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Problems in ozone determination in sea-water

by

H. Rosenthal and G. Hinz
Biologische Anstalt Helgoland,
Zentrale Hamburg,
Fed. Rep. Germany

INTRODUCTION

Ozone has been found useful in a number of applications related to human activities since its discovery by SCHÖNBEIN in 1840. In water sterilization and tertiary sewage treatment, ozone was virtually replaced by chlorine during the first half of this century because of higher production costs of ozone. In more recent years interest is returning to ozone as an effective agent in water pollution control. New and more efficient production methods have been developed that reduce operational costs.

Findings of HUBBS (1930) and DOUDOROFF and KATZ (1950) tended to discourage the use of ozone as a means of water treatment for aquaculture purpose. BENOIT and MATLIN (1966) were the first to state that a reexamination of ozone could be useful as a means for disease control in American fish hatcheries. While aquaculturists showed no interest in ozone during the last decade, ozonization has become a most beneficial standard method for water treatment of home aquaria.From their own experience the authors believe that ozone can play an important role in water treatment re-use systems (ROSENTHAL, 1974) (ROSENTHAL and WESTERNHAGEN, 1975).

COMMON METHODS FOR OZONE DETERMINATION

The impetus to select a suitable procedure for the determination of ozone dissolved in sea water arose from the requirement to evaluate the effectiveness of ozone application in sea-water treatment units. In fish culture units it is of great importance to control residual ozone levels because of its high toxicity.

Quantitative determinations of ozone have been troublesome, both in air and in aqueous solutions. Among the most important methods for low-level determination of ozone in air are the starch-iodine method (THORP, 1940), the phenolphthalein oxidation reaction (HAAGEN-SMIT and BRUNELLE, 1958), the long-path ultraviolet adsorption method (RENZETTI, 1957), the sodiom diphenylaminesulphonate reaction (BOVEE and ROBINSON, 1961), and the peroxy-isocyanate method (LAYTON et al., 1970).

Problems of determination of ozone in water arise from its rapid decomposition and its interaction with other ions in solution (INGOLS et al., 1959; SULZER, 1958; KOPPE and MÜHLE 1965; HOFMAN and STERN, 1969 a, b). as shown in Fig. 1 speed of ozone decompo-

Table 1: Methods of ozone determinations (modified after ROSENTHAL, 1974).

Method	Remarks	References
reaction with potassium iodide and back tritation of iodine with $Na_2 S_2 O_3$	neutral or slightly acidic tritation of iodine	ZEHENDER (1952)
Manganese oxidation and colour reaction with orthotolidine	$Mn^{++} \longrightarrow Mn^{+++}$ (Spectrophotometric determination at 440mµ; 5-20µM/l	ZEHENDER and STUMM (1953) SULZER (1958
Oxidation of Lenco-crystal violet	Redox indicator, colorometric procedure at a wave length of 592 mµ in acidic solution (sub-ppm levels)	LAYTON and KINMAN (1970 KINMAN (1975)
Spectrophotometry in distilled water (visible region)	typical absorption band at 260 mµ (< 0.4 µM/l)	ALDER and HILL(1950) KILPATRICK et al. (1956).
Oxidative decoloration of indigo-sulfonate	phosphate-buffer (pH 6.85)	DORTA-SCHAEPPI and TRADWELL (1949)
Reaction of ozone with potassium iodide	colorometric determination of the liberated iodine with starch	RAWSON (1953)
Ozone reaction with Mn (II) diphosphate complex $\longrightarrow$ Mn (III) disphosphate complex	Cr (III) as catalyst; O_3 determination in presence of chlorine, chlorine dioxide, hypochlorite, chlorate, perchlorate	HOFMANN and STERN (1969 a,b)
Reaction of ozone with potassium iodide	---	WANNER (1971)
Reaction with potassium iodide and colorimetric determination of iodine	two modified applications for low level (0.01-0.30 ppm) and high level determination (0.30-2.00ppm)	SHECHTER (1973
Reaction with potassium iodide and colorometric determination of iodine	Stoichiometry	PARRY and HERN(1973)

sition in fresh water is highly dependent on the pH of the medium. (ZEHENDER, 1952; ZEHENDER and STUMM, 1953; STUMM, 1954).

