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Ozone. Its Physiological Effects and Analytical Determination in Laboratory Air

SEPPO WILSKA

Department of Chemistry, Finland Institute of Technology, Helsinki, Finland

Since Schönbein discovered ozone in 1840, its occurrence and effects have been investigated extensively. Ozone, as is well known, occurs in the atmosphere, mainly in the upper layers where the ultraviolet radiation is more intense and the humidity lower. The latter fact is significant since ozone reacts with water vapour to form hydrogen peroxide. Ozone is formed by electrical discharges either silent or glowing, UV-radiation, and by some chemical and electrochemical processes.

Ozone has been used to purify air in storage rooms, underground spaces, cinemas *etc.* Witheridge and Yaglou [1] showed that 0.015 p. p. m. of ozone removed body odours and reduced by 50 % the amount of fresh air necessary for odour control. It seems, however, that the effect of the ozone depends more on its masking action than its oxidizing properties, and according to Elford and Ende [2], ozone does not sterilize air when used at a tolerable concentration, and gives no protection against infections. Because of its powerful oxidizing and catalyzing properties, ozone is widely used, particularly in organic chemistry.

The physiological effects of ozone have been investigated in both animal and human experiments. Hill and Flack [3] observed that a content of 1 p. p. m. of ozone in air provokes great changes in the metabolism of experimental animals, and exposure for two hours to air containing 15—20 p. p. m. of ozone causes fatal pneumonia. McDonnel [4] found that ozone administered continuously in the respiratory air for several months in concentrations even lower than 1 p. p. m. apparently shortens the lives of guinea pigs by irritating the lungs and bronchial tubes and causing pneumonia. Kunzmann [5] explains that an ozone — air mixture decomposes into oxygen at the skin surface and the oxygen enters the tissue through the sweat, diffuses into the veins and causes oxidation of organic acids, expulsion of carbon dioxide and a reduced fre-

quency of respiration. Peyre and Moricourt [6] have investigated the destructive action of ozonized oxygen on the haemolytic properties of serums. Fritz [7] attaches importance to the treatment of carbon monoxide poisoning with ozone, and points out that ozone is more poisonous than carbon monoxide. Thorp [8] claims that pure ozone is less poisonous than ozone containing nitrogen oxides. He found that ozone containing 47 % of nitrogen oxides destroys bacteria at a concentration of 3 p. p. m. of ozone, while pure ozone is ineffective below 50 p. p. m. Ewell [9] concluded on the basis of his bacteriological experiments that the addition of nitrogen oxides to ozone does not make the gas more poisonous. Thorp [10], however, maintained his opinion and found that different ozonizers produce gas mixtures of different toxicity. The alleged increase in toxicity caused by the addition of oxides of nitrogen has also been investigated by Watson [11] with negative results.

According to Dadlez [12] the presence of 4 mg ozone per cu.m. (1.5 p. p. m.) renders the atmosphere intolerable. He cites an investigation by D'Arsonval, who found that the average amount of ozone produced under normal conditions by the Hg-quartzlamp used in ultraviolet therapy does not exceed 0.5 mg/cu.m. (0.19 p. p. m.). This amount presents no danger, but when the concentration rises to 1 mg/cu.m. (0.4 p. p. m.) or more, discomfort and irritation result. These symptoms will be apparent in about 30 minutes. It is essential that rooms in which the ultraviolet installation is working should be well ventilated, especially if not spacious. Flury [13] gives the following symptoms characteristic of ozone:

0.001 mg/l (0.47 p. p. m.) causes distinct irritation.

0.002 mg/l (0.94 p. p. m.) causes, in 1 ½ hours, coughing irritation, and severe exhaustion.

0.006 mg/l (3 p. p. m.) causes sleepiness in one hour. At higher concentrations, ozone causes increased pulse frequency, sleepiness, and continued headache.

Striking data, however, have been published. According to Thorpes Dictionary [14] "the ozone content of city air is usually only (!) a few parts per million. If present in amounts larger than about one part in twenty thousand ozone is an irritant." The last mentioned concentration corresponds to 50 p. p. m. and is extremely high.

Edgar and Paneth [15] have determined the ozone content of London air and found it to be $0.4-4.5 \times 10^{-6}$ vol.-%. (C. A. *36* (1942) 988 erroneously gives these figures as 0.4—4.5 p. p. m.). For the air of Geneva, Briner and Perrottet [16, 17] have given the ozone content 7×10^{-9}, and Dauvillier [18] has determined the ozone in the air at Abisko, Swedish Lapland, with a result 1.6×10^{-7}.

