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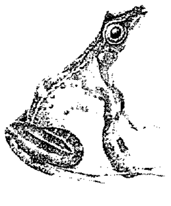

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EFFECTS OF DISINFECTANTS ON ORGANIC SUBSTANCES IN WATER

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Authors: M Fielding, J Haley, M Norris and K Smyth

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Any enquiries relating to this report should be referred to the following address:

WRc Medmenham, Henley Road, Medmenham, PO Box 16, Marlow,
Buckinghamshire SL7 2HD. Telephone: Henley (0491) 571531

SUMMARY

I OBJECTIVES

1. To study the effects of disinfection of water by chlorine and ozone on a range of selected substance likely to occur as contaminants in water.

2. To identify products of these reactions.

II REASONS

With a few exceptions, the chemistry of disinfection with respect to organic chemicals occurring in water sources is not well understood. Consequently, it is difficult to predict the reactions of disinfectants, such as chlorine or ozone, with such chemicals and the nature of any byproducts generated. Of particular concern are reactions with chemicals arising from specific pollution incidents and with any chemicals that commonly occur in surface water, eg hydrocarbons, surfactants and fatty acids. These chemicals may arise from waste water discharges, but although the chemicals themselves may not be of concern they may give rise to byproducts during disinfection which are undesirable owing to the production of tastes/odours or risks to health.

To date, few of the studies in this area have been conducted under conditions likely to arise during drinking water disinfection (eg concentration, pH, contact time). In contrast, WRc research has set out to investigate the effects of chlorine and ozone in a systematic manner under conditions as close as possible to those of treatment. This report provides some of the findings of the research at WRc.

III CONCLUSIONS

The data in the scientific literature on the reactivity of chlorine and ozone with organic substances and the likely reaction products must be treated with caution when trying to assess the effects of water treatment disinfection. Some of our findings in the laboratory produced under conditions related as far as possible to water treatment practice, disagreed with data in the literature.

Some types of potential or known water pollutants were shown to be unreactive and would not be expected to be of concern with respect to production of byproducts. However, a variety of potential or known water pollutants did react. The reactivities of the substances studied are summarised in Table 1.

In some cases where the organic chemical reacted, the products of the reaction were identified.

The presence of bromide during chlorination was an important factor. In certain cases bromide led either to more extensive consumption of organic chemical during chlorination or even reaction when no reaction could be found in the presence of chlorine alone

The data produced in this work should enable better prediction of the likely effects of chlorine and ozone, when applied during water treatment, on organic chemicals occurring in raw water. Such chemicals may occur as common constituents or specific pollutants from pollution incidents.

The work on using chlorine demand as a means of quickly assessing which chemicals react markedly with chlorine, and thus avoiding unnecessary analytical development work, gave promising results and indicated several chemicals likely to be found in water sources and some water treatment chemicals that need to be studied in more detail.

Ozone is currently proposed as an alternaive to chlorine, the latter being disliked in some quarters since it produces byproducts during disinfection. However, ozone also produces byproducts (of different type) and in some instances more readily.

IV RECOMMENDATIONS

Studies on the reaction of chlorine and ozone with further organic chemicals that are either common constituents of raw water or frequently involved in pollution incidents are needed.

Work is needed to determine whether or not products of chlorine and ozone disinfection mentioned in this report can be found in treated waters.

Studies are needed to explain why double bonds in some organic chemicals (eg permethrin) do not react as expected with chlorine. The influence of important inorganic species, such as bromide and bicarbonate, on the effects of disinfectants on organic substances needs further investigation. However, more study of the effects of pH (between a range of 6-9) is necessary.

Further work on rapid means of assessing general reactivity of chemicals (particularly those difficult to measure in water, such as treatment chemicals) towards disinfectants has been justified. The chemicals shown by the chlorine demand work to have marked reactivity to chlorine, need to be studied further to confirm the reactivity and assess the significance of the byproducts generated.

Many of the recommendations are being followed in on-going research, funded by the Department of the Environment, and the findings will be disseminated at a later stage.

V RESUME OF CONTENTS

Comparison of the effect of chlorine and ozone on saturated and unsaturated compounds has shown that both oxidants will react with unsaturated compounds such as alkenes, unsaturated fatty acids, unsaturated esters and unsaturated surfactants. After chlorination the products were found to be chlorohydrin derivatives of the starting material. Ozonation was shown to result in the formation of oxygenated cleavage products, such as aldehydes and carboxylic acids. Neither chlorine nor ozone could be shown to react with saturated substrates such as alkanes and saturated fatty acids.

Aromatic hydrocarbons containing more than one ring, such as naphthalene, phenanthrene, fluoranthene, fluorene and pyrene reacted readily with ozone, whereas toluene and xylenes (one ring aromatic hydrocarbons) were unreactive. Few of the products of these reactions have been characterised with the exception of phthalic acid (from naphthalene) and fluoren-9-one (from fluorene). In contrast only pyrene was found to react with chlorine; it yielded a mono- and a di-chloropyrene as products.

The chlorination of nonylphenyl ethoxylates (a nonionic surfactant) in the presence of bromide was shown to result in the formation of brominated products. Ozone completely consumed nonylphenyl heptakis ethoxylate; however, no products were detected.

From this work it is evident that some types of potential or known water pollutants do not react with either chlorine or ozone and are therefore of little or no concern with respect to the formation of byproducts. Some potential or known water pollutants were reactive. The reactivities of the substances studied and the byproducts formed (where known) are summarised in Table 1. The presence of bromide during chlorination was shown to be an important factor. In some cases bromide led either to more extensive consumption of the substrate or even to reaction when no reaction was found in its absence (ie with chlorine alone).

The data presented in this report should enable better prediction of the likely effects of chlorine and ozone on organic chemicals in water when applied during water treatment. However, more substances need to be studied and the apparently anomalous behaviour of some compounds needs to be understood.

Many compounds which need to be evaluated are, because of their physico-chemical properties, extremely difficult and tedious to analyse and consequently require considerable time to study. Consequently, some method of rapidly assessing the reactivity of these substances needs to be developed; with such a method only chemicals shown to have reactivity would need to be studied in greater detail. Investigations have shown that in the case of chlorine such an approach, based on chlorine demand, can give useful indications on the reactivity of a wide range of chemicals.

The studies were funded by the Department of the Environment. On-going work covers the reactivity of ozone, chlorine and chloramine with additional organic chemicals including pesticides of current concern.

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SECTION 1 - INTRODUCTION

With a few exceptions, the chemistry of disinfection with respect to organic chemicals occurring in water sources is not well understood. Consequently, it is difficult to predict the reactions of disinfectants, such as chlorine or ozone, with such substances and the nature of any byproducts generated. Of particular concern are reactions with chemicals arising from specific pollution incidents and with any chemicals that commonly occur in surface water, eg hydrocarbons, surfactants and fatty acids. These chemicals may arise from waste water discharges, but although the chemicals themselves may not be of concern they may give rise to byproducts during disinfection which are undesirable owing to the production of tastes/odours or risks to health.

Since the discovery that the disinfection of water by chlorine can result in the formation of halogenated products, there have been many studies on the effect of chlorine on organic substances likely to be found in raw water. In addition, similar investigations on the effects of alternative disinfectants such as ozone, chlorine dioxide, chloramines and ultraviolet (UV) irradiation have been carried out. To date, few of these studies have been conducted under conditions (eg concentration, pH, contact time) likely to arise during drinking water disinfection. In contrast, the present study, funded by the Department of the Environment, has set out to investigate the effects of chlorine and ozone in a systematic manner under conditions as close as possible to those of treatment. The work summarised in this report covers the initial part of the overall research.

The specific objectives of the work were:

i) to study the effects of disinfection of water by chlorine and ozone on a range of selected substances likely to occur as contaminants in water

ii) to identify products of these reactions.

Thus the report discusses the general reactivity of a selected range of chemicals towards chlorine and ozone and where possible outlines the chemicals produced during any reaction encountered . Work on the effect of ozonation was carried out under contract to WRc at the Department of Public Health Engineering, Imperial College, London.

The report also includes work aimed at developing a simple method of screening chemicals for possible reaction with chlorine under aqueous conditions. It should be noted that some chemicals are very difficult to measure in water. Thus it is difficult, by conventional methods, to determine their concentrations in water and consequently impossible to judge whether it has been affected by chlorination. However, an assessment of the effect that the chemical has on the concentration of chlorine (ie the chlorine demand) can give an insight into the reactivity of the chemical. A similar approach for ozone was not investigated due to difficulties posed by the chemistry of ozone.

SECTION 2 - EXPERIMENTAL

2.1 ANALYTICAL METHODS

2.1.1 Gas chromatography

Gas chromatographic (GC) analyses were performed on a Varian 3700 gas chromatograph fitted with a silica capillary column, DB-1, 60 m x 0.25 mm (Jones Chromatography) and an OCI-3 on-column injector (Scientific Glass Engineering Ltd (SGE), Milton Keynes, Bucks, UK) for sample introduction. A capillary column effluent splitter (SGE) allowed parallel use of flame ionisation (FID) and electron capture (ECD) detectors. The output from both detectors was recorded by a Servoscribe dual pen chart recorder (Labdata Instruments Services Ltd, Croydon, Surrey, UK). The output from the FID was also recorded on a Hewlett-Packard 3390A integrator (Hewlett-Packard Ltd, Winnersh, Berks, UK). Helium gas flow was set at 1.7 ml min^{-1} and the oven temperature was regulated in the following manner: 30 °C held for 4 minutes then linearly increased at 8° min^{-1} to 300 °C.

In the work on ozonation carried out at Imperial College, gas chromatographic analysis was performed using a Carlo-Erba Strumentazione Fractovap 4200 gas chromatograph (Carlo-Erba Instruments, Crawley, West Sussex, UK) equipped with a fused silica capillary column, BP5 25 x 0.24 mm (SGE) and an OCI-3 on-column injector (SGE) with detection of FID. Helium gas flow was set at 0.9 ml min^{-1} and the oven temperature was regulated as described above.

2.1.2 Gas chromatography - mass spectrometry

Gas chromatography-mass spectrometry (GC-MS) was performed using a Hewlett-Packard 5710-A gas chromatograph fitted with an OCI-2 on-column injector (SGE) and a fused silica capillary column DB-1 (60 m x 0.25 mm, J and W Chromatography) directly coupled to a VG 70-70E double-focussing mass spectrometer (VG Analytical, Manchester, UK). Data acquisition and processing were performed by a Super-Incos data system (Finnigan MAT, Hemel Hempstead, Herts, UK) with mass calibration using perfluorokerosene). Mass spectra were either obtained under electron impact (EI) conditions using 70eV electron energy, 200 µA trap current and 6 kV accelerating voltage or negative ion chemical ionisation (CI) using methane as reagent gas (source housing pressure about 2×10^{-5} τ), 200 µA trap current and -6 kV accelerating voltage.

Alternatively, GC-MS data were obtained using a Carlo-Erba Strumentazione Fractovap 4200 gas chromatograph fitted with a split-splitless heated injector at 250 °C and a silica capillary column, BP5 (25 m x 0.24 mm, SGE), directly coupled to a Jeol JMS D300 double-focussing mass spectrometer. Data acquisition and processing were performed by a Jeol MSDK 400 data system (Jeol, Tokyo, Japan). Mass spectra were obtained under EI conditions using 70 eV electron energy, 300 µA trap current and 3 kV accelerating voltage.

2.1.3 Fast atom bombardment mass spectrometry

Fast-atom-bombardment (FAB) mass spectrometry was carried out on a VG ZAB-IF double-focussing mass spectrometer (VG Analytical) with data acquisition and processing performed by a Super-Incos data system (Finnigan MAT). A commercial FAB source (VG Analytical) was used with a saddle-field atom gun (Ion-Tech, Teddington, UK) operated at 8 kV with xenon gas. Spectra were obtained at 8 kV accelerating voltage, a resolution of about 2000 m/Δm and the spectrometer continuously scanned over the mass range 20-1500 u at 5 sec decade^{-1}. Mass calibration was carried out using a mixture of rubidium, caesium and sodium iodides and samples introduced as solutions in methanol added to a glycerol matrix on a stainless-steel target.

