

Methodology for the determination of gaseous hydrogen peroxide in ambient air*

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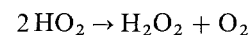
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Methodik zur Bestimmung von gasförmigem Wasserstoffperoxid in Umgebungsluft

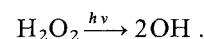
Zusammenfassung. Ein Verfahren zur Bestimmung von gasförmigem Wasserstoffperoxid in Umgebungsluft wird beschrieben. Die vorgeschlagene Verwendung eines Kryosammlers (-45°C) stellt insofern eine Verbesserung gegenüber der bisher üblichen Waschflaschen-Probenahme dar, als damit die bei Absorption in flüssiger Phase beobachteten Artefakte – Bildung und auch Zersetzung von Wasserstoffperoxid – deutlich vermindert werden. Feldmessungen, die zwischen Oktober 1984 und Juli 1985 auf dem Gelände der Universität Dortmund durchgeführt wurden, ergaben mittlere H_2O_2 -Gasphasenkonzentrationen um 30 pptv. Darüber hinaus werden die Ergebnisse erster Versuche mit beschichteten Diffusionsabscheidern als Sammler für gasförmiges Wasserstoffperoxid vorgestellt.

Summary. A method for the determination of gaseous hydrogen peroxide in ambient air is described. The cryogenic sampling technique (-45°C) employed represents an improvement compared with the impinger technique by diminishing artifacts which are bound to liquid phase production and decomposition, respectively. Results are given of H_2O_2 measurements from October 1984 to July 1985 in Dortmund (FRG), with mean concentrations of about 30 ppt (v/v). Preliminary results obtained with a coated denuder as a sampling device are also presented.

For several years increasing interest is focussed on atmospheric hydrogen peroxide, not only because of its oxidizing potential in the liquid phase [1–4], but also because of its impact on atmospheric radical chemistry. Here it may act as a sink for HO_2 [5]



and as a source of OH radicals [6]



These radicals on their part are the most important oxidizing species for the transformation of atmospheric pollutants [7].

* Dedicated to Prof. Dr. H. Monien on the occasion of his 60th birthday

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There is an urgent need to have a reliable method for H_2O_2 measurements in ambient air, not only to verify model calculations [8–11], but also to investigate the distribution of H_2O_2 between gas and liquid phase [9] under real atmospheric conditions.

The most widely employed collection method for gaseous H_2O_2 was the trapping in impingers [12–21] until Zika and Saltzman [22] and Heikes et al. [23, 24] showed the problems inherent in such a sampling approach. On the one hand, artificial H_2O_2 is produced by O_3 and other non-identified precursors at the glass surface during the sampling process, and on the other hand losses can be observed caused by the reaction of hydrogen peroxide with reducing air components, particularly SO_2 . Another sampling method is based on the condensation of water vapor onto a cooled surface [25–27], but with the same disadvantage of having a liquid medium and therefore favorable conditions for dissolution of other possibly interfering and reacting gases, such as SO_2 [23]. In the present study we chose the collection by water vapor condensation at about -45°C , thus avoiding a liquid phase being formed during sampling.

Several authors have determined hydrogen peroxide in aqueous solution photometrically [14, 18, 19, 25], by a chemiluminescence procedure using luminol as a reagent [12, 13, 15, 16, 20, 21, 27, 28], or by employing a fluorimetric enzyme technique [16, 21, 29, 32]. In this work we have made use of the chemiluminescent reaction between hydrogen peroxide and bis-(2,4,6-trichlorophenyl)oxalate (TCPO) in a borate buffer medium of pH 8. Method and instruments are described elsewhere [30].

Experimental

In the water vapor condensation approach for collection of gaseous substances, sampling device and experimental conditions are the result of a compromise between freezing temperature of gases to be sampled, volume of sample required, time resolution necessary, and load capacity of the cooling surface. (Too thick frozen layers lead to liquid film formation at the ice/air boundary layer.) The volume sampled depends on the sampling efficiency given by that fraction of airborne water vapor which is condensed to ice, assuming equal percentages of the present $(\text{H}_2\text{O}_2)_g$ to condensate. Cooling area, cooling surface temperature, and air flow rate are influencing efficiency, whereas the absolute water vapor content of ambient air determines the time necessary for sampling an amount of ice sufficient for analysis.

