Effect of pH and hydrogen peroxide on aldehyde formation in the ozonation process

Jacek Nawrocki and Iwona Kalkowska, *Adam Mickiewicz University, Department of Water Treatment Technology, ul. Drzymaly 24, 60–613 Poznañ, Poland*

ABSTRACT: This study presents the results of a bench-scale experiment on the formation of aldehydes as by-products of the ozonation process. The objective of this research was to investigate the influence of ozonation conditions during the process on aldehyde production. The results support a hypothesis that aldehydes are formed via a direct pathway. Higher pH and/or the addition of hydrogen peroxide during ozonation decreases the production of aldehydes.

INTRODUCTION

Aldehydes are the major ozonation by-products which are formed as a result of the oxidation of organic contaminants in water. It is important to recognise the factors that contribute to production of aldehydes, since many of them may lead to health problems. Ozonation by-products include mutagens such as, formaldehyde, acetaldehyde, propanal, glyoxal and methylglyoxal [1–5]. The formation of aldehydes can be used to evaluate the oxidation yield of organic matter, since the aldehydes are products of the partial oxidation of organics by ozonation. Aldehydes are a source of easily assimilable organic carbon and therefore these compounds may expose consumers to risks caused by the regrowth of micro-organisms in a distribution network.

Ozone can react with organic compounds which are dissolved in water by two pathways, either directly, or indirectly via a reaction of radicals [1,2,6]. The direct reaction is more selective than the radical one.

The decomposition of ozone and its reactions is dependent on the pH of the water and the raw water quality. The formation of hydroxyl radicals during the decomposition of ozone is initiated by an increasing pH. Acidic pH and the radical scavengers present in water (e.g. carbonates, bicarbonates, alcohols, acetate ions, phosphates) can decrease the concentration of hydroxyl radicals [1,2,6,7]. Ozone can attack humic substances at three types of sites: carbon–carbon double bonds (classical ozonolysis), aromatic rings, and at sites containing complexed metals (e.g. iron) [1,6].

Aldehyde formation depends on the water treatment conditions and the raw water quality. This study involved water ozonation employing various ozone doses on varying raw water qualities (pH, the presence of radical scavengers, various levels of TOC (total organic carbon), and different types of humic substances: commercial, and isolated from ground water on XAD resin). The aim of this work was to study the formation of aldehydes in water ozonation.

Oxidation reactions carried out by hydroxyl radicals are faster and less specific than those of molecular ozone. The combination of hydrogen peroxide and ozone (the Peroxone process) produces hydroxyl radicals which can oxidise contaminants in water. The aim of this study was also to examine the production of aldehydes in the H_2O_2/O_3 process. The effects of hydrogen peroxide dosage and pH are explored.

Aldehydes are polar, and occur in water at low concentrations (p.p.b. or p.p.t.), which leads to problems of analysis. A method for the determination of aldehydes in water was originally described by Yamada & Somiya [8] and was improved by other authors [9–13]. According to this method, low-weight aldehydes concentrations are determined using an aqueous-phase derivatisation with PFBOA (O-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine) and subsequent liquid–liquid extraction and GC analysis. The detection limit with this GC/ECD technique is in the p.p.t. range [8–13].

MATERIALS AND METHODS

Parameters of the water used

Two types of water were used: natural water and model water. The model water was prepared by dissolving humic acids (Aldrich) in it. Ground water (characterised in Table 1) was used in its natural state and was also used enriched with humic substances. The humic substances were isolated from the ground water using XAD4/XAD8 (1:1) resin, according to the procedure described by Thurman & Malcolm [14]. Prior to the extraction of humic substances, XAD resins were purified in Soxhlet using methanol, acetone, ethyl acetate. Pure resins were also washed with NaOH (0.1 N) and then in distilled water (to remove the NaOH). 0.1 N NaOH was used for the elution of the humic substances.

The pH values of these solutions were adjusted with H_2SO_4 or NaOH.

Butanol (0.7 mM/L) and $NaHCO_3$ (0.7 mM/L) were used as radical scavengers.