2.1.4 Preparative high-performance liquid chromatography

Preparative liquid chromatography was performed using a Varian 4060 solvent delivery system and a Cecil CE212 variable-wave length detector operating at 280 nm. Injections were made using a Rheodyne valve (Model 7125). The column (200 x 4.6 mm) was packed in our laboratory with 5 μm particle size Spherisorb NH_2 by a slurry procedure using acetone as the slurry medium.

The elution solvent consisted of two solutions A: 98% hexane and 2% propan-2-ol and B: 95% propan-2-ol and 5% water. A linear gradient from 95% B to 50% B over 30 minutes at a flow rate of 1.5 ml min^{-1} was employed.

2.1.5 Analytical high-performance liquid chromatography

Analytical liquid chromatography was performed using a Waters 510 delivery system with a Walters Model 680 automated gradient controller and a Hewlett-Packard 1040A diode array detector monitoring at 230, 260, 280 and 320 nm. The output of the detector was processed by a Hewlett-Packard 85 computer. Injections were made using a Rheodyne valve (Model 7125). The column (150 x 1.8 mm) was packed in our laboratory with 3 µm particle size Spherisorb NH_2 by a slurry procedure using acetone as the slurry medium. The following solvent systems were employed: A: 2% propan-2-ol in hexane, B: 5% water in propan-2-ol. Elution conditions were isocratic, utilising 15% A and 85% B at a flow rate of 200 µl min^{-1}.

2.2 REAGENTS

Organic compounds were obtained from a variety of sources and were the best quality available. Methanol, ethyl acetate and pentane distilled-in-glass grade were obtained from Rathburn Chemicals Ltd (Walkerburn, Peebleshire, UK) and were used without further purification. Diethyl ether was also obtained from Rathburn although this was re-distilled in glass prior to use.

Chlorine-demand-free water was obtained by passing tap water through ion exchange resins, Elga Cylinder Type C10 (The Elga Group, Lane End, Bucks, UK). The deionised water was passed through a column (90 x 5 cm) of granular activated carbon (Chemviron, Brussels, Belgium) to remove trace organic compounds. The water was either used immediately or stored in all-glass vessels, in the dark prior to use. Alternatively, for some ozonation studies, tap water was treated using a Milli-Q System (Millipore UK, Harrow, Middlesex, UK).

2.3 CHLORINATION PROCEDURE FOR ORGANICS OTHER THAN SURFACTANTS

The following chlorination procedure, was employed. In all cases the chlorine concentration refers to total available chlorine. However, repeated measurements by the ferrous ammonium sulphate method(1) showed that this consisted of >95% free chlorine.

Buffered 1 M potassium dihydrogen phosphate solution (20 ml) was diluted to 2 litres with chlorine-demand-free water to afford a final concentration of 10 mM at pH7. A solution of sodium hypochlorite was then added (where appropriate) to afford levels of approximately 1 or 10 mg l^{-1} of chlorine. The solution of organic substrates was then added (20 µl, to yield 10 µg l^{-1} of each component). The solutions of organic substrates each contained an appropriate internal standard for the purpose of assessing the effectiveness of solvent extraction and to provide data on the consumption of each substrate. The aqueous solutions containing all the components were maintained at 20 °C in the dark for either 1 or 4 hours; at the end of the selected reaction time, 1 litre of each solution was extracted with pentane (3 x 20 ml) (after readjusting the pH to 2 with 20% orthophosphoric acid, in the case of fatty acids). The organic extracts were dried by freezing out water and then concentrated by evaporation using a Junk vessel and a micro Snyder column to a final volume between 200 and 500 µl. On the occasions on which the effect of bromide on a reaction was assessed, potassium bromide was added to afford an initial concentration of 5 mg l^{-1} at the start of the reaction.

2.4 CHLORINATION PROCEDURE FOR SURFACTANTS

Methanolic solutions (10 µl of the required concentration) of the surfactant were diluted to 1 litre with 10 mM phosphate buffer (pH7) to afford 10 µg l^{-1} concentrations. One litre samples were then treated with sodium hypochlorite and potassium bromide. Thus, samples containing 10 mg l^{-1} Cl_2, both with and without the presence of 5 mg l^{-1} KBr were prepared. The solutions were maintained at 20 °C for 4 hours after which they were dechlorinated by treatment with an excess of aqueous sodium sulphite (3 ml of 10 mg ml^{-1} solution). The dechlorinated solutions were treated with Analar sodium chloride (100 g) and a 5% solution of sodium bicarbonate (100 ml) and extracted with ethyl acetate (2 x 100 ml). The solvent was removed under reduced pressure. The residual was dissolved in methanol, transferred to a centrifuge tube and concentrated under a stream of nitrogen. These solutions were analysed either by HPLC or FAB-MS.

2.5 OZONATION PROCEDURE FOR COMPOUNDS OTHER THAN SURFACTANTS

Solutions of ozone in water (5 mg l^{-1}) were obtained by bubbling dry ozonised air through purified water in a column contactor. A

TrailigazLabo 76 ozone generator (Ozotech Ltd, Burgess Hill, Sussex, UK) was employed, producing a maximum output of 9 g ozone per hour from dry air at a maximum flow rate of 800 litres per hour. Ozone concentrations in water were determined by the method of Schecter(2). After the desired ozone concentration was achieved, 1 litre of ozonised water was transferred to a reaction flask which was subsequently suspended in a recirculating water bath maintained at 10 °C. The required amounts of organic substrates were then added to afford concentration of 10 µg l^{-1} of each component. This mixture was maintained at 10 °C for 30 minutes. Aliquots were removed at the beginning and end of this reaction time to determine the degree of ozone consumption. At the end of the reaction the aqueous solution was either extracted with pentane (alkanes and alkenes) or after acidification to pH2 with diethyl ether (aromatic hydrocarbons and fatty acids). When diethyl ether was employed as the extracting solvent, an equal volume of pentane was added to the extract prior to drying. Diethyl ether extraction was used instead of pentane because it resulted in improved yields of polar substances from ozonated water. Where difficulties in detection of substrates and/or reaction products were encountered, extracts were methylated (by reaction with diazomethane) to make them more amenable to analysis. The extract to be methylated (500 µl) was placed in a reacti-vial. Diazomethane was produced in a reaction vessel by the action of 1 ml 60% w/v potassium hydroxide on 10 ml 4% methanol/ether solution of N-methyl-N-nitroso-p-toluene sulphonamide at 40 °C. The diazomethane/ether solution was distilled into the extract in the reacti-vial until a yellow colour persisted. After 1 hour, the diazomethane was removed under a stream of nitrogen, the samples were concentrated to about 50 µl and then diluted in the solvent of choice.

2.6 OZONATION PROCEDURE FOR SURFACTANTS

The above procedure (Section 2.5) was amended to include removal of ozone residual with sodium sulphite solution followed by treatment of the aqueous solution with sodium chloride (100 g) prior to extraction with ethyl acetate (2 x 100 ml). The organic layers were then treated as described in Section 2.4.

2.7 CHLORINE DEMAND STUDIES

2.7.1 Experimental procedure

All glassware used during these experiments had been pretreated with a standard chlorine solution to prevent their own chlorine demand interfering with test determinations. After treatment, the glassware was washed with carbon filtered, deionised water until no pink colouration was produced upon addition of DPD. Two 1 litre volumetric flasks were filled with about 800 ml of carbon filtered, deionised water. To each flask was added 10 ml of 1M potassium phosphate buffer (pH7) and the flasks shaken. A standard chlorine solution was prepared by the addition of 10 ml of approximately 1M sodium hypochlorite solution (low in bromine; BDH chemicals) to 240 ml carbon filtered, deionised water in a 250 ml volumetric flask. To each 1 litre flask was added 750 µl of stock chlorine solution after which the flasks were made up to the mark with deionised, carbon filtered water. This gave a 1 mg l^{-1} chlorine solution. The flasks were shaken and 200 ml of the solution taken for duplicate residual chlorine determinations using the procedure described below. These readings were noted as time zero for the experiment. In a 10 ml aliquot from one of the flasks was dissolved 8 mg of the compound and the solution returned to the same flask (final concentration 10 mg l^{-1}). (This concentration excluded highly insoluble substances from the investigation). Both flasks were wrapped in aluminium foil and placed into a water bath at 20 °C for the duration of the experiment.

Residual chlorine determinations were performed for both the control and test flasks over a twenty-four hour period.

2.7.2 Residual chlorine determination

A 100 ml aliquot of the test or control solution was removed from the flask and about 0.5 g DPD No 1 added. The solution was mixed and immediately titrated with ferrous ammonium sulphate (FAS) (0.028M) until the pink solution became colourless. The volume of FAS required to produce this change was noted as reading A. Two microspatula amounts of potassium iodide were added, the solution mixed and left to stand for 2 minutes, after which any pink colouration was titrated to a colourless end point with FAS and the volume required noted as reading B. Reading A represents the free chlorine in solution while reading B represents the combined chlorine. Duplicate residual chlorine determinations were performed for each flask at t=0, 1, 2, 4 and 24 hours.

SECTION 3 - RESULTS

3.1 HYDROCARBONS

3.1.1 Alkanes and alkenes

Solutions of undecane, dodecane, tridecane, tetradecane, pentadecane, hexadecane, heptadecane, pristane, octadecane, nonadecane, squalane and 1-chlorododecane as internal standard, were either treated with chlorine or with ozone under the conditions described above in Sections 2.3 and 2.5. The reactant solutions were then extracted with pentane and analysed by gas chromatography which showed that no consumption of any alkanes had occurred under either experimental regime.

A standard solution of alkenes containing 3,3,5-trimethylhex-1-ene, non-1-ene, non-4-ene, dec-1-ene, undec-1-ene, dodec-1-ene, tridec-1-ene, tetradec-1-ene, hexadec-1-ene, octadec-1-ene, eicos-1-ene, docos-1-ene squalene and 1-chlorododecane as internal standard, was prepared. This solution was treated with either chlorine or ozone under the conditions described in Sections 2.3 or 2.5. After treatment with ozone, all of the substrates were consumed and a homologous series of products were observed which were subsequently identified by GC-MS as aldehydes. In contrast, only a few of the alkenes were consumed by chlorine (Table 1). Further investigation of the conditions employed during the chlorination of alkenes revealed that many of the compounds had been used at concentrations above their solubility in water. Both experimentally measured solubility data published in the scientific literature(3) and solubility data calculated from mathematical models(4) showed that n-alkanes with a chain length greater than 12 carbon atoms and alkenes with a chain length greater than 13 carbon atoms were only partially soluble in water at the spiking concentration of 10 µg l^{-1}. Consequently, it was decided to repeat the chlorination of dec-1-ene, the most soluble (260 µg l^{-1}) alkene that exhibited anomalous consumption.

The conditions employed to investigate the chlorination of dec-1-ene were identical to those previously used to study the reaction of the mixture of alkenes with chlorine except that 3-chloroheptane was used as an internal standard. The consumption of dec-1-ene under these conditions was no longer anomalous.

Thus it is possible that under the conditions of the original alkene chlorination experiment when the alkenes were added to water at concentrations above their solubility limits, the existence of a two-phase system led to anomalous consumption data. However, the same conditions were used for the ozonation study but there was no evidence that the conditions used interfered with the reaction between the alkene substrates and ozone. However, this effect may be due to the more vigorous reaction between ozone and the unsaturated substrates.