According to Elkins[19] the concept of Maximum Allowable Concentration (MAC) of dusts and fumes is fundamental to industrial hygiene as practiced in the United States. The MAC values for different fumes and dusts are carefully determined by animal and human experiments, and are proposed to meet the following requirements. Illnes due to intoxication by the substance in question, and increased susceptibility to non-occupational diseases should not result from continued exposure to the MAC. There should be no marked discomfort to a major portion of exposed workers, and the capacity for working and carrying on a normal existence should not be reduced. When tolerance is acquired, the MAC should not be more than 3 times the concentration affecting unhardened persons, and should not exceed one-tenth of the concentration dangerous in a single exposure of ½ to 1 hours. A concentration 2 ½ times the MAC should fail to meet one or more of the preceeding requirements. If the MAC is based solely on animal experiment data, a safety factor of about 5 should be adopted.

For ozone, the MAC given by Elkins (*l. c.*) is 0.2 p. p. m., based on animal data. The MAC of hydrogen cyanide is 10 and that of phosgene 0.5 p. p. m., and ozone is, therefore, very poisonous. Elkins[20] points out that chronic poisoning by ozone has been reported, and the high toxicity of the substance is well established. In his opinion, ozone should never be intentionally introduced into workroom air, and when it is formed inadvertently, it should be removed by suitable ventilation. On the other hand he supposes that the concentrations of ozone produced by carbon arcs and welding arcs are usually negligible.

ANALYTICAL DETERMINATION

The characteristic strong odour of ozone is well known. The minimum concentration at which this becomes apparent is given in many handbooks as 1 : 500000, *i. e.* 2 p. p. m. This fact will be discussed later.

Of the chemical methods for the determination of ozone with sufficient sensitivity colorimetric and fluorometric methods, and methods depending on the oxidizing and catalytic properties of ozone will be mentioned. Arnold and Mentzel[21] determined ozone colorimetrically using tetramethyl-p:p′-diaminodiphenylmethane, and since then this reagent has been used extensively. Masterman[22] reports that ozone gives with this reagent colours initially blue, but changing to grassgreen, olive-green, orange, yellow and finally becoming complete bleached. This test is specific for ozone; only hypochlorites interfere. Benoist[23] determines ozone colorimetrically using fluorescein; Egorow[24] prefers the leuco-compound of fluorescein, fluorescin, which is oxided by ozone to fluorescein. This method is suitable, according to him, for concentrations of 1 p. p. m. or less. Allen[25] determines colorimetrically the iodine liberated by ozone from a KI-solution with a sensitivity of 10^{-6} g using starch as indicator. In the colorimetric method of Usher and Rao[26] $NaNO_2$-solution and the Griess-Ilosvay reagent are used. If O_3, N_2O_4

and H_2O_2 are present in the air, in the first test O_3 and H_2O_2 are removed by means of the combination $CrO_3 + MnO_2$. In a second test, H_2O_2 alone is destroyed by CrO_3, and the amount of ozone is calculated by difference. Dorta-Schaeppi and Treadwell [27] determine ozone colorimetrically in a concentration of 10^{-8} using indigodisulfonic acid in a phosphate buffered solution of pH 6.85. In the method of Konstantinowa-Schlesinger [28], the fluorescence of acridine, formed by ozone in a solution of dehydroacridine is measured.

The hypersensitive method of Briner and Perrottet [17] is based on the catalytic effect of ozone on the oxidation of aldehydes. They used benzaldehyde in carbon tetrachloride or butyraldehyde in hexane and obtained a sensitivity of 0.1—0.01 p. p. m. using samples of less than 10 litres. The sensitivity may be increased by small amounts of peracid, formed by air in the presence of light [29].

The oldest and best known method for the determination of ozone is by absorption in a solution of KI, and titration of the liberated iodine with sodium thiosulfate. In this procedure, other oxidizing agents such as nitrogen oxides, halogens, and hydrogen peroxide interfere. Teclu [30] introduced neutral instead of acid KI-solutions and Ladenburg and Quasig [31] have confirmed the correctness of this procedure. Ladenburg [32] further ascertained that a solution of $NaHSO_3$ unlike AsO_3'''-solution absorbs ozone completely, Lechner [33] recommends that the O_3-determination be made in alkaline KI-solution, because iodine should not be evaporated, but Riesenfeld [34] has shown that this method gives values which are too high due to the formation of iodate. Baskerville and Crozier [35] absorbed ozone either in acidic or neutral $CdKI_3 \cdot H_2O$-solution, and McDonnel [36] describes a rapid method in which the ozone is absorbed in a solution containing KI, $Na_2S_2O_3$ and starch, and the ozone concentration is proportional to the time required for the solution to become blue. Juliard and Silberschatz [37] used a KI-solution buffered to pH 7 by means of a boric acid-borate or mono-disodiumphosphate buffer. Ruyssen [38, 39], however, has not observed any differences in results using buffered or unbuffered solutions in the pH range 7—9.2. Between pH 5—7 and in the presence of boric acid, the results were too high by as much as 10 %. Dauvillier [40] proposes Na_3AsO_3-solution as adsorbent, but Briner and Paillard [41] have shown that a strong KI-solution is definitely superior.