Table 1 Ground water characteristics

Parameter	Value
TOC (mg/L)	3.8
Colour (°Pt)	3.0
Turbidity (mg/L)	1.0
pH	6.8
Alkalinity (mval/L)	6.1
BOD_7 (mgO_2/L)	0.1
COD (mgO_2/L)	2.1
$Fe_{tot.}$ (mg/L)	1.0
Mn^{+2} (mg/L)	0.1

The characteristic parameters of the ground water used in the experiment are shown in Table 1.

Characteristics of the bench plant

Ozone was generated from dry oxygen using a GS 0012 ozone generator (Sorbios, Switzerland). Ozonation was performed by bubbling an ozone-containing gas through a 1.5 L glass ozone contactor. The ozone concentration and ozone residue in the water were measured using iodometric and indigo methods, respectively.

The ground and model water (a solution of humic substances) were ozonated at various ozone-to-TOC ratios and different pH values. The contact time of water with the ozone was 15 min. In the experiments with the ozone–hydrogen peroxide system, various hydrogen peroxide doses were used in combination with different pH values and ozone doses. Hydrogen peroxide was used as a 3% solution.

Analysis of aldehydes in water

The concentration of aldehydes in the water were determined using an aqueous-phase derivatisation technique, as previously described [15]. The derivatising agent (PFBOA), was obtained from Aldrich and gravimetrically prepared as an aqueous solution in twice-distilled water (1 mg/mL). Aldehyde solutions were prepared in methanol from their pure compounds (Aldrich) and then diluted with twice-distilled water for the prepared standard solutions (and corresponding calibration curves). Hexane (Merck) was used as an extraction solvent. Organic extracts were analysed using a Fisons 8000 gas chromatograph with an electron capture detector.

RESULTS AND DISCUSSION

Formation of aldehydes

The ozonation of humic substances produces a variety of compounds of lower molecular weight than that of the initial substance. Among the ozonation by-products, which are usually oxygenated compounds, aldehydes (which are polar in nature) constitute an important group. We first examined the effect of humic acid concentration on aldehyde production during the ozonation of model water (the humic acid was obtained from Aldrich). When an excess of ozone was present, the concentration of aldehydes increased with increasing concentrations of humic acid (HA) (this was for a TOC which increased from 2.4 to 12 mg/L at 18 mg O_3/L). Doubling the HA concentration approximately doubled the production of aldehydes.

When the concentration of ozone was comparable to the concentration of TOC, then the concentration of aldehydes became dependent on the ratio O_3/TOC. At about O_3/TOC = 1 mg/mg, the concentration of aldehydes reached a maximum. Figure 1 presents the changes in aldehyde production during the ozonation of model water containing commercial humic acid. As follows from our results, the maximum concentration of aldehydes was generated at O_3:TOC = 1. Similar results were obtained with model water enriched in humic substances, but the maximum was shifted to an O_3:TOC ratio of 1.1. Such minor differences are due to differences in the nature of the humic substances we used. When the dose of ozone increased above the ratio O_3/TOC = 1, then concentration of aldehydes decreased. Such a correlation between ozone dose and the production of aldehydes has also been found by Schechter & Singer [2] and Garcia *et al.* [16].

Results showing aldehyde production, normalised per TOC are shown in Table 2.

For each water type, formaldehyde is the dominant aldehyde produced by ozonation. The same result has also been reported in other papers e.g. [9]. Humic substances undoubtedly act as precursors of oxidation by-products. However, the question as to which part of the dissolved organic carbon is responsible for the formation of aldehydes has not yet been answered. According to Schechter & Singer [2], XAD hydrophobic extracts from natural waters appeared to generate greater concentrations of aldehydes than was caused by hydrophilic organics. This means that aldehyde production can account for the hydrophobic material. On the other hand, results obtained by Andrew & Huck [17] showed that XAD extracts from water produce less than half the aldehyde formation in bulk water [17].

Our results support Schechter & Singer's observations rather than those of Andrew & Huck. The aldehyde formation level (normalised per TOC) in the ozonated natural water was similar to the concentration of aldehydes produced by ozonation of the extract from the natural water. In the model water containing commercial humic substances, the normalised aldehyde production level was higher than in both the natural water and the model water containing humic substances isolated from ground water (Table 2). It is also evident that the hydrophobic part of the TOC extracted from the ground water is slightly more responsible for the generation of aldehydes than is the hydrophilic part.

