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EFFECTS OF DISINFECTION ON ORGANIC SUBSTANCES IN WATER (EHT 9312 SLD)

Final report to the Water Research Centre of Work undertaken by Imperial College, October 1984 - February 1987

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PREFACE

In October 1984, the Department of the Environment placed a contract with the Water Research Centre to study the effects of disinfection of water by chlorine or ozone on organic substances likely to occur as contaminants in water.

That part of the contract dealing with ozone was sub-contracted by WRc to Public Health and Water Resource Engineering, sand Engineering Department at Imperial College. This report relates to that portion of the work undertaken at Imperial College and covers the period October 1984 to February 1987.

The work on chlorine undertaken by WRc ended in March 1987 and is reported separately.

SUMMARY

The long established practice of chlorination during water treatment in the UK and the potential hazard to human health of the THMs produced has led to a need to re-evaluate the use of alternative disinfectants. Ozone, currently widely used in Europe, the USA and Canada is believed to be the most promising candidate as an alternative disinfectant in UK potable water treatment.

In order to assess the effects of ozone on organic substances in water, systematic laboratory studies were undertaken to provide data on consumption of substrates, reaction pathways and end products.

This study investigated the effects of ozone on a large number of organic substances (including alkanes, alkenes, fatty acids, aromatics, polyaromatic hydrocarbons and surfactants) likely to occur as contaminants in water.

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1. INTRODUCTION

Recent development of specific and sensitive analytical techniques have enabled large numbers of organic compounds to be identified in water, at or below the microgram per litre levels. Certain compounds are naturally present, whilst others are of synthetic origin.

Natural organic material comprises the major part of the organic matter and is largely composed of humic substances. A great number of synthetic compounds are also present, however, concentrations of these contaminants are low (generally in the ngl^{-1} level) and rarely contribute more than 30% by weight to the total organic content. Compounds that have been detected include halogenated and non-halogented alkanes, alkenes, alicyclic, aromatic and polyaromatic compounds, trihalomethanes (THMs), polyaromatic hydrocarbons (PAHs) organochlorine pesticides, benzene and phenol (and their chlorinated and alkylated derivatives) petroleum hydrocarbons and phthalic acid esters (Bedding et al, 1982).

The chemistry of drinking water disinfection with respect to organic substances in raw water is poorly understood and consequently the impact of disinfection on natural and synthetic organic substances in water is uncertain. A major exception being the production of THMs and other halogenated conpounds during chlorination of raw waters largely through the action of chlorine on humic material present in the raw water (de Leer et al, 1985; Johnson et al, 1982; Bellar et al, 1974; Rook, 1974)

The long established practice of chlorination during water treatment in the UK and the potential hazard to human health of the THMs produced has led to a need to

re-evaluate the use of alternative disinfectants. Ozone, currently widely used in Europe, the USA and Canada is believed to be the most promising candidate as an alternative disinfectant in UK potable water treatment.

In order to assess the effects of ozone on organic substances in water, systematic laboratory studies are necessary to provide data on consumption of substrates, reaction pathways and end products. Although data exist on the reactions between ozone and organic compounds in water, results are often apparently contradictory and the majority of studies have not been carried out under realistic conditions of potable water treatment. However, some generalisations about the nature of reactions between organic compounds and ozone can be made.

Reaction may be direct [through 1,3-cycloaddition, electrophilic or nucleophilic attack (fig. 1)] or indirect, predominantly through the action of hydroxyl radicals (fig. 2). Direct reaction tends to be specific and occur at relatively slow reaction rates. Reaction frequently occurs at a C=C moiety to give 1,3-cycloaddition or ozonolysis across the double bond. Because of the time scales involved (minutes), most compounds are only partially degraded to other more oxygenated organic products such as aldehydes (or ketones in aromatic systems) and/or carboxylic acids. Depending on the nature of the compound and the contact time, aromatic compounds may either have the ring system preserved with increased functionality on the ring or the ring itself cleaved to yield aliphatic products or side chains (Patience, 1981).

Radical reactions occur as a result of the decomposition of ozone in water, predominantly to produce hydroxyl radicals. Such reactions occur at relatively fast rates and are less specific than direct reactions.

This study aimed to investigate the effects of ozone on a large number of organic substances (including alkanes, alkenes, fatty acids, aromatics, polyaromatic hydrocarbons and surfactants) likely to occur as contaminants in water and, where significant consumption was observed, to identify the products of reaction. Unlike the majority of studies previously undertaken, the individual substrate concentrations and ozone dose applied were selected to more closely represent those commonly encountered in potable water treatment. As experimental conditions used exert a major influence on the reactions occurring (eg. Gilbert, 1980), it is hoped that the results of this study will be representative of reaction products formed following ozonation in potable water treatment plants.

2. EXPERIMENTAL

An aqueous ozone solution was applied to selected organic substances and allowed to react for a fixed length of time in a static batch-type reactor. Substrates and reaction products were extracted, concentrated by evaporation and analysed by capillary column gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS).

Procedural details vary as modifications to the original experimental regime were carried out. Such modifications were primarily concerned with minimising contamination and increasing recovery efficiencies. Where such modifications occur, initial and subsequent procedures are given. The exact experimental conditions employed are indicated for each group of compounds investigated.

2.1 Reagents and preparation of glassware

2.1.1 Water

Purified water was used throughout for the production of aqueous ozone solutions and the cleaning of glassware.

Water was generally supplied by a Milli-Q system (Millipore, Harrow, UK) apart from a short period when work was carried out at the WRC, Medmenham. In the latter period, purified water was obtained by passing tap-water through ion exchange resins, Elga Cylinder Type C 10 (The Elga Group,Lane End,Bucks,UK) followed by passage of the deionised water produced through a column (90 x 5 cm) of granular activated carbon (Chemviron, Brussels,Belgium).

Aeration of Milli-Q water in the ozonation system contactor and subsequent sampling, extraction, GC and GC/MS analysis revealed negligible contamination (fig. 3).

2.1.2 Solvents

All solvents were HPLC grade (Rathburn Chemicals Ltd., Walkerburn, UK) and with the exception of diethyl ether (ether) which required redistillation from glass, were of sufficient purity to be used without further purification.

2.1.3

Organic compounds for ozonation and product identification

All organic compounds for investigation or to serve as standards for possible reaction products were supplied by the WRC and were of at least analytical grade quality. The exception being 9-oxo-nonanoic acid methyl ester which was synthesized by non-aqueous ozonation of hexadec-9-enoic methyl ester (see Appendix).

2.1.4

Preparation of glassware

New glassware was cleaned by soaking overnight in chromic acid solution and rinsing with Milli-Q water. Glassware was subsequently washed either with Decon 90 and rinsed with Milli-Q water or rinsed with methanol, heated at 100°C in an oven overnight and rinsed with the appropriate extraction solvent prior to use.

2.2.

Ozone Production

2.2.1

Ozone generation

Ozone was produced by the action of a silent electrical discharge on dry air using a Trailigaz Labo 76 ozone generator (Ozotech Ltd., Burgess Hill, Sussex, UK) of maximum generation capacity 9g O_3 h^{-1} at an outlet pressure of 0.5 bar.

Air at a pressure of between 5 and 6 bar, was supplied initially by compressor (Braun and Lubbe SYCGH 16-1) and later from a cylinder (BOC ltd., London) with an activated carbon filter fitted into the supply line. Ozone concentrations in the range 20-25 g/m^3 (under normal conditions of temperature and pressure) were typically found in the ozonized air (section 2.2.3)

2.2.2

Production of aqueous ozone solutions

Standard aqueous ozone solutions were prepared by passage of ozone through purified water contained in a recirculating bubble column contactor (fig. 4). Aqueous ozone concentrations of approximately 5 mg l^{-1} were typically produced after a 20 minute ozonation period (fig. 5) under the operating conditions given in Table 1.

Ozone concentrations in aqueous solution were determined as described in section 2.2.4

2.2.3

Determination of ozone production

The production of ozone from the ozone generator was checked intermittently and was calculated from the product of ozone concentration in ozonized air and the airflow.

Determination of the ozone concentration was based on the recommendations of the instrument manufacturer (Ozotech Ltd., 1986) and was determined by absorption into neutral potassium iodide solution, acidification with sulphuric acid and titration against sodium thiosulphate solution. Airflow was read directly from the instrument airflow meter.

2.2.4

Determination of ozone concentration in aqueous solution

Ozone concentration in aqueous solution was determined using the method described by Schechter (1973) involving spectrophotometric measurement at 352 nm of the triiodide ion liberated by ozone from neutral buffered 2% potassium iodide reagent.

2.2.5
Contamination problems

Gas chromatography analysis of ozonated Milli-Q water sample extracts (Procedure A, section 2.4.1) revealed a significant level of organic contamination with the majority of contaminant peaks appearing within the first 16 minutes of the GC run (fig.6). Such contamination prevented detailed identification of the products formed upon ozonation of the organic substrates under study. An investigation into the source of contamination was thus undertaken.

Initially, such aspects of the experimental procedure as purity of solvents, water supply and cleanliness of glassware were investigated as sources of contamination. The Milli-Q water supply system was found to be defective, however, replacement of the cartridges within the supply system improved contamination levels only marginally.

The air supply (Braun & Lubbe air compressor) was subsequently examined as a source of contamination. Bubbling air through the water sample in the contactor column produced few contaminant peaks in the resulting gas chromatogram (fig. 3). Such an observation suggested the contaminant peaks observed for ozonated water samples must correspond to compounds formed upon ozonation of a particular compound present in the air supply, water or ozoniser itself as the peaks did not appear in the gas chromatogram prior to ozonisation.

Use of an alternative air supply, namely an air cylinder, revealed a similar level of contamination (fig. 7) (although a carry over of contamination in the air lines cannot be discounted). A period of work at the WRC enabled the use of alternative air supply lines, air (air cylinder with an activated carbon filter fitted into the supply line), and water (section 2.1.1)

sources. Contaminant peaks were still evident (fig. 8), although the pattern observed was qualitatively different from that observed previously.

Contamination by trace organics was further investigated in a series of experiments in which ozonised and unozonised air/oxygen were bubbled through a column containing between 900 and 1000 ml hexane. Duplicate experiments with a second ozoniser (Wallace & Tiernan Limited, Tonbridge, Kent, UK) or with a complete by-pass of the ozoniser were carried out to identify any contamination resulting from the production of ozone by, or the passage of air through, the ozone generator (Trailigaz Labo 76) routinely used.

Details of the experimental conditions used are given in Table 2. The ozone dose applied (180 mgO_3) is similar to that applied in sample ozonation. Direct injection of hexane sample aliquots without pre-concentration was found to be adequate for GC analysis. A brief description and the results of each experiment undertaken with hexane are given in Table 3 and figures 9 & 10. Despite the numerous approaches made, the source/sources of contamination remained unidentified.

2.3 Ozonation of organic compounds

Limited experiments revealed that substantial degradation of ozone in water occurred at room temperature (21°C) whereas relatively little degradation was observed at 10°C, as shown in fig. 11. Consequently, all incubations were carried out in a darkened recirculating water bath maintained at 10°C.

2.3.1

Alkanes, Alkenes

Two 1 litre samples of ozonated water (ca 5mg O_3 l^{-1}) were transferred to 3-neck flasks (A and B) and suspended in the recirculating water bath.

To one flask (A), an appropriate quantity of the compounds under test were added in pentane solution by microsyringe to achieve a concentration of 10 µg l^{-1} of each component. The second flask (B) served as a procedural blank.

The contents were allowed to react for 30 minutes and the substrates and/or reaction products were subsequently extracted as described in section 2.4.1.

2.3.2

Fatty Acids, Aromatics

Preliminary results indicated partial comsumption of some fatty acids and aromatic hydrocarbons. However, this was based on the assumption that recovery efficiencies were invariable. To quantifiy the partial consumption more exactly, the experimental procedure was modified such that consumption calculations were based on the concentration of an unozonated sample incubated and extracted alongside the ozonated sample (unozonated samples had not previously been run concurrently; consumptions had been based on the concentration of unozonated sample recovered in the corresponding recovery experiment (section 2.5.3)).

Thus in addition to flasks A and B (containing 1 litre samples of ozonated water), a third flask (C), containing 1 litre unozonated water was incubated in the water bath. 10 µg of each compound under investigation were added in a methanol solution to flasks A and C. The contents of all flasks were allowed to react for a period of 30 minutes prior to extraction by the procedure described in section 2.4.2. Results were thus available for both ozonated and unozonated organic samples, thereby allowing calculation of the degree of consumption of individual compounds by ozone (section 2.5.4.).

At this level of substrate concentration GC and GC/MS analysis provided little information on the identity of the reaction products. Ozonations at a higher substrate concentration (500 µg l^{-1} for fatty acids; 200 µg l^{-1} for aromatics) were thus carried out on reacting organic compounds in order that the reaction products might be identified. Apart from the higher substrate concentrations, ozonation and extraction procedures were identical in all respects to those for the low substrate level ozonations.

2.3.3
Surfactants

Ozonation was carried out at a single relatively high substrate concentration (500 µgl^{-1} for cationic surfactants; 240 µgl^{-1} for non-ionic and anionic surfactants). Such substrate levels were necessary to allow subsequent analysis using positive and negative ion FAB mass spectrometry. All other procedural details are identical to those for fatty acid and aromatic compounds (Section 2.3.2)

2.4
Extraction and concentration of samples

2.4.1
Alkanes, Alkenes

Procedure A

Following the 30 minute incubation with aqueous ozone, the reaction mixtures were transferred with pentane washings of the 3-neck flasks to separating funnels. A total volume of 30 ml pentane was added and the samples shaken by hand for 3 minutes.

Following separation of the phases (15 minutes), the water phase was discarded and the pentane extract collected in a second separating funnel (100 ml) together with pentane washings (10 ml) of the original separating funnel. After discarding further small volumes of separated water, the extract was transferred with washings (5 ml) to a Kuderna/Danish evaporator. After slow evaporation of the solvent over a water bath (at approximately 65°C for alkanes and thereafter at 40-50°C) using a macro 3-ball Snyder column to approximately 2 ml, the extract was further concentrated to the required volume (50-1000 µl) under a stream of clean dry nitrogen.

Extracts were stored at -18°C prior to analysis by GC and GC/MS.

2.4.2
Fatty Acids, Aromatics

The nature of the substrates and the possible reaction products necessitated modifications to be made to the initial extraction procedure (i.e., Procedure A). In addition, the development of a suitable internal standard for fatty acids was required.

Dodecanoic acid (C12) was selected for study as the internal standard and recovered from ozonated and unozonated water spiked at $10\mu g^{-1}$. An external standard tetradecanoic acid (C14) ($10\mu g^{-1}$) was added immediately prior to extraction (initially, a pentane extraction at pH 2) low recoveries for ozonated as compared to unozonated samples were observed: recoveries of both dodecanoic and tetradecanoic acids from ozonated solutions were reduced by approximately 50% compared to unozonated samples. Although it was possible that ozone had consumed both of the acids, tetradecanoic acid had been added to the aqueous ozone solution immediately prior to extraction and it was felt unlikely that consumption would have occurred to this extent in the

limited period of contact of tetradecanoic acid with the ozone (Hoigné and Bader, 1983).

This phenomenon was further investigated by determining the efficiency of extraction of dodecanoic and tetradecanoic acids from ozonated water using the more polar solvents dichloromethane (DCM) and diethyl ether. The results from this study (Table 4) indicated ether to be the more efficient extraction solvent. The improved recoveries achieved for the fatty acids indicated that neither comsumption by ozone nor irreversible adsorption onto the glassware had taken place.

Subsequent GC analysis of the samples produced a drifting baseline which was found to be due to stripping of the liquid phase off the capillary column. Dilution of ether extracts with pentane overcame this problem by production of a precipitate. Methylation and GC-MS analysis of the ether extracted/pentane diluted solutions showed the presence of phosphoric acid trimethyl ester. From this it is apparent that phosphoric acid was extracted by ether and most probably removed the liquid phase during chromatography of the sample solution. The practice of ether extraction and subsequent pentane dilution was thus introduced (Procedure B).

Investigations into the use of dodecanoic acid as an internal standard were resumed using ether extraction at pH 2 and pentane dilution. Table 5 gives the results for ozonated and unozonated samples, from the table it is apparent that dodecanoic acid (C 12) does not appear to react with ozone and can therefore be used as an internal standard.

Procedure B

After incubation with aqueous ozone, the reaction mixtures were acidified to pH2 by addition of approximately 10 ml 20% phosphoric acid (Analar Grade, BDH Chemicals Ltd., Poole, UK.) and transferred with ether washings to separating funnels. A total volume of 150 ml ether was added and the samples shaken. Following separation of the phases, the aqueous phase was returned to the reaction vessel and subsequently re-extracted with 2 x 50 ml ether. The extracts were combined and diluted with approximately 120 ml pentane.

The extracts were dried by freezing out water at a temperature of -18°C (for at least 2 hours and preferably overnight), the organic fraction decanted into a Kuderna/Danish evaporator and concentrated using macro and micro 3-ball Snyder columns to approximately 500µl. Further concentration was achieved, when necessary, under a stream of clean dry nitrogen.

2.4.3
Surfactants

The nature of the substrates and the anticipated nature of the reaction products formed upon ozonation of surfactants necessitated further modifications to the extraction procedure. This modified procedure has been termed Procedure C.

Procedure C

Following the 30 minute incubation with aqueous ozone solution, ozone remaining within the reaction mixture was quenched by addition of sodium sulphite (approximately 2 mls of a 10mg ml^{-1} solution). Complete reaction of all ozone present was indicated by the absence of colour formation upon the addition of the diethyl-p-phenylene diamine (DPD). The reaction solutions were then transferred to a separating funnel, 100g NaCl added and the mixture shaken to ensure

dissolution. The resulting solution was extracted with 2 x 100 ml ethyl acetate and dried by freezing out water (for at least two hours and preferably overnight), rotary evaporated down to dryness, redissolved in 5-10 ml methanol and concentrated (to a volume of 1 ml) under a stream of dry nitrogen.

2.5 Analysis of Samples

2.5.1 Instrumental analysis

2.5.1.1 Gas chromatography (GC)

GC was generally carried out using a Carlo Erba Strumentazione Fractovap 4200 fitted with a flame ionization detector (FID), on column injector OCI-3 (Scientific Glass Engineering Ltd., (SGE) Milton Keynes, UK) and fused silica capillary columns (BP5 25m x 0.32mm id (SGE)). Instrument operating conditions are given in Table 6.

The output was linked to a Shimadzu C-R3A Chromatopac integrator (Dyson Instruments Ltd., Tyne & Wear, UK) or Venture Servoscribe 15 chart recorder (Labdata Instrument Services Ltd., (LIS), Croydon, Surrey, UK).

During the period when work was carried out at the WRC, a Varian 3700 gas chromatograph fitted with an FID, on column injector OCI-3 (SGE) fused silica column (DB-1 60m x 0.25mm (Jones Chromatography Llanbradach, Mid Glamorgan,UK)) was employed. Instrument operating conditions remained unchanged with the exception of the helium flow rate which was increased from 0.9 ml min^{-1} to 1.7 ml/min^{-1}.

The output was linked to both a Servoscribe dual pen chart recorder (LIS) and a Hewlett-Packard 3390A integrator (Hewlett-Packard, Winnersh, Berks, UK).

2.5.1.2

Gas chromatography - Mass spectrometry (GC-MS)

GC-MS analysis was generally carried out on a Carlo Erba Strumentazione Fractovap 4200 connected to a Jeol JMS-D300 double focussing mass spectrometer (Jeol Ltd., Tokyo, Japan) in electron impact mode.

GC operating conditions were as for GC analysis (section 2.5.1.1) with the exception that sample introduction was carried out on an on column injector OCI- 3 (SGE) and a narrow bore (0.22mm) fused silica capillary column (BP5 25m x 0.22mm id (SGE)). MS operating conditions are given in Table 7. Data acquisition and processing was carried out on a Jeol MS DK 400 Disc system (Jeol Ltd., Tokyo, Japan). Mass calibration of the spectrometer was achieved using perfluorokerosine.

Whilst work was carried out at the WRC, a Hewlett-Packard 5710A GC (on column injector OCI-2 and DB-1 60m x 0.32mm capillary column (Jones Chromatography)) directly coupled to a VG 70-70E double focussing mass spectrometer (VG Analytical, Manchester, UK) operated in both electron impact and chemical ionization modes, was utilised. GC operating conditions were similar to those used in GC analysis (section 2.5.1.1); MS operating conditions are given in Table 8. Data acquisition and processing was provided by a Super-Incos data system (Finnigan MAT, Hemel Hempstead, Herts, UK), with mass calibration again achieved using perfluorokerosine.

2.5.1.3

Fast Atom Bombardment (FAB) Mass spectrometry

A VG ZAB-1F double focussing mass spectrometer (VG Analytical) was used for the production of FAB ± Mass Spectrums in conjunction with a Super-Incos data system (Finnigan MAT) for data acquisition and processing.

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. Samples were introduced as solutions in methanol added to a glycerol matrix on a stainless steel target. Operating conditions are given in Table 9. Mass calibration was achieved using mixtures of rubidium, caesium and sodium iodides.

2.5.2 Diazomethane methylation

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 apparatus required for methylation is shown schematically in Figure 12.

The extract to be methylated (500 µl) is contained in the reaction vial (A). Diazomethane is produced in the reaction vessel (B) by the action of 1 ml 60% v/v potassium hydroxide on 10 ml 4% methanol/ether solution of N-methyl N-nitroso-p-toluenesulphonamide at 40°C.

The diazomethane/ether solution is distilled over into the extract in a reaction vial until a yellow colour persists. After a 1 hour reaction period, the diazomethane is removed under a stream of nitrogen, the samples taken down to approximately 50 µl and subsequently taken up in the solvent of choice.

2.5.3

Determination of recovery efficiencies

Recovery efficiency determinations were carried out in triplicate. Known concentrations (10 $\mu g l^{-1}$) of each standard compound were spiked into 1000 ml volumes of purified water contained in separating funnels, shaken for 30 seconds and allowed to stand for 30 minutes prior to extraction.

Pentane (for alkanes and alkenes) or ether (for fatty acids and aromatic hydrocarbons) was added and the standard extracted by Procedure A or B respectively in accordance with that adopted for the corresponding sample solution. A 1 µl aliquot (typically from 500 µl volume samples) was analysed by GC. Percentage recovery was calculated as follows from the mean results of 3 determinations:

$$\% \text{ recovery} = \frac{\text{peak area after extraction}}{\text{peak area of standard}} \times 100$$

2.5.4

Determination of the degree of consumption of substrates upon ozonation

The degree of consumption of organic substrates was estimated by comparison of the gas chromatographs for ozonated and unozonated spiked water samples at the 10 μl^{-1} level.

From gas chromatograms resulting from the injection (in duplicate) of 1 µl reaction mixture (typically from a 500 µl sample volume), the ratio of the mean compound area (A) to the mean internal standard area (IS) was calculated for all peaks of interest in both ozonated and unozonated samples.

Consumptions were calculated as follows:

$$\text{Consumption (\%)} = 1 - \frac{A' \; IS''}{A'' \; IS'} \times 100$$

where ' = ozonated samples

" = unozonated samples

A positive value indicates that the substrate has been consumed upon ozonation.

3. RESULTS

3.1 Alkanes

3.1.1 Recovery efficiencies

The compounds studied and their recoveries (based on duplicate analyses) are given in Table 10.

3.1.2 Consumption of alkanes by ozone

Alkane consumption experiments were conducted without the use of an internal standard. Absolute values of peak area or height were therefore utilised in the calculations. Comparison of the retention times and peak areas/heights in the GC chromatogram for ozonated and unozonated alkane samples (fig. 13) indicated that with the exception of undecane and docecane, no consumption had taken place.

This is further illustrated by superimposing GC-MS traces (fig. 14). Similar retention times are observed for both ozonated and unozonated samples. Within experimental error, for alkanes with C > 13 little difference in peak height/area between ozonated and unozonated samples were observed, indicating negligible consumption had taken place. The identities of the peaks in the ozonated sample were confirmed to be those of the original hydrocarbons by searching of a mass spectra library data base.

The apparent partial consumption of undecane and dodecane is some what suprising and is believed to be anomalous. Although ozone can react with saturated substrates such reactions generally involve the free radical species which are unlikely to have been produced under the experimental conditions used, although their production cannot be ruled out. Further work has since been carried out which indicates that undecane and dodecane are not consumed.

3.2. Alkenes

3.2.1 Recovery efficiencies

The alkenes investigated are listed in Table 11 together with the recovery efficiencies (based on triplicate analyses) recorded.

3.2.2 Consumption of alkenes by ozone

GC analysis was hampered by the presence of contaminating peaks of a similar retention time to those of many of the alkene compounds under test (that is, within the first 15 minutes of the GC run). The source of this contamination remained unidentified (section 2.2.5). No convincing explanation can be found for the appearance of this contamination which was to persist for the remainder of the project. Nevertheless comparison of the gas chromatograms for ozonated sample and blank solutions and the unozonated standard solutions suggested near complete consumption of the longer chain alkenes studied (that is, tetradec-1-ene to squalene - see figure 15). In addition, GC-MS analysis indicated the absence of these compounds in the ozonated sample solutions.

On account of interference by contaminating organics, the fate of the lower chain alkenes is more difficult to assess. However, analysis of both gas chromatograms and library searching of mass spectra would suggest near complete consumption of these compounds also.

3.2.3 Identification of reaction products

Further analysis of the GC chromatograms reveals the presence of an homologous series of peaks present in the ozonated sample extract, but not in either of the control extracts.

As aldehydes and ketones are likely products of the ozonation of alkenes in water (Bailey et al (1978) and Bailey (1979)), a set of standard aldehyde solutions (octanal to dodecanal) in methanol was analysed by GC for comparative purposes. The resulting chromatogram is shown in Figure 16. Based on retention times, a tentative identification of dodecanal was made.

GC-MS analysis provided further evidence for the identification of the reaction products as aldehydes (fig. 17). Based on retention times of the standard aldehyde solutions and the uncharacterised peaks observed in the ozonated sample extract, tentative assignment of nonanal through to dodecanal was made to a number of uncharacterised peaks. The correspondence between the mass spectra and GC-MS retention times for an aldehyde standard and an uncharacterised peak from the ozonated sample extract is illustrated for dodecanal in Figure 18.

Library searching of mass spectra confirmed the presence of the aldehydes decanal to tetradecanal, although not dodecanal, in the ozonated sample extract (fig. 19). Examination of the dodecanal library spectrum shows a base peak of 45 whereas the dodecanal standard and sample have base peaks of 57. This may account for the non-identification of dodecanal by library searching despite the visual similarity in the spectra.

3.3 Aromatics

Extraction of reaction mixtures resulting from ozonation of aromatic compounds was undertaken intitially using pentane (Procedure A, section 2.4.1) with a pH 2 adjustment. Few non-attributable peaks were apparent in the gas chromatograms produced from these extracts possibly on account of inefficient extraction by pentane. As the expected reaction products include relatively polar polyhydroxylated aromatic compounds, quinoids, aliphatic acids and aldehydes (Legubé et al (1983); Decoret et al (1984)), the use of a solvent of greater polarity (namely diethyl ether with pentane dilution (Procedure B, section 2.4.2)) was introduced.

3.3.1 Recovery efficiencies

Recovery values for the aromatic compounds studied (ether extraction with pentane dilution) are given in Table 12.

3.3.2 Consumption of aromatic hydrocarbons by ozone

The apparent degree of consumption of the various aromatic hydrocarbons studied are given in Table 13. Negligible consumption of toluene, the xylenes and fluorene was observed (fig 20); significant consumption (at least 50%) of the polyaromatic hydrocarbons, naphthalene, phenanthrene, fluoranthene and pyrene was found.

3.3.3 Identification of reaction products

3.3.3.1 Low substrate concentration (10 $\mu g l^{-1}$)

Comparison of the GC and GC-MS chromatograms of the ozonated and unozonated sample solutions and the ozonated water blank yielded little information on the identity of the products of reaction at the 10 $\mu g l^{-1}$ substrate level. However, possible reaction product peaks were observed in the GC chromatagram (fig. 20). Methylation of extracts and subsequent GC and GC-MS analysis did not improve identification ability.

Ozonation at a higher substrate concentration (200$\mu g l^{-1}$) was thus undertaken so as to produce sufficiently high levels of ozonation products to enable identification.

3.3.3.2 High substrate concentration (200 $\mu g l^{-1}$)

In addition to those polyaromatic compounds showing significant consumption by ozone (that is naphthalene, phenanthrene, fluoranthene and pyrene), ozonation of fluorene at the higher substrate level was also undertaken as the reactivity of fluorene towards ozone had been demonstrated in other studies (Helleur et al (1979)).

GC analysis of extracts revealed a series of unknown peaks in the ozonated sample extract, one of which, by retention time, appeared to be 9-fluorenone (fig. 21) GC-MS analysis and subsequent library searching suggested two of the other peaks to be phenanthradiol and phenanthrene dione (fig. 22).

GC analysis of methylated extracts provided tentative identification of diphenic acid based on GC retention time as compared to that of a diphenic acid standard (fig. 23). However, diphenic acid could not subsequently be detected by GC-MS analysis. A series of unidentified peaks was again present and most probably corresponded to reaction products.

GC-MS analysis in CI mode was also carried out on methylated samples, but this did not reveal any additional information.

3.3.4
Ozonation of individual polyaromatic compounds (PAHs)

Ozonation of the five PAHs selected for high substrate level ozonation (section 3.3.3.2) was repeated on an individual basis with the concentrations of naphthalene, phenanthrene and fluorene being increased to 1 mgl^{-1}. The solubility of pyrene and fluoranthene in water is approximately 200 μgl^{-1}; individual ozonations were therefore repeated at this level.