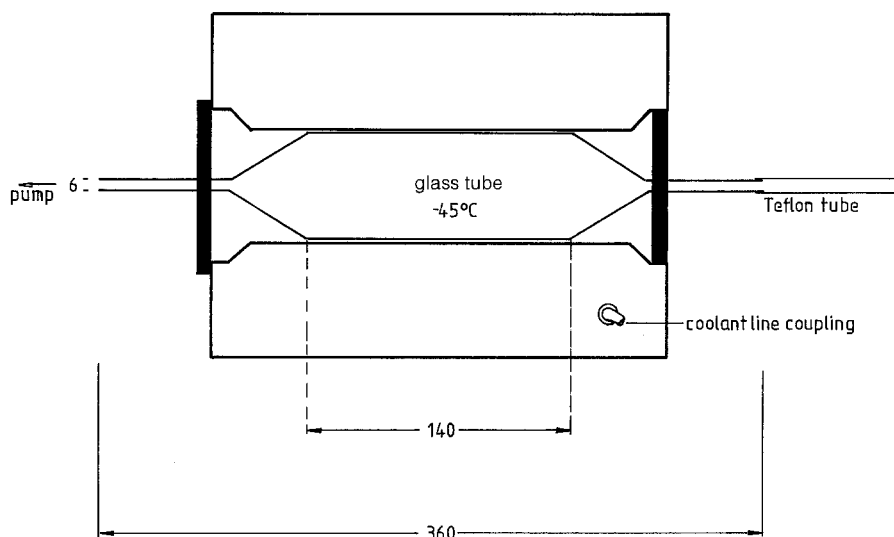


Fig. 1
Cryogenic sampling system, dimensions in mm (Refrigerator: Products for Research, Inc.; Type: TE-149 TS-RF)

The cooled trap used consists of an electrically operated cooling house normally applied for photomultiplier cooling and a glass tube of compatible dimensions (Fig. 1). The lowest surface temperature possible of the sampling tube, -45°C (reached within 20–30 min after switching on the cooling aggregate), was used to avoid the formation of liquid droplets or even a liquid film at the cooled surface. The sampling flow rates were between 0.7 and $1.3 \text{ m}^3 \cdot \text{h}^{-1}$. Too slow fluxes, e.g. 100 l/h, led to clogging of the inlet of the glass tube by frozen water. The smaller the temperature difference is between incoming and outgoing air, the lower is the collection efficiency. In our sampling conditions, temperature differences of about 20°C were obtained for air at 0 – 27°C passing through the cooled trap, such yielding sampling efficiencies of 40–30%.

Higher ambient temperatures may lead to a decrease in temperature differences between incoming and outgoing air, with additional danger of liquid film formation at the ice/air boundary layer. However, this effect can be overcome by employing lower air flow rates. The necessary sampling time depends on the water vapor content of the air under study.

At a relative humidity range of 30–100%, a sample volume sufficient for analysis (ca. 2 ml) can be obtained within 1 h, which enables a reasonable resolution in time. Maximum sampling time is limited by the load capacity of the cooling surface.

Although a liquid nitrogen trap would work with higher efficiency, its use would be unsuitable in the particular case of H_2O_2 sampling. This is because ozone would also be condensed and this represents a potential source of artificial hydrogen peroxide.

Air samples have been taken in 1.5 m altitude above ground during the period of August 1984 to July 1985 at a site on the campus of the University of Dortmund. After sampling, the glass tubes, internally coated with ice and condensed atmospheric trace components, were closed at both ends with little polypropylene tubes (type Eppendorf) and stored in a freezer (-20°C) until being taken for analysis. Alternatively, the content of a sampling tube was directly melted under warm tap water and transferred to a polypropylene vessel for immediate analysis, thus allowing only little time for decomposition of H_2O_2 by possibly present reducing agents. 1 ml of a sample solution was buffered

with 200 μl of 0.5 M borate buffer (pH 8) and injected into the flow analyser. Results were obtained by standard addition technique [30].