In order to obtain sufficient material for identification of the products it was decided to chlorinate non-4-ene at a much higher concentration. Therefore, non-4-ene (1 mg l^{-1}) was treated with chlorine at 10 mg l^{-1} for 4 hours at 20 °C. After the reaction, analysis of the solvent extract by GC and GC-MS spectra and comparison of retention times of these products with those of the epoxide synthesised from non-4-ene showed that the products were not epoxides. It was not possible to draw further conclusions about the structure of these products just on the basis of their electron impact mass spectra. However, analysis by GC-MS using identical chromatographic conditions but using negative ion chemical ionisation showed that the products contained chlorine by the presence of ions at mass to charge (m/z) ratios of 35 and 37 with an intensity ratio of 3:1. It was likely that these products were chlorohydrins. Confirmation of this was provided by comparing the mass spectra and retention times of these chlorination products with those of chlorohydrin standards.

3.1.2 Aromatic hydrocarbons

The following aromatic hydrocarbons were treated with either chlorine or ozone under the conditions described in Sections 2.3 or 2.5; toluene, _ortho_, _meta_ and _para_ xylenes, naphthalene, fluorene, phenanthrene, fluoranthene and pyrene. Of these compounds only pyrene exhibited any reaction with chlorine. In order to facilitate the identification of the reaction products a higher concentration of pyrene (100 $\mu g\ l^{-1}$ _cf_ 10 $\mu g\ l^{-1}$) was chlorinated under the same reaction conditions. Analysis by GC-MS indicated that two products were formed, the major product being identified as a monochloropyrene and the minor product, which was barely detectable was identified as a dichloropyrene (Table 1).

In contrast, after ozonation, all of the substrates with more than one aromatic ring were consumed, whereas those substrates with a single aromatic ring did not appear to be consumed (Table 1).

In order to facilitate further the identification of products, reactive aromatic hydrocarbons were ozonated individually. Thus phthalic acid was tentatively identified as a product of naphthalene ozonation by comparison with the mass spectrum of a library standard held on the data system. Fluoren-9-one was confirmed as a product of the ozonation of fluorene by comparison of both gas chromatographic retention time and mass spectrum with those of a standard. To date, no products of ozonation of fluoranthene or pyrene have been identified although these compounds reacted extensively.

3.2 FATTY ACIDS

The following fatty acids were treated with either chlorine or ozone under the conditions described in Sections 2.3 or 2.5; octanoic, decanoic, dodecanoic, tetradecanoic, hexadec-9-enoic, hexadecanoic, heptadecanoic, octadec-9,12-dienoic and octadecanoic acids. Only the unsaturated fatty acids, namely hexadec-9-enoic and octadec-9,12-dienoic acids were consumed by either chlorine or ozone. Therefore, in order to identify reaction products the chlorination and ozonation of the unsaturated fatty acids were repeated at much higher initial substrate concentrations (500 $\mu g\ l^{-1}$ cf 10 $\mu g\ l^{-1}$). Dodecanoic acid was used as the internal standard in each case. Other reaction conditions were unchanged. After chlorination, only one product was observed by GC or GC-MS. However, when the product solution was examined using FAB-MS in negative ion mode, comparison with control solutions revealed the presence of several reaction products.

Examination of the unchlorinated control solution showed intense $[M-H]^-$ ions at m/z ratios of 199, 253 and 279 for dodecanoic, hexadec-9-enoic and octadec-9,12-dienoic acids respectively, together with their corresponding glycerol adduct ions at m/z 291, 345 and 371. In contrast, after chlorination only the ions corresponding to dodecanoic acid (m/z 199 and 291) remained. However, a number of new peaks could be seen at m/z 305 and 307 ($[M-H]^-$ ions for ^{35}Cl and ^{37}Cl chlorohydroxyhexadecanoic acid) and at m/z 383 and 385 ($[M-H]^-$ ions for ^{35}Cl and ^{37}Cl dichlorodihydroxyoctadecanoic acid). In addition fragment ions were observed at m/z 269, 347 and 349 corresponding to elimination of one equivalent of HCl from the parent ions of the chlorohydrins during ionisation. The peaks were assigned on the basis of accurate mass measurements.

The product observed by GC and GC-MS was shown to be the chlorohydroxyhexadecanoic acid by comparison of its GC retention time and FAB mass spectrum with that of a standard (Table 1).

After ozonation, extraction and methylation, a number of products were identified by GC and GC-MS. These included hexanal, heptanal, their methylation products, heptan-2-one and octan-2-one and also the methyl esters of hexanoic and heptanoic acids. In addition, two other products, namely, the methyl esters of 9-oxononanoic acid and 9-oxodecanoic acid were tentatively identified. Support for the identification of 9-oxononanoic acid methyl ester was provided by negative ion FAB mass spectral analysis of the unmethylated extracts obtained with and without ozonation. Thus, the extract of the unozonated solution showed intense $[M-H]^-$ ions at m/z ratios of 199, 253 and 279 corresponding to dodecanoic, hexadec-9-enoic and octadec-9,12-dienoic acids respectively together with their corresponding glycerol adduct ions at m/z 291, 345 and 371. In contrast, the FAB mass spectra obtained after ozonation showed ions corresponding to dodecanoic acid (namely m/z 199 and 291) and some new peaks. These included m/z 171 identified as an $[M-H]^-$ ion for 9-oxononanoic acid and m/z 187 identified as an $[M-H]^-$ ion of nonanedioic acid. Accurate mass measurements using peak matching techniques demonstrated that the $[M-H]^-$ ions were consistent with empirical formulae of $C_9H_{15}O_3$ (9-oxononanoic acid) and $C_9H_{15}O_4$ (nonanedioic acid) respectively. From the above data, it is evident that unsaturated fatty acids undergo ozonolysis followed by some degree of oxidation during treatment with ozone under aqueous conditions (Table 1).

3.3 ESTERS

The following esters were treated with chlorine under the conditions described in Section 2.3; triethylphosphate, methyl tetradecanoate, dibutyl adipate, methyl hexadec-9-enoate, dibutylphthalate, methyl octadec-9-enoate, methyl octadecanoate, tris (butoxyethyl) phosphate and di(2-ethylhexyl)-phthalate.

Of these compounds, only the unsaturated esters, namely, methyl hex-9-enoate and methyl octadec-9-enoate were consumed. The reaction mixtures were extracted (see Section 2.4) and examined by GC and GC-MS which showed that one product was observed for each reaction. The mass spectra of the new peaks indicated that the products were chlorohydrin derivatives of the unsaturated esters (Table 1). Comparison of the mass spectra of the products with synthetic standards confirmed this assignment. As yet, no studies on the aqueous ozonation of the esters have been conducted.

3.4 SURFACTANTS

3.4.1 Nonionic surfactants

For the purposes of these studies it was necessary to separate single oligomers of nonylphenyl ethyoxylate from a commercial product containing a mixture of oligomers using preparative liquid chromatography (Section 2.1.4) so that the analyses could be simplified as much as possible.

Nonylphenyl heptakis ethoxylate (300 µg l^{-1}) was treated with either chlorine or ozone using the procedures described in Sections 2.4 or 2.6.

Analysis of the product solutions after chlorination using FAB-MS (positive ion mode) showed that whilst in the absence of bromide no products were formed, chlorination in the presence of bromide resulted in the formation of a brominated product (Figure 4 and Table 1). Analysis by HPLC (Section 2.1.5) confirmed that the nonylphenyl heptakis ethoxylate (NP7), was only consumed (by about 50-60%) during chlorination in the presence of bromide and only a single product was observed.

Further confirmation of the reactivity of nonylphenyl ethoxylates with chlorine in the presence of bromide was provided when a mixture of nonylphenyl hexakis (NP 6) and octakis ethoxylates (NP 8) (250 µg l^{-1}) and also the parent mixture of the nonionic surfactant, namely Synperonic NP10, were used as substrates for the reaction.

After ozonation, neither nonylphenyl heptakis ethoxylate (NP7) (300 µg l^{-1}) nor any products derived from the substrate were observed in the product solution. As yet, no HPLC analysis of the reaction solution has been undertaken.

3.4.2 Anionic surfactants

A single isomer of sodium dodecylbenzenesulphonate (250 µg l^{-1}) was treated with chlorine and with ozone. Analysis by FAB-MS indicated that the substrate did not react with either oxidant under the conditions used. However, as stated previously, FAB-MS analysis is not quantitative. Consequently another method is required, probably HPLC analysis, to establish whether sodium dodecylbenzenesulphonate is consumed or not.

3.4.3 Cationic surfactants

The reactivities of three types of cationic surfactants towards ozone and chlorine, in the presence or absence of bromide, were investigated using similar procedures to those described in Sections 3.4.1 and 3.4.2. Neither cetylpyridinium chloride (500 µg l^{-1}) nor Arquad 2HT (500 µg l^{-1}) reacted with either ozone or chlorine and chlorine in the presence of bromide. However, Prapagen WKT (500 µg l^{-1}) (a mixture of dimethyl dialkyl and trimethyl alkyl ammonium chlorides in which some of the alkyl chains are unsaturated) (Figure 5) reacted extensively with both chlorine and ozone.

After chlorination in the presence and absence of bromide, FAB-MS analyses showed that peaks corresponding to unsaturated substrates at m/z 310, 520, 546 and 548 were smaller relative to peaks representing the corresponding saturated substrates at m/z 312, 522 and 550 respectively. Halogenated products were tentatively identified in product solutions obtained in the presence and absence of bromide (Table 1). After chlorination in the absence of bromide, new pairs of peaks corresponding to the addition of HOCl to m/z 310, 520 and 548 at m/z 362, 364 (M^+ ions for ^{35}Cl and ^{37}Cl $(CH_3)_3{}^+N(C_{18}H_{36}OCl)$); 572 and

574 (M^+ ions for ^{35}Cl and ^{37}Cl $(CH_3)_2{}^+N(C_{18}H_{36}OCl)(C_{16}H_{33})$); 602 ($M^+$ ions for ^{35}Cl and $^{37}Cl(CH_3)_2{}^+N(C_{18}H_{36}OCl)(C_{18}H_{37})$) were observed in the FAB mass spectrum.

After chlorination in the presence of bromide, new peaks were observed at m/z 406, 408 (310 + HOBr); 616, 618 (520 + HOBr); and 644, 616 (548 + HOBr). The identifications indicated are tentative and await accurate mass measurements to confirm the assignments. In a previous experiment, it was observed that when Prapagen WKT was chlorinated in the presence of bromide and the product mixture was subsequently exposed to alkaline pH (ca 9-10), no halogenated products were found. However, a new peak was observed at m/z 536. Accurate mass measurement showed that this was consistent with a compound having the formula $(CH_3)_2{}^+N(C_{18}H_{35}O)(C_{16}H_{33})$. It is likely that this compound is an epoxide formed by the elimination of hydrogen bromide from the corresponding bromohydrin at alkaline pH. There are many examples of this type of reaction in the literature(5,6). It is possible that in some chlorinated waters where the pH is high such epoxides are likely to be found.

After ozonation, the peaks corresponding to the unsaturated substrates in the FAB mass spectrum had almost completely disappeared. In addition, a series of new peaks at m/z 426, 440, 454 and 468 were observed. Accurate mass measurements of the product peaks indicated that the compositions of these compounds were consistent with the products being carboxylic acid derivatives of the substrates.

Examination of ether extracts of reaction mixtures acidified to pH2 by GC and GC-MS (after methylation) with diazomethane indicate that aldehydes (especially n-nonanal) and carboxylic acids (heptanoic, octanoic, nonanoic and decanoic) are generated as products (see Table 1)

3.5 PESTICIDES

3.5.1 Permethrin

No consumption of a commercial mixture of <u>cis</u> and <u>trans</u> permethrin (Figure 6) (10 µg l^{-1}) substrates was observed after chlorination (8 mg l^{-1} chlorine) in either the presence or absence of bromide (5 mg l^{-1}). Neither were any products observed when the reaction solutions were examined by GC-MS.

In contrast, ozone (5 mg l^{-1}) after 30 minutes led to over 90% consumption of both cis and trans isomers. However, no products of ozonation were detected by the techniques applied.