The generation of aldehydes is dependent on pH, as shown in
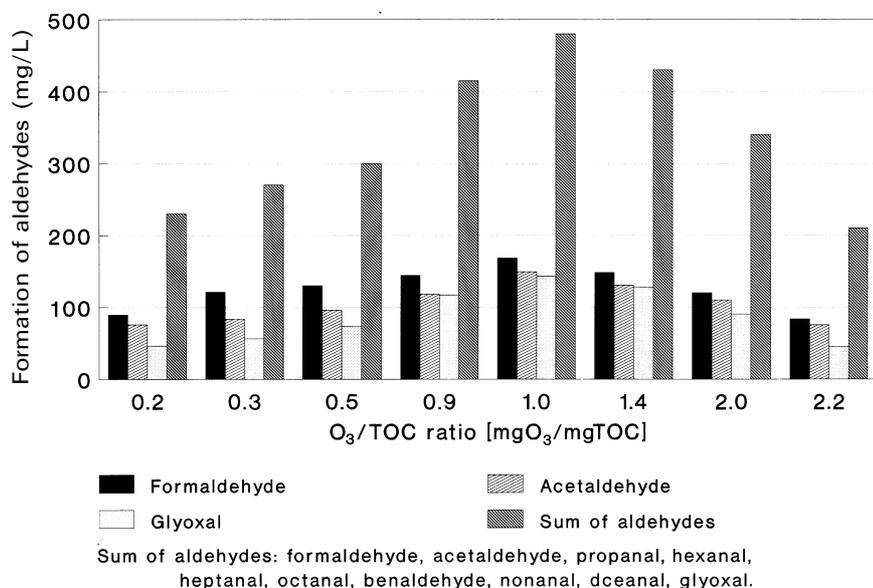
Fig. 1 Effect of ozone dose on aldehyde production during ozonation of model water (distilled water spiked with commercial humic acid).

Fig. 2 for the ozonation of model water containing commercial humic substances. With a pH that increased from 3.5 to 8.0, the generation of aldehydes decreased. These results confirm the hypothesis that aldehydes are formed by the direct reaction of ozone molecules with organic matter. This is probably a general rule concerning the formation of aldehydes, as it has already been observed by Schechter & Singer [2], Andrews & Huck [17] and Zhou *et al.* [18]. It is known that higher pH values favour the decomposition of ozone molecules into radicals [1,6,7]. However, as it is also clear that a higher pH inhibits the formation of aldehydes, there is some controversy concerning the reason for this constraint. Weinberg & Glaze [19] have speculated that hydroxyl radicals may oxidise a part of the aldehydes at higher pH. Our results indirectly show that the radicals do not influence aldehyde formation, since the addition of radical scavengers does not change the concentration of

aldehydes generated. We are thus tempted to say that the availability of molecular ozone is the limiting factor in the production of aldehydes.

In order to confirm the direct reaction as a main mechanism for the formation of aldehyde by ozonation, the influence of introduced radical scavengers was examined. Figure 3 shows the effect of the presence of organic (butanol) and inorganic (NaHCO₃) radical scavengers on aldehyde production during the ozonation of model water containing commercial humic acids. A comparison of the concentration of aldehydes produced during the ozonation process, performed both with and without radical scavengers, showed that it did not depend on the concentrations of radicals. It should be noted that the same effect was also observed at various pH values: 3.5, 7 and 8. These results again support the hypothesis that aldehydes are formed via the direct reaction pathway. Some authors have

	Model water containing commercial humic substances	Natural water (ground water)	Model water containing humic substances isolated by XAD
TOC (mg/l)	16.0	3.8	16.0
O₃/TOC ratio (mgO₃/mgTOC)	1.0	1.0	1.0
Formaldehyde	10.2	4.0	6.5
Acetaldehyde	9.6	1.3	2.1
Glyoxal	8.6	2.0	2.5
Sum of aldehydes *	31.0	8.0	12.5

Table 2 Normalised aldehydes production (μg/mgTOC) during the ozonation of different types of water

* Sum of aldehydes: formaldehyde, acetaldehyde, propanal, hexanal, heptanal, octanal, benzaldehyde, nonanal, decanal and glyoxal.