3.3.4.1
Naphthalene

GC analysis of unmethylated and methylated sample and control extracts yielded a series of uncharacterised peaks. GC-MS analysis and library searching of mass spectra for unmethylated sample and control extracts revealed the presence of phthalic acid in the ozonated sample extract (fig. 24). A parallel analysis of methylated samples confirmed the presence of this compound by identifying the dimethylphthalic ester (fig. 25).

3.3.4.2
Fluorene

GC and GC-MS analysis of unmethylated samples revealed a single product peak which was identified as 9-fluorenone based on a matching of GC-MS retention time and mass spectra with that of a standard (figs. 26 and 27) and library searching of mass spectra. GC analysis of the

high substrate concentration PAH mixture had also suggested the presence of 9-fluorenone in the ozonated sample extract (section 3.3.3.2).

Then GC and GC-MS analysis of methylated samples, although revealing the presence of additional possible product peaks, was unable to provide any identification.

3.3.4.3
Fluoranthene

The presence of unidentified compounds in ozonated sample extracts were apparent from GC analysis of both methylated and unmethylated sample extracts. However, GC-MS analysis was unable to identify any of these compounds.

3.3.4.4
Phenanthrene

GC analysis of both methylated and unmethylated extracts revealed the presence of a series of possible product peaks. However, GC-MS analysis and subsequent library searching of mass spectra did not identify any reaction products.

3.3.4.5
Pyrene

GC and GC-MS analysis of the unmethylated extracts did not reveal any ozonation products. GC analysis of the methylated extracts indicated the presence of several unknown compounds; however, GC-MS analysis provided no indication as to the identity of the reaction products.

3.4 Fatty Acids

3.4.1 Recovery efficiencies

The fatty acids studied and recovery efficiencies recorded are listed in Table 14. No significant difference was noted between the recoveries for unsaturated and saturated fatty acids.

3.4.2 Consumption of fatty acids by ozone

Consumption data for the reaction of fatty acids with ozone is given in Table 15. Due to the problems initially encountered in GC analysis (see section 2.4.2), consumption data is presented for the methylated sample extracts.

A clear distinction between the reaction of saturated and unsaturated fatty acids with ozone is observed: near complete consumption (at least 95%) of unsaturated fatty acids occurs whilst little consumption of saturated fatty acids can be seen (fig. 28). The apparent consumption/formation of saturated fatty acids is most probably within experimental error although an increase in octanoic acid (C_8) of approximately 40% is surprising. It should be noted that significant contaminations of the ozonated blank extract by fatty acids was recorded. Examination of the corresponding GC-MS chromatograms also revealed the presence of contaminating fatty acids, although not necessarily the same fatty acids as observed in the GC chromatogram. However, the extent of this contamination would not account for the 40% increase in octanoic acid observed. Repeat consumption experiments are to be carried out to confirm or refute this finding.

3.4.3 Identification of reaction products

3.4.3.1 Low substrate concentration (10 $\mu g l^{-1}$)

Analysis of the sample and control extracts by GC analysis both prior to and following methylation revealed the presence of a series of unknown compounds in the ozonated sample extracts. GC-MS analysis did not provide any identification of these peaks.

3.4.3.2 High substrate concentration (500 $\mu g l^{-1}$)

Having established that the unsaturated fatty acids react extensively with ozone, further investigation was confined to hexadec-9-enoic and octadec-9,12-dienoic acids.

Ozonation was carried out at a higher substrate concentration (500 $\mu g l^{-1}$). Significant consumption of the two acids was again observed. GC analysis revealed the presence of a series of uncharacterised peaks in the unmethylated sample extract. Methylation and subsequent GC analysis of the sample extract enabled tentative identification of hexanal and heptanal based on the comparison of the chromatogram with that of standard solutions (fig. 29).

Propandioic acid was anticipated as a possible reaction product. However, comparison of the GC retention time of the methylated derivative (propandioic acid dimethyl ester) with that of the methylated sample extract did not suggest its presence (fig. 29).

GC-MS analysis of the methylated sample confirmed the presence of hexanal and heptanal in the ozonated sample extracts (fig. 30). The methyl ketones 2-octanone and 2-heptanone, products of methylation of the aldehydes, and the methyl esters, methyl hexanoate and methyl

heptanoate, were also found. (The methyl esters resulted from the methylation of the corresponding carboxylic acids (hexanoic and heptanoic acids) arising from oxidation of the aldehydes).

Identification of 9-oxononanoic acid methyl ester was made by comparison of mass spectra from sample extracts and from the reaction products formed during the non aqueous ozonation of hexadec-9-enoic acid methyl ester (fig. 31). Library searching of a mass spectra data bank provided identification of 9-oxodecanoic acid methyl ester (fig. 32).

Unmethylated extracts were further analysed by fast atom bombardment (FAB) mass spectrometry in both the positive and negative ion mode. Negative ion FAB indicated the presence of 9-oxo nonanoic and nondioic acid (fig. 33). The presence of the semialdehyde and diacid was confirmed by accurate mass determinations which were carried out at a resolution of 2500 to within 2mmu.

3.5

Surfactants

The reaction of a range of surfactants with ozone was studied. Cationic, anionic and non-ionic surfactants were included. The structures of the compounds investigated are given in fig. 34.

3.5.1

Cationic surfactants

Ozonation of cationic surfactants was carried out at a substrate concentration of $500\mu gl^{-1}$. Sample and control extracts were analysed by FAB mass spectrometry.

3.5.1.1

Prapagen WKT

Ions corresponding to the unsaturated (m/z 310, 520, 546, 548) and saturated (m/z 312, 522, 550) components of Prapagen WKT were observed in the unozonated sample extract (fig. 35). Following ozonation, ions corresponding to the unsaturated components largely

disappeared. Additional ions, most probably corresponding to reaction products, were produced at m/z 426, 440, 456 and 468. The probable empirical formulae and accurate mass determinations for these newly formed ions are given in Table 16.

3.5.1.2

Arquad 2HT

Ions attributable to cationic Arquad 2HT components (m/z 312,522,550) were present in both ozonated and unozonated extracts. All the peaks representing Arquad 2HT were present in similar proportions in both the ozonated and unozonated extracts. Additional ions (m/z 380,422,438,532) absent from control extracts were also present in ozonated sample extracts (fig. 36). The reason for the presence of these ions is not known.

3.5.1.3

Cetyl pyridinium chloride

The presence in both ozonated and unozonated sample FAB positive spectra of the ion at m/z 304 corresponding to the cetyl pyridinium chloride (CPC) cation (fig. 37) would suggest no reaction between CPC and ozone. The lack of reaction product cations observed supports this.

3.5.2

Anionic surfactant

Extracts produced following the ozonation of 4-dodecylphenylsulphonate (240 $\mu g l^{-1}$) were analysed by FAB negative ion mass spectrometry. The presence of the 4-dodecylphenylsulphonate (DPS) anion at m/z 325 in both ozonated and unozonated sample spectra and the absence of reaction product anions (fig. 38) indicates no reaction between DPS and ozone.

3.5.3
Non-ionic surfactant

Extracts produced following the ozonation of nonyl phenyl ethoxylate NP7 ($240\mu gl^{-1}$) were analysed by FAB positive ion mass spectrometry. The absence of the 529$[M+H]^+$ peak in the FAB positive ion mass spectrum suggests the consumption of this surfactant. However, no reaction product ion peaks were apparent (fig. 39). Future analysis by GC, GC-MS and HPLC may reveal the presence of reaction products not amenable to FAB positive ion mass spectrometry.

4. DISCUSSION AND CONCLUSIONS

Ozone can react with organic compounds by two mechanisms; either directly (by 1,2-dipolar cycloaddition, electrophilic or nucleophilic attack) or indirectly (through the action of hydroxyl radicals). The type of reaction occurring is largely dependent upon pH (Doré, 1985); the neutral or slightly acidic reaction conditions of this study should result in reaction products arising principally from direct reactions of ozone. Such reactions are based on the resonance structure of ozone which gives the molecule an electric dipole. Attack of aliphatic saturated hydrocarbons by this dipole can be expected to be minimal. Thus, the lack of reactivity observed between alkanes and ozone in this study is as anticipated although this does not seem to have been reported previously. (The 'apparent' consumption of the two alkanes undecane and dodecane is believed to be anomalous. Work is being carried out at present to confirm or refute the initial findings).

In contrast, almost complete reaction of unsaturated aliphatic (that is, alkene) compounds was demonstrated The formation of aldehydes as the only products would suggest the occurrence of a classic 1,3-dipolar cycloaddition reaction with initial addition of ozone

across the carbon-carbon double bond to form an ozonide intermediate and subsequent breakdown (at 10°C) to produce the aldehyde (fig. 1a). Further oxidation of the aldehyde to form the carboxylic acid has been demonstrated (Doré, 1985); although, in this study, carboxylic acids were not detected following ozonation of alkenes; however, alkene ozonation and product extraction at pH 2 will be necessary to confirm that carboxylic acids are not formed.

The reactivity of fatty acids with ozone followed a similar pattern: reaction of unsaturated, but not saturated fatty acids was observed. The reaction products resulting from the ozonation of the unsaturated fatty acids (namely hexanal, heptanal and 9-oxnonanoic acid) would again imply a mechanism proceeding via 1,3-dipolar cycloaddition of ozone. However, in addition to the formation of aldehydes subsequent oxidation resulted in the formation of the corresponding carboxylic acids and also at least one diacid (fig. 40).

Reaction of aromatic hydrocarbons with ozone was observed only in the case of the polyaromatic hydrocarbons (PAHs) investigated. Negligible consumption of the single ring aromatic compounds (that is, xylene and toluene) was observed. Significant consumption of PAHs (naphthalene, phenanthrene, fluoranthene and pyrene - but not fluorene) occurred.

Ozonation of the PAH's idividually at a higher substrate concentration (200 to 1000 $\mu g l^{-1}$ cf 10 $\mu g l^{-1}$) permitted some reaction products to be identified. These products were generally in agreement with the findings of other studies.

Various authors have described the reaction between ozone and aromatic hydrocarbons in terms of a 2 or 3 stage process (Decoret et al., 1984; Legubé et al., 1983). The first stages involve the formation of polyhydroxy aromatic species and loss of some or all of the aromaticity via electrophilic attack; subsequent stages involve the ozonation of the non-aromatic products of the first stage.

In this study, the identification of phthalic acid as a product of the ozonation of naphthalene is consistent with such a reaction pathway and also with the work of Legubé et al., (1986) for which high performance liquid chromatography was used. From kinetic studies they speculated that the initial reaction mechanism involved an electrophilic substitution of ozone on carbon 1 or 2 of naphthalene (fig. 41).

The production of fluoren-9-one upon ozonation of fluorene has been demonstrated by other workers (Helleur et al., 1979). However, fluoren-9-one was a minor product of fluorene ozonation. The majority of reaction products were found to result from the action of ozone on the aromatic ring system rather than at the CH_2 group. It is thus likely that other products of reaction were produced but not identified in this study.

Although significant comsumption of phenanthrene, fluoranthene and pyrene was observed and non-attributable peaks were apparent in the ozonated sample GC chromatograms, no products of reaction were identified. Of the cationic surfactants studied, reactivity towards ozone was demonstrated only for the unsaturated component of Prapagen WKT. Examination of the structure of Prapagen and the reaction products identified indicates reaction at the unsaturated side chain with no reaction occurring at the nitrogen. A

classic 1, 3 dipolar cycloaddition of ozone across the carbon-carbon double bond and subsequent oxidation would lead to the carboxylic acids identified as likely reaction products (Table 17).

No reaction between ozone and the other cationic surfactants studied (Arquad 2HT and cetyl pyridinium chloride) or the anionic surfactant, 4-dodecyl phenylsulphonate, was demonstrated. The lack of reaction of Arquad 2HT with ozone is consistent with the lack of reaction of saturated Prapagen components with which it is structurally similar. The absence of reaction observed for cetyl pyridinium chloride and 4-dodecyl phenylsulphonate may be attributable to the presence of the pyridinium ion and the sulphonate group, respectively, deactivating the ring system and making it less susceptible to ozone attack (Rice et al., 1980; Morrision and Boyd, 1973; Millar and Springall, 1969).

FAB mass spectral data indicated consumption of nonyl phenyl ethoxylate NP7 although no reaction products were identified. The reaction of the ether linkage with ozone in aqueous solution does not seem to have been studied previously. However, from the general chemistry of ethers and aromatic ring systems (Morrison and Boyd, 1973), the C-O group is likely to activate the ring system facilitating attack by ozone. Cleavage of the C-O bond requires relatively severe conditions (e.g. high temperatures and concentrated acids). Products of reaction are thus most likely to result from attack of the aromatic ring system by ozone.

The difficulties in identification of reaction products indicate the need for the application of different analytical techniques. HPLC analysis may provide additional information on polyaromatic hydrocarbon ozonation products whilst, for surfactants, extraction

techniques suitable for volatile products and subsequent GC and GC-MS analysis together with HPLC analysis may provide further indications as the identity of reaction products.

The substrate concentrations and initial ozone concentration used in this study were selected to approximate to those used in potable water treatment. However, although the ozone and individual organic substrate concentrations are realistic, the ratios of disinfectant to organic substrate will be inordinately high. Natural surface waters contain organic material in the concentration range 0.5-30 mg l^{-1} whereas the total concentration of organic material undergoing ozonation in this study was most commonly in the 100µg l^{-1} range.

Thus during water treatment, the ratios of disinfectant-to-substrate will be considerably lower than those used in this study. In addition, competition between organic substrates for the available ozone will occur. Consequently reactions will tend to be incomplete with possible interaction occurring between by-products, reaction intermediates and substrates. Competition for ozone by inorganic species such as ferrous and manganous ions, nitrite, sulphide, sulphite and the halides will also occur. Apart from raising the effective organic substrate to disinfectant ratio, reaction with inorganic species may result in the formation of reactive oxidants, such as hypobromous acid, which can significantly affect the by-products formed.

It must thus be concluded that this study has served primarily to indicate those organic compounds/groups of compounds which are likely to demonstrate reactivity towards ozone. However, the reaction products observed in this study would not necessarily be formed under typical water treatment conditions where competition and/or modifying reactions by other organic and the inorganic species may affect the products formed.

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Table 1

Operating Conditions for the Production of Aqueous Ozone Solutions

Ozonation period	20 minutes
Aqueous Ozone concentration	5 mgl^{-1}
Ozone concentration in feed line	20 - 25 $g.m^{-3}$
Current applied (approximate)	0.9 Amps
Air flow rate	100 $l.hr^{-1}$ under conditions of Normal temperature and pressure
Flow rate through column	40 $l.hr^{-1}$
pH of ozone solution	4.5 - 6

Table 2

Experimental Conditions - Hexane Extraction

Hexane volume	900 - 1000 ml	
Ozone applied	180 mg	
Ozone generator	Ozotech	Wallace and Tiernan
Flow rate ($l\ hr^{-1}$)	18	50
Ozonation time (mins.)	20	8
Dissolved ozone in water ($mg.l^{-1}$)	5.5	5.6

Table 3

Experiments using Hexane Extraction

Experiment	Description	Ozone Generator	Results/Comments
(1)*	Ozonated air passed through hexane	Ozotech	High level of contamination in unconcentrated sample
(2)	Unozonated air passed through hexane	Ozotech	little contamination even in concentrated sample
(3)*	Ozonated oxygen passed through hexane	W + T	reduced contamination as compared to (1)
(4)	Unozonated oxygen passed through hexane	W + T	little contamination
(5)	Air passed through hexane (by-passing the ozonator)	Ozotech	similar contamination present as compared to (1) NB 200 x more concentrated
(6)	Hexane concentrated 100 ml to 500 µl	-	similar contamination present as compared to (1) NB 500 x more concentrated
(7)	Ozonated water blank	W + T	ether extraction followed by pentane dilution level of contamination significantly greater than Ozotech water blank (8)
(8)	Ozonated water blank	Ozotech	ether extraction followed by pentane dilution

* performed in duplicate

W + T = Wallace and Tiernan

Table 4

Recovery efficiencies for dodecanoic acid (C_{12} - internal standard) and tetradecanoic acid (C_{14} - external standard)

Extracting solvent	% Recoveries *			
	Ozonated		Unozonated	
	C12	C14	C12	C14
Pentane	23.2	23.3	36.7	57.2
DCM	15.9	10.9	46.8	53.62
Ether	45.0	30.3	74.1	110.3

* compared to standards as used for recovery efficiencies for fatty acids (Table 14).

Table 5

Internal Standard Development. Ratio of C12 to C14 peak area in ozonated and unozonated samples

	Ozonated	Unozonated
Average peak area ratio	1.051	1.053
Relative Standard Deviation % (N = 3)	23.1	16.1

Table 6

Gas-Chromatograph Operating Conditions

Temperature Programme	30°C for 4 min; 8°C min^{-1} to 300°C
Detector Temperature	350°C
Carrier Gas	Helium
Carrier flow rate	0.9 ml min^{-1}

Table 7

Mass Spectrometer Operating Conditions - I

MS System	Jeol JMS-D300 Double focussing
Accelerating voltage	3 KV
Ionization voltage	70 eV
Ionization current	300 µA
Resolution	800
GC/MS transfer line	275°C
Source temperature	250°C
Scan range	40 - 500 u
Scan speed	1 second per decade

Table 8

Mass Spectrometer Operating Conditions - II

MS System	VG 70 - 70E Double focussing
Electron energy	70 eV
Trap current	200 μA
Accelerating voltage	6 KV
Resolution	2000
Scan range	20 - 700 u
Scan speed	0.5 second decade^{-1}

Table 9

Fast Atom Bombardment Mass Spectrometer Operating Conditions

Accelerating voltage	8 KV
Resolution	2000
Scan range	20 - 1500 u
Scan speed	5 second decade^{-1}

Table 10

Recovery of Alkanes from Spiked Water Samples at 10 $\mu g l^{-1}$

Compound	Mean recovery %	Relative standard deviation (N = 3) %
undecane	43	7.2
dodecane	47	4.6
tridecane	39	8.3
tetradecane	48	3.7
pentadecane	46	5.1
hexadecane	58	6.2
heptadecane	58	6.2
pristane	62	2.2
octadecane	54	7.5
nondecane	57	6.8
squalane	44	4.0

Table 11

Recovery of Alkenes from Spiked Water Samples at 10 $\mu g l^{-1}$

Compound	Mean recovery %	Relative standard deviation (N = 3) %
3,5,5, trimethylhex-1-ene (TMH)	26	16
non-1-ene ($C_{9(1)}$)	39	5
non-4-ene ($C_{9(4)}$)	39	5
dec-1-ene (C_{10})	25	1
undec-1-ene (C_{11})	29	13
dodec-1-ene (C_{12})	36	21
tridec-1-ene (C_{13})	42	17
tetradec-1-ene (C_{14})	49	13
hexadec-1-ene (C_{16})	66	1
octadec-1-ene (C_{18})	78	1
eicosene (C_{20})	77	1
docosene (C_{22})	69	7
squalene (Sq)	82	2

Table 12

Recovery of aromatic hydrocarbons from spiked water samples at 10 $\mu g l^{-1}$

Compound	Mean recovery %	Relative standard deviation* %
Toluene (T)	44.5	4.5
o/p Xylene (o/pX)	43.6	3.1
m Xylene (mX)	46.7	2.6
Naphthalene (N)	59.4	2.9
Fluorene (F)	57.7	2.3
Phenanthrene (PA)	62.7	6.0
Fluoranthene (FA)	65.4	5.5
Pyrene (P)	64.6	4.0

* N = 3 except for o/p Xylene where N = 2

Table 13

Apparent consumption of aromatic hydrocarbons (%)

Toluene	10
o/p Xylene	17
m Xylene	9
Naphthalene	49
Fluorene	14
Phenanthrene	77
Fluoranthene	75
Pyrene	85

Table 14

Recovery of Fatty Acids from Spiked Water Samples at 10 $\mu g l^{-1}$

Fatty Acid	Mean recovery %	Relative standard deviation (N = 3) %
Octanoic acid (C_8)	50.5	8.6
Decanoic acid (C_{10})	49.1	16.9
Dodecanoic acid (C_{12})	48.7	12.7
Tetradecanoic acid (C_{14})	51.3	14.5
Palmitoleic acid ($C_{16:1}$)	50.8	14.3
Hexadecanoic acid (C_{16})	56.4	14.6
Heptadecanoic acid (C_{17})	49.4	19.3
Linoleic acid ($C_{18:2}$)	49.6	3.6
Octadecanoic acid (C_{18})	49.0	25.3

Table 15

Apparent Consumption of Fatty Acids (%)

C_8	- 40
C_{10}	- 8
C_{12} *	0
C_{14}	14
$C_{16:1}$	95
C_{16}	12
C_{17}	15
$C_{18:2}$	98
C_{18}	17

* internal standard

Table 16

Accurate mass data for Ozonated Prapagen WKT

Sample/ion m/z	Experimental mass amu.	Proposed empirical formula and accurate mass
426	426.43649	426.43056 $C_{27}H_{56}NO_2$
440	440.446218	440.446218 $C_{28}H_{58}NO_2$
454	454.463500	454.461869 $C_{29}H_{60}NO_2$
468	468.48101	468.47751 $C_{30}H_{62}NO_2$

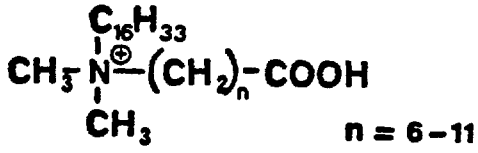
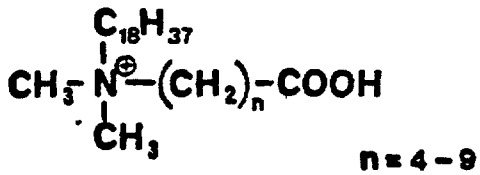
Table 17

Structures of unsaturated components of Prapagen WKT and their reaction products

Prapagen WKT

mwt	Structure
310	$(CH_3)_3\ N^+\ C_{18}H_{35}$
520	$(CH_3)_2\ N^+\ (C_{16}H_{33})\ (C_{18}H_{35})$
546	$(CH_3)_2\ N^+\ (C_{18}H_{35})_2$
548	$(CH_3)_2\ N^+\ (C_{18}H_{37})\ (C_{18}H_{35})$

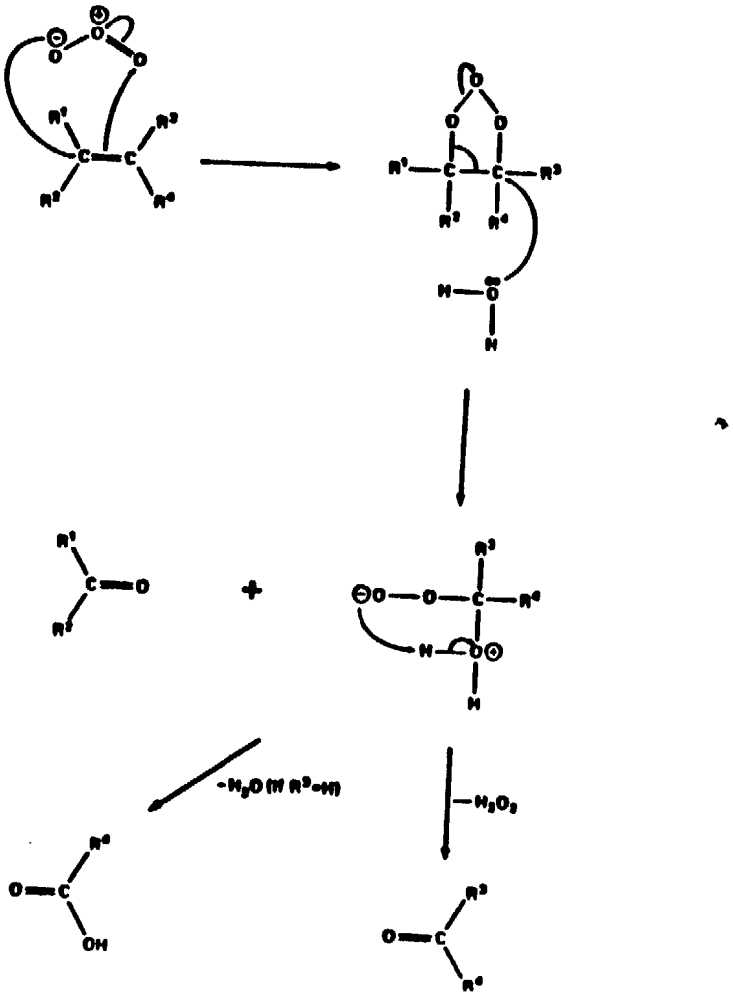
Reaction products

A	B	mwt	Possible structure
6	4	398	A 
7	5	412	
* 8	6	426	
* 9	7	440	B 
*10	8	454	
*11	9	468	

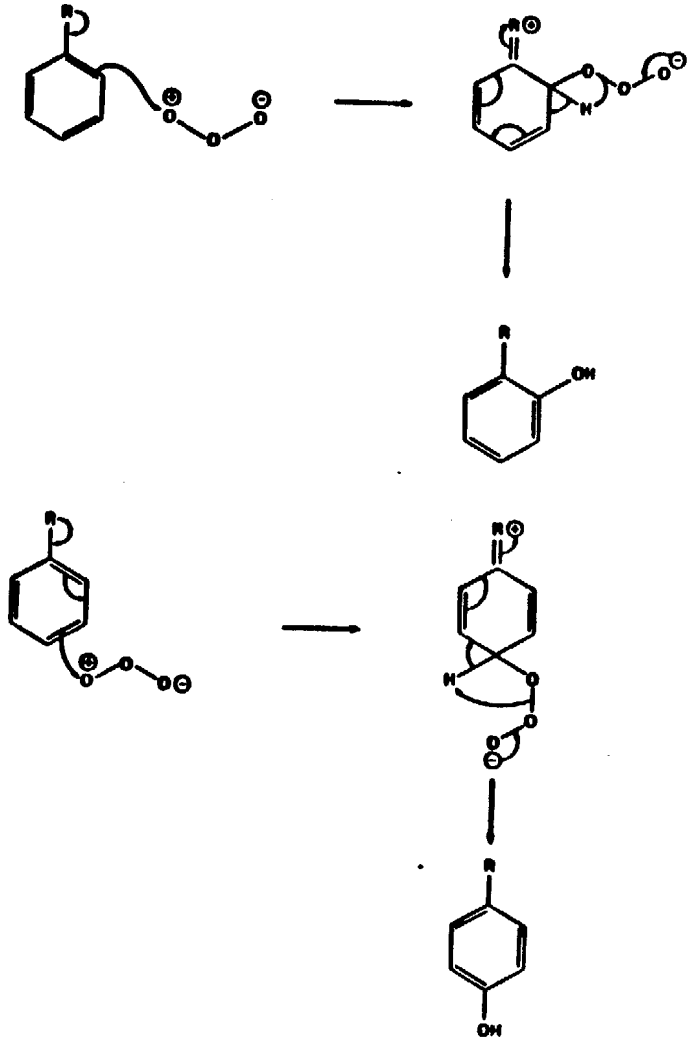
* Peak matched, accurate mass measurements - see Table 16

Figure 1 Direct reactions of ozone (Doré, 1985)

a Reaction scheme for 1,3 - dipolar cyclo-addition



b Reaction scheme for electrophilic attack



ig. 1 (cont) c Reaction scheme for nucleophilic attack

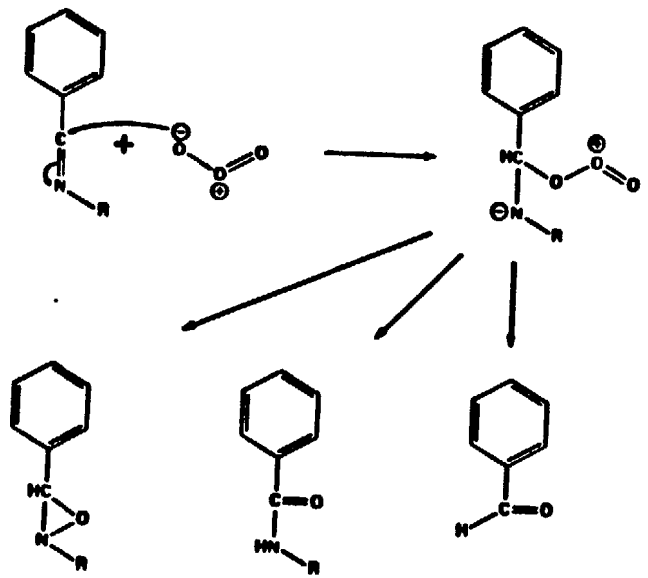


Figure 2. Indirect reaction (action of OH• on phenol)