Ozone may be adsorbed by silica gel at low temperatures and liberated by destillation (Briner [42] and Paneth and Edgar [43]). Separation of ozone from N_2O_4 is carried out by destillation at a temperature below — 120° C. The procedure of Ladenburg-Quasig (*l. c.*) is recommended by Paneth and Edgar for ozone determinations. Thorp [44] sensitizes the reaction between ozone and KI with a solution of $AlCl_3 \cdot 6H_2O + NH_4Cl$. Glückauf *et al.*[45] have obtained a continuous recording of the local ozone concentration with an automatic apparatus. KI-solution buffered to pH 7 is used, the liberated iodine being titrated electrometrically. As regards nitrogen peroxide, these authors made the observation that with the buffered KI-solution used the quantity of I liberated by NO_2 corresponds to less than 2 % of the amount of peroxides present. The reaction

$$NO_2 + 2\ H^+ + 2\ I^- = H_2O + NO + I_2$$

requires hydrogen ions, and the concentration of these is reduced by buffering the solution. If the concentration of NO_2 is increased (10^{-5}), the reaction occurs more rapidly.

Boelter *et al.*[46] determined ozone in higher concentrations (4 to 20 weight %) iodometrically, and found that KI-absorbents in the pH range 2.3 to 12.3 gave correct results if the solution was acidified with strong acid before titration with sodium thiosulfate. Addition of aluminum chloride to the absorption solution caused no error at concentrations up to 0.055 N. Strongly acidified potassium iodide absorbents gave high results.

Briner and Monnier [47] remove nitrogen oxides by absorption in concentrated sulfuric acid. In the presence of ozone the oxides of nitrogen are in the form of peroxide, or even nitric acid anhydride, and thus they will be almost completely absorbed by sulfuric acid. Kawamura [48] previously reported on the low solubility of ozone in concentrated sulfuric acid.

EXPERIMENTAL

In this work, the concentration of ozone in the immediate vicinity of a spectrograph and of an ultraviolet lamp has been determined. The spectrograph was used with spark excitation, the spark source being the commercial type of Heraeus, Hanau, with the inductance marked 1/10, full capacitance and a primary resistance of 40 ohm. The ultraviolet lamp was a laboratory model made by Hanovia, England, and was used without any filter. The spectrograph was in a room of about 100 cu.m. volume, the ultraviolet lamp in a room of about 50 cu.m. No ventilation was used.

Collection of the samples.

Two fritted bubblers in series were used, the first containing 50 ml of concentrated sulfuric acid to remove nitrogen oxides, the second 50 ml of KI-solution protected from light. The latter solution was either buffered to pH 7 or unbuffered. The samples, either 50 or 100 litres (measured by means of a gas meter) were collected at a rate of about 7 l/min.

Analysis.

The sample was transfered to a 250-ml Erlenmeyer flask, 1 ml 6N-H_2SO_4 and one drop of starch solution were added and the solution was titrated immediately to the colourless end-point with 0.01 N sodium thiosulfate using a micro buret. Before each sample, three blanks were run with a reproducibility of $\pm$ 0.05 ml in titration. The average of these was subtracted from the titration value of the sample.

The reaction is:

$$O_3 + 2\ KI + H_2O = 2\ KOH + O_2 + I_2$$

and hence 1 ml of 0.01 N sodium thiosulfate corresponds to 1.12 p. p. m. of ozone. The results were calculated to NTP.

Sensitivity and accuracy.

On the basis of the reproducibility of the blanks and titrations, a sensitivity of 0.1 p. p. m. and an accuracy of $\pm$ 0.05 p. p. m. are to be expected.

Reagents.

KI solution. 100 g of KI dissolved in distilled water and diluted to 500 ml.

Buffered KI solution. Prepared according to Glückauf *et al.*[45], 1.38 g of NaH_2PO_4 and 0.20 g of NaOH were added. The solutions were protected from light and used immediately.