Formation of aldehydes (μg/L)
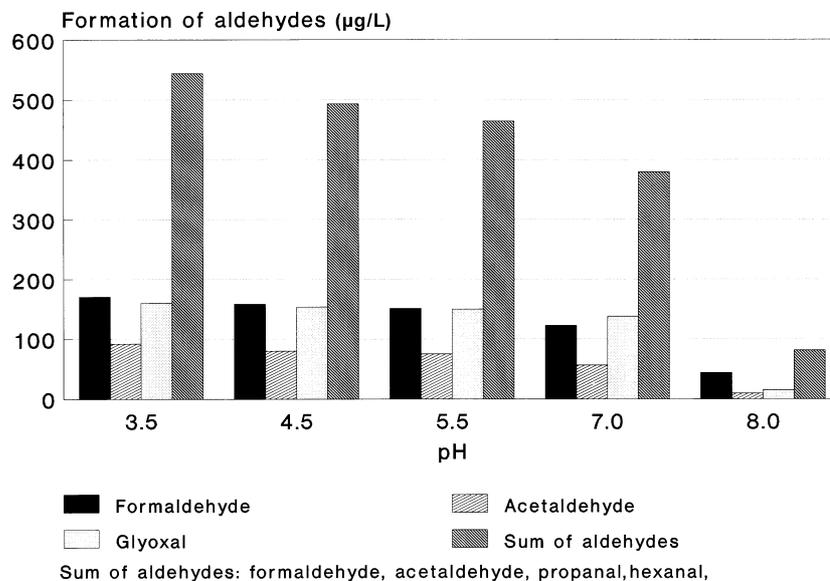
Fig. 2 Effect of pH on aldehyde production during ozonation of model water (ozone dose/TOC ratio = 1.1 mg O_3/mg TOC).

Sum of aldehydes: formaldehyde, acetaldehyde, propanal, hexanal,

Formation of aldehydes (μg/L)
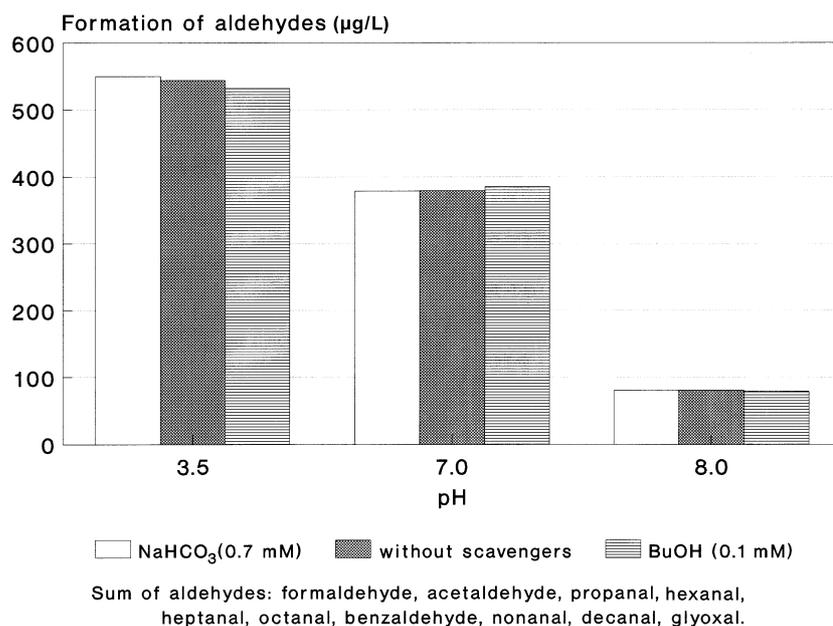
Fig. 3 Effect of the presence of radical scavengers on aldehyde production during ozonation of model water (ozone dose/TOC ratio = 1.1 mg O_3/mg TOC).

Sum of aldehydes: formaldehyde, acetaldehyde, propanal, hexanal, heptanal, octanal, benzaldehyde, nonanal, decanal, glyoxal.

confirmed the direct reaction as a source of aldehydes [1,6], but in contrast, some have reported the opposite conclusion [1].