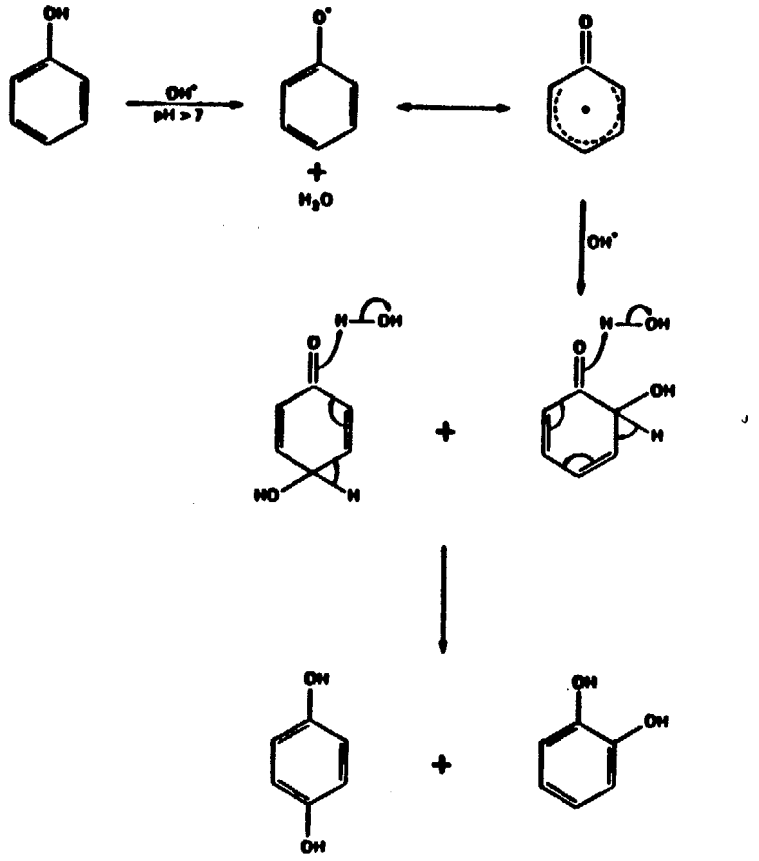


Figure 3. GC-MS Trace. Air blank from air compressor source

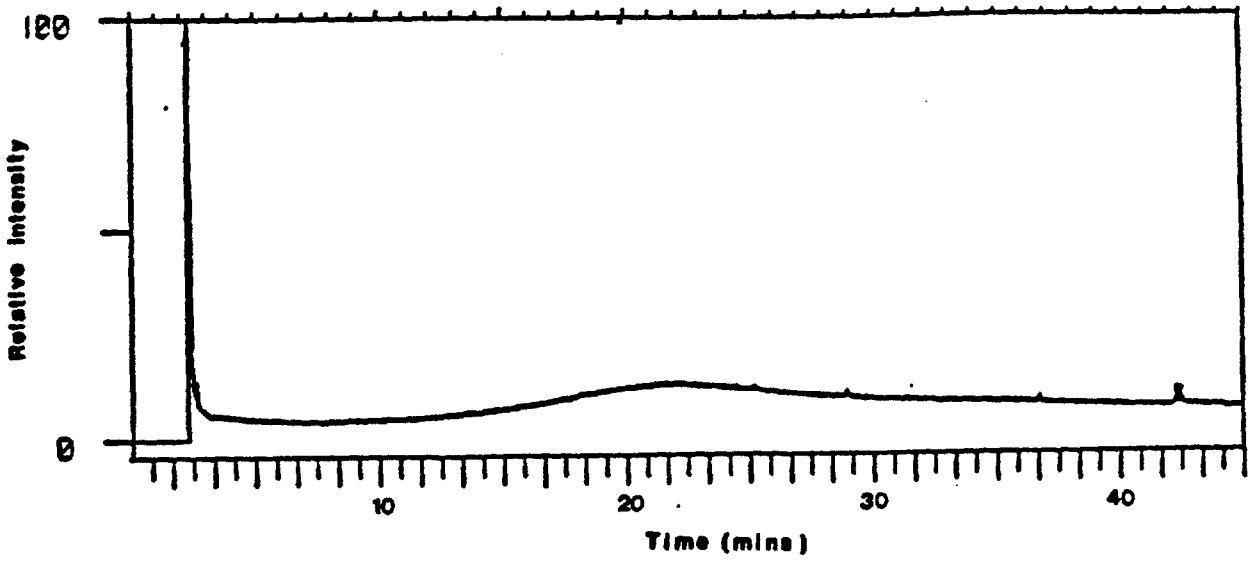


Figure 4. Ozone generator for the production of aqueous ozone solutions using a recirculating bubble contact column

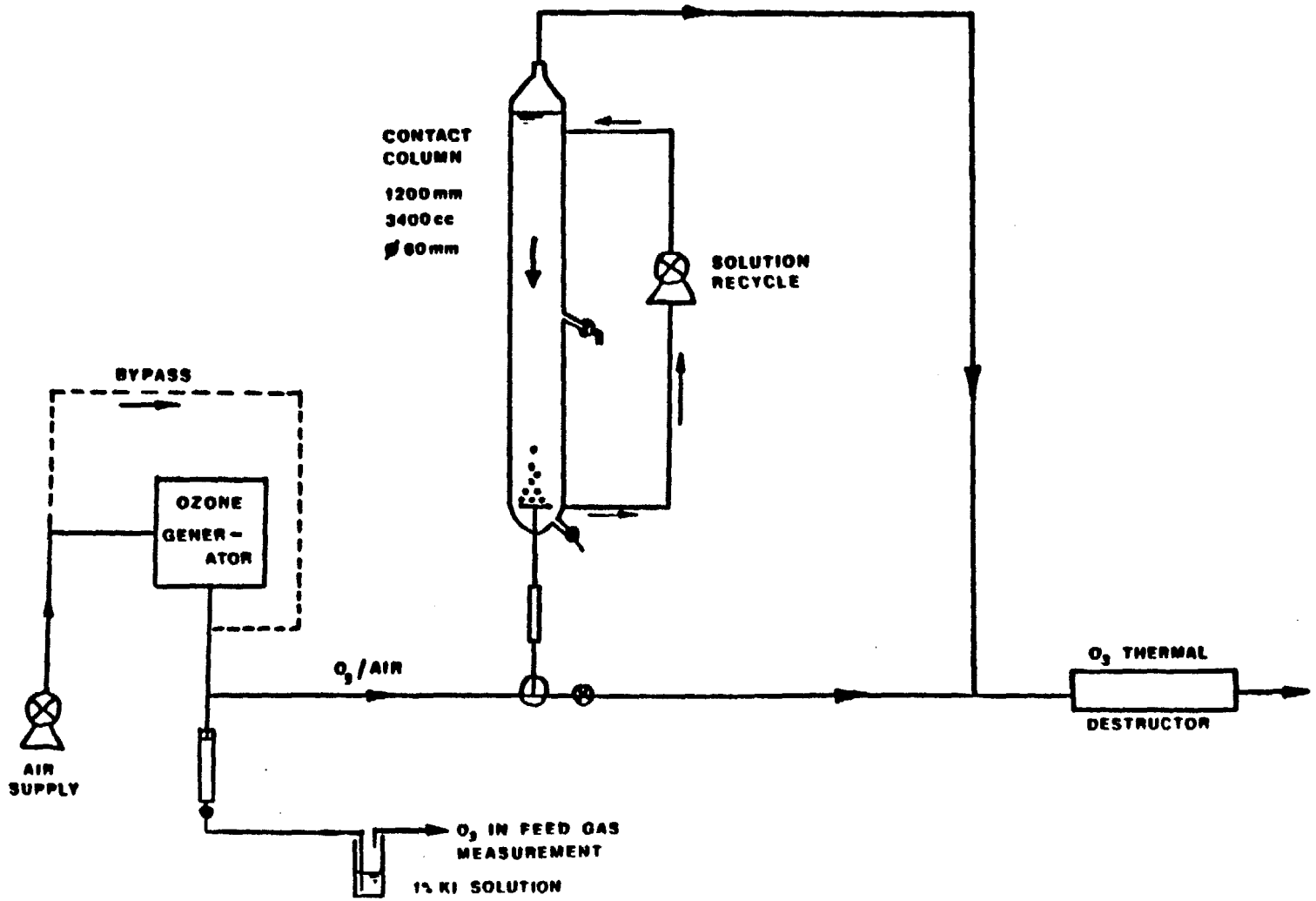


Figure 5. Production curve for aqueous ozone solution

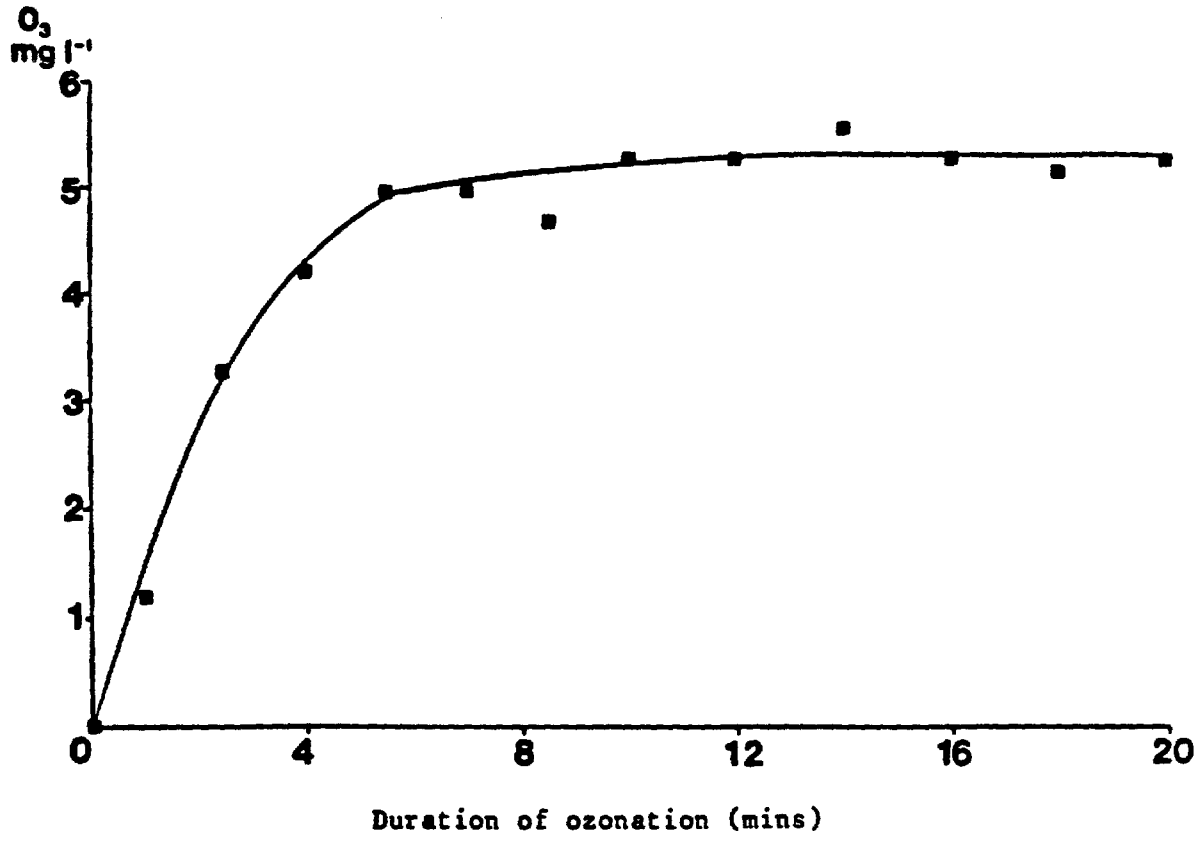


Figure 6. GC-MS Trace. Ozonated water blank from air compressor source

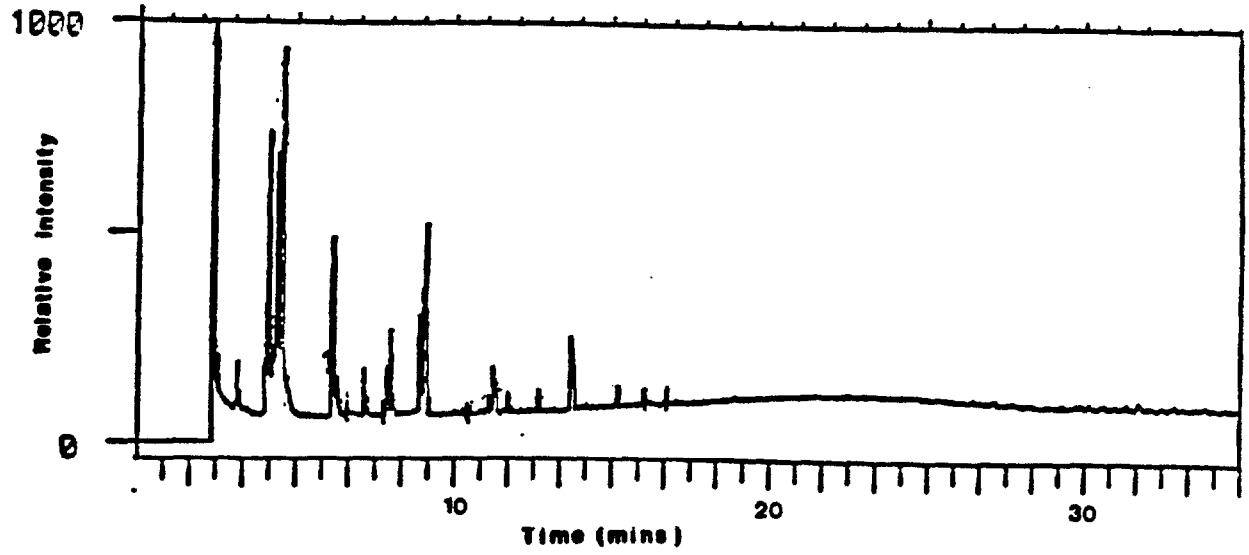


Figure 7. GC-MS Trace. Ozonated water blank from air cylinder

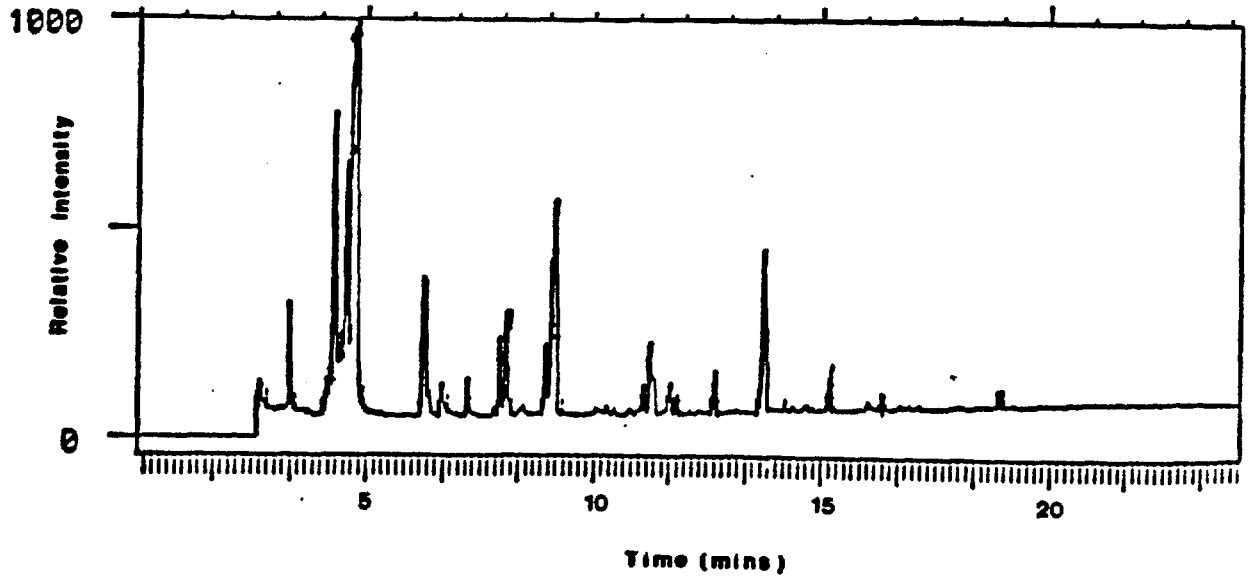
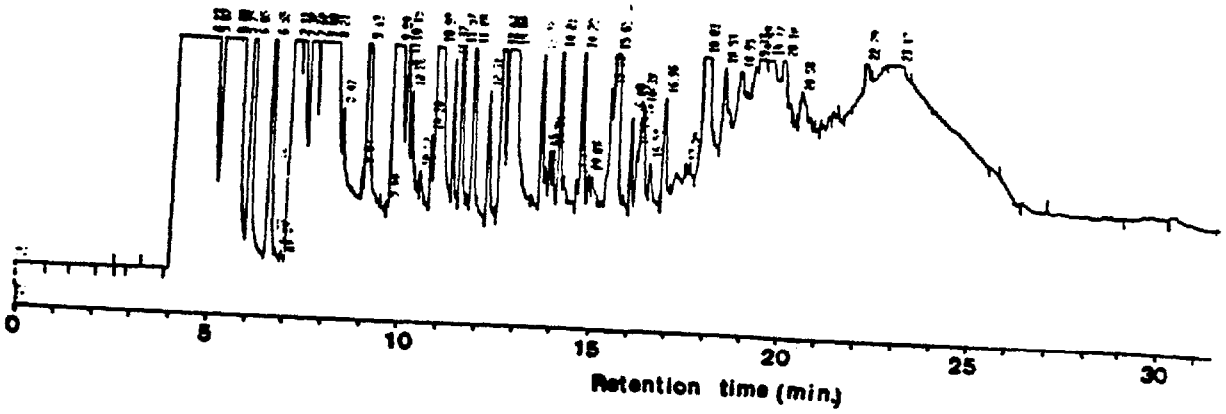


Figure 8. Contamination investigation at the WRC

a GC Trace. Air blank from air cylinder



b GC Trace. Ozonated water blank from air cylinder

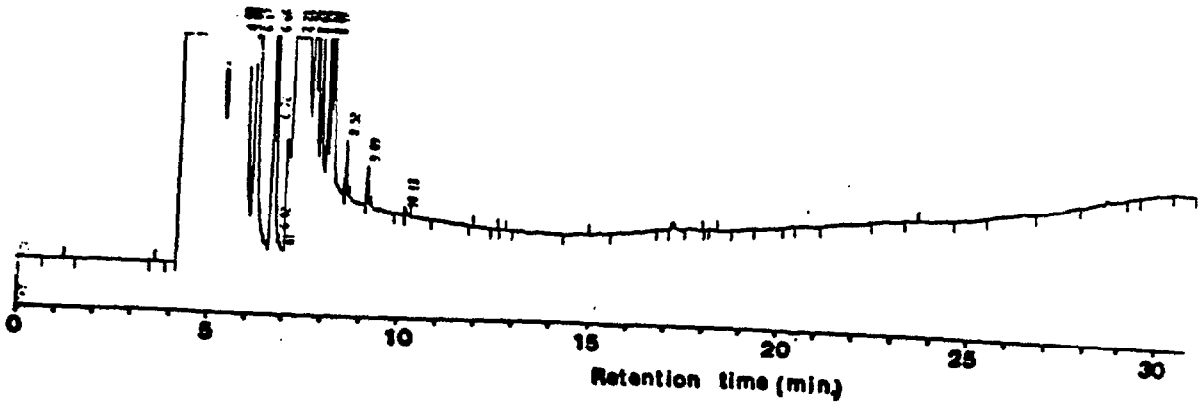
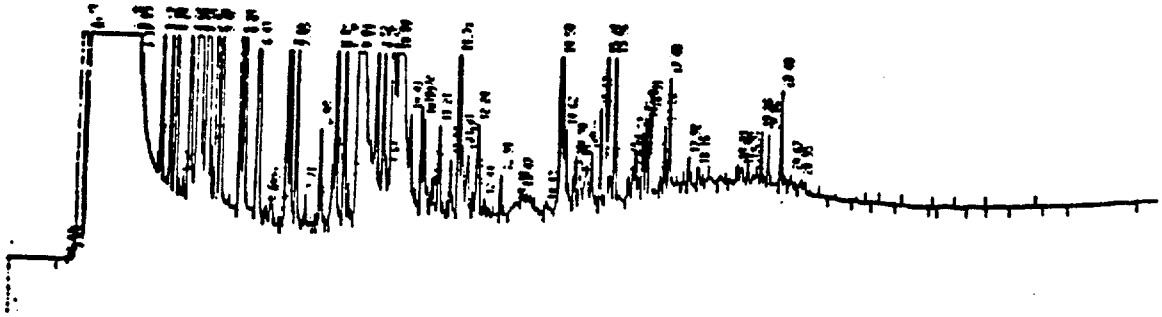
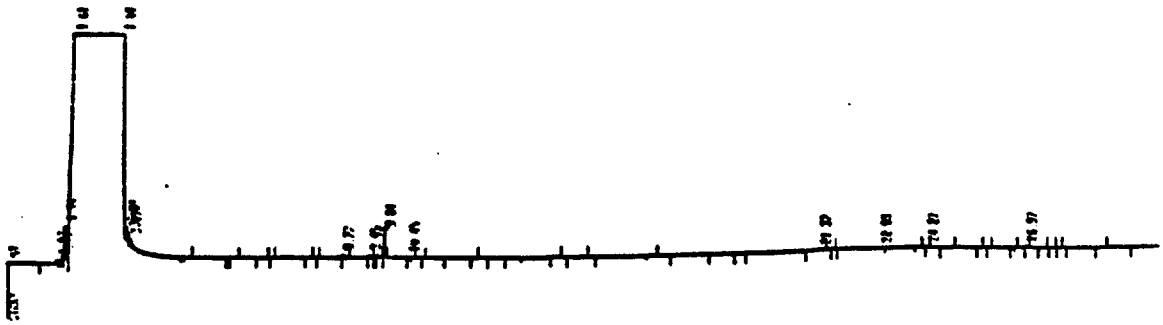


Figure 9. Results of experiments using Hexane Extraction

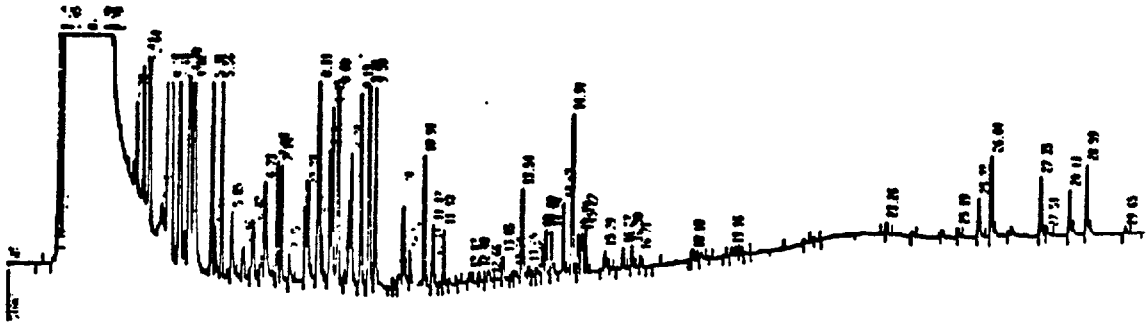
a Experiment 1



b Experiment 2



c Experiment 3



d Experiment 4

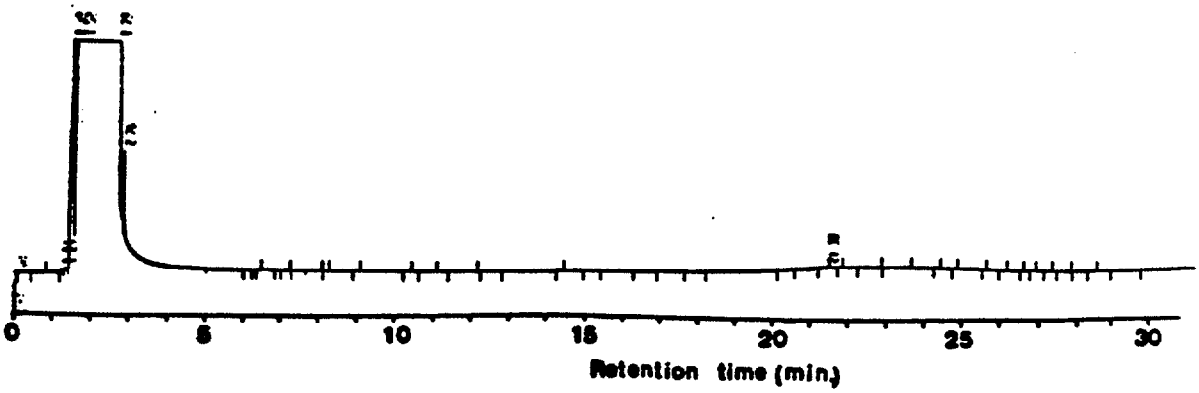
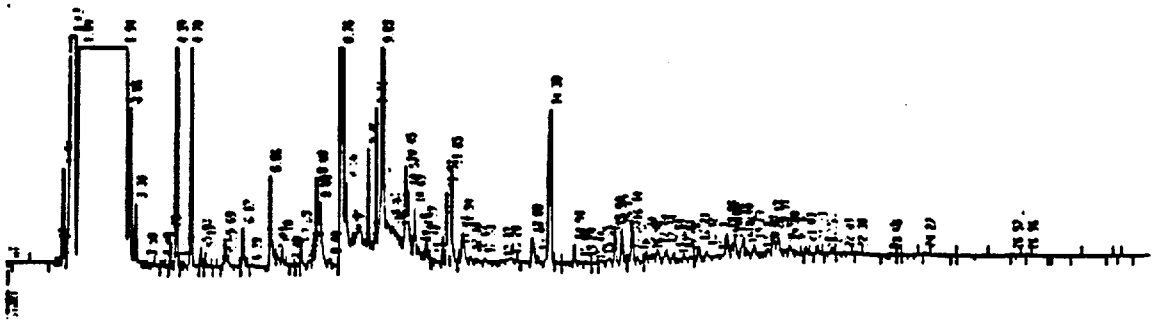
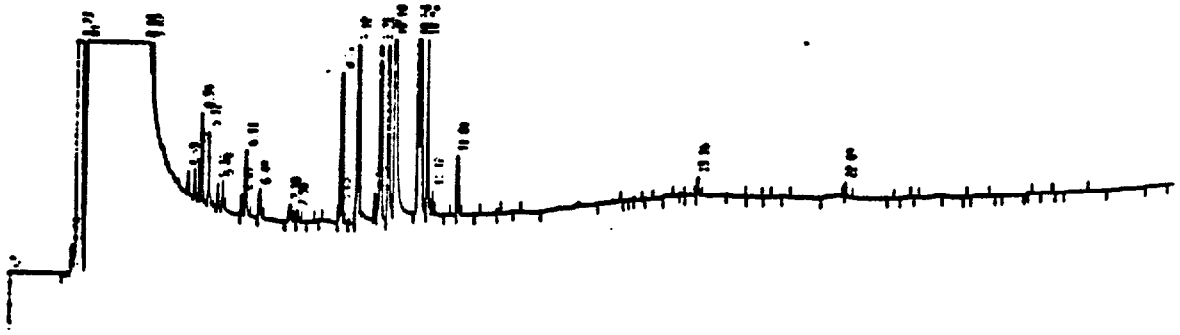


Figure 10. Results of experiments using Hexane Extraction

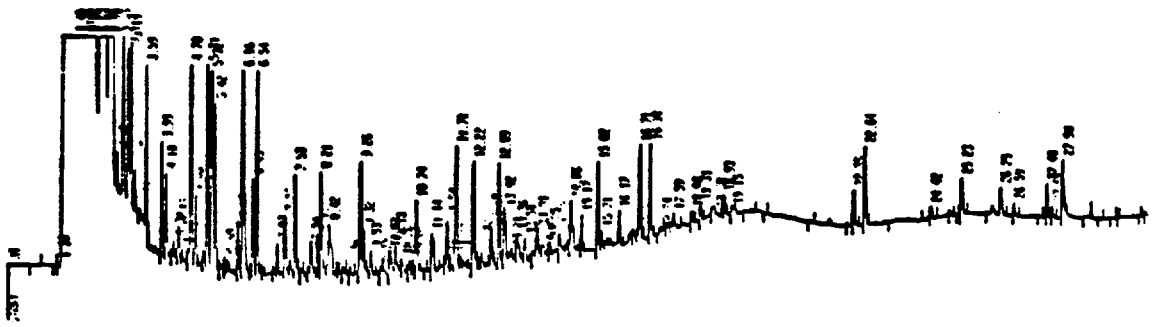
a Experiment 5



b Experiment 6



c Experiment 7



d Experiment 8

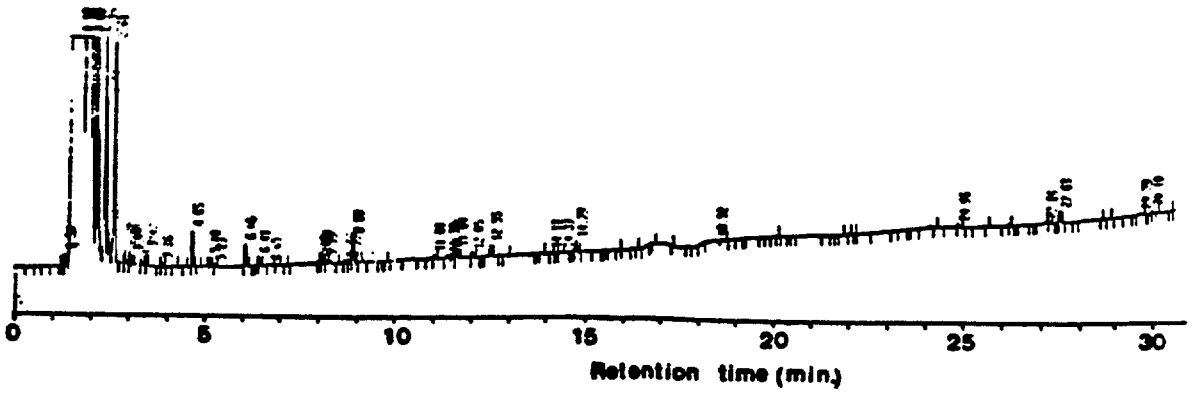


Figure 11. Comparison of the Degradation of Ozone at 10°C and 21°C (pH of Milli-Q water = 5.5)