The usual methods for the determination of ozone in water are iodine titration (ZEHENDER and STUMM, 1953; INGOLS et al, 1959; RAWSON, 1953), the colorometric Mangan-o-Tolidin-method (STUMM,1956), the Aminodimethylaniline-method (PALIN, 1953), the Indigo-method (DORTA-SCHAEPPI and TRADWELL, 1949) and the Tetramethyldiaminodiphenylmethan-method (KOPPE and MÜHLE, 1965). Some further methods are summarized in Table 1.

The method developed by DORTA-SCHAEPPI and TRADWELL (1949) using Indicocarmin (which is oxidized to isatin) is highly sensitive but is not specific enough to be employed for determination of residual ozone in polluted water because it also reacts with nitrate. Most of the methods described in the literature are inappropriate for determining ozone in the presence of chlorine and chlorine-compounds.

EXPERIMENTS ON OZONE DETERMINATION IN SEA-WATER

Selection of method.

The following criteria were employed to select a method which satisfies our requirements:

- a) the method should allow ozone determination in the presence of high chloride, nitrate and sulphate concentrations.
- b) the method should be sufficiently sensetive to detect residual ozone down to levels of 0.1 ppm

c) the method should be simple, easy to handle, and not time consuming.

After a thorough survey of the literature, the method developed by ZEHENDER (1952) and ZEHENDER and STUMM (1953) was selected and modified (see also KINMAN, 1975). The reaction of ozone and iodide is based on the following equation:

$$O_3 + 2\,I^{(-)} + 2\,H^+ \rightarrow I_2 + H_2O + O_2$$

The liberated iodine will usually be determined by back titration with thiosulphate:

$$I_2 + 2Na_2S_2O_3 \longrightarrow 2\,NaI + Na_2S_4O_6$$

Experimental procedure.

The experimental design is shown in Fig. 2. Ambient air is thoroughly dried passing through two 200 ml bottles (a and b) containing $CaCl_2$ and Silica gel.

The air was ozonized in an electrical discharge ozonizer (c) (Typ IV, Fa. Sander) at a flow rate of 200 l/h resulting in a total ozone production of approximately 700 mg O_3/h (Fig. 3). Ozone containing air was bubbled through a water column of a 500 ml sample (e) for different periods of time (i.e. 30, 60, 120, 300, 600 sec). Immediately after ozonization a 100 ml sample of the treated water was poured into a jar containing a mixture of potassium-iodide solution (1 ml; 0. 1 normal) and acetate-buffer (10 ml; pH = 4.62). The liberated iodine was titrated with sodium thiosulphate (0.01 n). The endpoint of tritation was determined by measuring the redox-potential with a Platin-Calomel-electrode. Some minor modifications of the methods described by ZEHENDER (1952) were made in order to meet pH requirements for iodine titration in sea-water. Fig. 4 shows an example of a typical tritation curve.

The stoichiometry of the ozone-iodide reaction is based on the assumption of the 1 : 1 ration, i.e. one molecule of ozone liberated one molecule of iodine. The assumption of 2 moles of sodium thiosulphate $\hat{=}$ 48 g ozone. 1 ml of an 0.01 N sodium thiosulphate solution corresponds to 0.00079 g thiosulphate. Therefore, the amount of ozone can be calculated by the expression

$$\frac{48 \times 0.79 \times (\mathrm{ml}) \times (F)}{316.4} = \mathrm{mg}\ O_3/l$$

where ml is the amount of thiosulphate titrated in millilitres and F a factor correcting the sample volume to 1 liter.

Table 2 illustrates the results obtained from ozone determination trials when clean (filtered) sea-water and polluted sea water of different organic loads was aerated with ozone containing air for different periods of time. Polluted water was obtained from the outlet of the fish-rearing tanks.