In order to verify that the H_2O_2 concentration found in the condensed water phase can be directly related to the water vapor content of ambient air, a second cooling trap with dry ice/acetone has been used in series with the first one in a number of experiments. The H_2O_2 concentrations in the solutions obtained from the two traps differed by less than 10% most of the time, indicating that no serious fractionation of $(\text{H}_2\text{O}_2)_g$ and water vapor takes place during sampling. Therefore, the concentration of gaseous H_2O_2 in ambient air, $[\text{H}_2\text{O}_2]_g$, expressed in $\text{ng} \cdot \text{m}^{-3}$, can be calculated in the following way:

$$[\text{H}_2\text{O}_2]_g = [\text{H}_2\text{O}_2]_l \times [\text{H}_2\text{O}]_g$$

Here $[\text{H}_2\text{O}_2]_l$ is the concentration of H_2O_2 in the liquid water from the trap in ppbw, and $[\text{H}_2\text{O}]_g$ is the water vapor content in $\text{g} \cdot \text{m}^{-3}$ of the air under investigation at given temperature and relative humidity.

The limit of detection of the chemiluminescence technique is 0.4 ppbw of H_2O_2 in aqueous solution. For the determination of H_2O_2 in the gas phase, combining cryo sampling with chemiluminescence analysis, meteorological parameters such as temperature and relative humidity have to be taken into account for the estimation of the overall detection limit. This can be taken from the examples in Table 1.

As can be seen, the limits of detection are higher during summer. But generally the H_2O_2 concentrations in air are also higher in summer, so that reliable determinations can be carried out during all the year (see Table 2).

For comparison three sampling trains were operated in parallel, one containing the cryogenic collector, and two equipped with an impinger. Both impingers were fitted with a glass frit as air inlet, filled with 10 ml of water, stored in an ice bath at 0°C and protected against light. The results obtained are shown in Table 3.

The rather low pH-values and high conductivities of the absorber solutions suggest that the impingers are much more unselective and are collecting a significantly higher mass fraction of airborne matter, gases and particles, than the cryogenic trap. Most probably the higher levels of H_2O_2

Table 1. Limits of detection, $(LD)_g$, for the determination of $(H_2O_2)_g$ in ambient air employing cryogenic sampling as a function of relative humidity and temperature

Parameter	Water vapor content (g/m^3)	$(LD)_g$ (pptv)
r.h.: 95% T: 25°C	21.5	6
r.h.: 80% T: 0°C	3.8	1
r.h.: 50% T: -15°C	0.8	0.2

Table 2. Mean and maximum $(H_2O_2)_g$ concentrations in air at Dortmund in different seasons

Month	Number <i>n</i> of days with measurements	Daily concentrations (pptv)	
		mean	maximum
8.84	5	39	220
10.84	7	35	110
11.84	20	15	55
12.84	12	5	10
6.85	7	52	220
7.85	6	60	215

found with impinger sampling are due to uncontrolled artificial H_2O_2 production.

Results of field measurements

Results of measurements in the period between October 1984 and July 1985 are shown in Figs. 2–5. From these some conclusions can be derived:

– The $(H_2O_2)_g$ concentrations are very low compared to those found by other authors [12, 15, 16, 19, 27, 28]. Exceptional agreement is achieved with results reported already in 1878 by Schöne (150–300 pptv) [25].

– On days with a clear sky the concentrations exhibit a distinct diurnal variation with maxima in the afternoon.

The daytime mean concentration between October and December 1984 is 27 pptv compared with 14 pptv at night. In June and July the relation is 55 pptv to 16 pptv. The fast decrease of the $(H_2O_2)_g$ concentrations during evening and night is not easy to interpret, considering that the estimated lifetime of H_2O_2 is about 1 day (Chameides and Davis [33]) and that only photolysis and rain-out or wash-out should be effective sinks. It might be possible that deposition with dew is responsible for the observed phenomenon.

– Rain events lead to wet removal of gas phase H_2O_2 . Observations have shown, however, that a decrease in concentration starts already with increasing cloudiness. This may be due to advection of humid air masses which have lost a substantial fraction of gaseous H_2O_2 by uptake through liquid droplets.

In order to describe the behaviour of H_2O_2 in ambient air, its distribution between gas and liquid phase under atmospheric conditions has to be investigated. For this reason H_2O_2 concentrations in rain and in the gas phase were measured simultaneously during a complete 52 min event on September 13, 1985 (Fig. 6). From the concentrations found in rain and with a Henry's law constant for pure water of 1.7×10^5 moles l^{-1} atm $^{-1}$ (15°C) [3] gas phase concentrations of H_2O_2 were calculated and then compared with measured ones (Table 4).