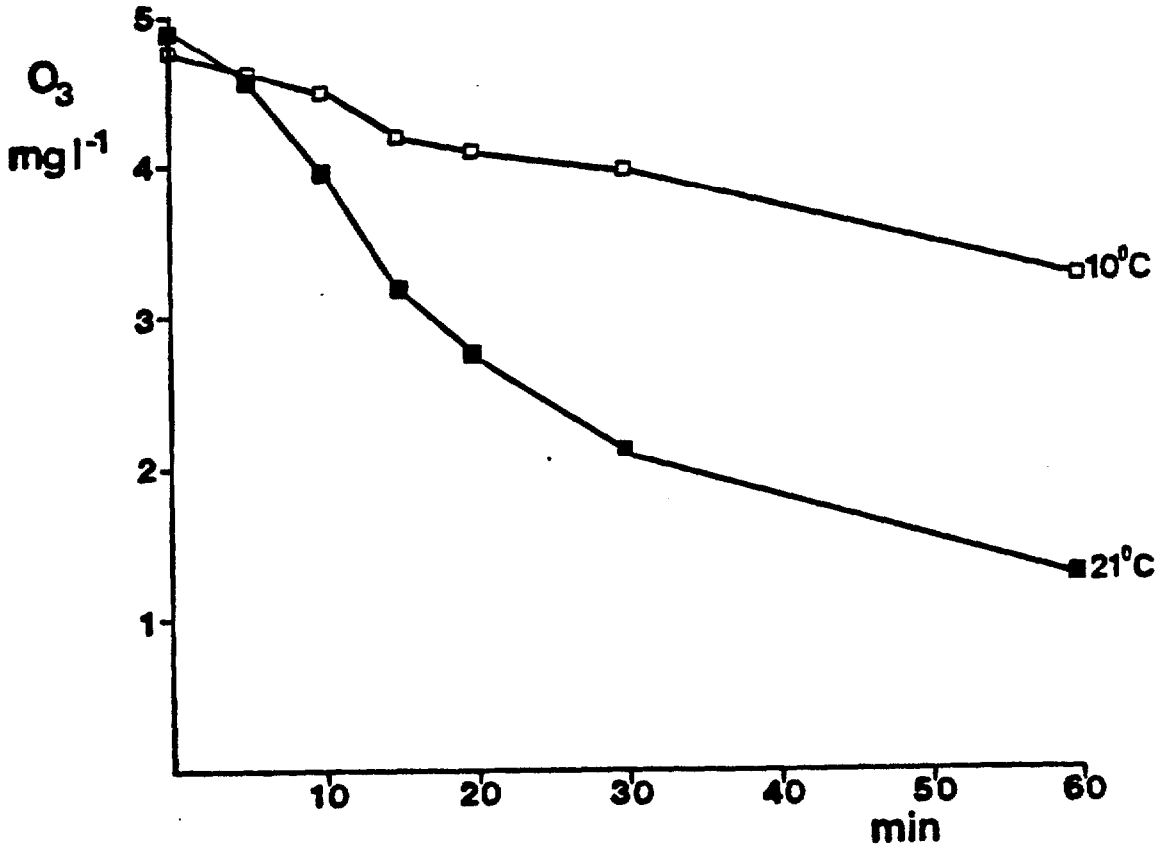
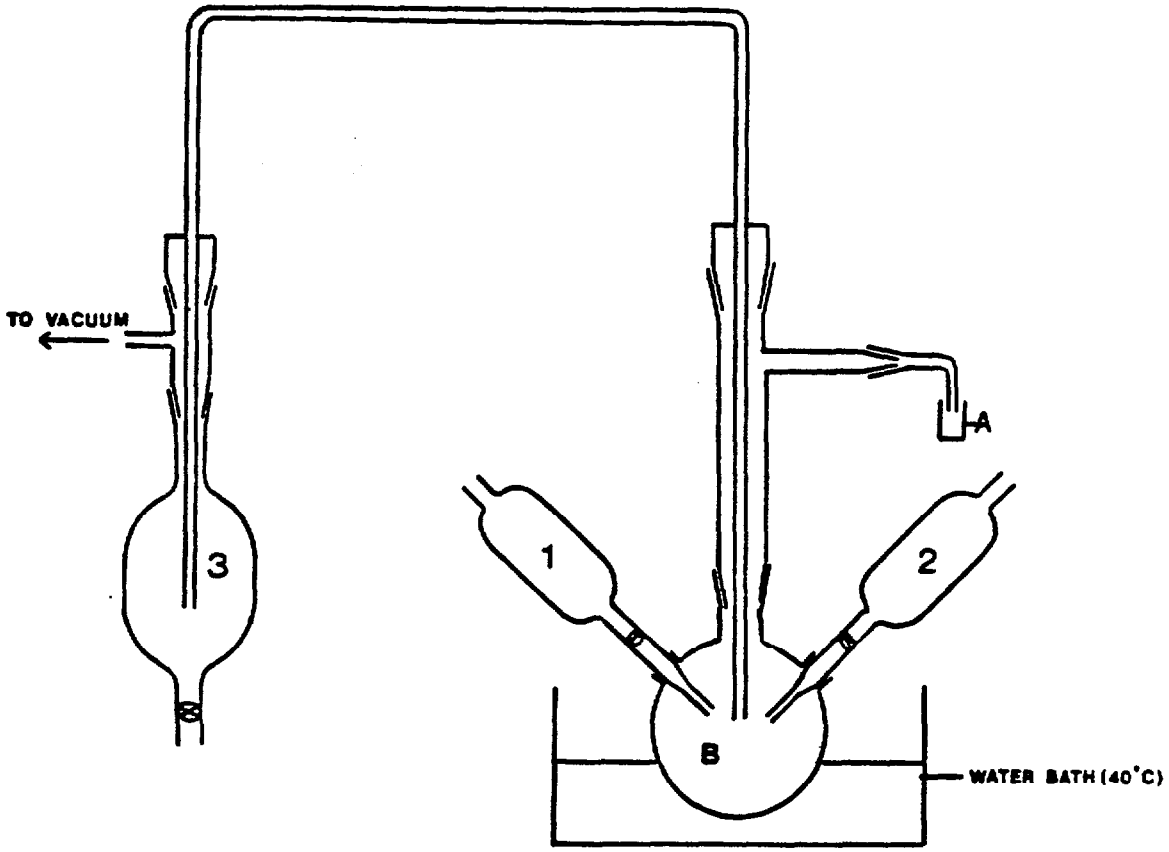


Figure 12. Apparatus for Diazomethane Generation



KEY

1	60% KOH
2	49% N-Methyl N-Nitroso-p-toluene sulphonamide
3	Glacial Acetic Acid
A	Reaction vial
B	Reaction vessel

Figure 13. GC chromatogram for (a) ozonated and (b) unozonated Alkane samples

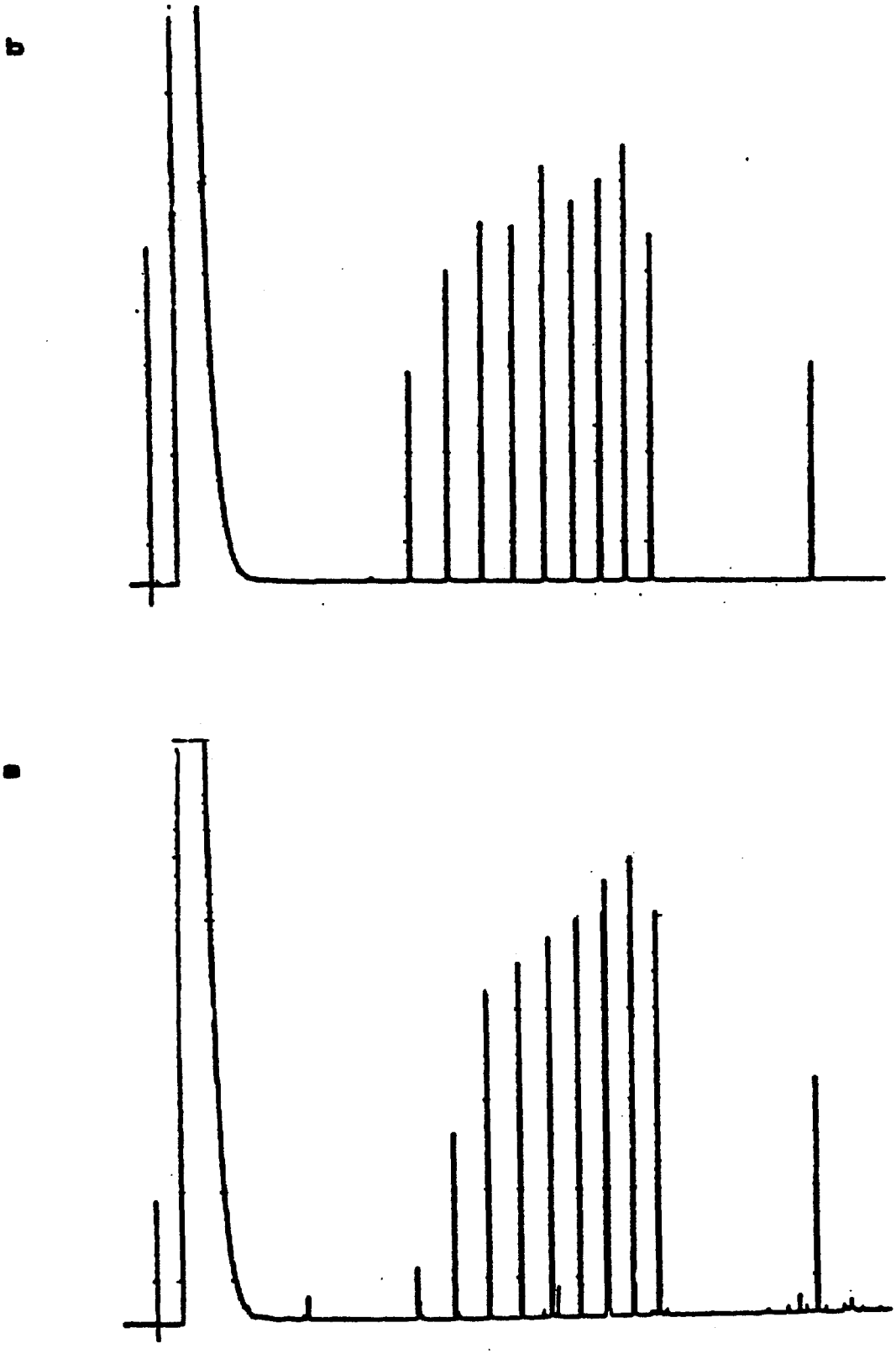
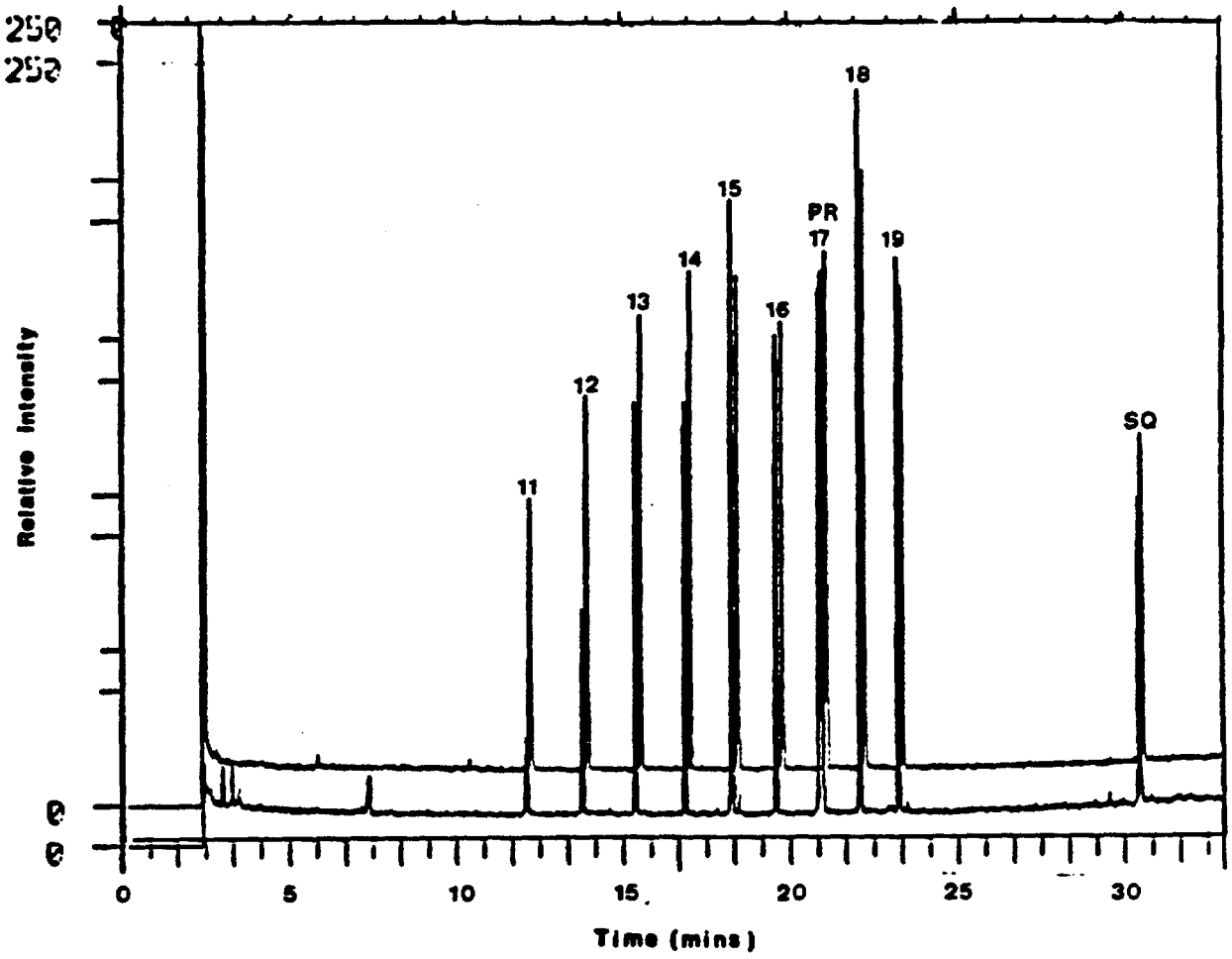


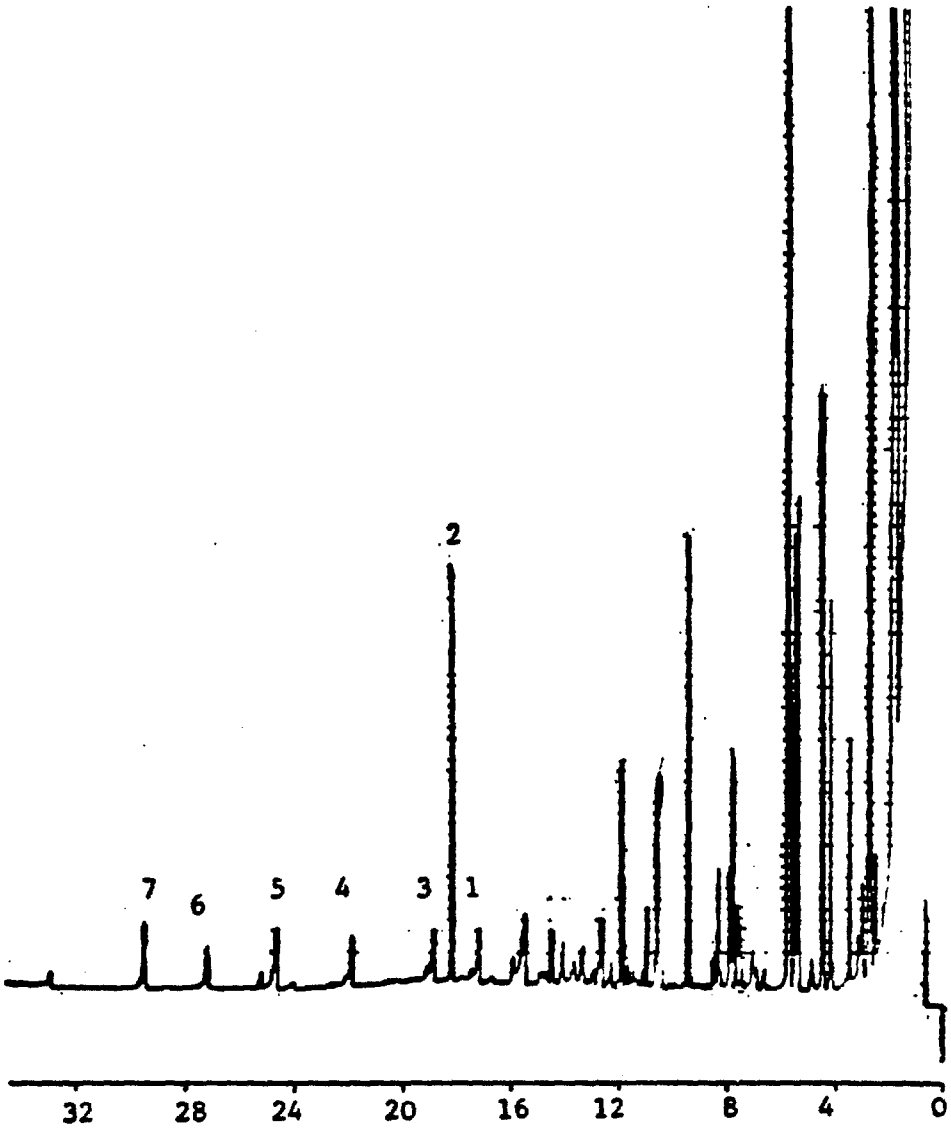
Figure 14. GC-MS chromatograms for unozonated (upper) and ozonated (lower) Alkane solutions.



Peak	Compound
11	undecane
12	dodecane
13	tridecane
14	tetradecane
15	pentadecane
16	hexadecane
17	heptadecane
PR	pristane
18	octadecane
19	nondecane
SQ	squalane

Figure 15. GC chromatograms for alkenes

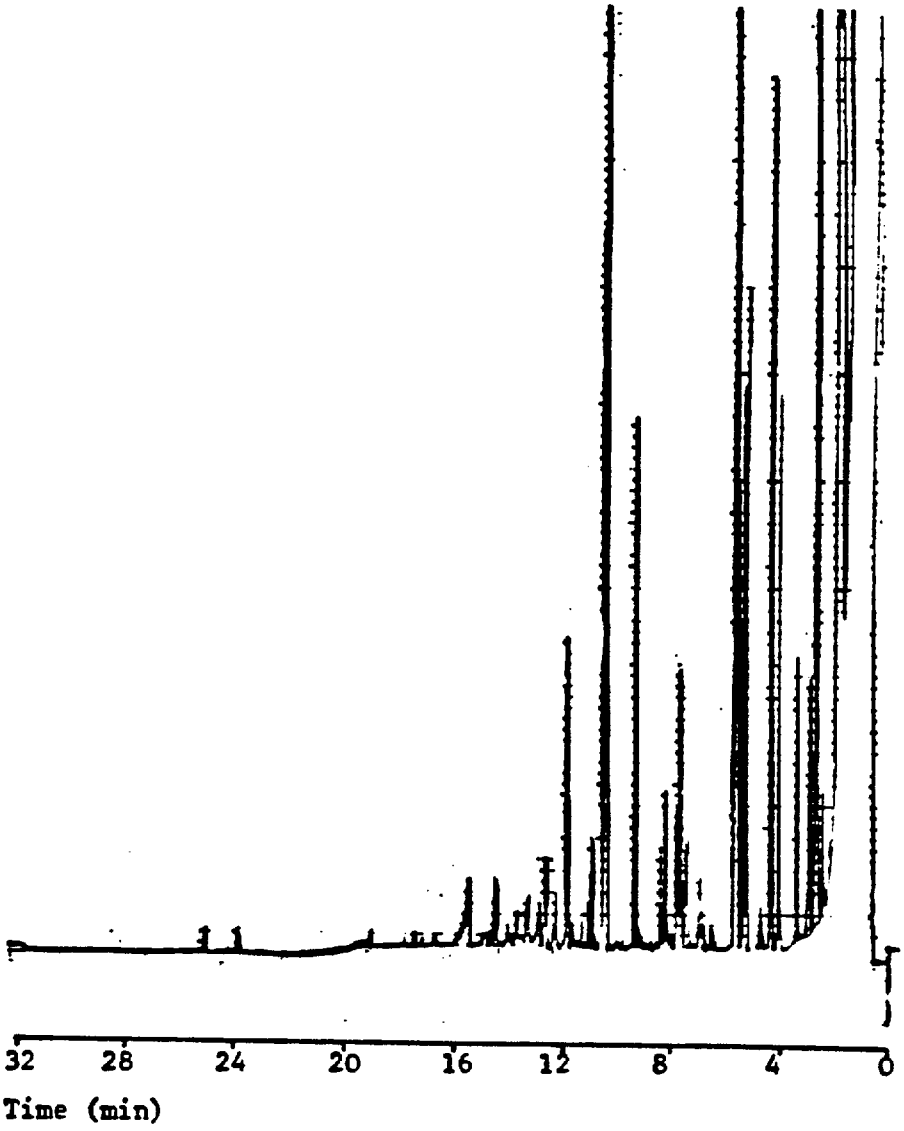
a Ozonated Alkenes



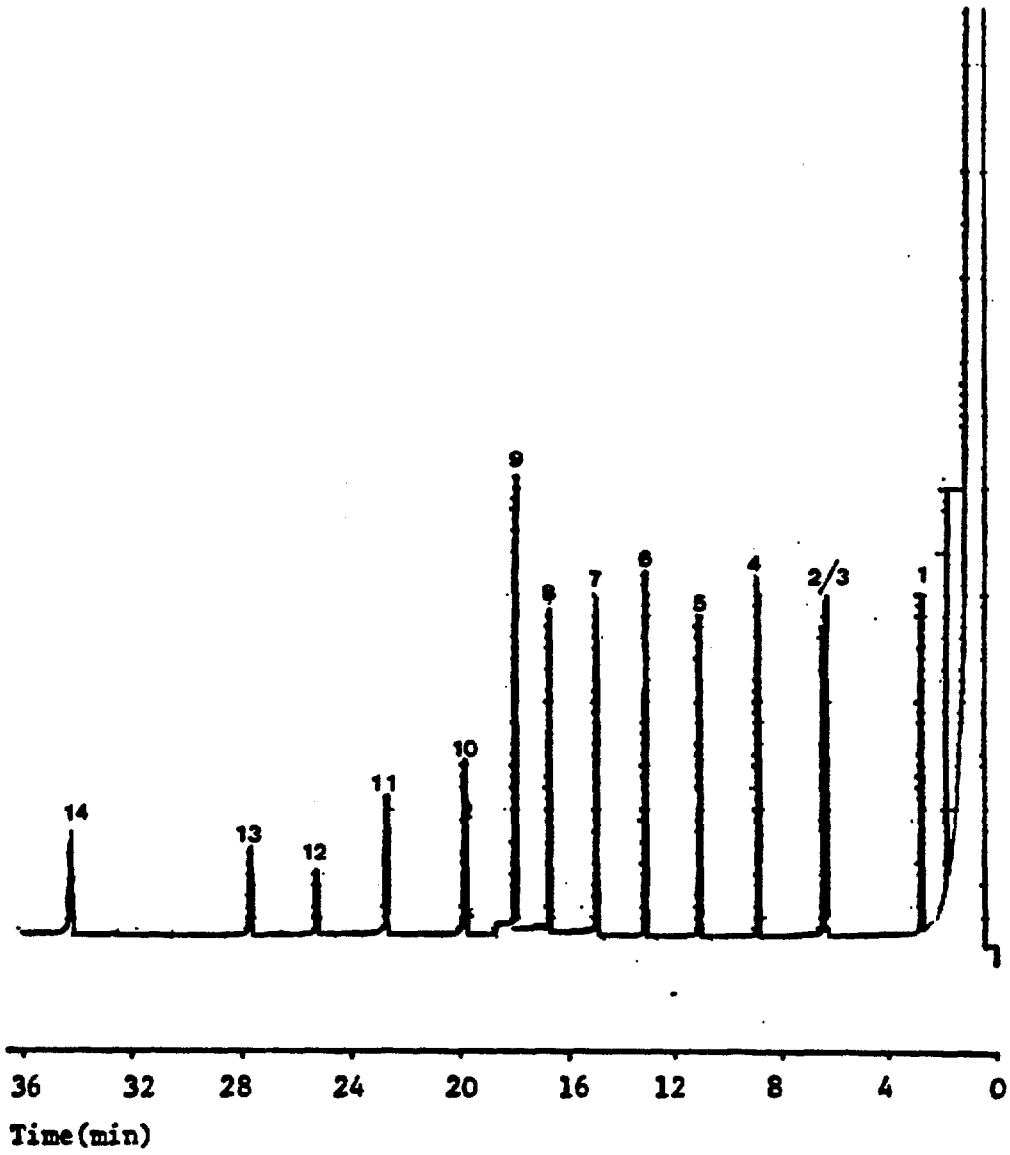
Peak	Compound	Retention Time(min)
1	x	17.2
2	Internal standard	18.0
3	x	18.9
4	x	21.9
5	x	24.6
6	x	27.2
7	x	29.5

x = unidentified product

b Ozonated Blank

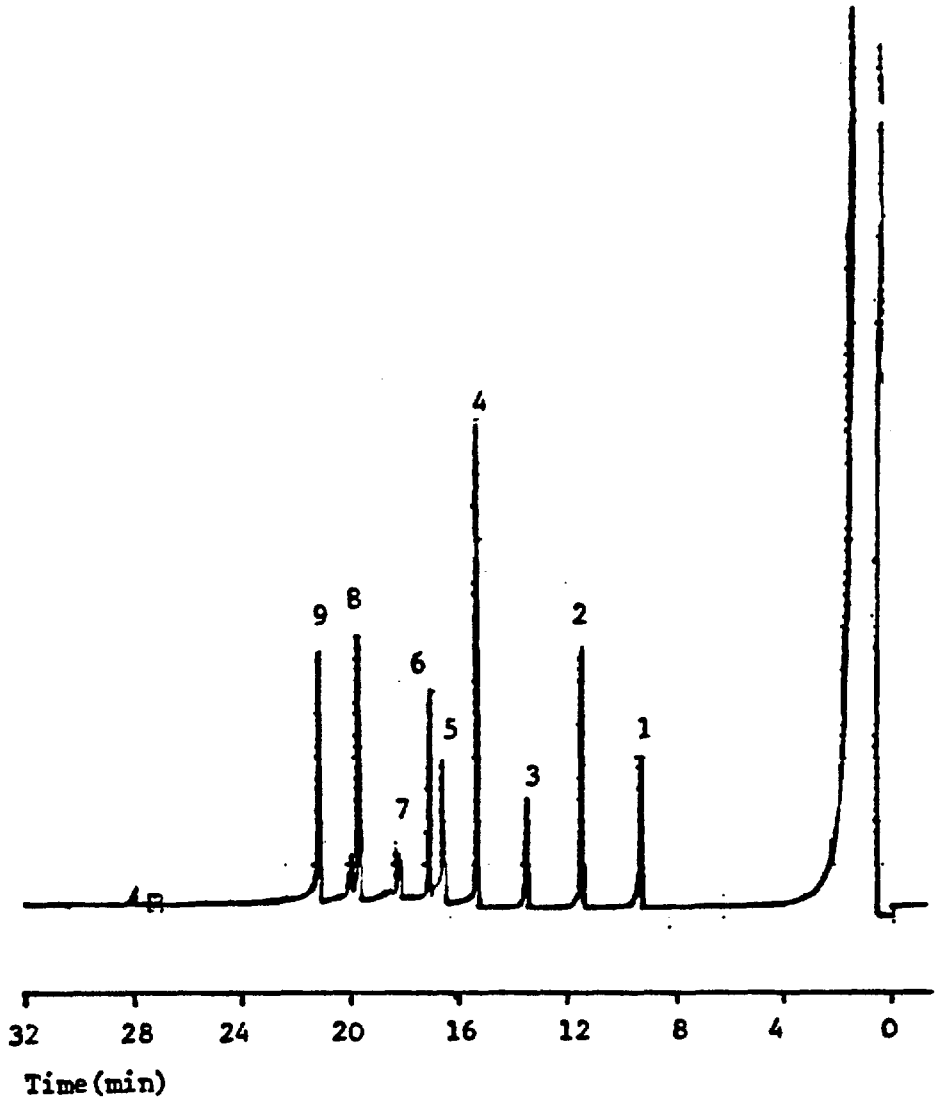


c Unozonated Alkenes



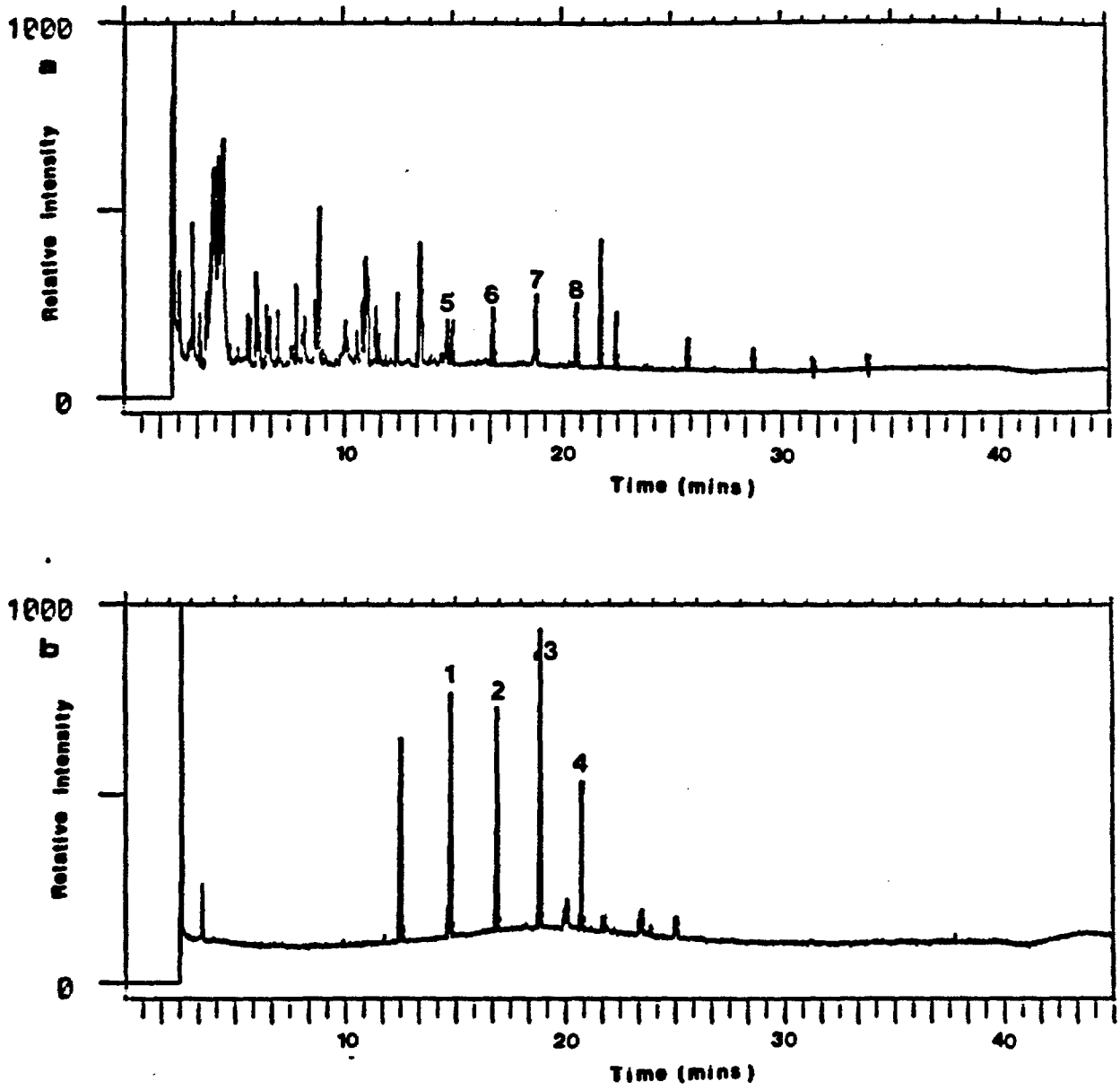
Peak	Compound	Retention time (min)
1	3,5,5, trimethylhex-1-ene (TMH)	2.8
2	non-1-ene ($C_{9(1)}$)	6.3
3	non-4-ene ($C_{9(4)}$)	6.5
4	dec-1-ene (C_{10})	8.9
5	undec-1-ene (C_{11})	11.1
6	dodec-1-ene (C_{12})	13.1
7	tridec-1-ene (C_{13})	14.9
8	tetradec-1-ene (C_{14})	16.6
9	Internal standard (1-chlorododecane)	18.0
10	hexadec-1-ene (C_{16})	19.8
11	octadec-1-ene (C_{18})	22.7
12	eicosene (C_{20})	25.2
13	docosene (C_{22})	27.6
14	squalene (Sq)	34.3

Figure 16. GC chromatogram for Aldehyde standard compounds



Peak	Compound	Retention time (min)
1	octanal	9.4
2	nonanal	11.5
3	decanal	13.5
4	undecanal	15.3
5	decanoic acid	16.5
6	dodecanal	17.1
7	undecanoic acid	18.2
8	dodecanoic acid	19.7
9	tridecanoic acid	21.1

Figure 17. GC-MS chromatograms for (a) ozonated Alkene compounds and (b) Aldehyde standards.