3.6 CHLORINE DEMAND AS A TOOL FOR ESTABLISHING THE REACTIVITY OF CHLORINE WITH ORGANIC CHEMICALS IN WATER

The analytical methods required to quantify the reactivity of organic compounds with chlorine usually have to be tailored to each substrate and are consequently time-consuming and expensive. For some chemicals of interest specific analytical methods do not exist and would need to be developed. The purpose of the work described below was to establish a simpler and quicker method for screening organics for reactivity with chlorine by measuring the chlorine demand of an aqueous solution of the organic compound concerned. Chemicals which show significant reactivity may justify more detailed investigations using more elaborate analytical procedures. (Due to the instability of its aqueous solutions, this approach is not readily applicable to ozone.)

3.6.1 Selected chemicals

Table 2 lists the compounds which were selected for investigation. Some of these compounds were already known to be reactive towards aqueous chlorine and were included as reference compounds.
All the compounds selected were of analytical grade and from various commercial sources. The list also includes pesticides which were

selected due to the lack of information concerning their reactivity towards aqueous chlorine.

3.6.2 Water treatment chemicals

In addition to the compounds discussed above, a range of polyacrylamides (used as flocculating agents during water treatment) was also studied.

The water treatment chemicals, supplied by three companies, and their physico-chemical characteristics are presented in Table 3. Three compounds from each supplier, which covered the range of ionic characteristics, were selected for testing with this system using the same concentrations of substrate (10 mg l^{-1}) and chlorine (1 mg l^{-1}) previously described.

3.6.3 Reactivity of selected organic chemicals

The data obtained for each compound was expressed as a percentage of the initial chlorine concentration (IC) (t=0 reading) and graphically represented by plotting percentage of initial chlorine versus time. For comparison the control was also plotted on the same graph. Examples of the plots obtained are given in Figures 8, 9, 10, 11 and 12 for phenol, aniline, EDTA, ethylene glycol and formaldehyde respectively. The time taken for the residual chlorine to fall to 75% of the initial chlorine concentration (IC75) was calculated for each compound and used to produce a ranking order of reactivity. Graphical representation of the data obtained for most of the compounds revealed that the IC75 was obtained during the period giving the maximum slope gradient, ie during the maximum rate of reaction, and was therefore, a better index of reactivity than the IC remaining after 24 hours.

Table 4 gives the IC75 values for the compounds investigated and also the percentage of initial chlorine after 24 hours to give a ranking order to the compounds of low reactivity. The water treatment chemicals have also been included in this table to give an indication of their reactivity in comparison to the other chemicals.

The results suggest that this system can effectively identify those compounds of high reactivity, ie those that are very likely to react with chlorine under water treatment conditions. However, uncertainty arises when assessing compounds that show little or no reactivity, such as Synperonic NP10. Although reactivity appears minimal, it is possible that under different conditions at the treatment works, ie low substrate-to-chlorine ratio, they may react with aqueous chlorine to some degree.

3.6.4 Reactivity of water treatment chemicals

Table 5 contains the data for all of the treatment chemicals tested. The information is separated into the individual company products and, as can be seen, reactivity appears to be dependent upon ionic character.

From the results obtained it would appear that the highly anionic water treatment chemicals are less reactive towards aqueous chlorine than the other compounds. Consideration of the IC75 values obtained suggest that there is little difference in reactivity between the non-ionic, and low or medium anionic compounds.

The highly anionic A45 reacts at about 1/30 as fast as the highly cationic LT31 (not based on acrylamide) suggesting a trend in reactivity from cationic (high reactivity) to anionic (low reactivity). Although it must be emphasised that all of the water treatment chemicals tested were reactive towards aqueous chlorine under these conditions.

SECTION 4 - DISCUSSION

No reaction was observed between either chlorine or ozone and any of the saturated substrates, alkanes, fatty acids, esters, surfactants. Although both chlorine and ozone can react with saturated substrates such reactions generally involve free radical species and require conditions (such as high temperatures and pressures and UV irradiation) which do not occur during drinking water treatment.

Addition of hypohalous acid across carbon-carbon double bonds to form halohydrins (Figure 1) is a well known reaction(5,7) and it is therefore not surprising that halohydrins are produced on aqueous chlorination of alkenes, or other compounds such as fatty acids, esters and surfactants - provided they contain some unsaturation. Several authors have reported the formation of chlorohydrins from unsaturated substrates under aqueous conditions; Carlson and Caple(8) studied the chlorination of octadec-9-enoic acid (oleic acid) at various pH; Ghanbari et al(9) studied the chlorination of unsaturated acids and esters. However, neither of these studies used typical water treatment conditions. Morris(10) speculated that the formation of chlorohydrins under water treatment conditions would be too slow to be of significance unless the unsaturated substrate was activated in some way. The results presented here show that rapid consumption of alkenes, and other unsaturated substrates, takes place under conditions likely to be found during water treatment. At neutral pH halohydrins are the only observed products, but at pH9 the halohydrins can form epoxides (Figure 1). This was encountered with Prapagen (see Section 3.4.3). Not all unsaturated compounds seem to react, eg permethrin, and thus the presence of unsaturation within a molecule does not guarantee that that compound will react with chlorine. However, appropriate techniques for the analysis of halohydrins or epoxides have yet to be applied to drinking water samples.

Mechanisms proposed for the reaction of ozone with organic compounds have been divided into two categories(11). The conditions used in this study (pH 5.5-6.5) should result in reactions via direct mechanisms with ozone, which are specific in nature and relatively slow.

Direct reactions of ozone are a consequence of the resonance structure of the ozone molecule which forms an electric dipole. This form is insufficiently reactive to attack saturated carbon chains as is demonstrated by the lack of consumption observed of alkanes, saturated fatty acids and saturated surfactants. In contrast, the direct reaction of ozone is well illustrated by its 1,3-dipolar cyclo addition across unsaturated double bonds such as alkenes, unsaturated fatty acids and unsaturated surfactants, in which an ozonide (1,2,3-trioxolane) is first produced (Figure 2). In aqueous solution, the ozonide reacts further to form a hydroxy hydroperoxide(12) which undergoes further decomposition to form hydrogen peroxide and carbonyl compounds (aldehydes or ketones). Aldehydes so formed can be oxidised further to form carboxylic acids and peracids. This last stage was found during the ozonation of the unsaturated cationic surfactant, Prapagen WKT, since only products bearing a carboxylic acid group were observed. The ozonation of unsaturated fatty acids resulted in the formation of aldehydes, the corresponding carboxylic acids, an aldehydo acid and its corresponding di-acid. Only aldehydes were found in this study from the ozonation of alkenes although acids may have been produced because these were not analysed for.

Chlorine did not react with aromatic hydrocarbons in the manner expected from previously published studies. Oyler et al(13,14), Carlson et al(8) and Smith et al(15) all reported that most of the hydrocarbons examined in this study reacted with chlorine under aqueous conditions to yield chlorine- or oxygen-containing products (Figure 3). However, examination of the conditions employed in these earlier studies(16) revealed that in most cases the reactions were carried out under conditions of substrate and chlorine concentrations, pH and contact time different from those used in this study and consequently further removed from conditions likely to be found during drinking water treatment.

The formation of mono- and di-chlorinated pyrenes during chlorination at pH7 is surprising, since many of the above studies indicated that chlorinated products tend to be formed at low pH with oxidation products being produced at neutral pH and above. It should be noted that the chlorinated pyrenes identified accounted for about 50% of the observed pyrene consumption and, consequently, there must have been other product(s) formed which were not amenable to the extraction/identification methods used.

The identification of only brominated products from the chlorination of nonylphenyl ethoxylates (in the presence of bromide, Figure 4), contrasts with the study of Rivera et al(17). These authors reported the occurrence of both chlorinated and brominated derivatives of nonylphenyl ethoxylates in extracts of drinking water but not in the corresponding untreated raw water.

The lack of reactivity of permethrin (a compound with some similar structural features to nonylphenyl ethoxylates) towards chlorine in the presence and absence of bromide is surprising. At present, there is no obvious reason to account for the stability of permethrins under the reaction conditions used. Lack of reaction with the double bond in the side chain could be explained by steric factors. However, by analogy with nonylphenylethoxylates, some reaction of the aromatic rings with chlorine, especially in the presence of bromide, could be expected.

Various authors have described the reaction between ozone and aromatic compounds in terms of a two or three stage process(18,19). The first stage involves the formation of polyhydroxy aromatic species and loss of some or all of the aromaticity via electrophilic attack. Subsequent stages involve ozonation of the non-aromatic products of the first stage. In the present study, the tentative identification of phthalic acid from the ozonation of naphthalene and fluoren-9-one from fluorene (Figure 7) are consistent with observations reported in the literature(19,20,21). The fact that no products were observed from the ozonation of either fluoranthene or pyrene, although both were extensively consumed, suggests that the products were not amenable to the analytical techniques used.

Nonylphenyl heptakis ethoxylate was totally consumed by ozonation. Although no products were observed FAB-MS work is under way to examine the products of reaction by GC and LC methods.

The work on developing chlorine demand as a way of identifying substances that are likely to react provided useful findings and therefore may need to be studied further. Several chemicals likely to be found in water sources, and some water treatment chemicals were found to react. Some of these will be studied in more detail in on-going research at WRc. Some further investigation of the approach is needed, particularly on whether chemicals shown to be more or less inactive remain so under the high chlorine-to-chemical ratio that may exist under water treatment conditions, a condition difficult to simulate with the chlorine demand approach since the small changes in chlorine level likely would be difficult to measure. Also some further investigation of whether some chemicals merely catalyse decomposition of aqueous chlorine is needed.

SECTION 5 - CONCLUSIONS

The data in the scientific literature on the reactivity of chlorine and ozone with organic substances and the likely reaction products must be treated with caution when trying to assess the effects of water treatment disinfection. This is because the conditions used to produce the data were in many circumstances far removed from those related to water treatment. Consequently, some of our findings in the laboratory, produced under conditions related as far as possible to water treatment practice, disagreed with data in the literature.

Some types of potential or known water pollutants were shown to be unreactive and would not be expected to be of concern with respect to production of byproducts, eg saturated hydrocarbons, anionic and some cationic surfactants and, in the case of chlorination, permethrin. However, a variety of potential or known water pollutants did react, including unsaturated fatty acids, aromatic hydrocarbons, unsaturated cationic surfactants, and non-ionic surfactants. The reactivities of the substances studied are summarised in Table 1.

In some cases where the organic chemical reacted, products of the reaction were identified. However, in some case little data appeared to be available on their general toxicity and it is likely that many of the by-products have never been investigated or even produced as pure substances.

The presence of bromide during chlorination was an important factor. Although this possibility was known already to some extent, from the generation of brominated haloforms in the production of haloforms during water treatment chlorination, in this work the presence of bromide was often crucial. In certain cases bromide led either to more extensive consumption of organic chemical during chlorination or even reaction when no reaction could be found in its absence.

The data produced in this work should enable better prediction of the likely effects of chlorine and ozone, when applied during water treatment, on organic chemicals occurring in raw water. Such chemicals may occur as common constituents or specific pollutants from pollution incidents. However, more substances need to be studied and some anomolous behaviour needs to be explained to improve ability to predict. For example, in the latter case why is the double bond in permethrin unreactive to chlorine when in other chemicals it led to extensive reaction.

The work on using chlorine demand as a means of quickly assessing which chemicals react markedly with chlorine, and thus avoiding unnecessary analytical development work, gave promising results and indicated several chemicals likely to be found in water sources and some water treatment chemicals that need to be studied in more detail.

Ozone is currently proposed as an alternative to chlorine largely because of the chlorination byproducts produced during disinfection. However, ozone also produces byproducts - of different character - and consequently needs to be investigated thoroughly before major changes in disinfection policy are undertaken

SECTION 6 - RECOMMENDATIONS

Work on the reaction of chlorine and ozone with further organic chemicals that are either common constituents of raw water or frequently involved in pollution incidents is needed.

Work is needed to determine whether or not products of chlorine and ozone disinfection mentioned in this report can be found in treated waters.