From Fig. 6 and Table 4 it can be seen that, in the beginning of the rain event, high concentrations of H_2O_2 are present in the liquid phase. Close to the ground, the H_2O_2 mixing ratio found in the gas phase is much lower than correspondent to the gas-liquid equilibrium. Therefore no significant change in the H_2O_2 gas phase concentration due to wash-out was noticed in the first period of the event. As the event proceeds, the rain becomes poorer in H_2O_2 , so that slowly a transition state is achieved, where calculated and measured $(H_2O_2)_g$ concentrations are in agreement. Towards the end of the event, rain becomes subsaturated with respect to H_2O_2 and starts to scavenge H_2O_2 from the gas phase where measured $(H_2O_2)_g$ concentrations are higher than the calculated ones.

Different processes can account for the observed changes in H_2O_2 concentrations in collected rain water during the event: below-cloud scavenging of gaseous H_2O_2 (different in different altitudes), partial evaporation of rain drops in the initial period of the event, production or consumption of H_2O_2 [23], and decrease of H_2O_2 gas phase concentration in clouds during the event.

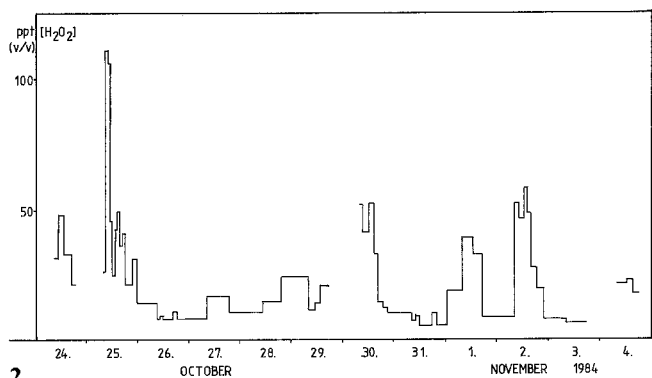
Table 3. Results of comparative measurements of $(H_2O_2)_g$ obtained by employing two different sampling procedures, a cryogenic trap and two impingers in parallel, respectively

Sampling technique	Sampling periods							
	December 18, 1984, from 11.00–18.00 h				December 19, 1984, from 9.30–15.30 h			
	$(H_2O_2)_g$ (pptv)	V^a (ml)	pH	cond. ($\mu S/cm$)	$(H_2O_2)_g$ (pptv)	V^a (ml)	pH	cond. ($\mu S/cm$)
Cryogenic	12	15	5.08 ^b	8.00 ^b	13	12	5.51 ^b	7.31 ^b
Imp. I	32	10	4.20	29.3	37	10	4.45	23
Imp. II	75	10	4.12	34.2	32	10	4.29	34

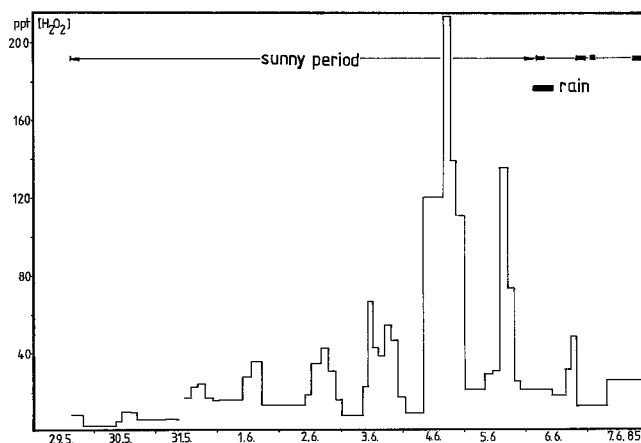
Sampling rate was 700 l/h for the cryogenic trap and 65 l/h for Imp. I and 69 l/h for Imp. II

^a V Total volume of the aqueous sample solution

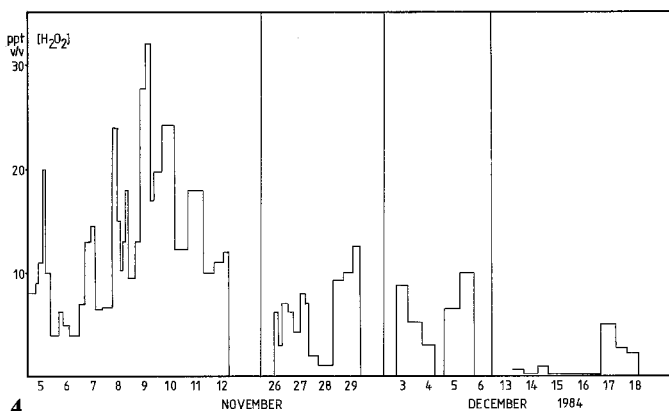
^b pH-values and conductivities of the melted samples