The results indicate that detection of ozone in sea-water is possible down to levels of about 0.002 mg/l, but the error of the method remains high (about 10 to 15%). Nevertheless, we find this accuracy sufficient to determine retention time of sea-water in the storage tanks and thus to ensure complete decomposition of ozone before the water enters the fish tanks.

Nothing is known about the total amount of ozone absorbed by sea-water because a considerable amount of the introduced gas may have escaped with the air bubbled through the water column. From our determination trials it has become obvious that most of the ozone reacts and/or is decomposed immediately after introduction into the water. Residual ozone levels found in water of low initial organic load ($KMnO_4$ value : 12.5 mg/l) are about 1% and 7% of the total amount of ozone gas introduced into the medium when ozonization lasts for 0.5 and 5.0 minutes, respectively. In sea-water with high organic loads, ozone levels reached after a five minutes treatment period were 0.1% of the total amount of ozone introduced. Thus, over short periods (minutes), intensive ozonization of sea-water with a high organic load will not lead to detrimental residual ozone levels which may damage the fishes in the tanks.

Decomposition of residual ozone in relatively unpolluted water ($KMnO_4$ value : 44 mg/l) is still rapid compared with values obtained in destilled water. About 85% and 50% of the ozone level reached within a 30 second treatment period remained after one and five minutes, respectively.

At present nothing is known on interference of other ions with the ozone determination method employed except the fact that chloride, nitrite and nitrate ions do not significantly effect the reaction between iodide and ozone in solution.

DISCUSSION

The major problems in using the iodine titration method arise from the fact that the amount of iodine liberated when ozone is added to iodide solutions is markedly dependent on pH. After INGOLS et al (1959) twice as much iodine was liberated at pH 2 than at pH 9. BYERS and SALTZMAN (1959) obtained an increased ratio in the I_3^- / O_3 in similar investigations. They assumed that at pH 7 the ratio of molecules of iodine to molecules of ozone was 1 : 1 (SALTZMAN and GILBERT, 1959). Our results are based on this assumption in order to get a first approximation. We are well aware that the results obtained by BOYD et al (1970) give a stoichiometry for neutral pH of 1.53 molecules of sodine liberated per molecule of ozone absorbed. PARRY and HERN (1973) have shown that the oxidation of iodide to iodate is also thermodynamically feasible, especially at higher ozone concentrations. On the other hand HODGESON et al (1971) and KOPCZYNSKI and BUFALINI (1971) have reaffirmed the stoichiometry for the reaction as 1 : 1.

Using redox potential measurements as indication of titration endpoint has several advantages compared to the starch-iodide procedure which is believed to give a precision of about ± 1%. At low ozone levels this procedure of determination of ozone in water begins to show significant error when the released iodine is less than about 2.0 mg/l. An iodine concentration of 2.0 mg/l in neutral solution is equivalent to an ozone concentration of about 0.4 mg/l. Thus the starch-iodide procedure has a large error when ozone concentration is less than about 1.0 mg/l (KINMAN, 1975).

KINMAN (1975) recommends amperometric titration for measuring low ozone residuals in water. Commercial equipment is available for measuring 0 to 1.00 mg/l of ozone in water directly by means of a copper-gold electrode combination.

Further experiments are planned to examine the applicability of this method of ozone determination in sea-water. We also intend to investigate whether or not some chlorine is liberated by ozonization in sea-water. This could be done by the method developed by HOFMAN and STERN (1969 a, b) where ozone reacts with the manganese(II) diphosphate complex in acidic media , to form the manganese (III) diphosphate complex which reacts with o-tolidine. The method allows the determination of ozone in the presence of chlorine, chlorine dioxid, hypochlorite, chlorite, chlorate and perchlorate.