Studies are needed to explain why double bonds in some organic chemicals (eg permethrin) do not react as expected with chlorine. The influence of important inorganic species, on the effects of disinfectants on organic substances needs further investigation. In particular, the role of bromide in chlorination reactions needs more study. In addition the effect on bicarbonate ions on the nature of ozonation byproducts (not covered in this report) needs investigation. However, more study of the effects of pH (between a range of 6-9) is necessary.

Further work on rapid means of assessing general reactivity of chemicals (particularly those difficult to measure in water, such as treatment chemicals) towards disinfectants has been justified. The chemicals shown by the chlorine demand work to have marked reactivity to chlorine, need to be studied further to confirm the reactivity and assess the significance of the byproducts generated.

Many of the recommendations are being followed in on-going research, funded by the Department of the Environment, and the findings will be disseminated at a later stage.

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Table 1. Summary of reactivities of organic compounds towards chlorine or ozone

	Reactivities*		Products		Relevant Section
Compounds	Chlorine	Ozone	Chlorine	Ozone	
Alkanes	0	0	0	0	3.1.1
Alkenes	1	2	chlorohydrins	aldehydes	3.1.1
Aromatic hydrocarbons					
toluene	0	0	0	0	
m-xylene	0	0	0	0	
o/p-xylene	0	0	0	0	3.1.2
naphthalene	0	2	0	phthalic acid	
fluorene	0	1	0	fluoren-9-one	
phenanthene	0	2	0	?	
fluoranthene	0	2	0	?	
pyrene	1	2	chloropyrenes	?	
Fatty acids					
octanoic	0	0	0	0	
decanoic	0	0	0	0	
dodecanoic	0	0	0	0	
tetradecanoic	0	0	0	0	
hexadec-9-enoic	2	2	chlorohydrin	heptanal heptanoic acid 9-oxononanoic acid nonanedioic acid	3.2
hexadecanoic	0	0	0	0	
heptadecanoic	0	0	0	0	
octa dec-9,12-dienoic	2	2	bis chlorohydrin	hexanal hexanoic acid 9-oxononanoic acid nonanedioic acid	
octadecanoic	0	0	0	0	

Table 1. continued

	Reactivities*		Products		Relevant Section
Compounds	Chlorine	Ozone	Chlorine	Ozone	
Esters					
dibutyl adipate	0	-	0	-	
methyl hexadec-9-enoate	2	-	chlorohydrin	-	
dibutyl phthalate	0	-	0	-	
methyl octadec-9-enoate	2	-	chlorohydrin	-	3.3
methyl octadecanoate	0	-	0	-	
tris (butoxyethyl) phosphate	0	-	0	-	
dioctyl phthalate	0	-	0	-	
Nonionic surfactants					
NP6	1	-	bromoderivative	-	
NP7	1	2	bromoderivative	?	3.4.1
NP8	1	-	bromoderivative	-	
Cationic surfactants					
Prapagen WKT unsaturated components	2	2	halohydrins	aldehydes, carboxylic acids, 'quaternary' carboxylic acids	3.4.3
saturated component	0	0	0	0	
Arquad 2HT	0	0	-	-	3.4.3
cetylpyridinium	0	0	-	-	
Anionic surfactant					
SDBS	0	0	-	-	3.4.2
Permethrins					
cis	0	2	0	?	3.5.1
trans	0	2	0	?	

* 0 = no detected reaction
1 = partial reaction
2 = complete or extensive reaction

? = products not characterised
\- = not determined

Table 2. Compounds selected for determination of chlorine demand.

- ANILINE
- ATRAZINE
- CHLORTOLURON
- CREOSOTE
- ETHANEDIOL
- FORMALDEHYDE
- ISOPROTURON
- MALACHITE GREEN
- MCPA
- MELAMINE
- METHANOL
- NAPHTHALENE
- NITRILOTRIACETIC ACID
- PHENOL
- POLYETHYLENE GLYCOL
- m-XYLENE
- SIMAZINE
- SYNPERONIC NP10
- TOLUENE
- UREA
- SODIUM DODECYLBENZENESULPHATE
- 2,4,5-TRICHLOROPHENOXYACETIC ACID
- 2,4-DICHLOROPHENOXYACETIC ACID
- ETHYLENEDIMINETETRAACETIC ACID (DISODIUM SALT)
- ETHYLENEDIMINETETRAACETIC ACID (TETRA SODIUM SALT)

Table 3. **Polyacrylamide water treatment chemicals and their physico-chemical properties supplied by three commercial companies.**

FOSPUR LIMITED

High molecular weight polyacrylamides agents

C330*	Cationic character
N50*	Non-ionic character
N100	Trace anionic character
A30	Low anionic character
A33	Low/medium anionic character
A36*	Medium anionic character
A39	Medium/High anionic character
A45*	High anionic character

NALFLOC LIMITED

High molecular weight polyacrylamides

A378*	Cationic character
A3701*	Non-ionic character
A3721*	Anionic character
A3731*	Strongly anionic character

ALLIED COLLOIDS LIMITED

Ultra high molecular weight polyacrylamides

LT27	Anionic character
LT22s	Medium/low cationic character

High molecular weight polyacrylamides

LT26*	Anionic character
LT20*	Non-ionic character
LT25	Low/medium anionic character

Medium molecular weight polyacrylamides

LT22	Medium/low cationic character
LT24*	Cationic character

Liquid grade polyelectrolytes

LT31*	High cationic character (not based on polyacrylamide)

* Chemicals selected for testing

Table 4. Ranking order of compounds investigated based upon their respective IC75 values.

IC75	Compound	% IC remaining after 24 hours
.14 hr	Aniline	8.18
.27 hr	Phenol	3.12
.29 hr	Creosote	3.82
.40 hr	LT31 liquid cationic	12.0
.42 hr	EDTA Tetra sodium salt	7.08
.42 hr	EDTA Di sodium salt	9.63
.82 hr	LT22 cationic	23.7
.85 hr	A3701 non-ionic	28.1
.85 hr	A36 med anionic	39.4
.93 hr	A378 cationic	24.1
.94 hr	LT20 non ionic	28.0
1.0 hr	N50 non ionic	18.2
1.4 hr	LT26 anionic	56.4
1.4 hr	A330 cationic	43.2
1.7 hr	A3721 anionic	38.6
1.7 hr	Nitrilotriacetic acid	14.3
2.2 hr	Urea	9.48
2.7 hr	Malachite green	15.3
3.5 hr	Toluene	50.4
4.1 hr	A3731 strongly anionic	43.5
11. hr	A45 high anionic	58.7
22. hr	Synperonic NP10	73.9
>24 hr	Atrazine	77.7
>24 hr	Isoproturon	82.1
>24 hr	MCPA	83.7
>24 hr	Polyethylene glycol	84.9
>24 hr	2,4,D	85.0
>24 hr	Simazine	85.8
>24 hr	2,4,5,T	86.4
>24 hr	Chlortoluron	86.8
>24 hr	m-Xylene	89.7
>24 hr	SDBS	90.9
>24 hr	Formaldehyde	91.3
>24 hr	Methanol	94.7
>24 hr	Naphthalene	94.9
>24 hr	Melamine	96.1
>24 hr	Ethanediol	98.6

SDBS	Sodium dodecylbenzenesulphate
2,4,D	2,4-Dichlorophenoxyacetic acid
2,4,5,T	2,4,5-Trichlorophenoxyacetic acid
EDTA	Ethylenediaminetetraacetic acid
IC75	Time taken for total residual chlorine to fall to 75% of the initial total chlorine concentration taken at t=0.

Table 5. Reactivity data for the water treatment chemicals tested using the chlorine demand system.

Company	Compound	IC75
FOSPUR	A36 medium anionic	0.85
	N50 non-ionic	1.0
	C330 cationic	1.4
	A45 high anionic	11.0
NALFLOC	A3701 non-ionic	0.85
	A378 cationic	0.93
	A3721 anionic	1.7
	A3731 strongly anionic	4.1
ALLIED COLLOIDS	LT31 liquid cationic	0.4
	LT22 cationic	0.82
	LT20 non-ionic	0.94
	LT26 anionic	1.7

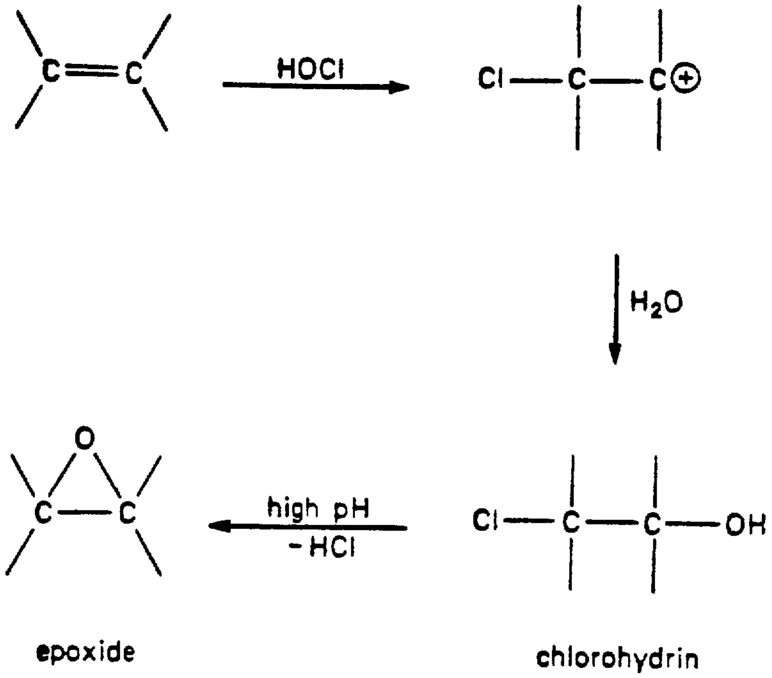


Figure 1. Addition Reaction of HOCl across a double bond.

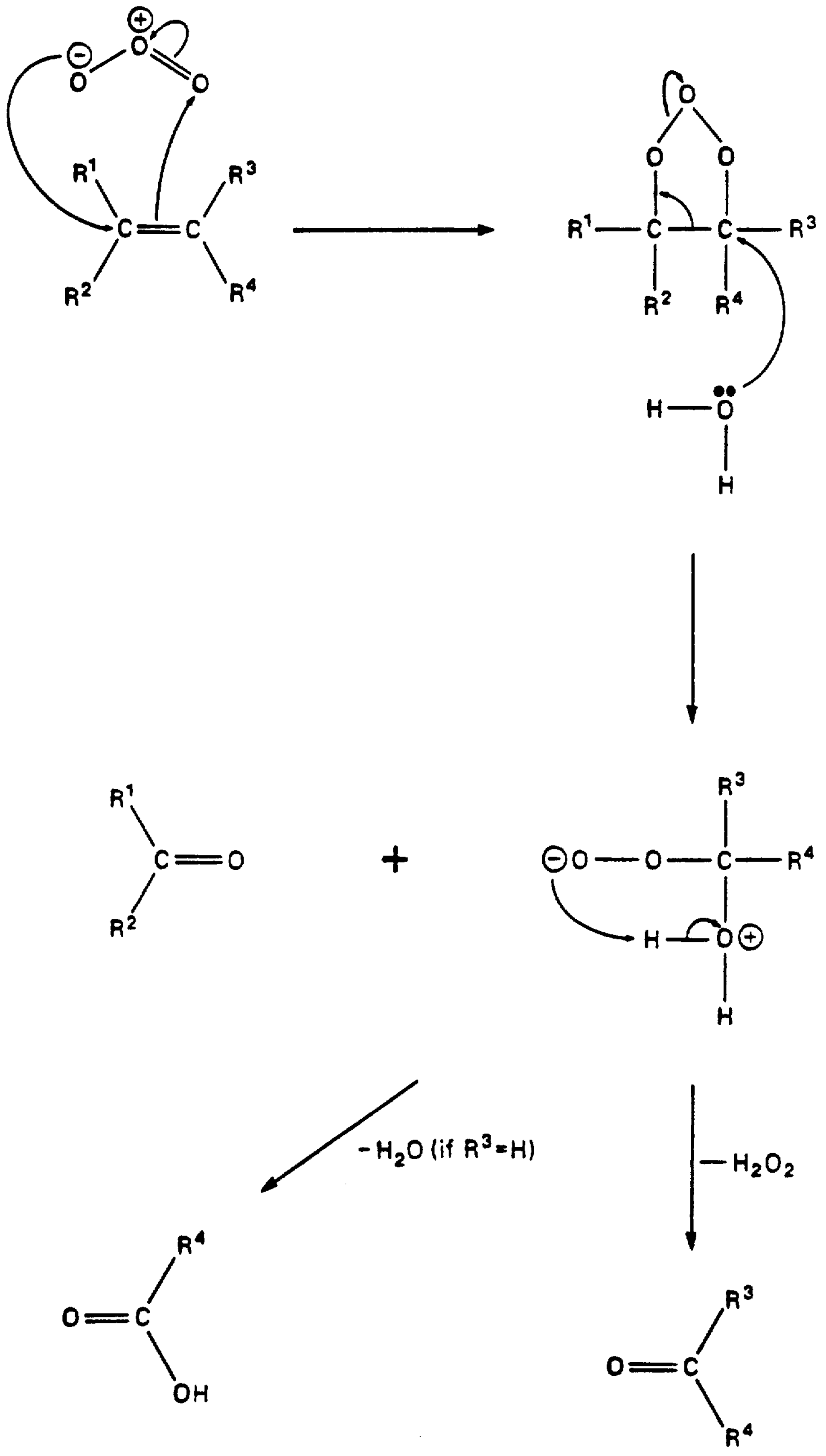


Figure 2. Reaction scheme for 1,3-dipolar cyclo-addition. (reference 11)