Retention Time(min)	Aldehyde standards (peak no.)	Ozonated alkene spectra (peak no.)
14' 50"	Nonanal (1)	(5)
16' 56"	Decanal (2)	(6)
18' 54"	Undecanal (3)	(7)
20' 46"	Dodecanal (4)	(8)

Figure 18. Mass spectra for (a) dodecanal standard and (b) reaction product for ozonated tridec-1-ene.

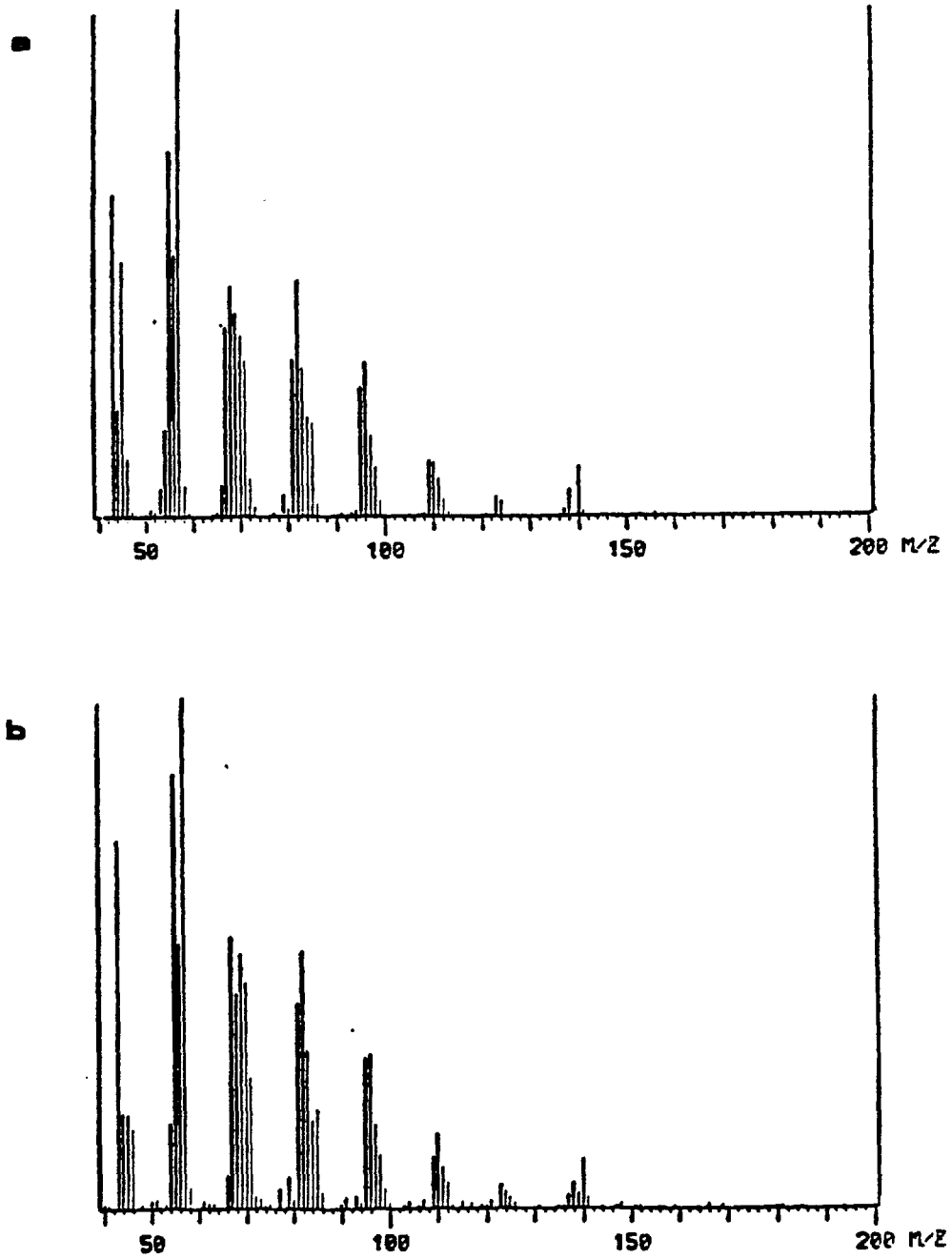
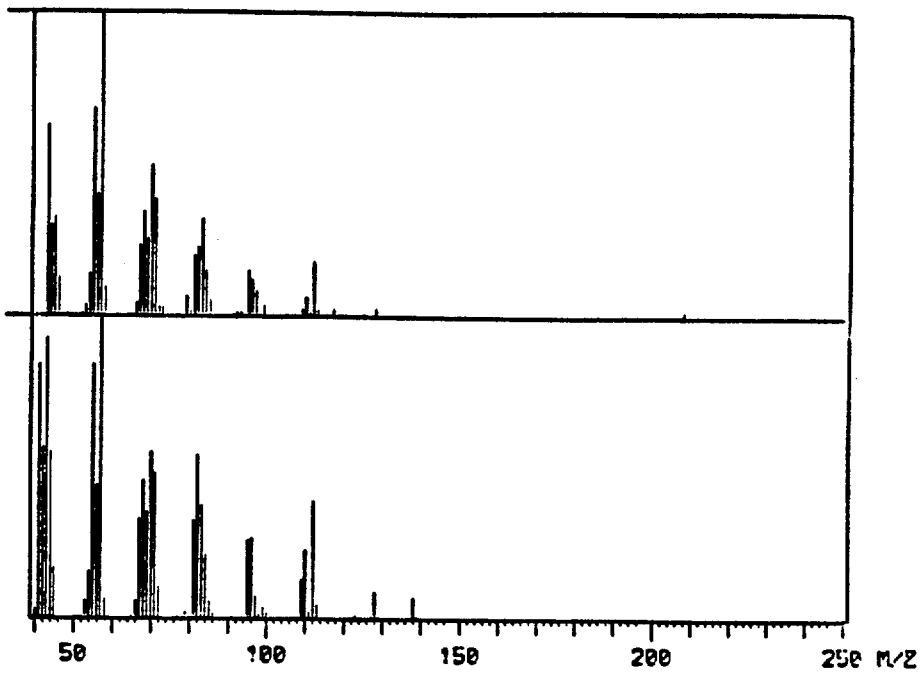
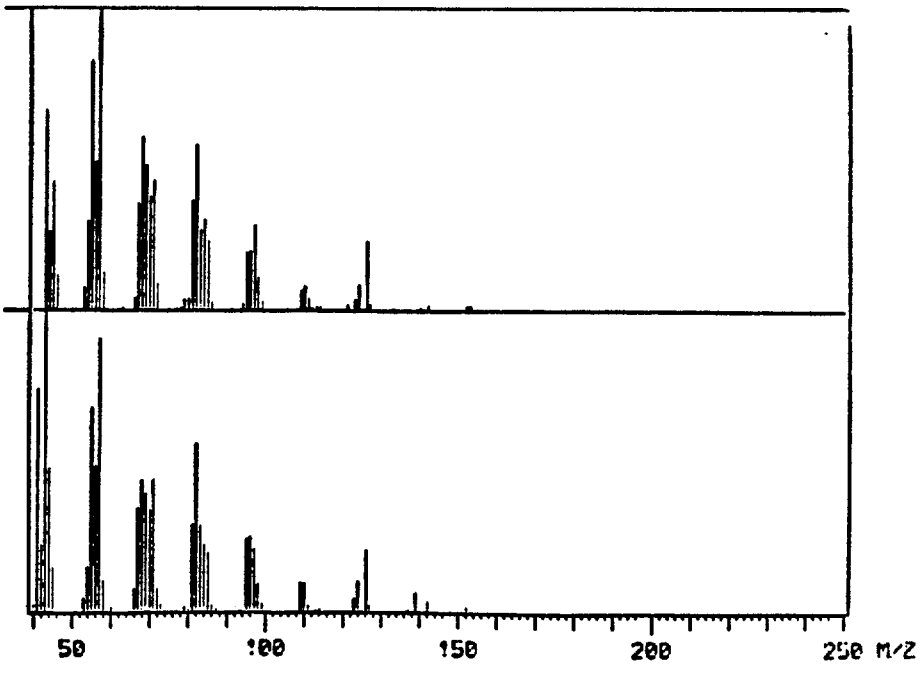


Figure 19. Mass spectra (upper, sample; lower, library), for Reaction Products of ozonated Alkenes

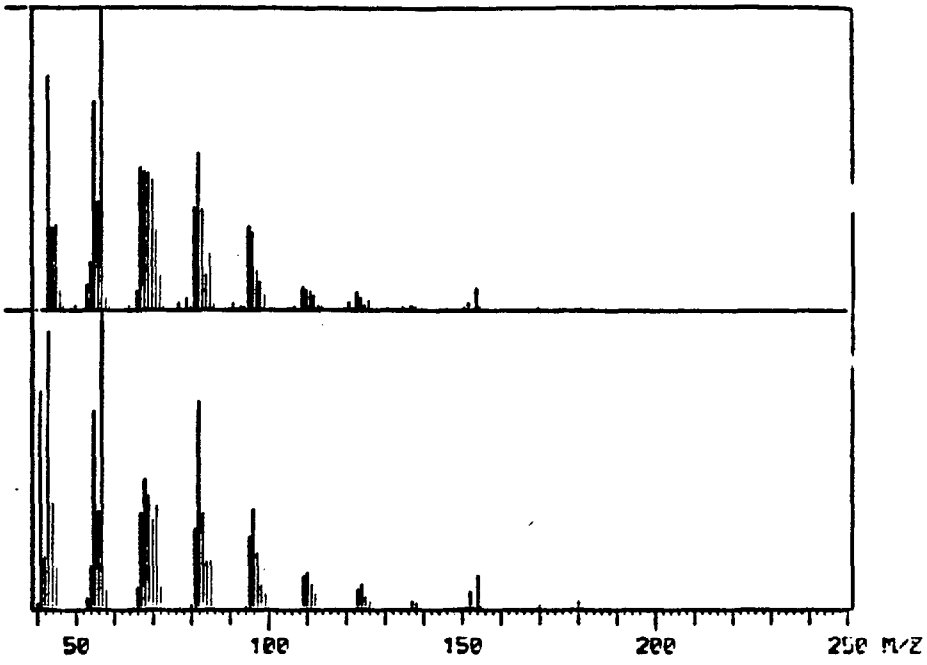
a decanal



b undecanal



c tridecanal



d tetradecanal

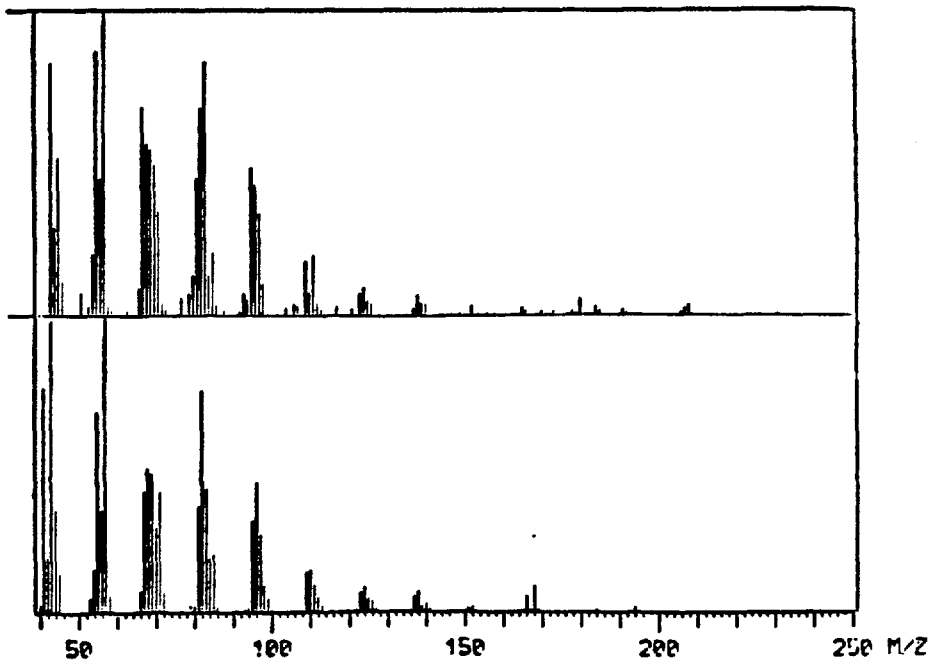
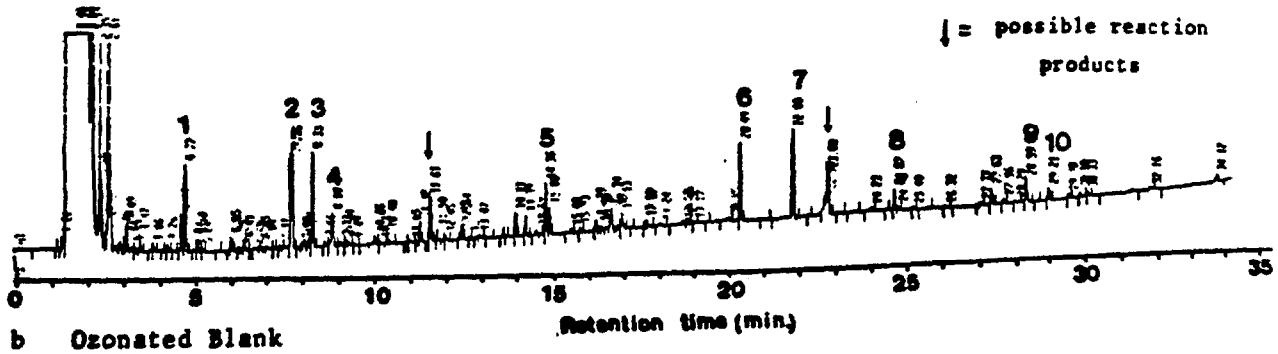
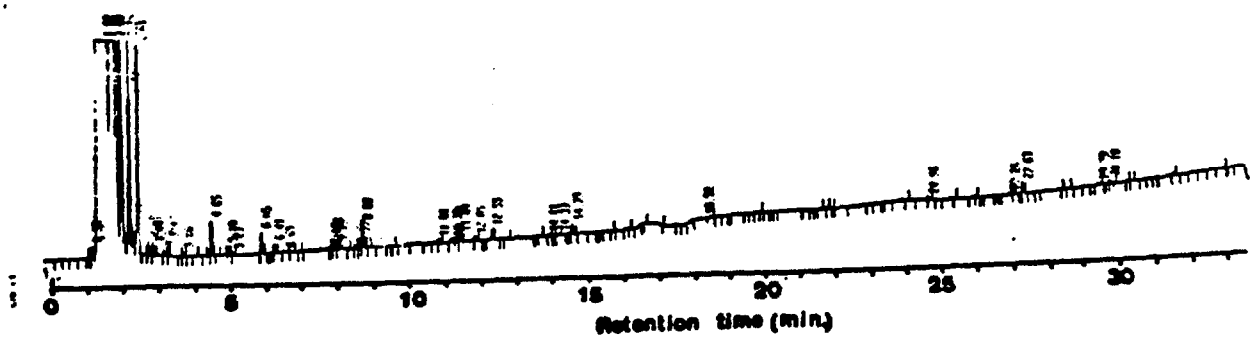


Figure 20. GC chromatograms for Aromatic Consumption

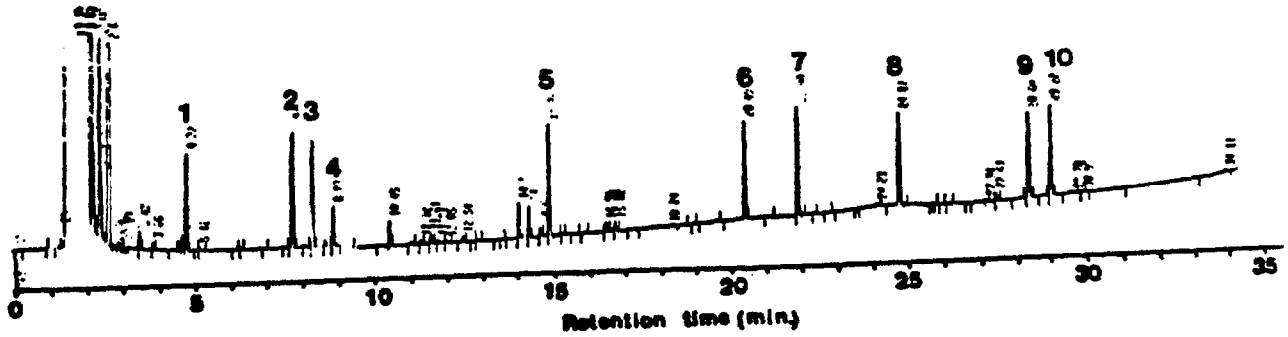
a Ozonated Aromatics



b Ozonated Blank

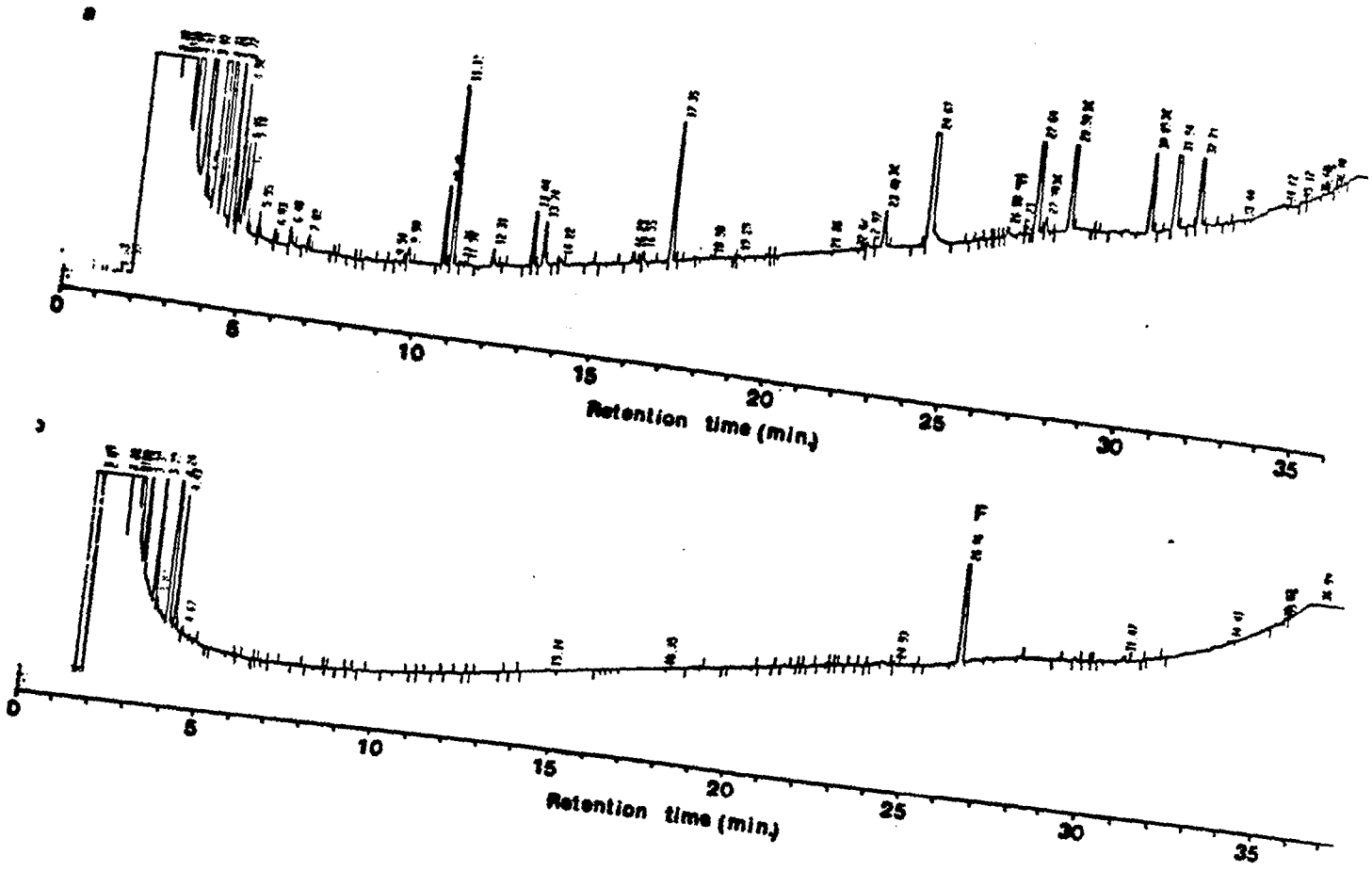


c Unozonated Aromatics



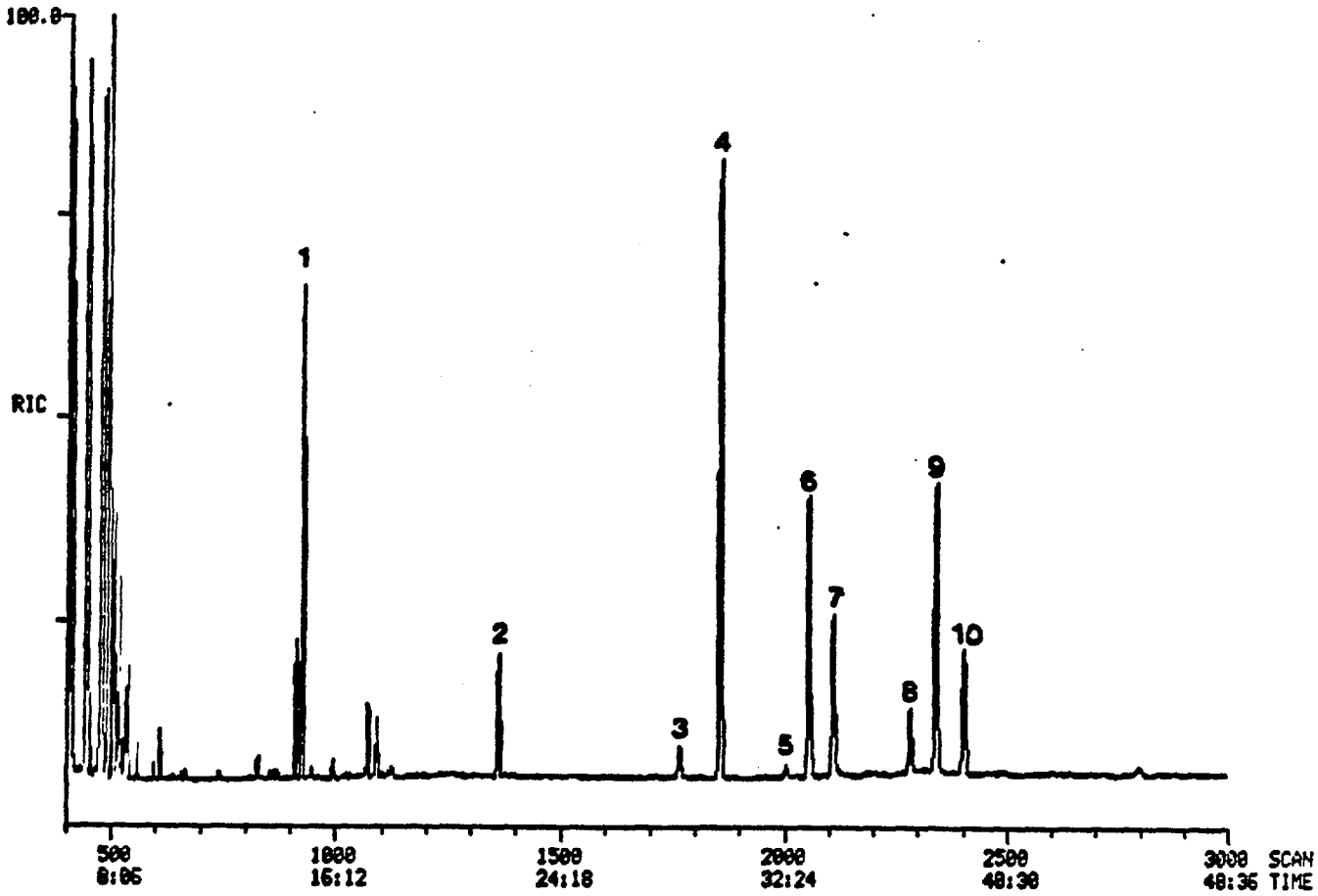
Peak	Compound	Retention time (min)
1	Toluene	4.77
2	o/p Xylene	7.74
3	m Xylene	8.34
4	Internal standard (3-chloroheptane)	8.09
5	Naphthalene	14.96
6	1-chlorododecane (Initial internal standard)	20.49
7	Fluorene	22.00
8	Phenanthrene	24.87
9	Fluoranthene	28.60
10	Pyrene	29.22

Figure 21. GC chromatograms for (a) ozonated Aromatic compounds ($200\mu gl^{-1}$) and (b) 9-fluorenone standard compounds



Compound	Retention time (mins)	
	a	b
9-fluorenone (F)	26.86	26.88
Unidentified compounds (x)	23.40	
	27.90	
	28.58	
	30.85	

Figure 22. GC-MS chromatogram for ozonated Aromatic compounds ($200\mu gl^{-1}$)