Peroxone process

Since hydroxyl radicals are the main oxidising species in the peroxone process [20], one could expect that aldehydes will be generated in negligible quantities, as they are formed mainly by the direct pathway [2,17,18]. Our experiments have shown that this is not the case. We have observed the formation of aldehydes in the peroxone process at lower concentrations than in ozonation.

The concentration of aldehydes generated in the peroxone process may vary depending on O_3/TOC ratio, H_2O_2/O_3 ratio or pH. Figures 4 and 5 shows the interdependencies that govern the generation of aldehydes. The addition of hydrogen peroxide to the ozonation process decreases the concentration of aldehydes. However, the process does not remove the aldehydes entirely.
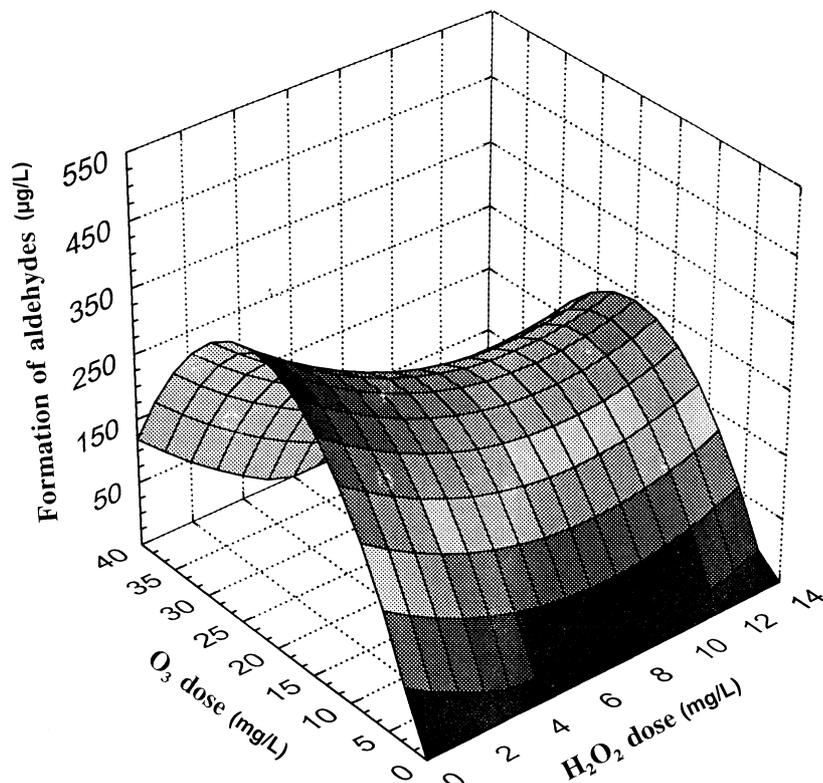
Fig. 4 Effect of O_3 and H_2O_2 dose on aldehyde production during ozonation of model water (TOC = 16.0 mg/L).

Earlier observations showed that the H_2O_2/O_3 process breaks down the contaminants in water more effectively than ozone or hydrogen peroxide alone [16,21,22]. As we have shown above, hydroxyl radicals do not influence aldehyde formation. Thus, we cannot assume that aldehydes are destroyed by the radicals in the Peroxone process. The decrease in aldehyde concentration must be caused by a decreasing effective ozone concentration, concurrent with ozone reacting with the hydrogen peroxide to form radicals.

Figure 4 shows how the doses of ozone and hydrogen peroxide affect aldehyde formation. The results obtained for the ground water indicate that the optimum hydrogen peroxide concentration is close to 1 mg H_2O_2/mg O_3 ($\approx 50\%$ less aldehydes are generated compared to the ozonation process, while at higher ratios the concentration of aldehydes again increases).

The optimum value for the H_2O_2/O_3 ratio should be determined for the water treated. Theoretically, this is a 1:2 molar ratio [22], because two hydroxyl radicals are formed from one molecule of hydrogen peroxide plus two molecules of ozone. This has been confirmed for slightly polluted water, but the optimum ratio can change for more polluted waters [22]. This can be explained by the fact that if there are more hydrogen peroxide molecules than contaminant molecules, the hydroxyl radicals react primarily with hydrogen peroxide to form water and oxygen [21].