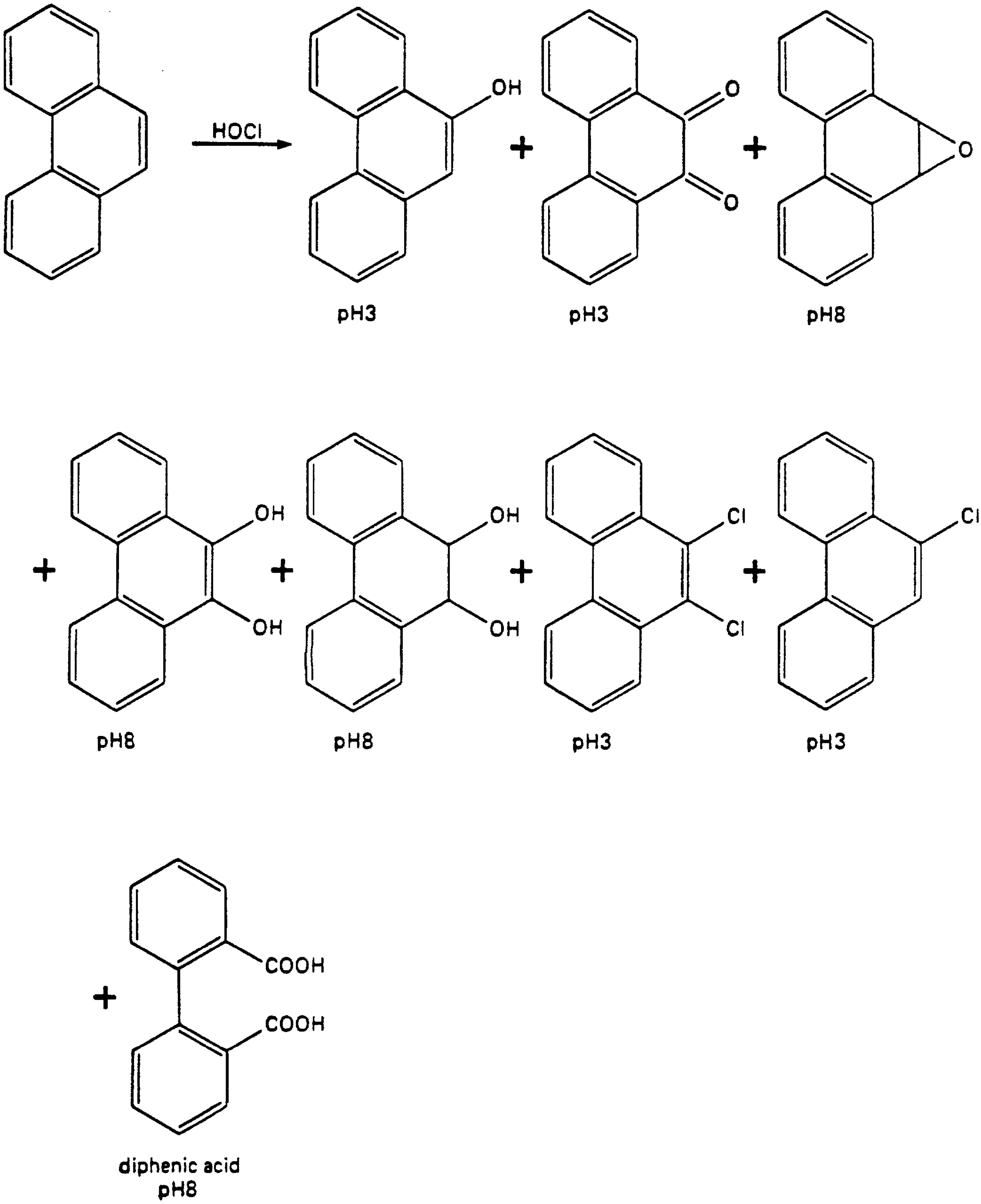
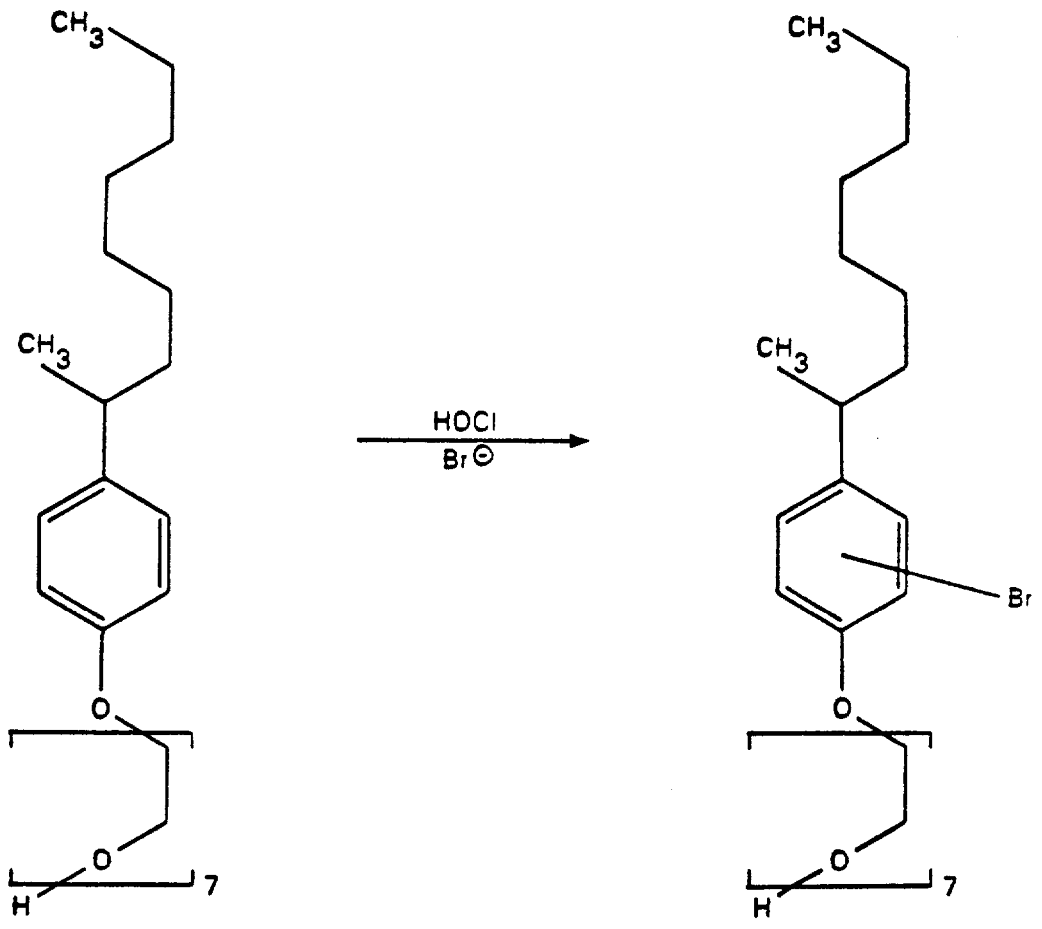
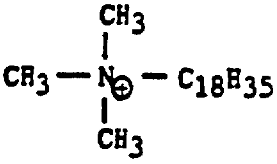


Figure 3. Reaction products from chlorination of phenanthrene at different pH's. (reference 13)



n = 4 - 16

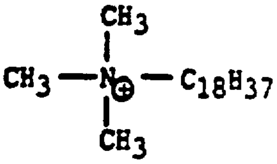
Figure 4. Chlorination of nonylphenyl heptakis ethoxylate in the presence of bromide.



$\mathrm{CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{N^{\oplus}}}-C_{18}H_{35}}$

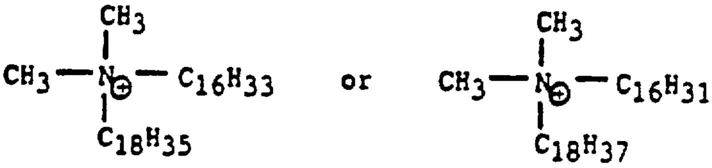
m/z 310

*



$\mathrm{CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{N^{\oplus}}}-C_{18}H_{37}}$

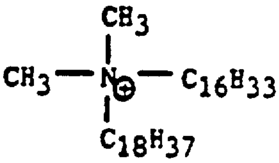
m/z 312



$\mathrm{CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle C_{18}H_{35}}{N^{\oplus}}}-C_{16}H_{33}}$ or $\mathrm{CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle C_{18}H_{37}}{N^{\oplus}}}-C_{16}H_{31}}$

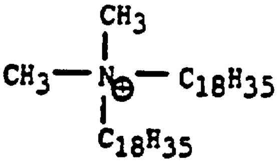
m/z 520

*



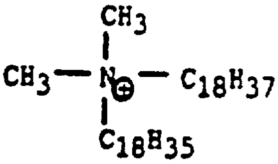
$\mathrm{CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle C_{18}H_{37}}{N^{\oplus}}}-C_{16}H_{33}}$

m/z 522



$\mathrm{CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle C_{18}H_{35}}{N^{\oplus}}}-C_{18}H_{35}}$

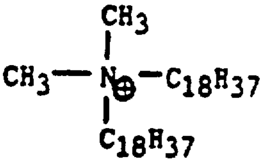
m/z 546



$\mathrm{CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle C_{18}H_{35}}{N^{\oplus}}}-C_{18}H_{37}}$

m/z 548

*



$\mathrm{CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle C_{18}H_{37}}{N^{\oplus}}}-C_{18}H_{37}}$

m/z 550

Figure 5. Structures of the cationic components of Prapagen WKT and Arquad 2HT and major ions in their mass spectra