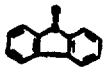
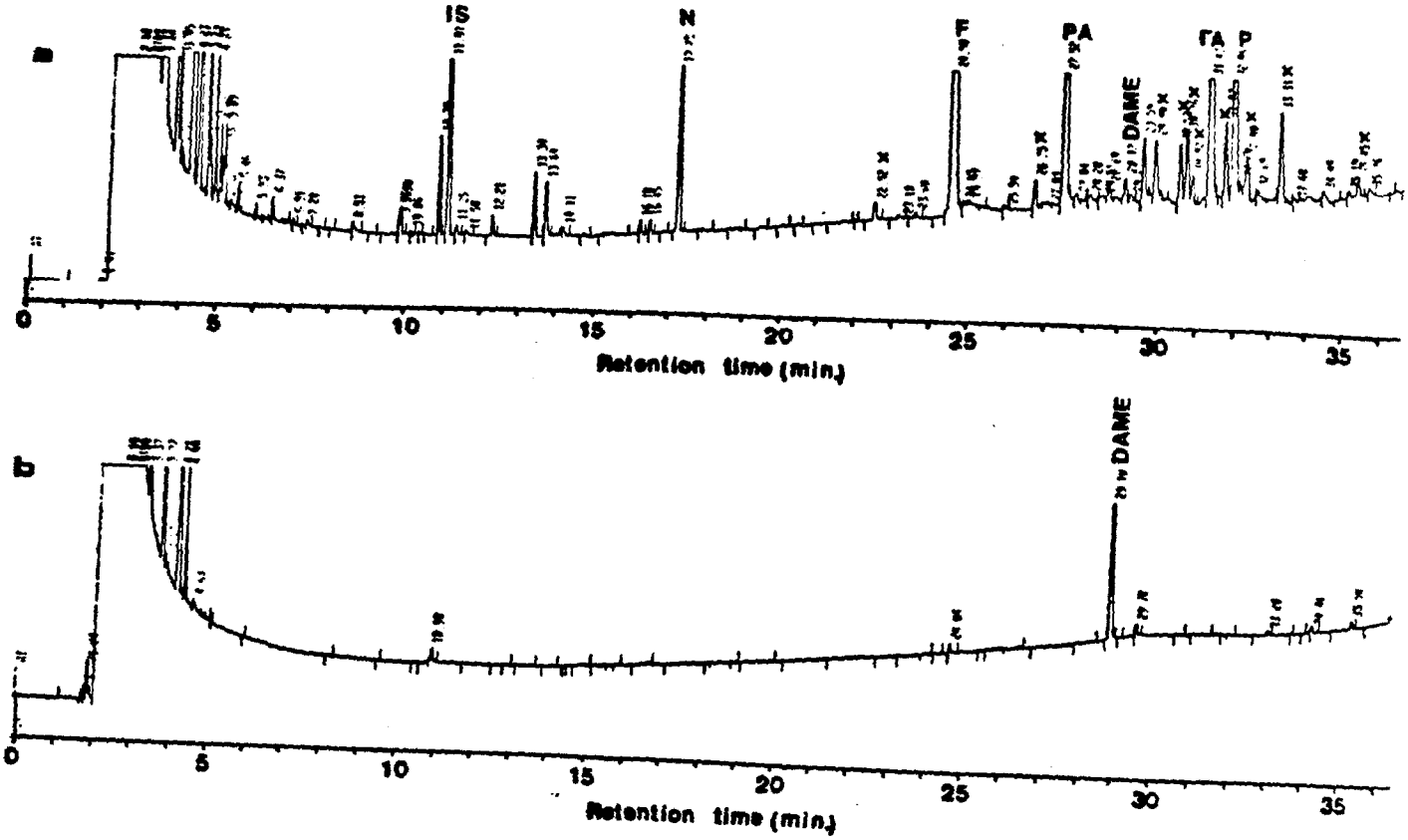
Peak	Compound	Major peaks in mass spectra	Possible identification	Structure
1	Internal standard (3-chloroheptane)			
2	napthalene			
3	-	131, 103, 77, 51, 44		
4	fluorene			
5	-	180, 152, 76	9-fluorenone	
6	phenanthrene			
7	-	210, 181, 152	phenanthrediol	
8	-	208, 180, 152	phenanthrene dione	
9	fluoranthene			
10	pyrene			

Figure 23. GC chromatograms for (a) ozonated Aromatic compounds ($200\mu gl^{-1}$; methylated extracts) and (b) diphenic acid standard (methylated)



Compound	Retention time (mins) a	b
Internal standard (IS)	11.01	
Naphthalene (N)	17.25	
Fluorene (F)	24.58	
Phenanthrene (PA)	27.52	
Diphenic acid methyl ester (DAME)	29.12	29.10
Fluoranthene (FA)	31.42	
Pyrene (P)	32.06	
Unidentified compounds (x)	22.52	
	26.75	
	29.90	
	30.58	
	30.76	
	30.92	
	31.82	
	32.40	
	33.31	
	35.47	

Figure 24. Mass spectra (upper, sample; lower, library), fo
acid reaction product of Naphthalene

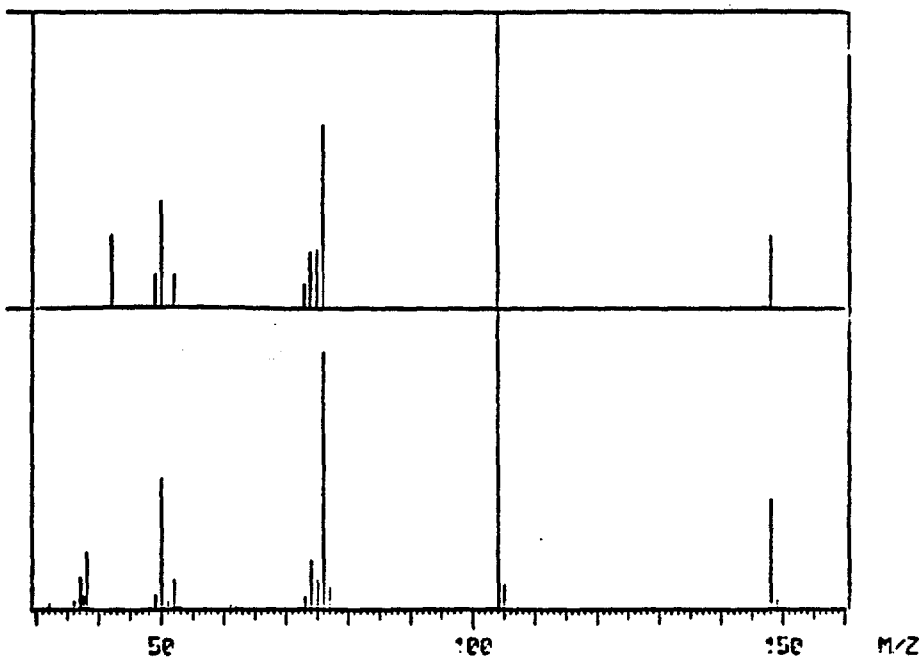


Figure 25. Mass spectra (upper, sample; lower, library), fo
dimethylphthalic ester, (methylated) reaction pr
Naphthalene ($1mgl^{-1}$)

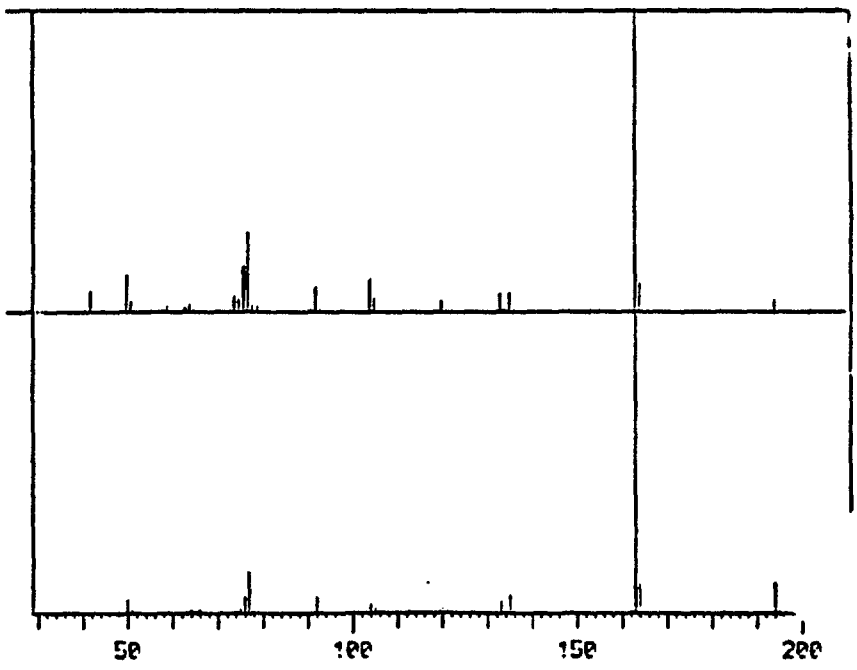
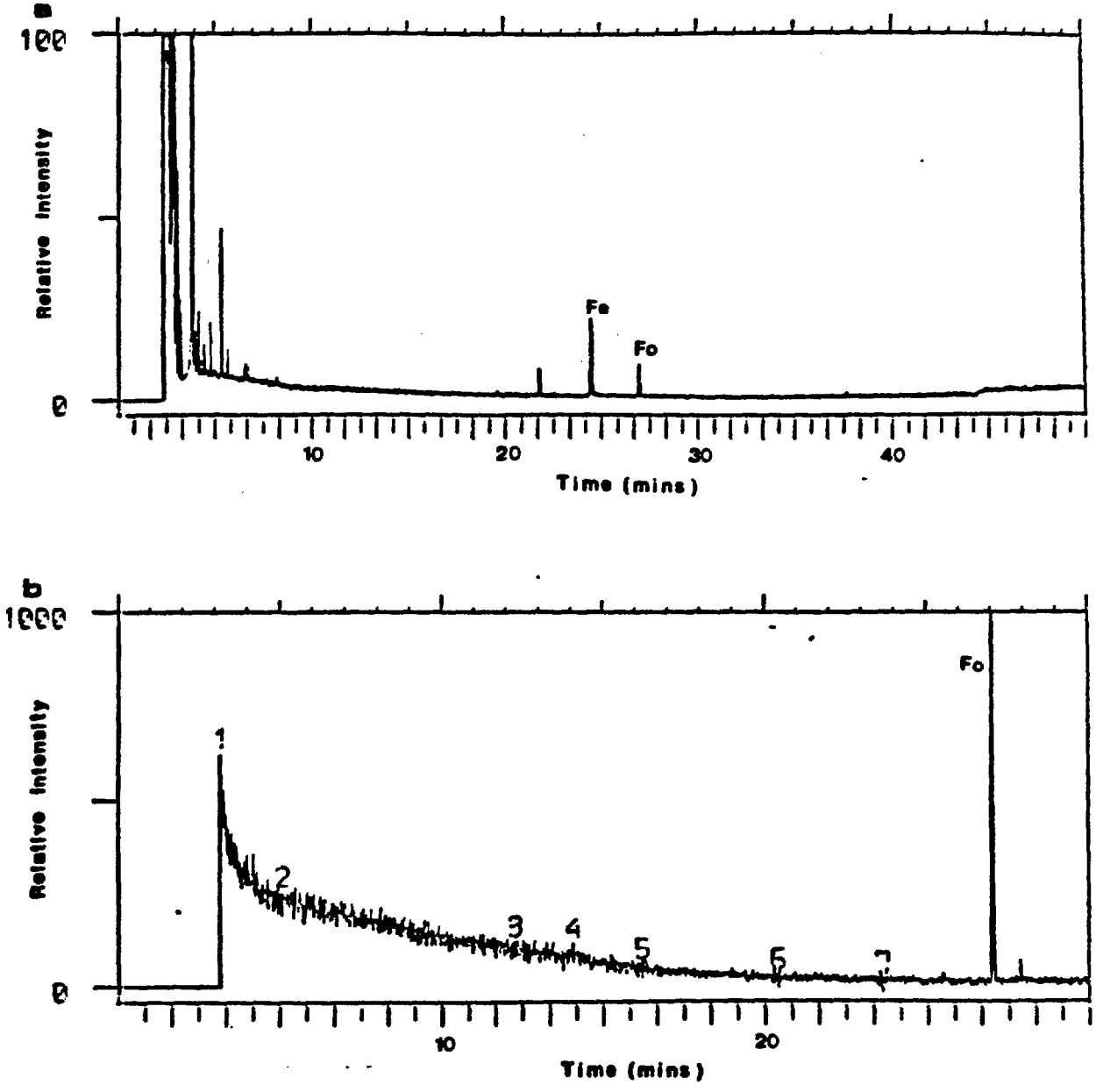


Figure 26. GC-MS chromatograms for (a) ozonated fluorene ($1mgl^{-1}$) and (b) 9-fluorenone standard



Compound	Retention time (mins)	
	(a)	(b)
fluorene (Fe)	24.34	-
9-fluorenone (Fo)	27.02	27.03

Figure 27. Mass spectra for (a) 9-fluorenone standard and (b) reaction product for ozonated fluorene ($1mgl^{-1}$)

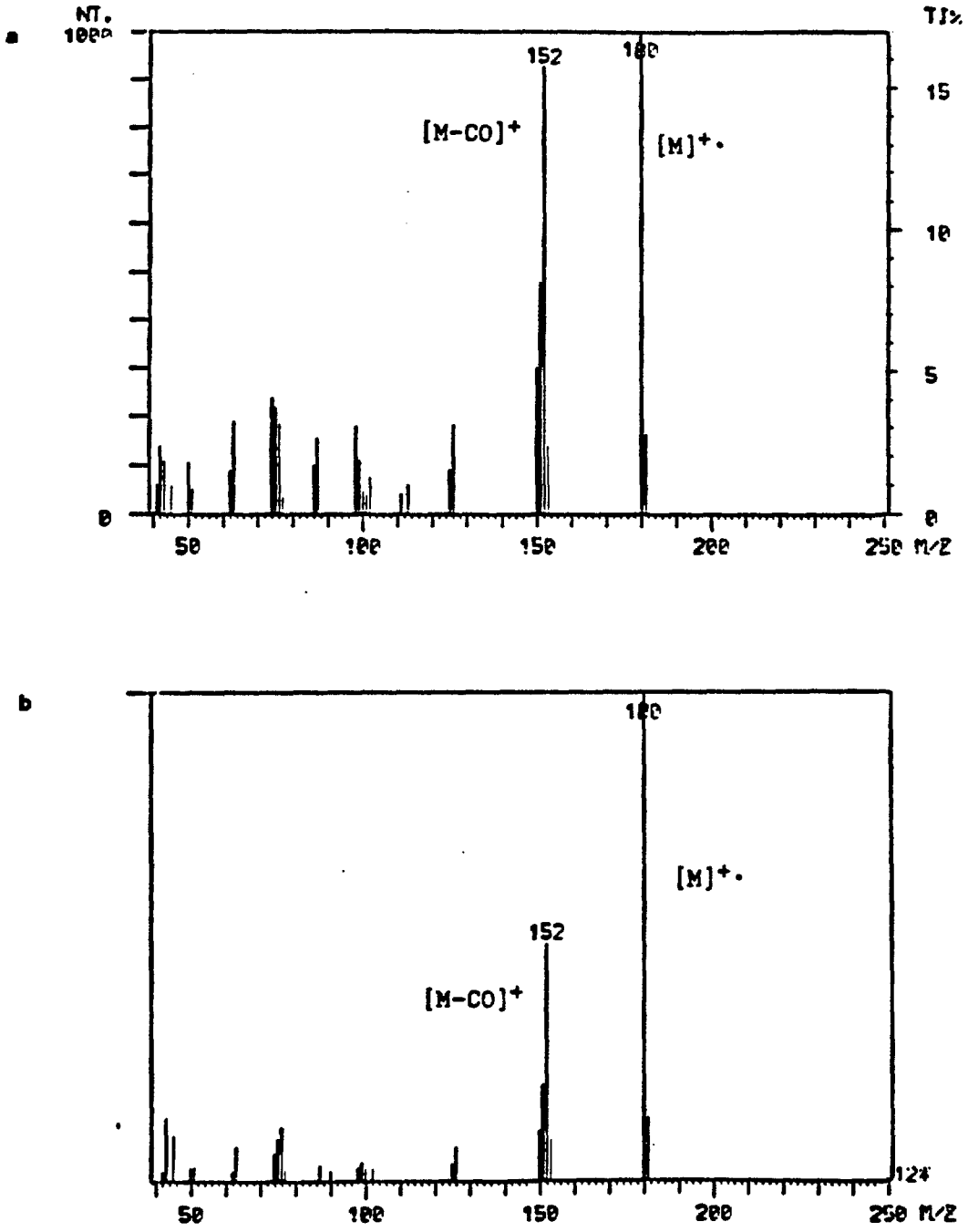
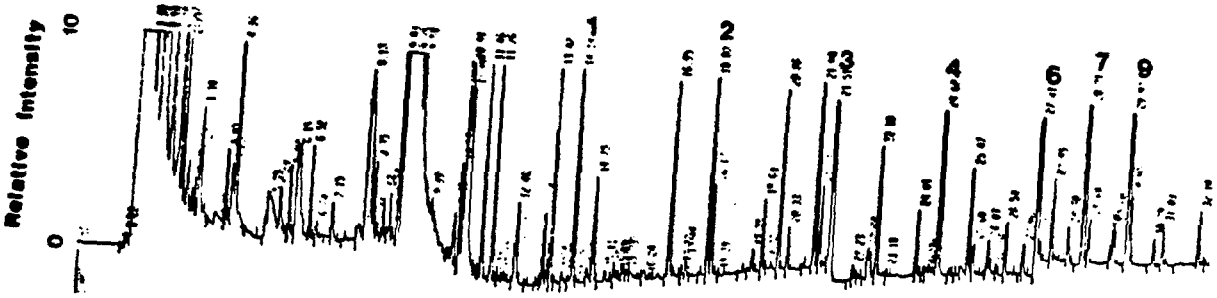
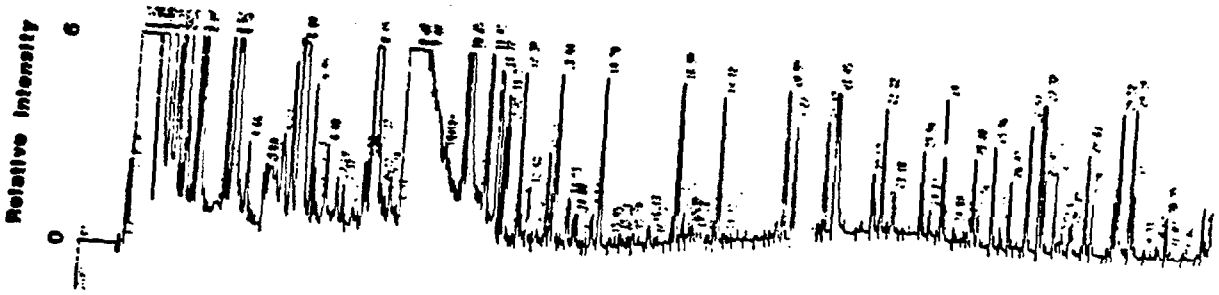


Figure 28 GC chromatograms for Fatty Acid consumption (Methylated sam

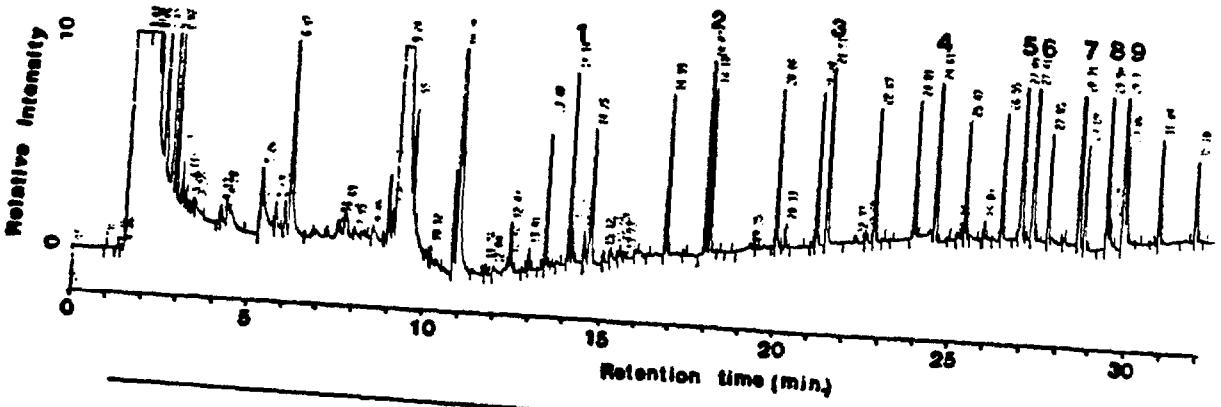
a Ozonated Fatty Acids



b Ozonated Blank

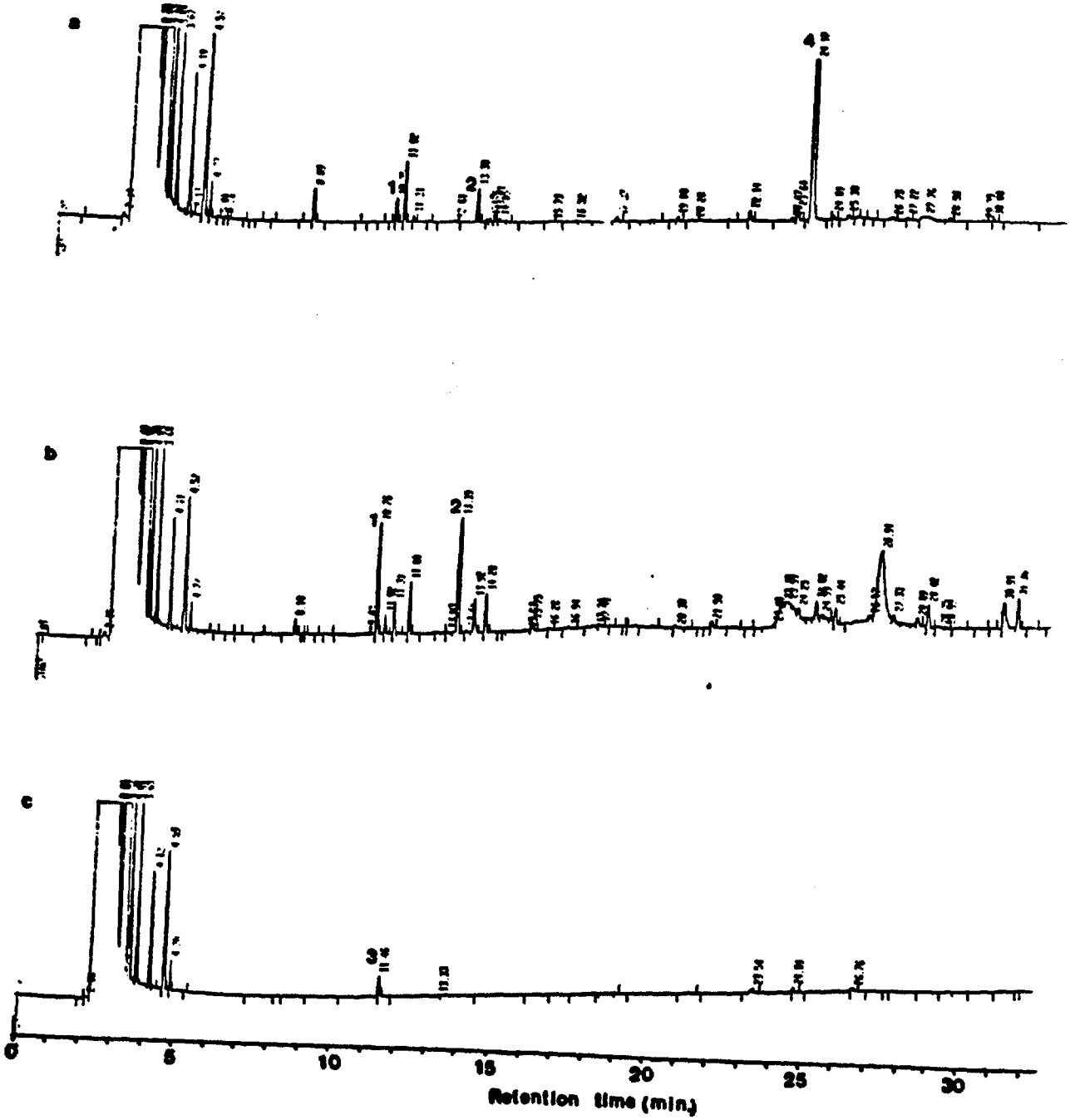


c Unozonated Fatty Acids



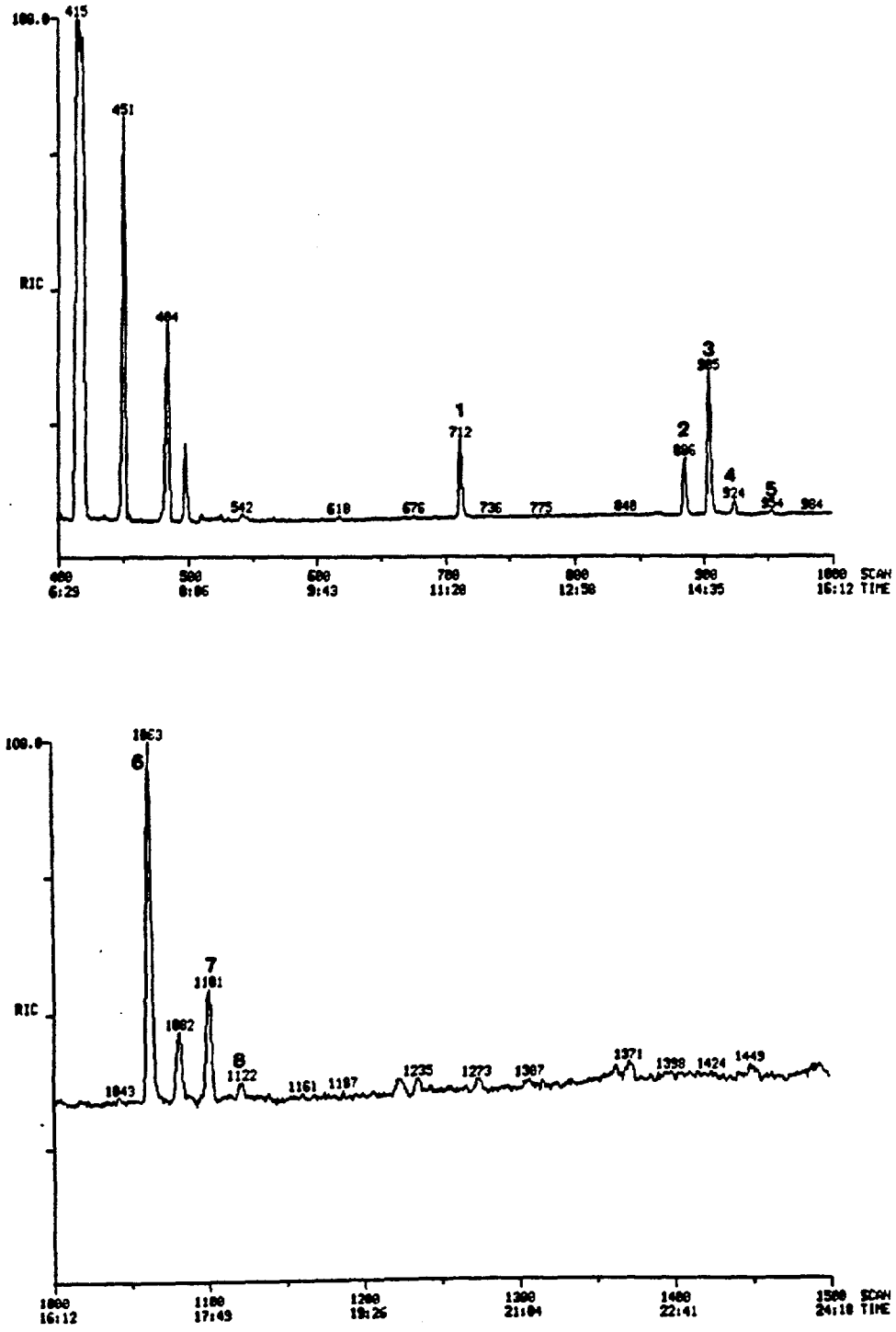
Peak	Compound	Retention time (mins)
1	Octanoic acid (C_8)	14.14
2	Decanoic acid (C_{10})	18.07
3	Dodecanoic acid (C_{12})	21.51
4	Tetradecanoic acid (C_{14})	24.61
5	Palmitoleic acid ($C_{16:1}$)	27.09
6	Hexadecanoic acid (C_{16})	27.41
7	Heptadecanoic acid (C_{17})	28.71
8	Linoleic acid ($C_{18:2}$)	29.50
9	Octadecanoic acid (C_{18})	29.97