Figure 5 shows changes in aldehyde production with a hydrogen peroxide dose (presented as hydrogen peroxide dose:ozone dose) at different pH values. This example shows that the reaction of ozonation with hydrogen peroxide produces less aldehydes in the alkaline pH of the solution. Figure 5 also confirms that aldehyde generation strongly depends on pH.

CONCLUSIONS

Aldehydes are formed as ozonation by-products from the ozonation of natural and model waters. In both cases, formaldehyde is the dominant species which is formed. Aldehyde production changes under different ozonation conditions and water qualities. Overall aldehyde production is the greatest at a ratio which is close to 1 mg O_3/mg TOC. Higher pH values decrease the amount of aldehydes formed during ozonation. The presence of organic or inorganic radical scavengers has no effect on aldehyde production. These results confirm that aldehydes are formed through a direct reaction involving ozone molecules. The H_2O_2/O_3 process appears to be effective in the reduction of aldehyde production, particularly at higher pH values.

In conclusion, aldehyde production has been shown to correlate with ozonation conditions and water quality. Factors (higher pH, H_2O_2) which shift the ozone decomposition process
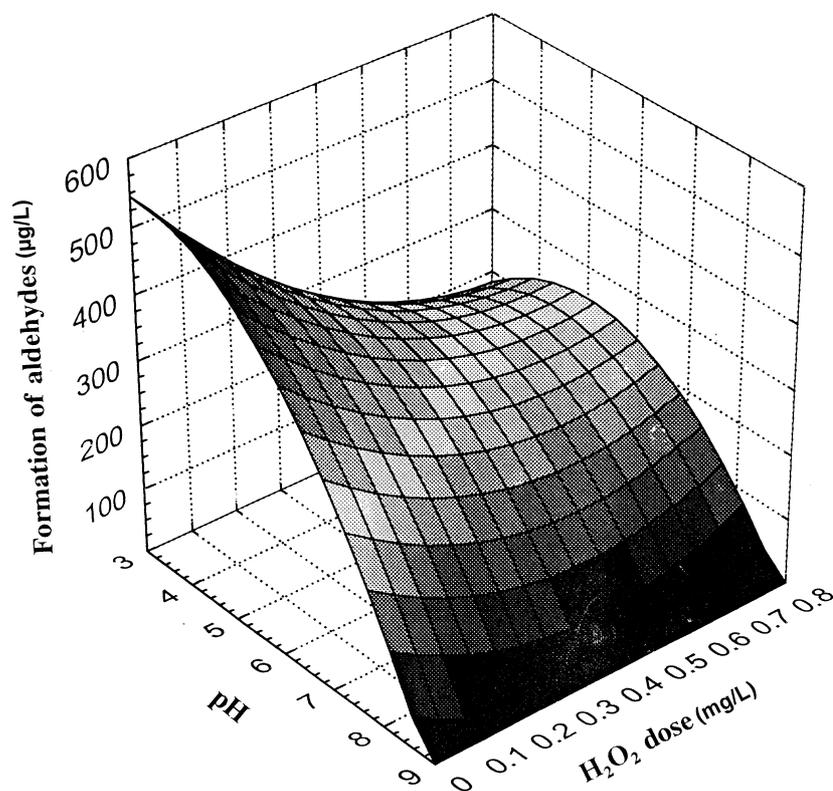
Fig. 5 Effect of H_2O_2 dose on aldehyde production during ozonation of model water (ozone dose/TOC ratio = 1.1 mg O_3/mg TOC) at different pH values.

to the formation of hydroxyl radicals decrease the amount of aldehydes produced by the ozonation process.

BIBLIOGRAPHY

1 Rice RG, Bollyky WJ, Lacy WJ. *Analytical Aspects of Ozone Treatment Water and Wastewaters*. Lewis Publications, Inc., Chelsea, Michigan, 1986.

