peroxide in rainwater. Atmos. Environ., **14**, 653–656.

Laj, P., Drummey, S. M., Spencer, M. J., Palais, J. M. and Sigurdsson, H. (1990): Depletion of H_2O_2 in a Greenland ice core: Implications for oxidation of volcanic SO_2. Nature, **346**, 45–48.

Lazrus, A. L., Kok, G. L., Gitlin, S. N. and Lind, J. A. (1985): Automated fluorometric method for hydrogen peroxide in atmospheric precipitation. Anal. Chem., **57**, 917–922.

Möller, D. (1980): Kinetic model of atmospheric SO_2 oxidation based on published data. Atmos. Environ., **14**, 1067–1076.

Neftel, A., Jacob, P. and Klockow, D. (1984): Measurements of hydrogen peroxide in polar ice samples. Nature, **311**, 43–45.

Neftel, A., Jacob, P. and Klockow, D. (1986): Long-term record of H_2O_2 in polar ice cores. Tellus, **38B**, 262–270.

Radojevic, M. (1983): H_2O_2 in the atmosphere and its role in the aqueous oxidation of SO_2. Environ. Technol. Lett., **4**, 499–508.

Sigg, A. and Neftel, A. (1988): Seasonal variations in hydrogen peroxide in polar ice cores. Ann. Glaciol., **10**, 157–162.

Yoshizumi, K., Aoki, K., Nouchi, I., Okita, T., Kobayashi, T., Kamakura, S. and Tajima, M. (1984): Measurements of the concentration in rainwater and of Henry's law constant of hydrogen peroxide. Atmos. Environ., **18**, 395–401.

Zeller, E. J., Dreschhoff, G. A. M. and Laird, C. M. (1986): Nitrate flux on the Ross ice shelf, Antarctica and its relations to solar cosmic rays. Geophys. Res. Lett., **13**, 1264–1267.

Zika, R., Saltzman, E., Chameides, W. L. and Davis, D. D. (1982): H_2O_2 levels in rainwater collected in South Florida and the Bahama Island. J. Geophys. Res., **87**, 5015–5017.

(Received January 14, 1991; Revised manuscript received April 12, 1991)