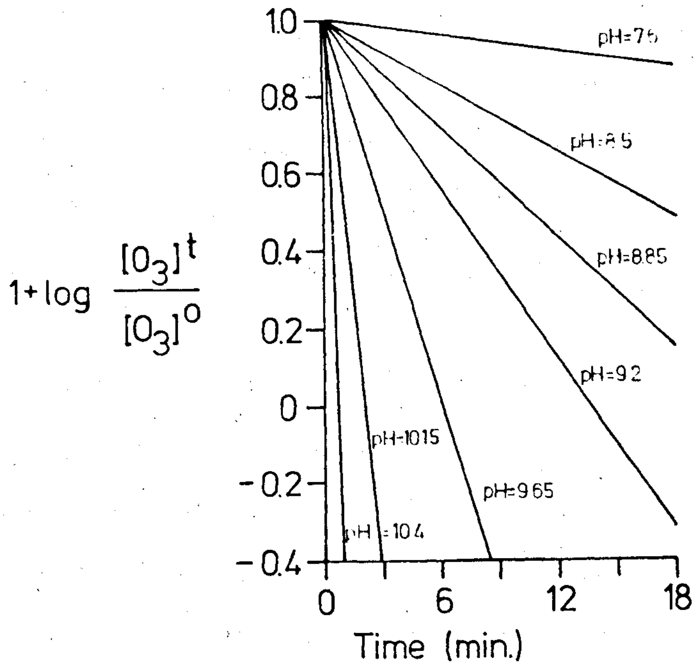

Fig. 1: Decomposition of ozone in aqueous solution in relation to pH value of the medium (after STUMM, 1954)

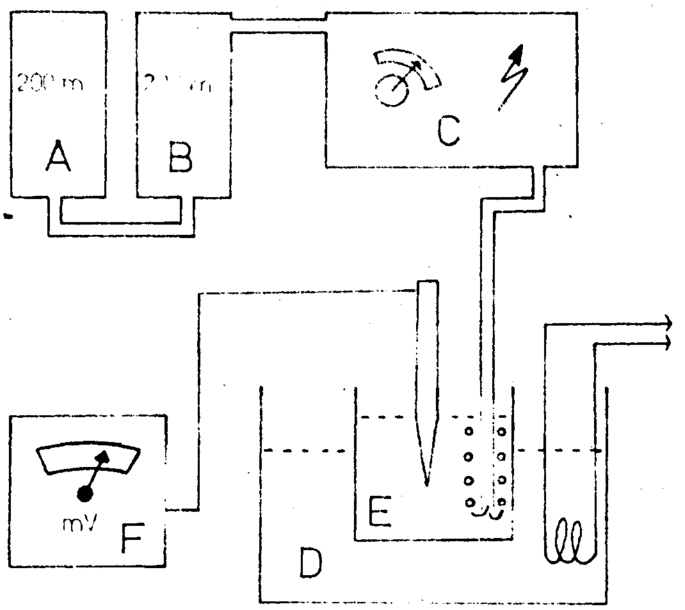

Fig. 2: Experimental design used in ozone determination trials
A and B = Air drying tubes (200 ml volume each);
C = ozonizer; D = water bath (20°C); E = sample jar(500 ml);
F = Voltmeter