* components found in Arquad 2HT

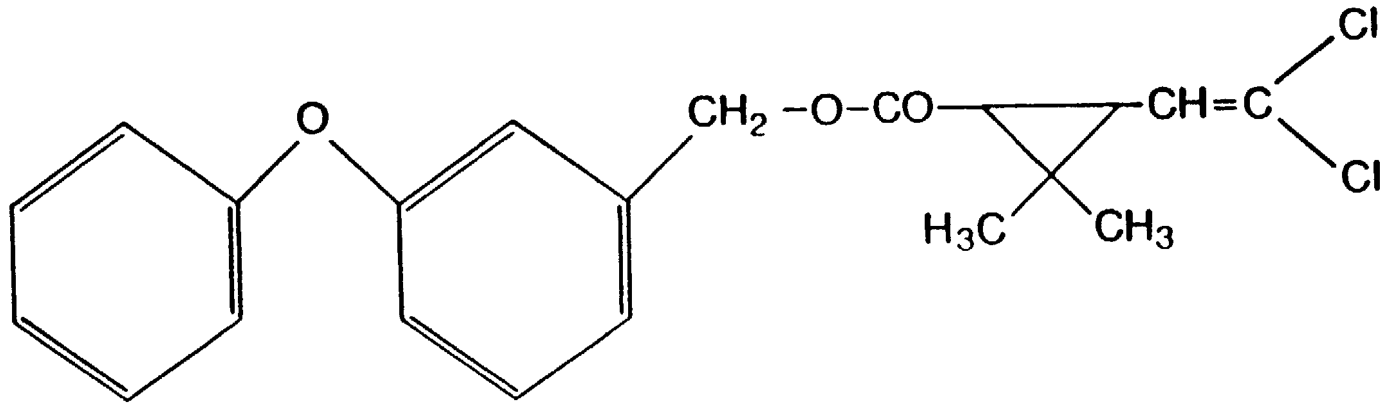


Figure 6. Permethrin

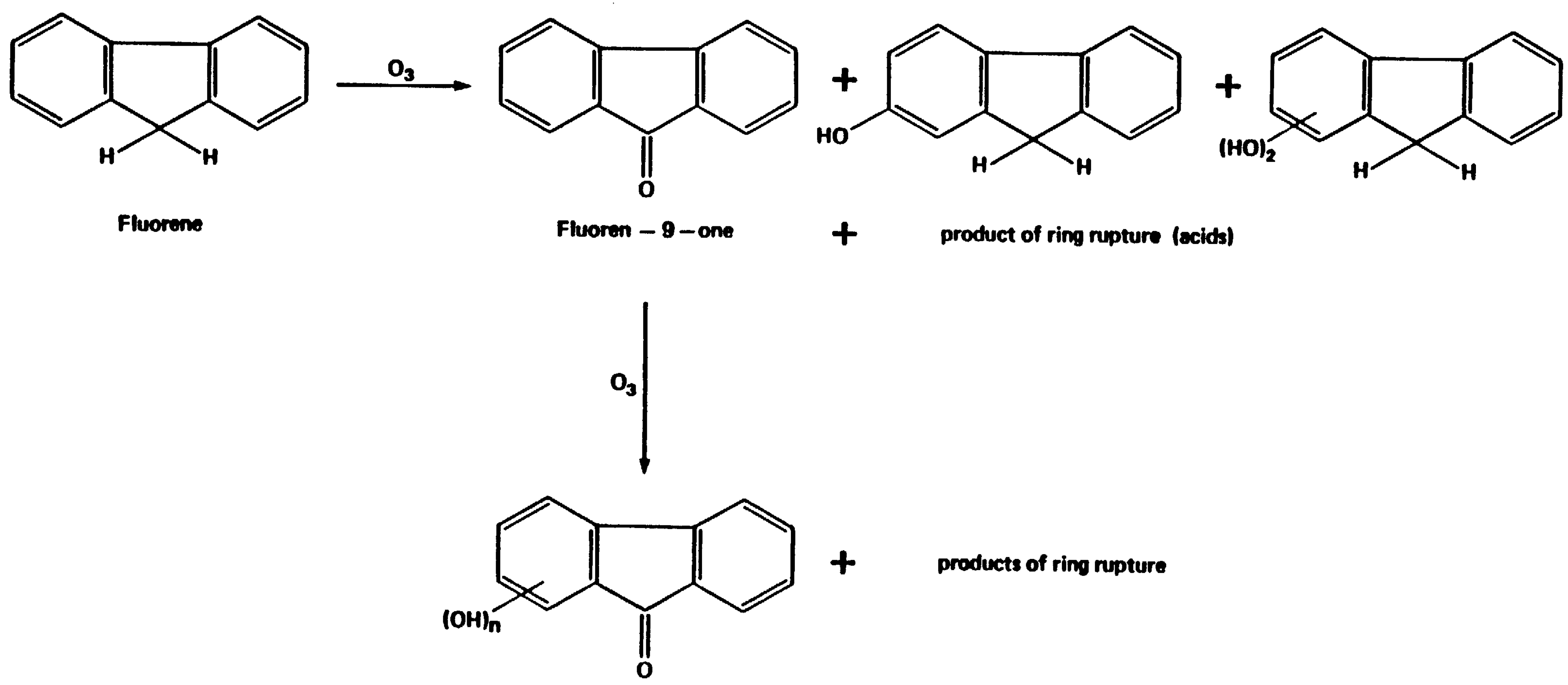


Figure 7. Reaction scheme for ozonation of fluorene and fluoren-9-one.
(reference 21)

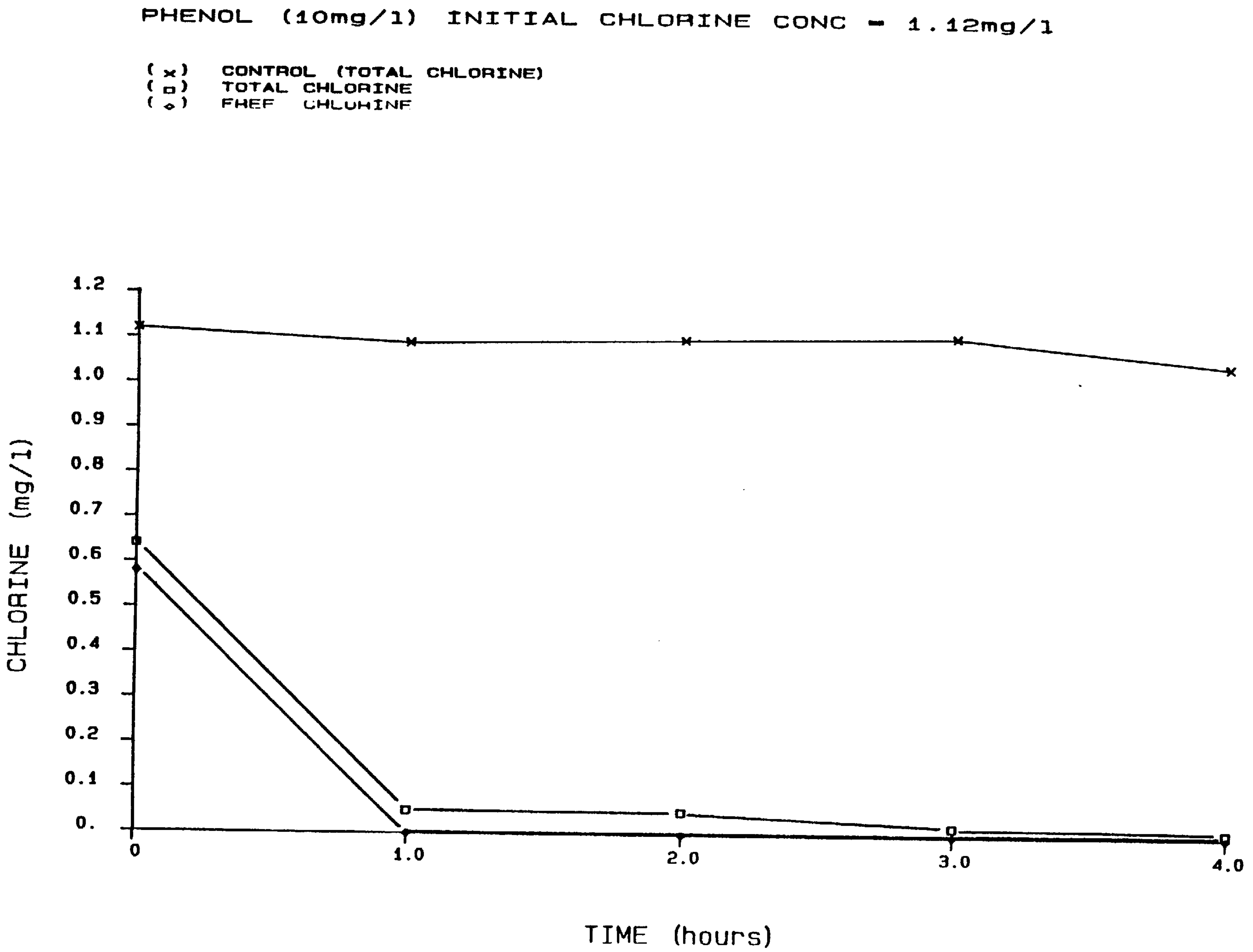


Figure 8. Chlorine demand of phenol.

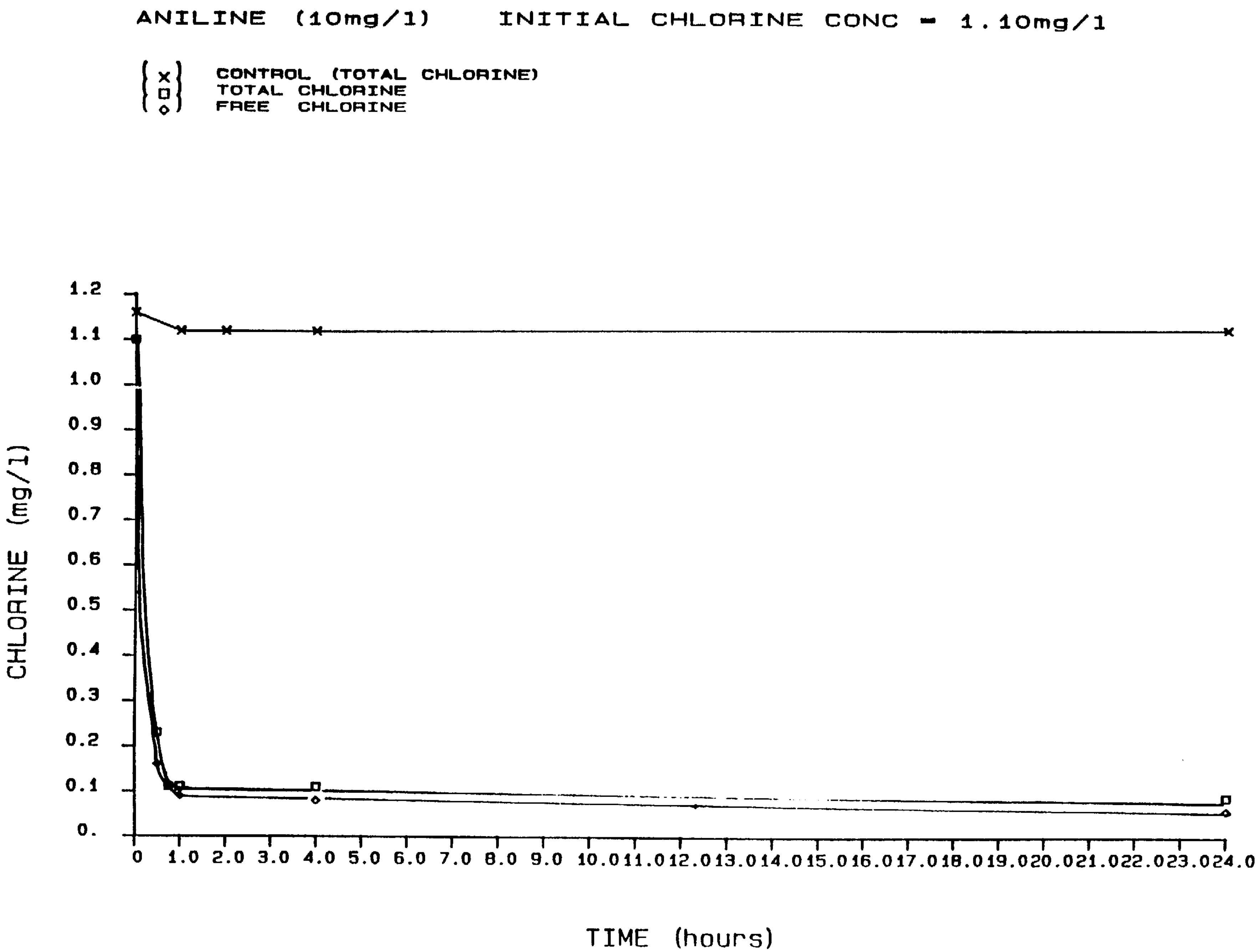


Figure 9. Chlorine demand of analine.