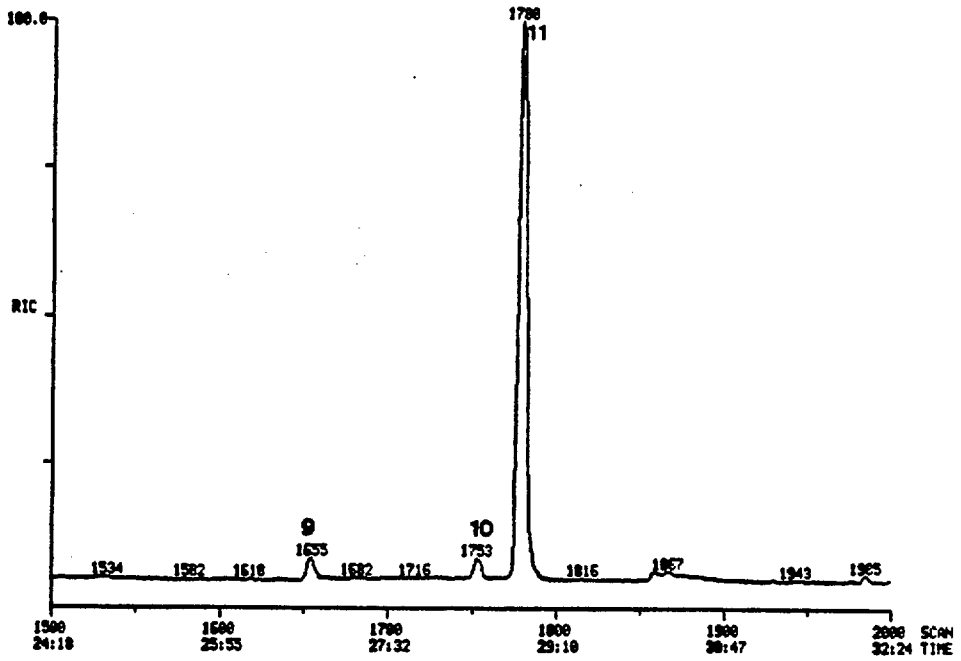
Figure 29 GC chromatograms for (a) ozonated unsaturated Fatty Acids ($500\mu gl^{-1}$; methylated extracts) and (b) heptanal and hexanal standards (methylated) and (c) propanedioic acid methyl est standard



Peak	Compound	Retention time (mins) a	b	c
1	hexanal	10.76	10.76	
2	heptanal	13.38	13.39	
3	propanedioic acid methyl ester			11.46
4	dodecanoic acid (internal standard)	24.18		

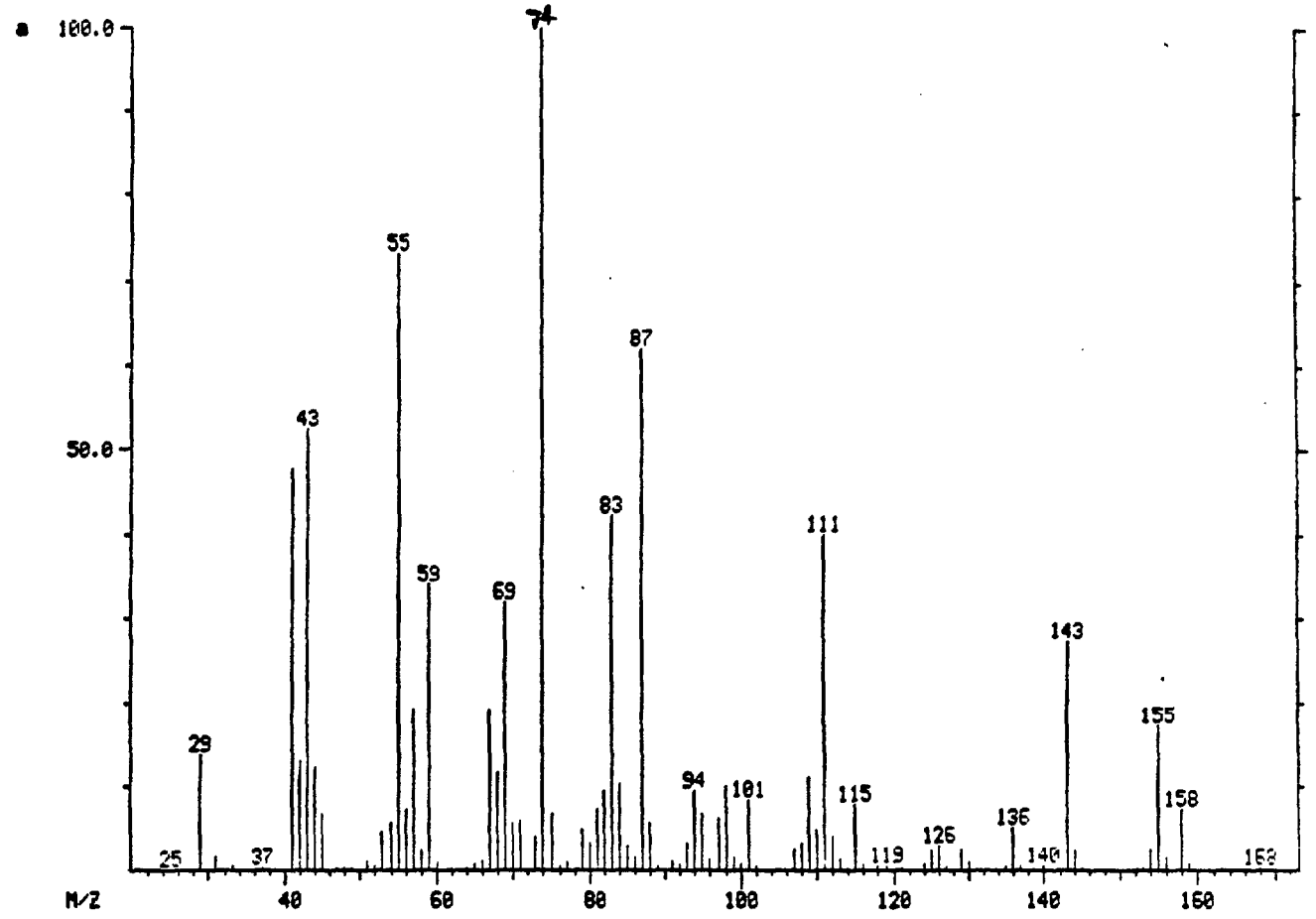
Figure 30 GC-MS chromatogram for ozonated unsaturated Fatty Acids (500$\mu g l^{-1}$; methylated extracts)





Peak	Compound	Major peaks in mass spectra
1	hexanal	82, 72, 56, 44, 79
2	2-heptanone	114, 99, 85, 71, 58, 43, 29
3	heptanal	114, 96, 81, 70, 44, 29
4	unidentified	96, 85, 71, 56, 44, 19
5	methyl hexanoate	133, 101, 99, 87, 74, 55, 53
6	2-octanone	128, 95, 85, 71, 58, 43, 29, 27
7	unidentified	130, 115, 71, 55, 43, 29
8	methyl heptanoate	101, 87, 74, 59, 43
9	9-oxononanoic acid methyl ester	see fig. 31
10	9-oxodecanoic acid methyl ester	see fig. 32
11	dodecanoic acid (Internal standard)	

Figure 31 Mass spectra for (a) 9-oxononanoic acid methyl ester from non aqueous ozonation of hexadec-9-enoic acid methyl ester (b) reaction product of ozonated unsaturated Fatty Acid extracts (methylated)



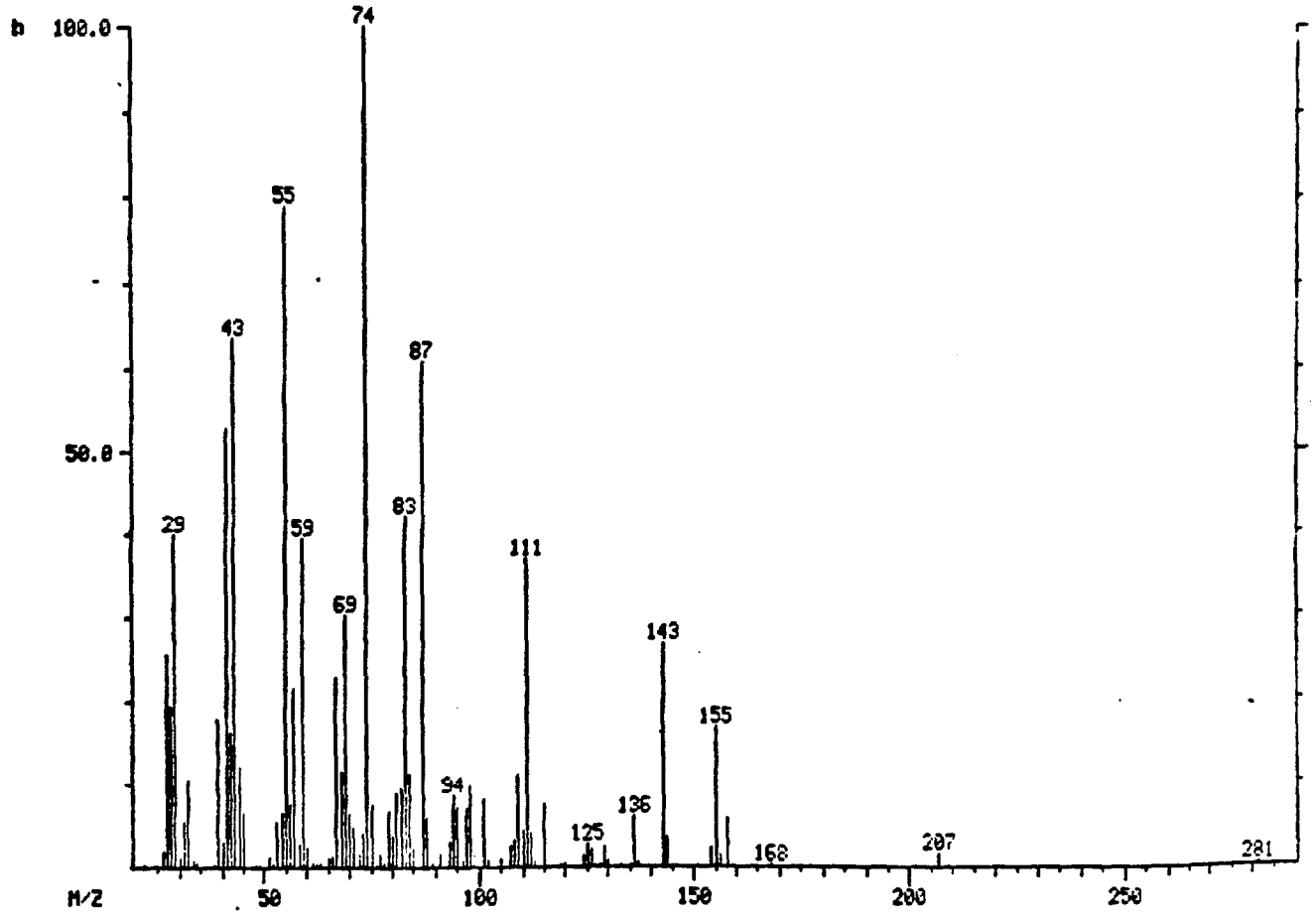


Figure 32 Mass spectra (upper, sample; lower, library), for 9-oxodecanoic acid methyl ester

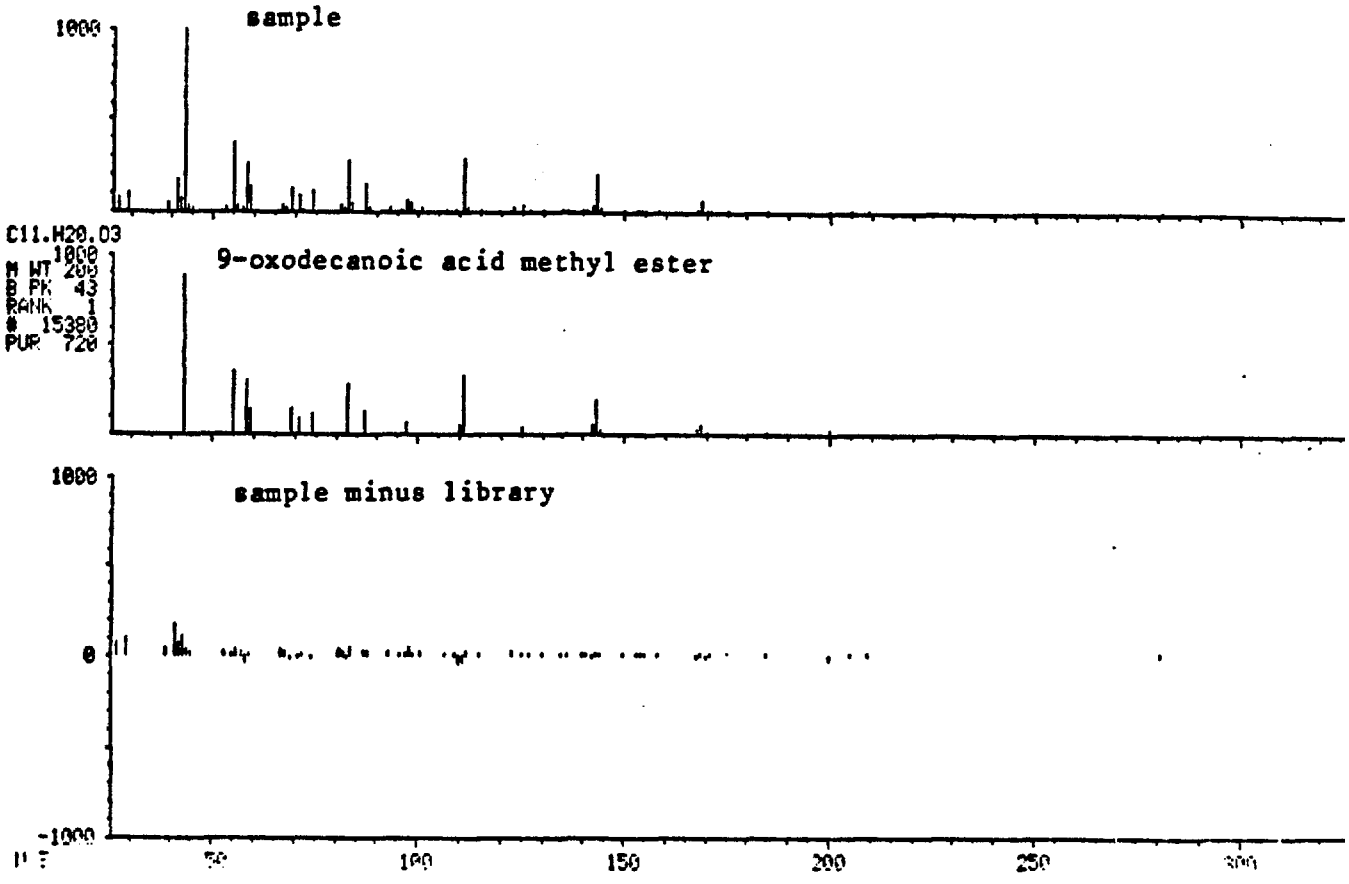
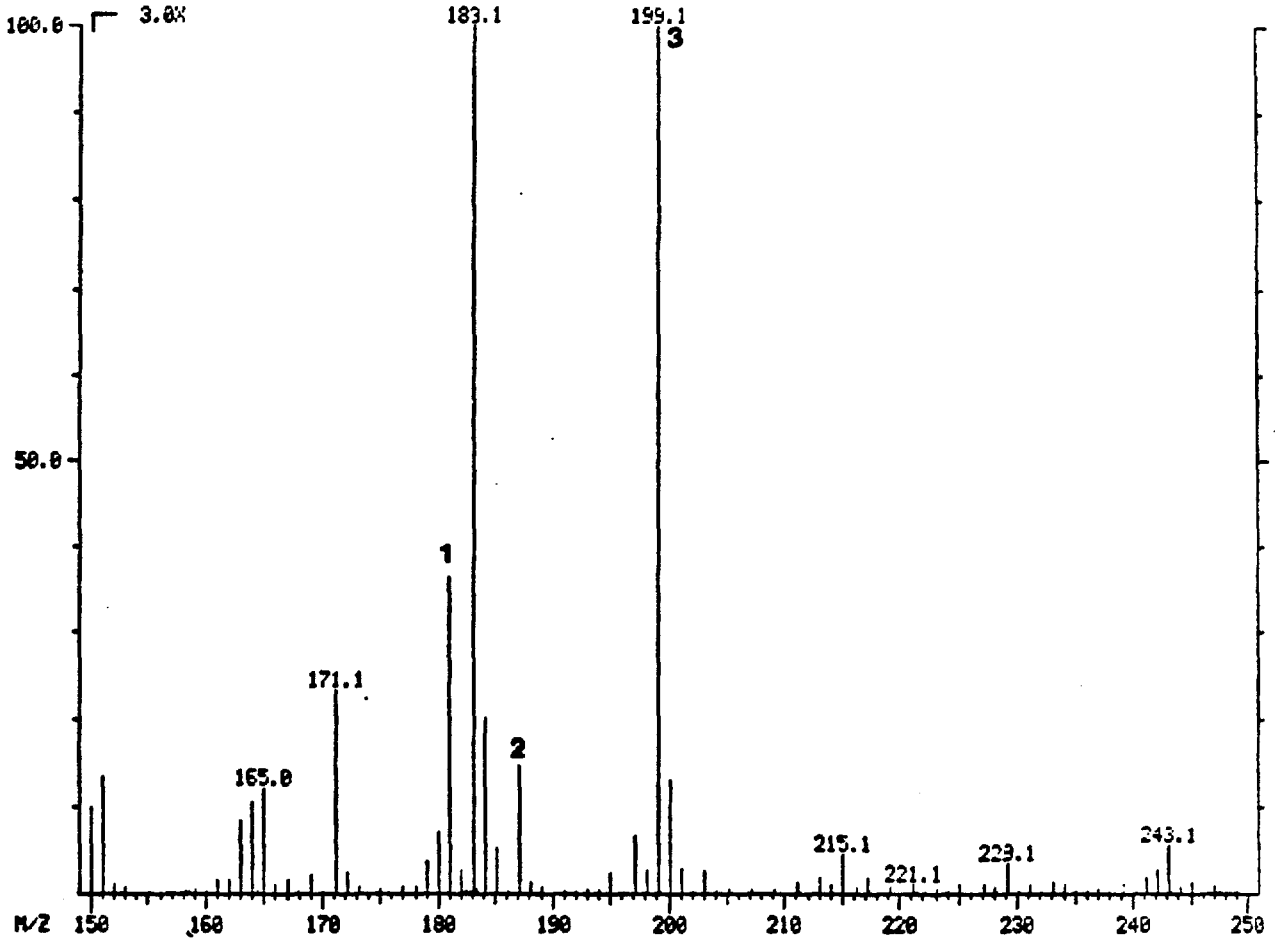


Figure 33 FAB negative ion mass spectrum for ozonated unsaturated fatty acids ($500\mu g l^{-1}$)

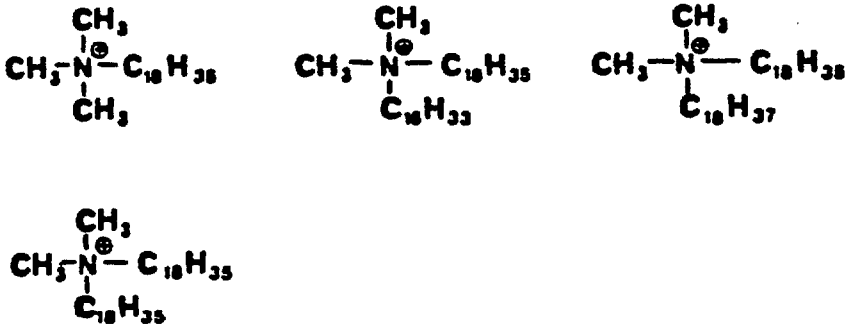


Peak	Compound
1	9-oxononanoic acid $[M - H]^-$ ion
2	nonandioic acid $[M - H]^-$ ion
3	dodecanoic acid $[M - H]^-$ ion

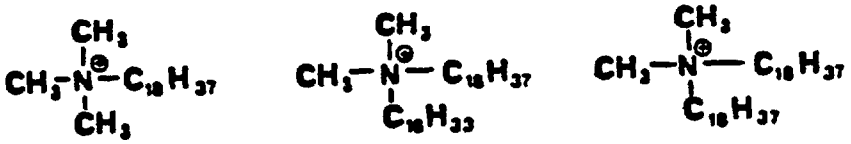
Figure 34. Structures of (a) cationic (b) anionic and (c) non-ionic surfactants studied

(a) Cationic surfactants

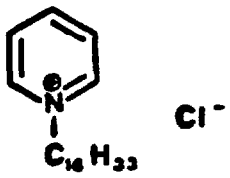
Prapagen WKT (unsaturated components)



Prapagen WKT (saturated components) and Arquad 2HT

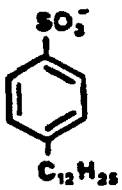


cetyl pyridinium chloride



(b) Anionic surfactant

4-dodecylphenylsulphonate



(c) Non-ionic surfactant

nonylphenyl ethoxylate NP7

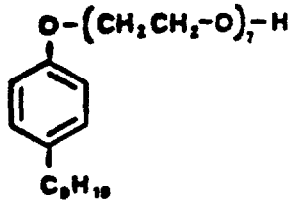
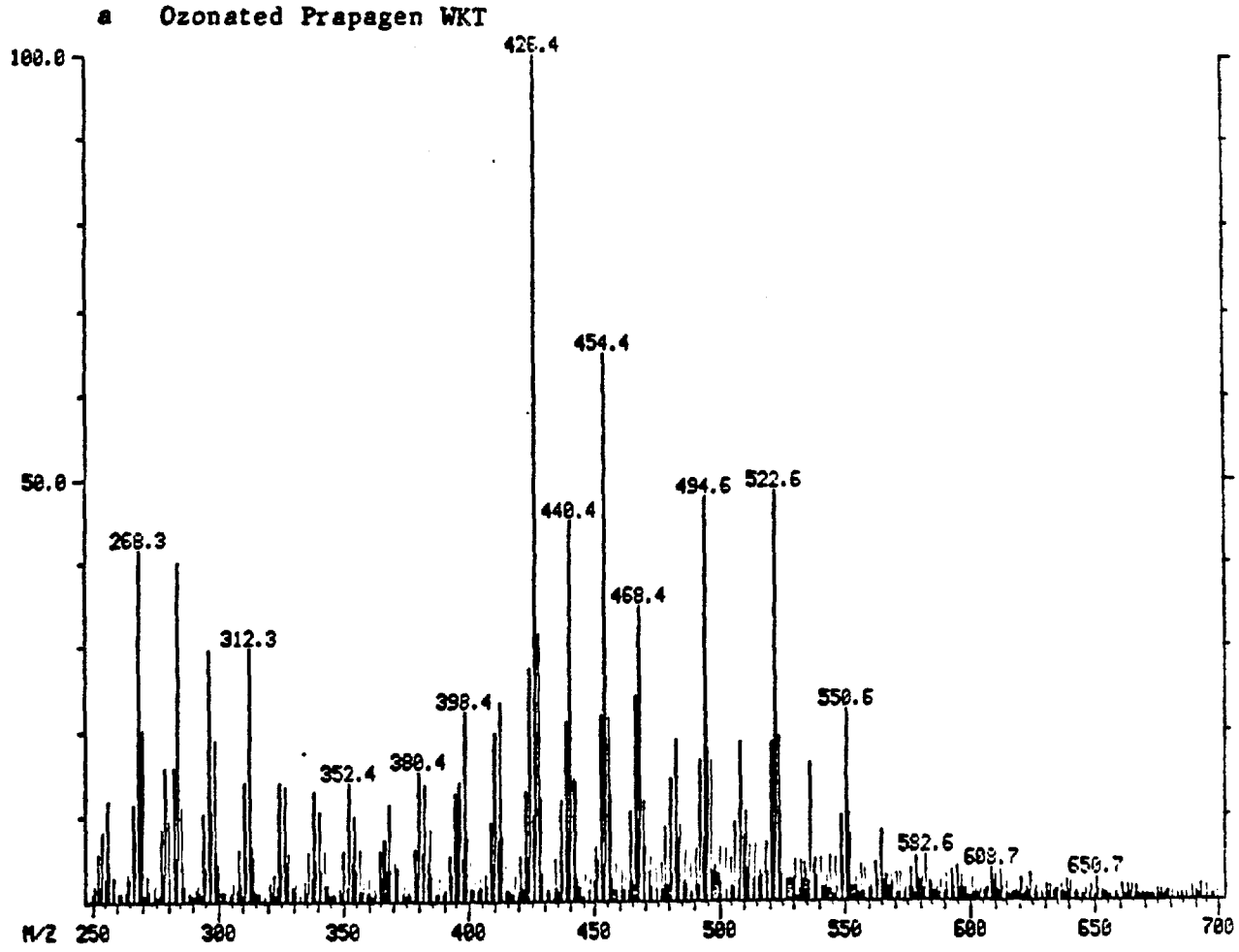
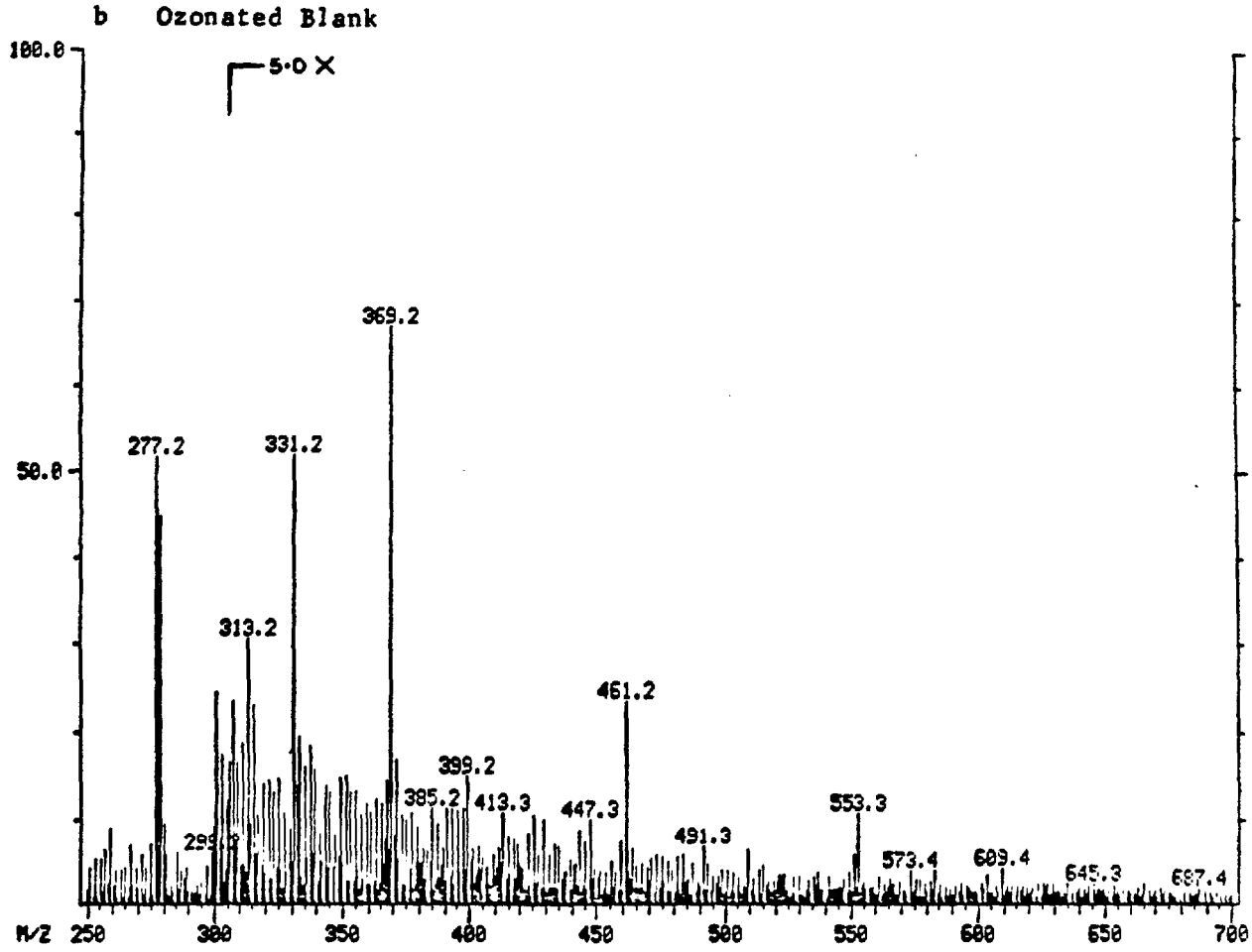


Figure 35. FAB positive ion mass spectra of Prapagen WKT



m/z	identification
426.4, 440.4 456.4, 468.4	unidentified
310.3, 520.6 546, 548	unsaturated cationic components of Prapagen WKT ion
312.3, 522.6 550.6	saturated cationic components of Prapagen WKT ion


b Ozonated Blank
100.0
5·0 X
50.0
369.2
277.2
331.2
313.2
461.2
399.2
385.2
413.3
447.3
491.3
553.3
573.4
609.4
645.3
687.4
M/Z
250
300
350
400
450
500
550
600
650
700