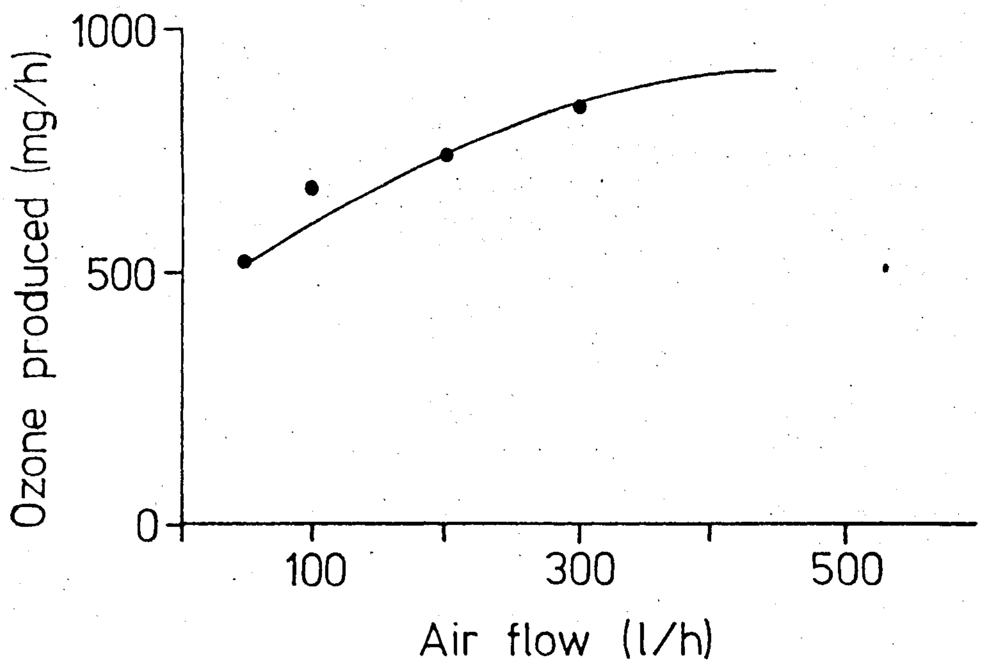

Fig. 3: Ozone production (mgO_3/h) of the ozonizer used (Typ IV, Fa. Sander) in relation to air flow rate.

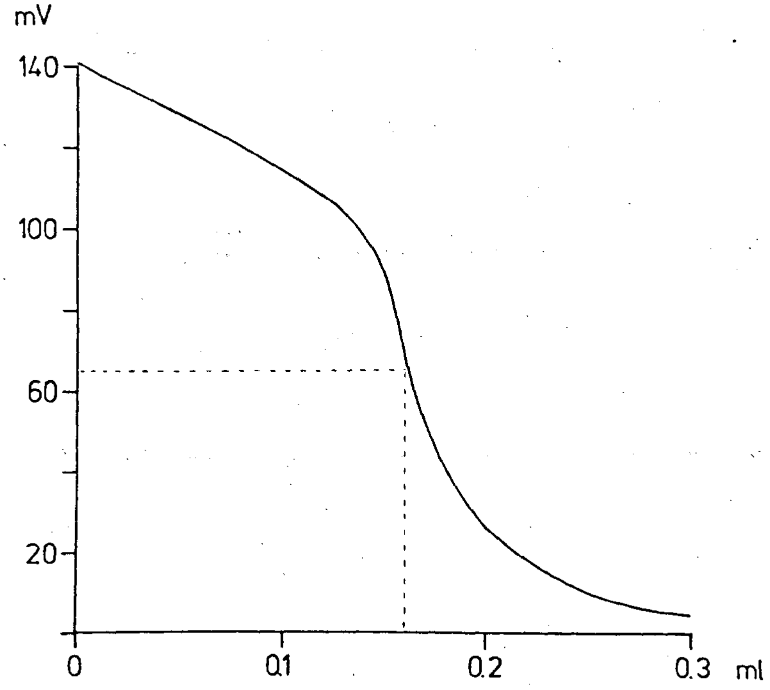

Fig. 4: Typical mV-curve for iodine-thiosulphate titration using a Pt-Calomel-Redox electrode.

Table 2: Residual ozone concentrations (mg/l) in relation to the organic load of the water treated, the duration of ozonization (in brackets: total amount of ozone introduced into the medium), and decomposition within 0.5; 1.0 and 5.0 minutes after treatment.
Temperature 20 °C; salinity 32 °/oo; initial pH = 7.95-8.14; n = number of determinations; $\bar{x}$ = mean; $s_{\bar{x}}$ = error of the mean.

duration of ozonization (sec) organic load of the medium (KMn O_4 values)		30 " (5.81 mg O_3)			60 " (11.65 mg O_3)	300 " (23.3 [illegible] O_3)
		time after treatment (min)				
		0.5	1.0	5.0		
12.5	n	5			2	2
	$\bar{x}$	0.121	-	-	0.216	1.248
	$s_{\bar{x}}$	0.020				
44.0	n	10	9	8		
	$\bar{x}$	0.041	0.035	0.021	-	-
	$s_{\bar{x}}$	0.005	0.004	0.002		
105.0	n	3			2	9
	$\bar{x}$	0	-	-	0	0.028
	$s_{\bar{x}}$					0.002

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