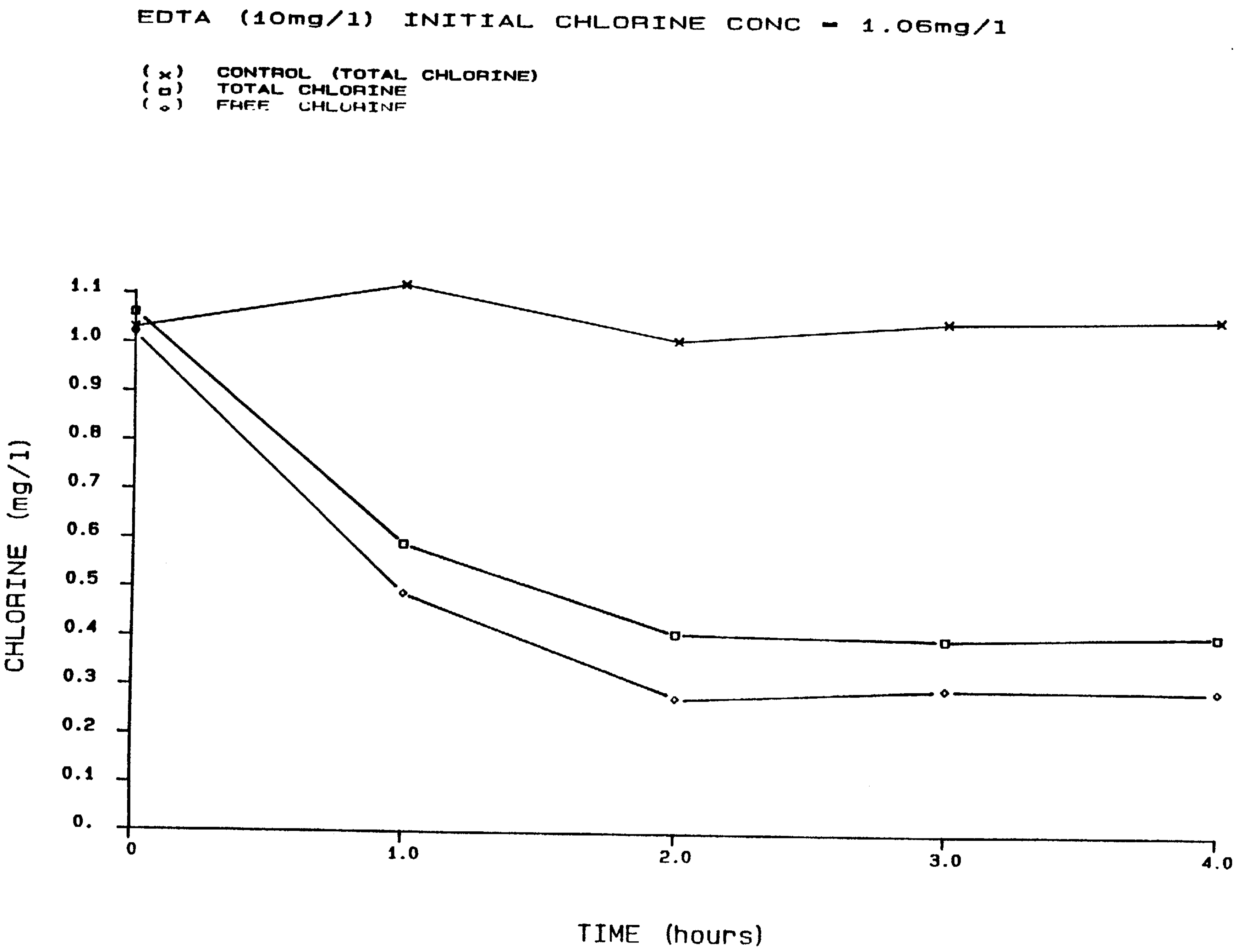


Figure 10. Chlorine demand of EDTA.

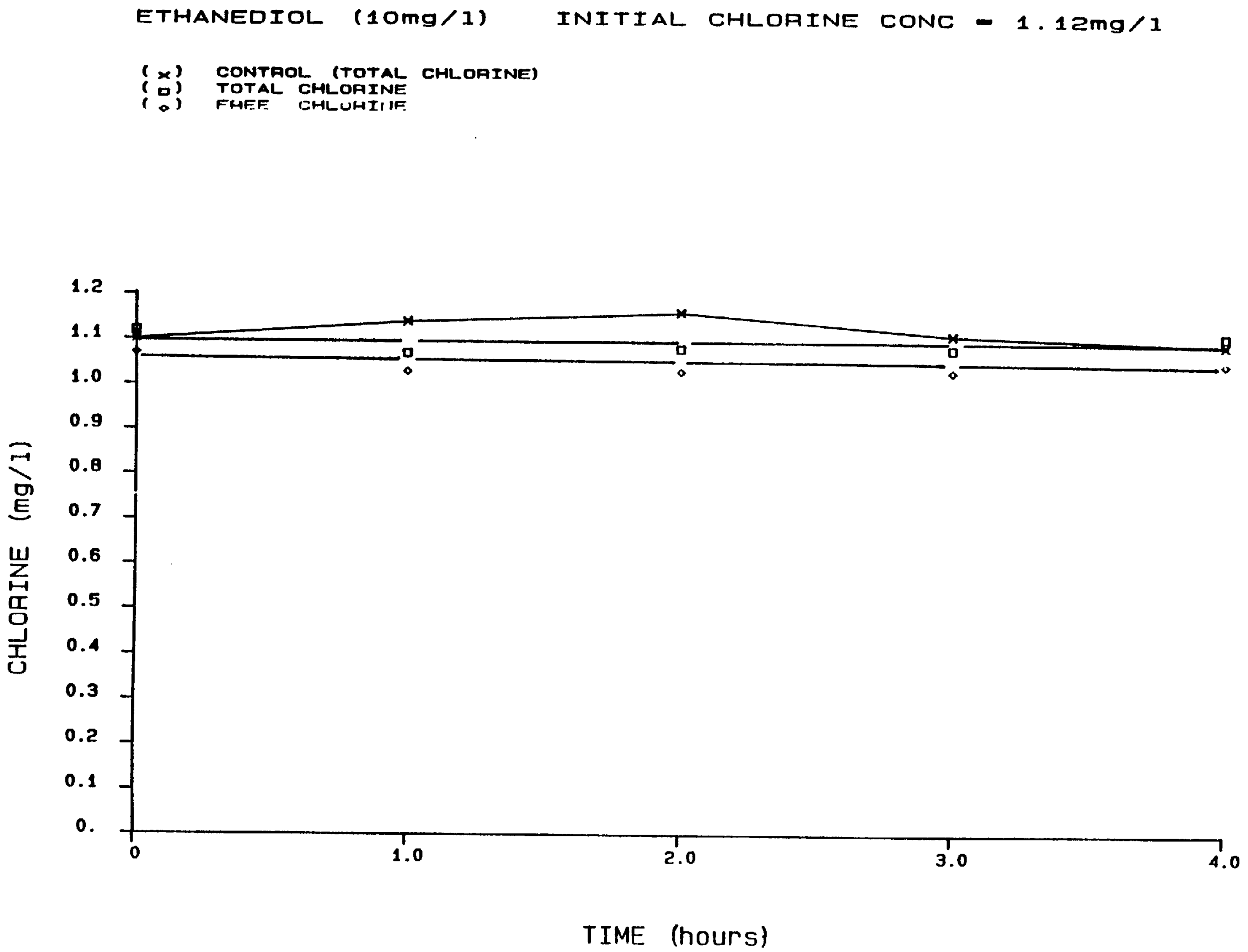


Figure 11. Chlorine demand of ethanediol (ie ethylene glycol).

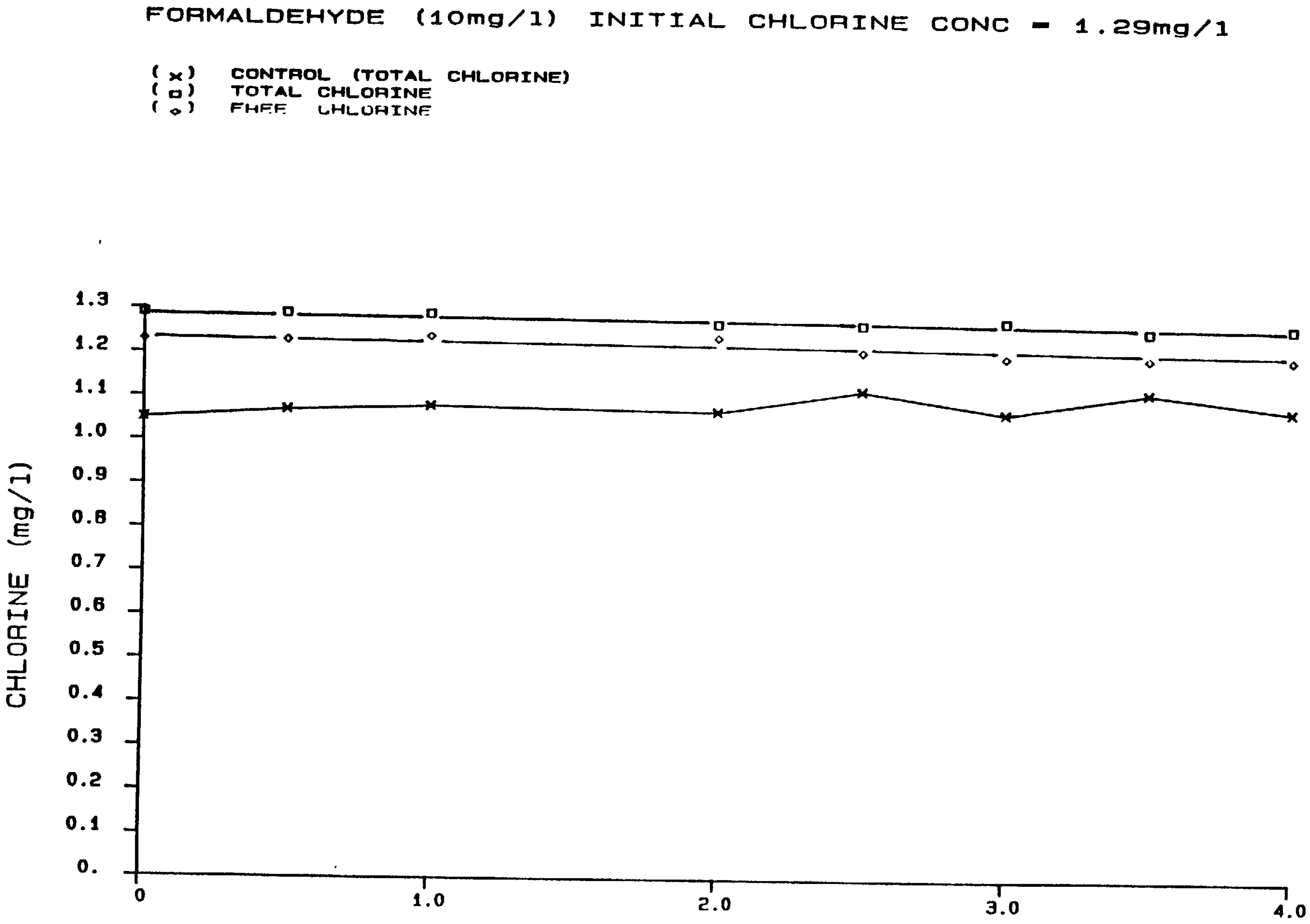


Figure 12 Chlorine demand of formaldehyde