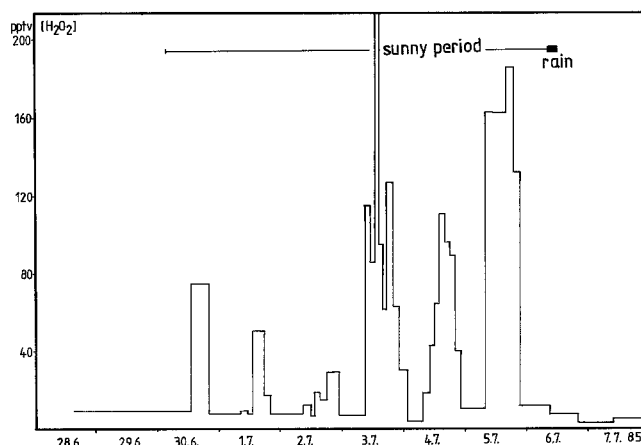
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Figs. 2–5. H_2O_2 concentration in ambient air; Campus of the University of Dortmund

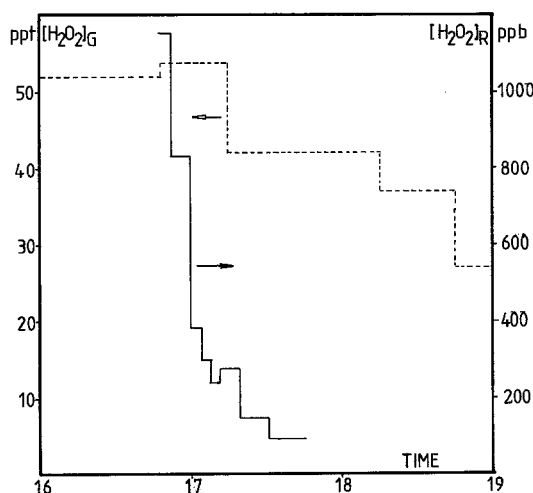


Fig. 6. H_2O_2 concentration in rainwater (—) and in ambient air (---) during a precipitation event on September 13, 1985

Further investigations

In order to make the sampling equipment smaller and more convenient for field use, and also to avoid possible losses of H_2O_2 due to scavenging by non-settling ice particles formed in the cryogenic sampling tube during the condensation process, some laboratory investigations employing coated

Table 4. Measured and calculated $(H_2O_2)_g$ concentrations in air during a rain event on September 13, 1985

Time	Rain $(H_2O_2)_l$, meas. (w/w)	Air $(H_2O_2)_g$, calc. (v/v)	Air $(H_2O_2)_g$, meas. (v/v)
16.50	1114 ppb	192 ppt	54 ppt
17.15	273 ppb	47 ppt	42 ppt
17.42	95 ppb	16 ppt	42 ppt

denuders as collectors [36–38] were undertaken. Sodium tetraborate proved to be a very effective coating material, with the advantage of being the right buffer for the chemiluminescence determination method.

Reproducible generation of $(H_2O_2)_g$ test gas was obtained both with a capillary dispenser (Fig. 7) and a PTFE porous membrane diffusion tube (Fig. 8), both thermostated at $18^\circ C$ to avoid water vapor condensation on the internal walls of the PTFE tubing and silicon rubber connections used for carrier gas and test gas mixture transport, respectively. Both generators gave a sufficiently stable output over 24 h but the day to day reproducibility of the diffusion tube was better than that of the capillary dispenser (Fig. 9). Figure 10 shows the complete laboratory set-up for generation and collection of H_2O_2 .