2 Schechter DS, Singer PC. Aldehydes formation during ozonation. *Ozone Sci Engng* 1995; **17**: 53–59.

3 Anderson WB, Huck PM. Ozone byproducts formation in three different types of surface waters. *Proc. Water Quality Technology Conference*. Amercian Water Works Assoc., San Francisco, CA, Part I. 6–10 November 1994: 871–9.

4 Fawell JK. Carcinogenic micropollutants in drinking water— risks and regulation. *Water Sci Technol* 1992; **25**(11): 473–478.

5 Matsuda H, Yammamori H. Mutagenicity of ozonation products from humic substances and their components. *Water Sci Technol* 1992; **25**(11): 363–370.

6 Hoigne J. *The Chemistry of Ozone in Water*. In: Stucki S, ed. *Process Technologies for Water Treatment*. New York, Plenum Publ. Corp., 1988.

7 Singer PC. Assessing ozonation research needs in water treatment. *JAWWA* 1990; **82**(10): 78–91.

8 Yamada H, Somiya I. The determination of carbonyl compounds in ozonated water by the PFBOA method. *Ozone Sci Engng* 1989; **11**(2): 125–132.

9 Glaze WH, Koga M, Cancilla D. Ozonation byproducts. 2. Improvement of an aqueous-phase derivatization method for the detection of formaldehyde and other carbonyl compounds formed by the ozonation of drinking water. *Environ Sci Technol* 1989; **23**(7): 838–845.

10 Sclimenti MJ, Krasner SW. Ozone disinfection by-products. *Proc. Am. Water Works Assoc. Water Quality Techn. Conference*, San Diego, CA, 1990.

11 Cancilla DAChCh, Chou ChCh, Barthel R. Characterization of the O-(2,3,4,5,6-pentafluorobenzyl) hydroxylamine hydrochloride (PFBOA) derivatives of some aliphatic mono and dialdehydes. *J AQAC Int* 1992; **75** (5): 824–830.

12 Weinberg HS, Glaze WH, Krasner SW, Sclimenti MJ. Formation and removal of aldehydes on plants that use ozonation. *JAWWA* 1993; **85** (5): 72–80.

13 Nawrocki J, Kalkowska ID, Dabrowska A. Optimization of solid-phase extraction method for analysis of low ppb amounts of aldehydes—ozonation by-products. *J Chromat* 1996; **749**: 157–163.

14 Thurman EM, Malcolm RL. Preparative isolation of aquatic humic substances. *Environ Sci Technol* 1981; **15**(4): 463–472.

15 Nawrocki J, Kalkowska ID, Dabrowska A. Analysis of ppb amounts of aldehydes in water by solid phase extraction. *Polish J Environ Studies* 1996; **5**(3): 41–47.

16 Garcia R, Aragues JL, Cortes S, Ovelleiro JL. Study of the catalytic ozonation of humic substances in water and its ozonation by-products. *Ozone Sci Engng* 1996; **18**(3): 195–201.

17 Andrew S, Huck PM. NOM quantitation of ozonation by-products. *Ozone Sci Engng* 1994; **16**(1): 1–7.

18 Zhou X, Reckhow DA, Tobiason JE. Formation and removal

of aldehydes in drinking water treatment processes. *Proc. AWWA Water Quality Technology Conference*, Toronto, 1993.

19 Weinberg HS, Glaze WH. An overview of ozonation and disinfection by-products. In (Minear RA, Amy GL, eds), *Disinfection By-products in Water Treatment. The Chemistry of Their Formation and Control*. CRC Lewis Publications, Boca Raton, 1996: 165.

20 Huang CP, Dong C, Tang Z. Advanced chemical oxidation: its present role and potential future unhazardous waste treatment. *Waste Mngmt* 1993; **13**: 361–377.

21 Brunet R, Bourbigot MM, Dore M. Oxidation of organic compounds through the combination ozone-hydrogen peroxide. *Ozone Sci Engng* 1984; **6**: 163–169.

22 Schulte P, Bayer A, Khun F, Luy Th, Volkmer M. H_2O_2/O_3, H_2O_2/UV and H_2O_2/Fe^{2+} processes for the oxidation of hazardous wastes. *Ozone Sci Engng* 1995; **17**: 119–125.