H_2SO_4 concentrated. M & B "for analysis".

H_2SO_4 6 N.

$Na_2S_2O_3$ 0.01 N.

Starch solution. 1 gram in 100 ml hot water.

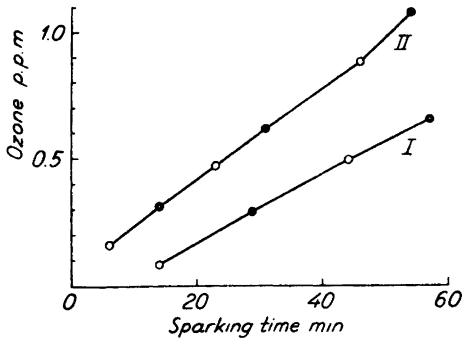

Fig. 1. The concentration of ozone in air at various distances from the spectrograph electrodes using either buffered and unbuffered KI-solutions in the analysis.

RESULTS

A. The concentration of ozone caused by the spectrograph

I. Horizontal distance from the electrodes 50 cm.

Sparking time (minutes)	Ozone p. p. m. (Air samples 100 l)
14	0.08
29 B[1]	0.29
44	0.49
57 B	1.65

[1] Buffered solution.

II. Horizontal distance from the electrodes 40 cm.

Sparking time (minutes)	Ozone p. p. m. (Air samples 50 l)
6	0.16
14 B[1]	0.31
23	0.47
31 B	0.61
46	0.87
54 B	1.07

[1] Buffered solution.

These results are shown graphically in Fig. 1. The time is measured from the start of the test to the end of each sampling. As may be seen, no differences between the buffered and unbuffered solutions are detectable.

A series of tests was carried out omitting the sulfuric acid pre-treatment, and it was observed that the increase in the titres was about 20 %, this representing the oxidizing agents absorbed by the sulfuric acid.

B. The concentration of ozone caused by the ultraviolet lamp

No significant concentration of ozone could be determined. When the lamp was lit the odour of ozone was easily noticeable, but it disappeared rapidly. This result agrees with the data given in the literature [12, 17].

DISCUSSION

The odour of ozone corresponding to a concentration of about 0.1 p. p. m. could be observed immediately after igniting the spark, and continued thereafter. A distinct irritating effect on the respiratory organs appeared in 15 minutes and increased towards the end of the test. These observations agree with those of Flury [13]. During these tests the usual ventilation system of the spectrograph, a powerful suction just above the electrodes, was not used, but during normal operation of the spectrograph the author has observed the same irritation, although after a longer working time. The author has used rather long exposure times (3—4 min.), the total working time being as long as 3—4 hours without a break. After two weeks, distinct symptoms of chronic ozone poisoning were observed — shortness of breath and continuous headache. It is evident that ventilation efficient enough to remove the hazard of contamination during the analysis is not sufficient to eliminate the possibility of ozone poisoning. Oxides of nitrogen, of course, cause irritation, too, but according to the test values, the amount of ozone is of greater significance. It seems possible that ozone may be formed by the ultraviolet radiation of the spark or an arc at a comparatively long distance from the electrodes, where it is not immediately removed by the ventilation system but is inhaled by the worker.

The hazard of ozone poisoning caused by ultraviolet lamps reported on by Dadlez [12] is worthy of note, even although the present test has not shown an unusual concentration of ozone around such a lamp. The possible effect depends on the size of the lamp and the room, on the ventilation and, of course, on individual sensitivity to ozone.

It is evident that the great toxicity of ozone is not widely appreciated, and more attention should be paid to this fact in all cases where ozone may occur in air, e. g. in electric machine halls, transformer stations, artificial sun treatment rooms and laboratories working with ozonizers, spectrographic equipment and ultraviolet lamps. The MAC-value given by Elkins [19], 0.2 p. p. m. for ozone, seems to be too high, as irritation is distinctly noticeable at this concentration. The concentration meeting all the requirements of the MAC is close to or below the minimum, at which ozone may be detected by its odour, i. e. 0.05—0.1 p. p. m.

SUMMARY

The properties, physiological activity and analytical determination of ozone are reviewed. The concentration of ozone in the vicinity of a spectrograph has been determined iodometrically and was found to rise to 1 p. p. m. in one hour. The ozone concentration near an ultraviolet lamp was found to be below the limit of determination, 0.1 p. p. m. Personal experiences of symptoms caused by ozone are presented. Finally the author stresses that the great toxicity of ozone should be better known, and considered wherever ozone may be formed.

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