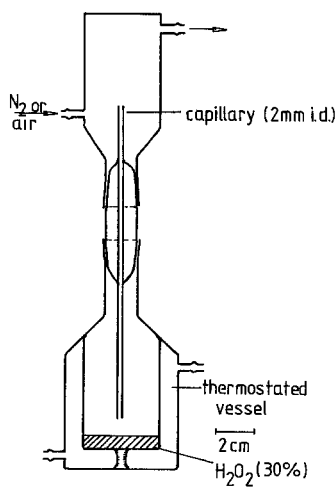


Fig. 7.
Capillary dispenser

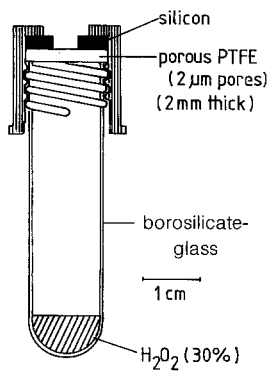


Fig. 8.
Diffusion tube

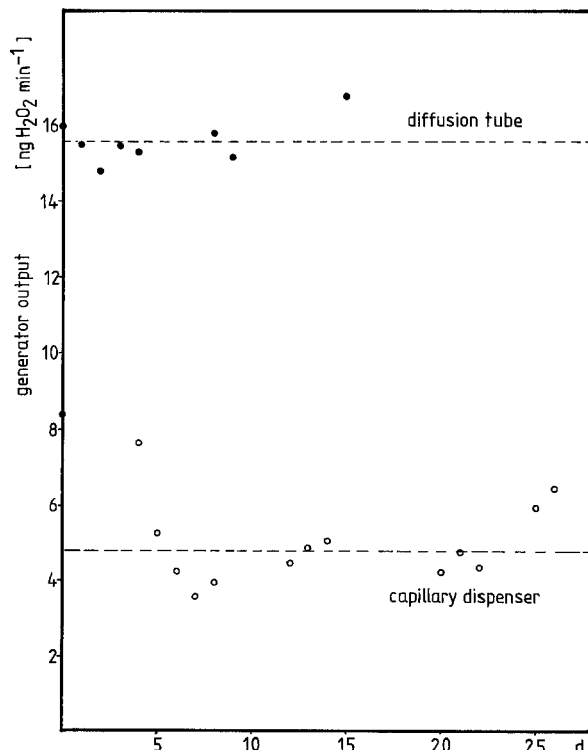


Fig. 9. Day to day variations in the output of the H₂O₂ test gas source

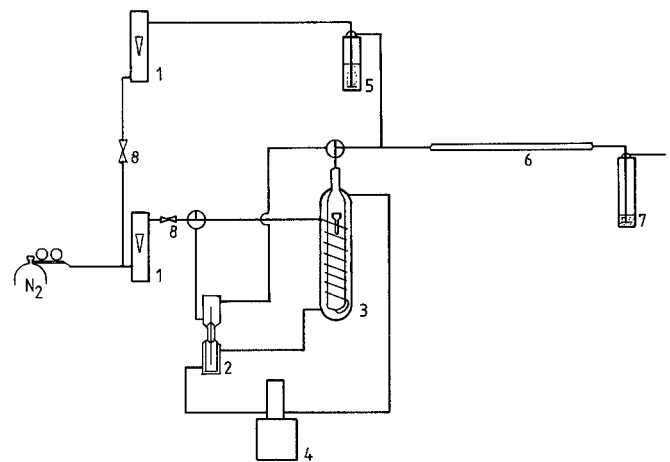


Fig. 10. Laboratory set-up for H₂O₂ generation and collection: 1 Flowmeter; 2 capillary dispenser; 3 thermostated diffusion tube; 4 thermostat; 5 humidifier; 6 denuder; 7 H₂O₂ scrubber (water); 8 needle valve

Brown borosilicate glass tubes, 6 mm i.d., 60 cm length, were coated with sodium tetraborate by employing 500 μ l of a 0.026 M solution of Na₂B₄O₇ in methanol and used as denuders. Brown tubes (or other light protecting means) are necessary to avoid photochemically induced production or decomposition of H₂O₂. Because diffusivity of (H₂O₂)_g is 0.18 cm² · s⁻¹ (20°C) [31] the dimensions of the denuder tubes chosen allow air sampling flow rates up to 100 l/h according to Davies' equation [34, 35]. This implies 2–6 h sampling time for the (H₂O₂)_g concentration ranges generally found at Dortmund (cf. Figs. 2–5). After sampling, the tetraborate coating was removed from each tube with 1 ml of bidistilled water, and 200 μ l aliquots of each extract were analysed by the chemiluminescence technique already described [30].

Laboratory investigations of denuder sampling of (H₂O₂)_g employing test gas mixtures showed very good collection efficiency (95%) and overall recovery (96%). However, ozone interferes by formation of artifact H₂O₂. Therefore field results obtained by denuder sampling were higher by a factor of 3–10 compared with the (H₂O₂)_g levels found by cryogenic sampling. The elimination of the ozone interference is presently being studied by our group.

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