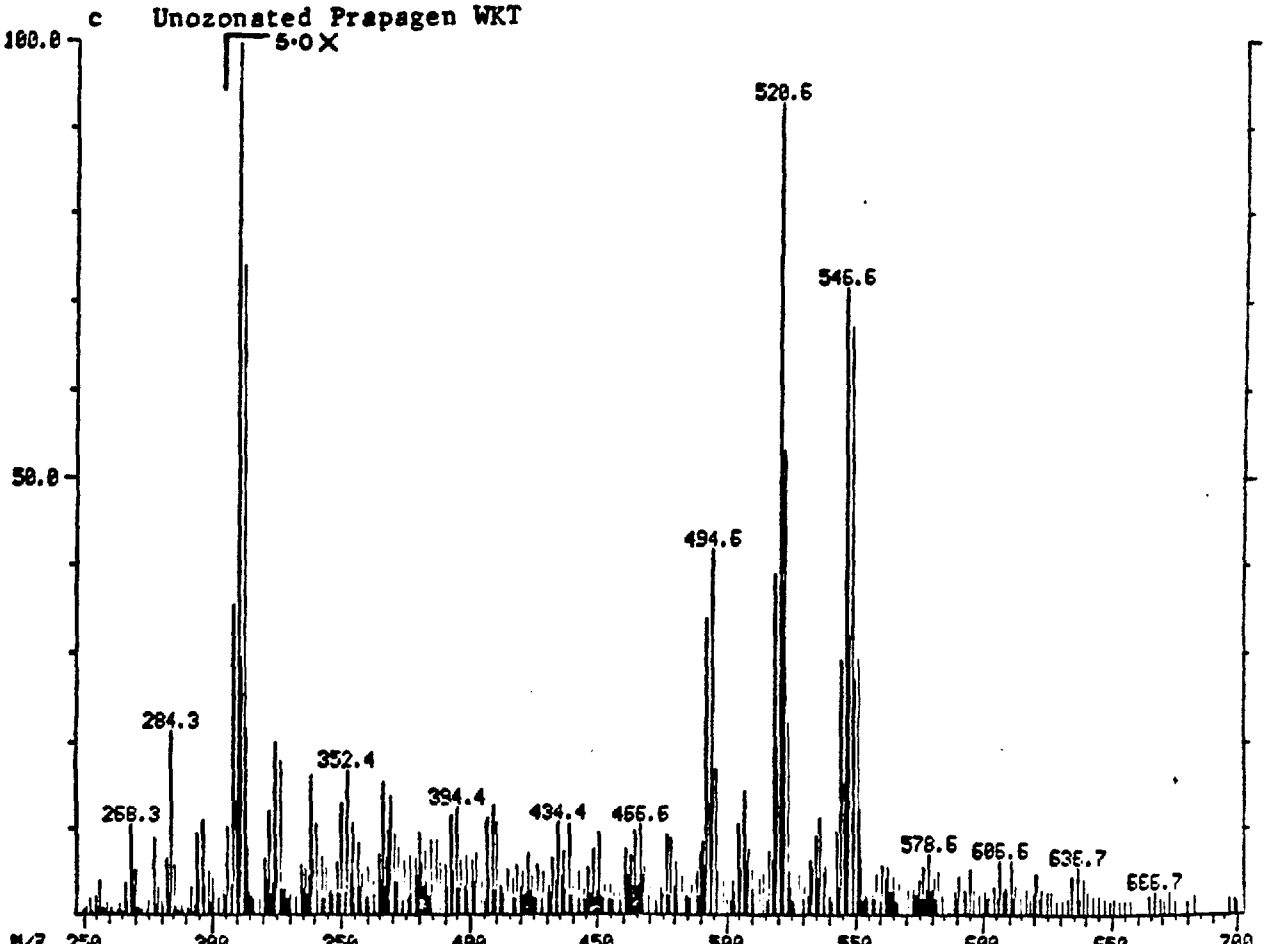
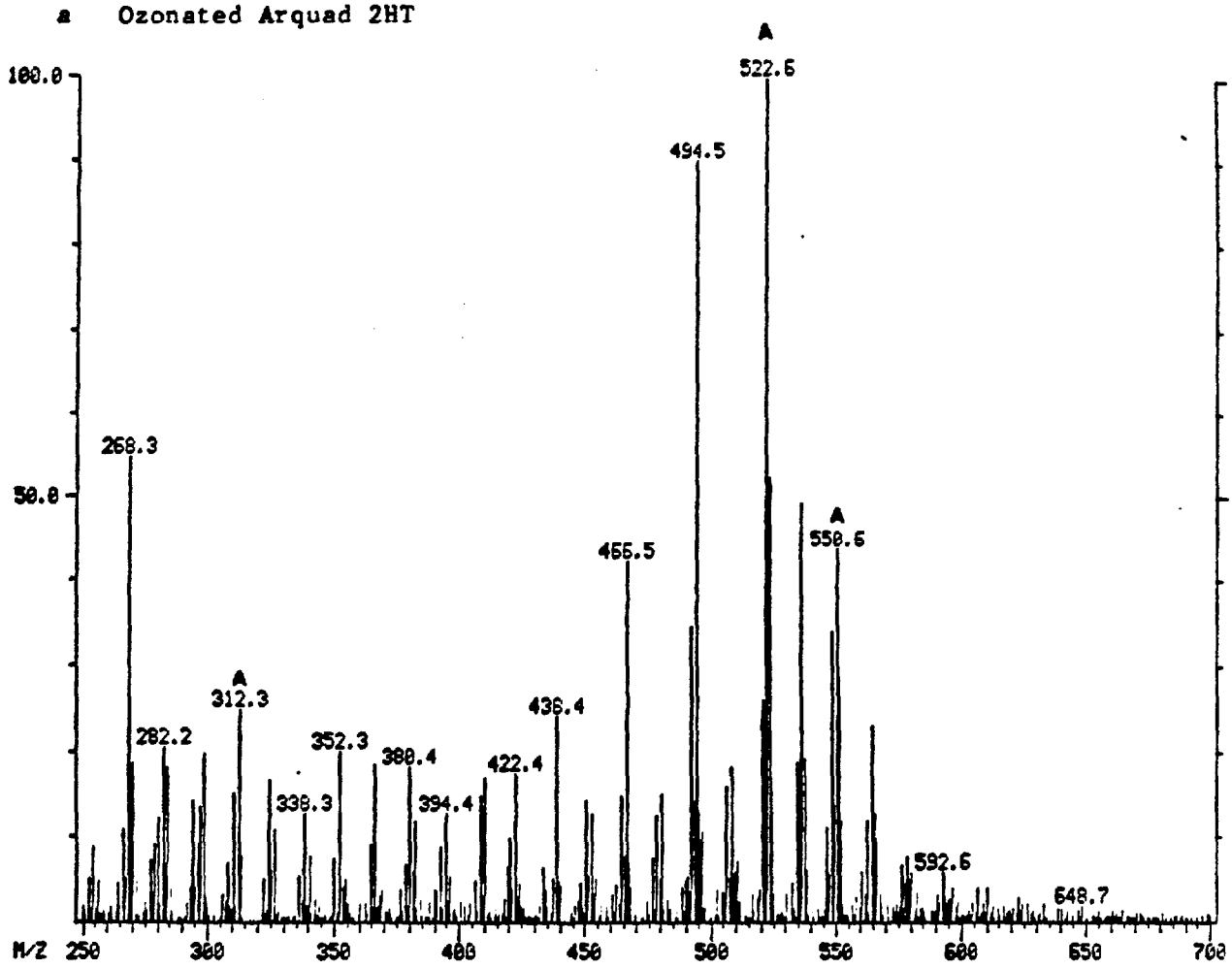

c Unozonated Prapagen WKT
100.0
5·0 X
50.0
520.6
546.6
494.6
284.3
352.4
268.3
394.4
434.4
466.6
578.6
606.6
638.7
666.7

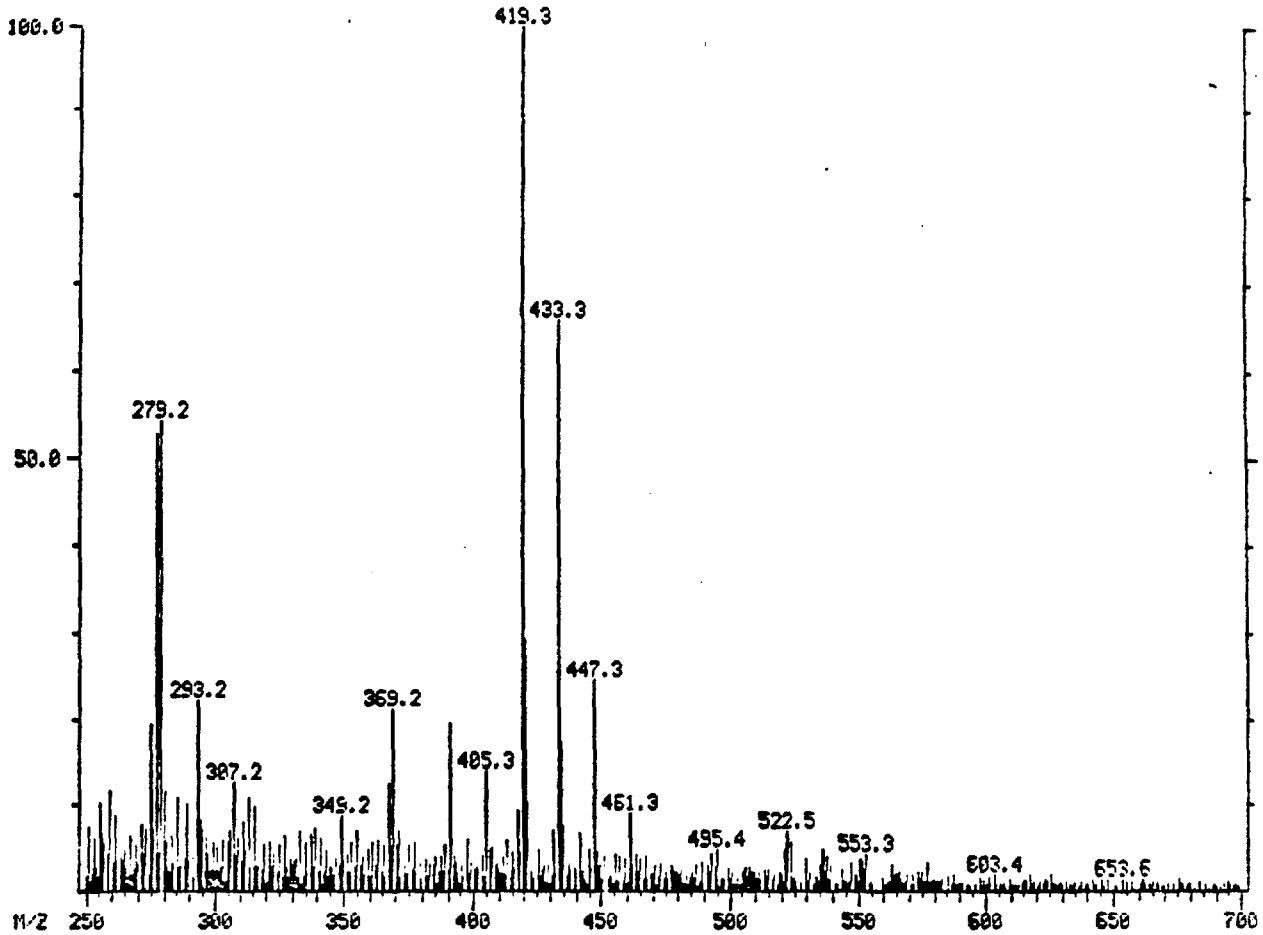
Figure 36. FAB positive ion mass spectra of Arquad 2HT

a Ozonated Arquad 2HT



m/z	identification
312.3, 522.6, 550.6	Arquad 2HT components (A)
380.4, 422.4 438.4, 537	unidentified

b Ozonated Blank



c Unozonated Arquad 2HT

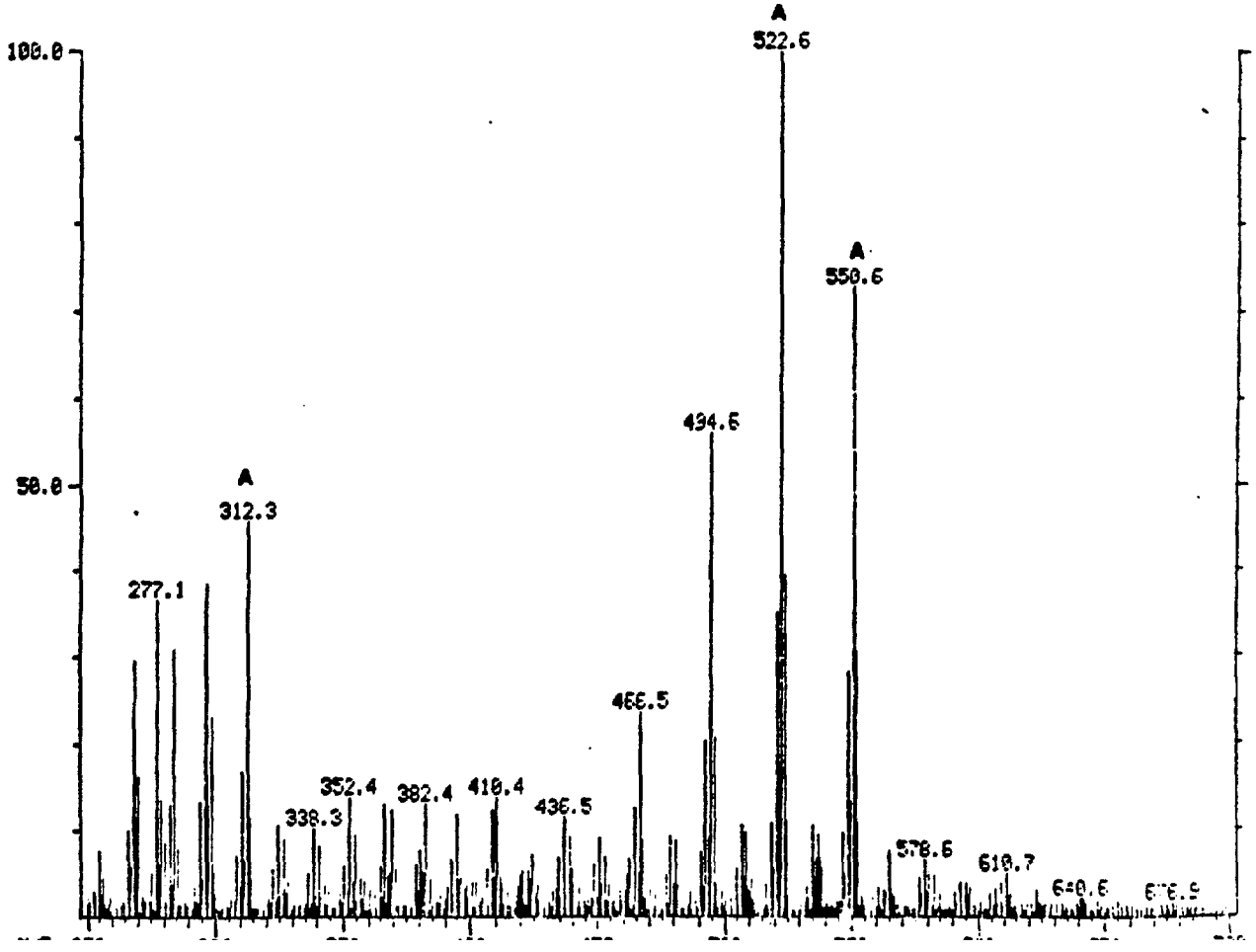
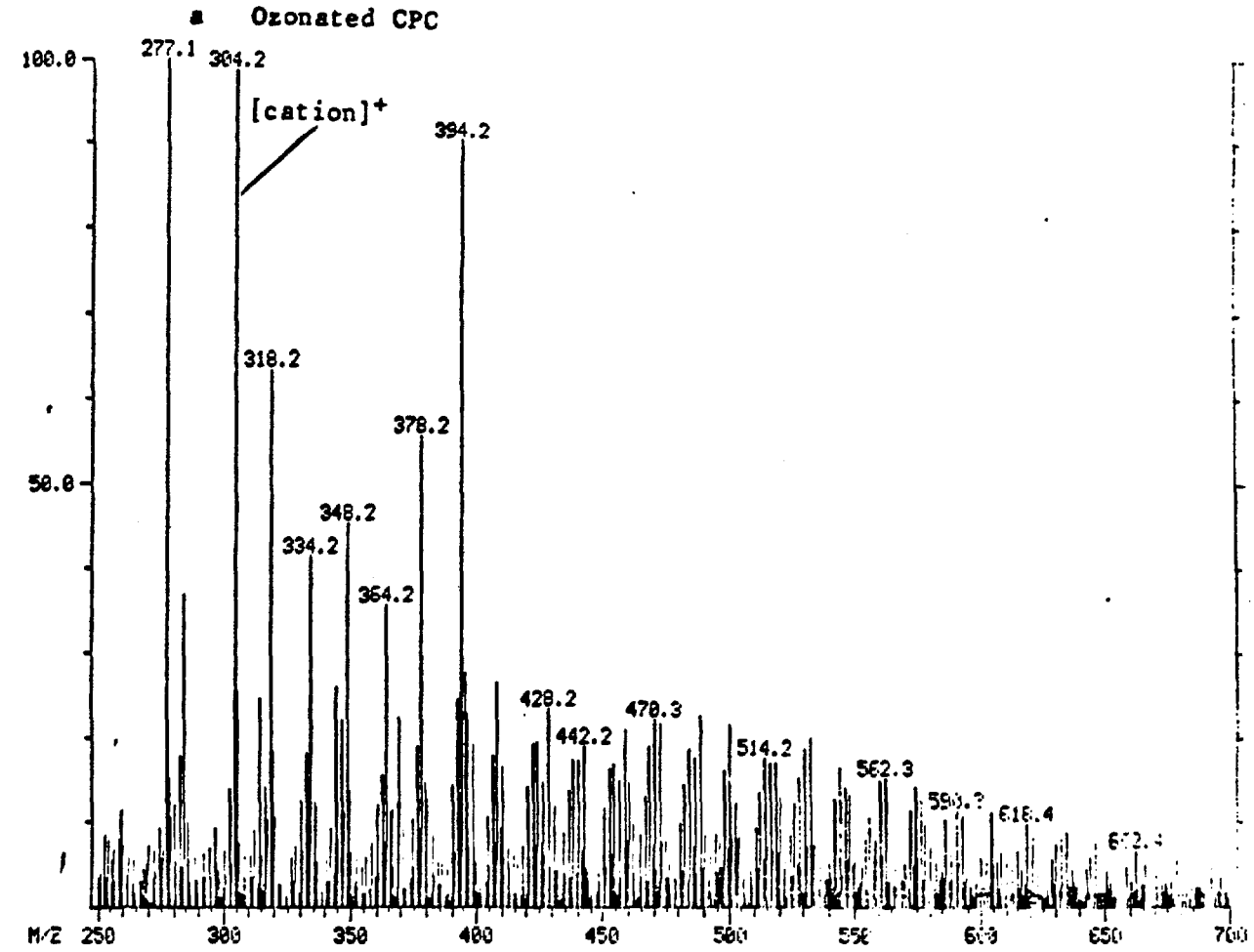
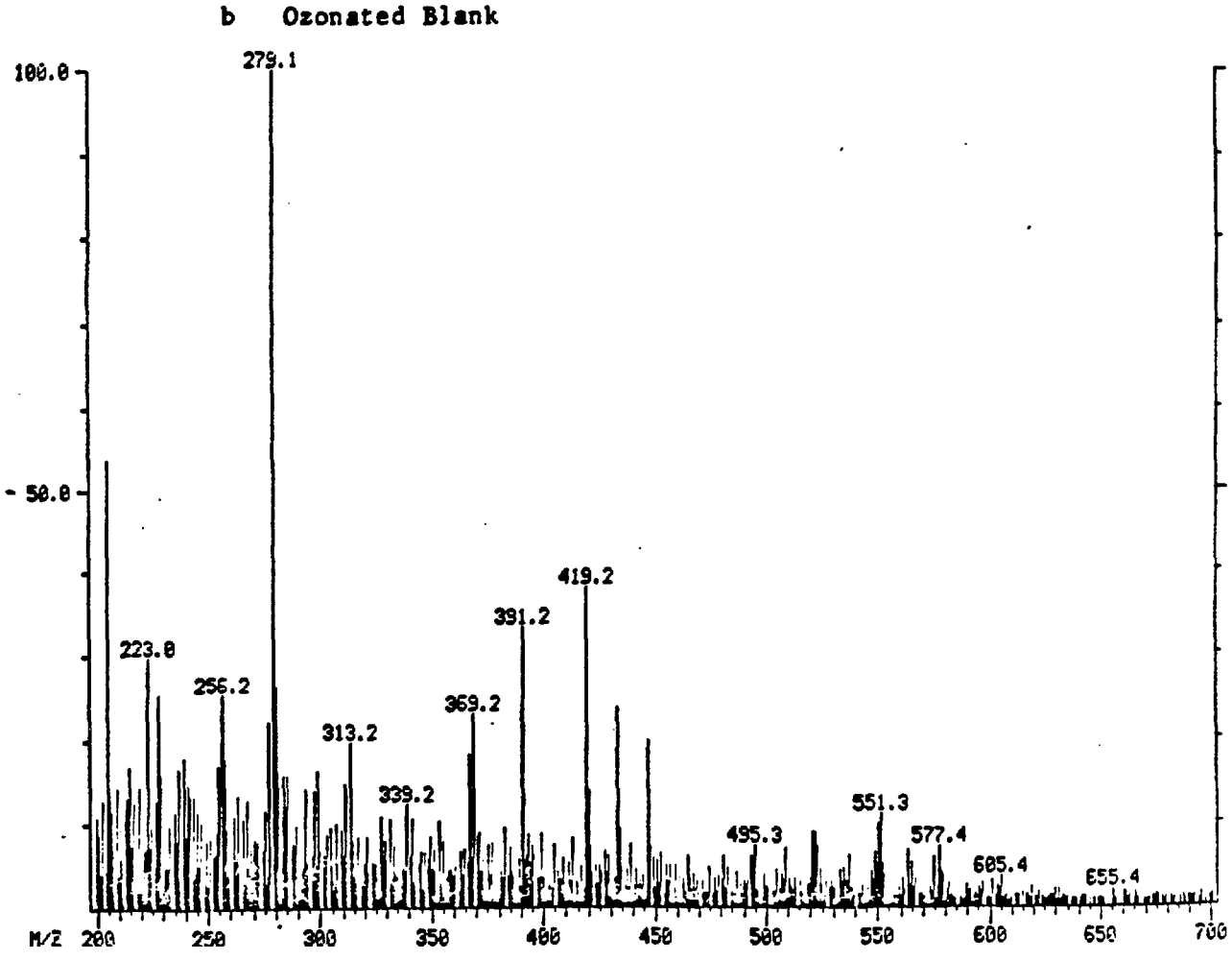


Figure 37. FAB positive ion mass spectra of cetyl pyridinium chloride (CPC)





c Unozonated CPC

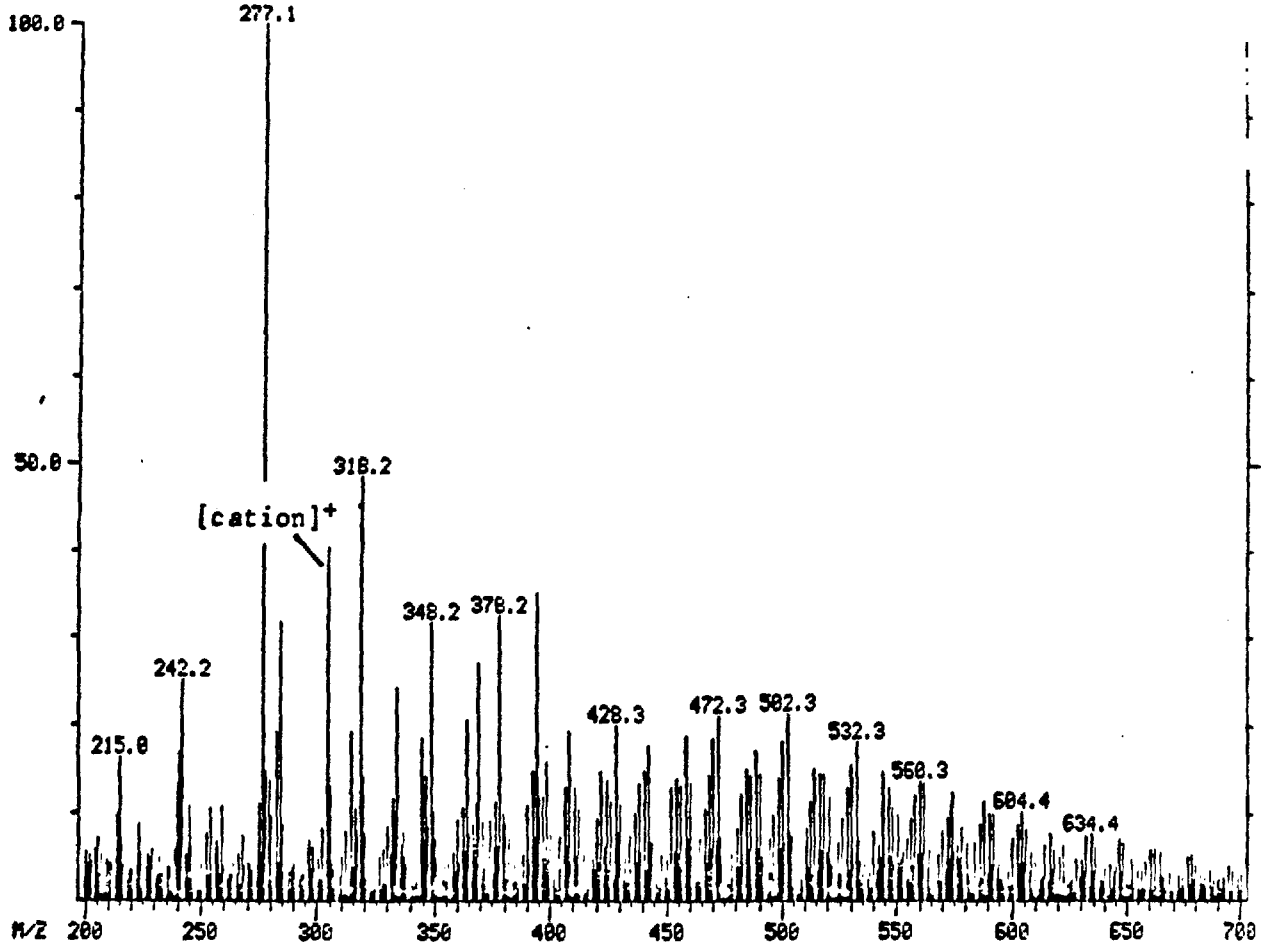
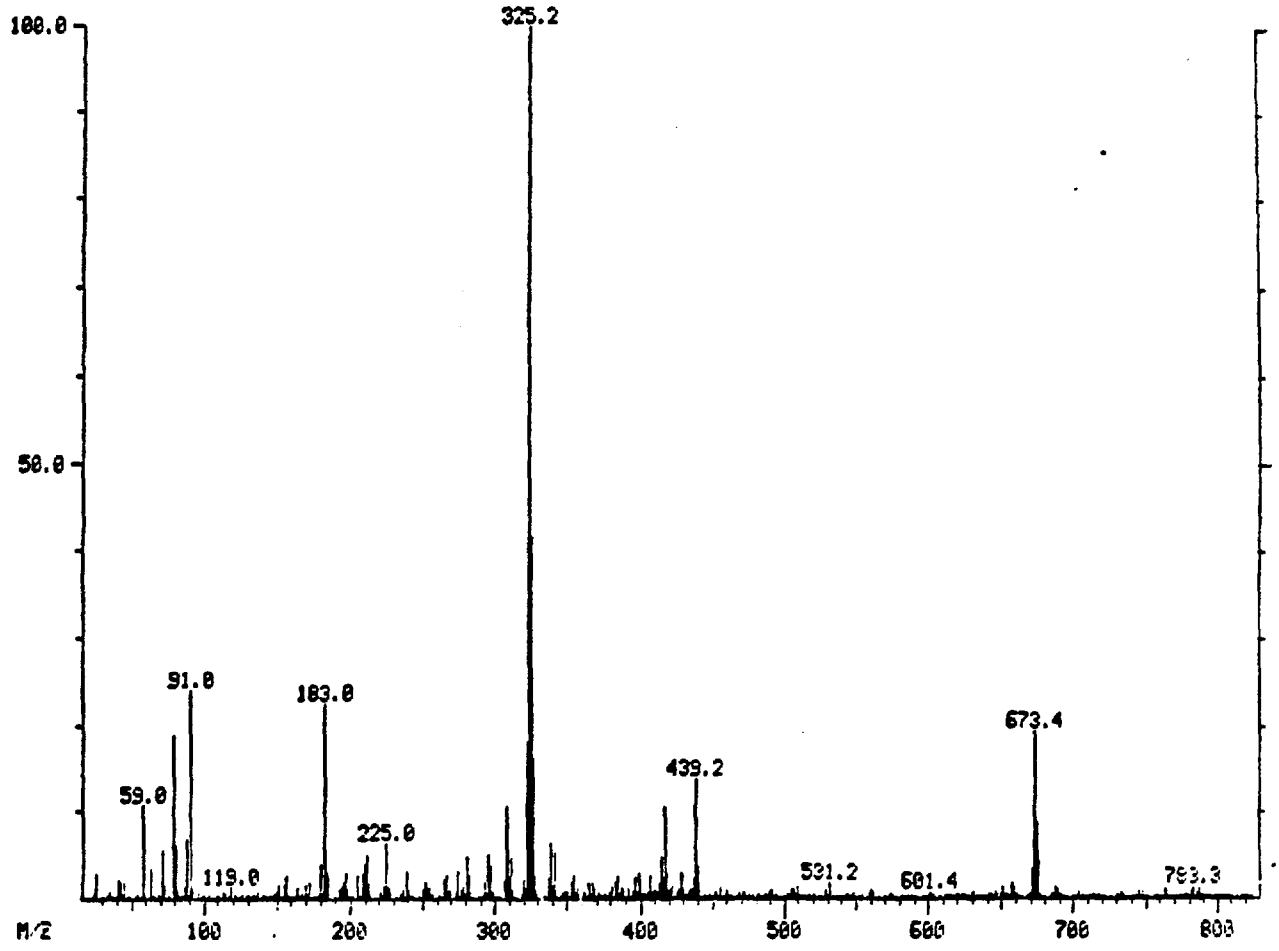


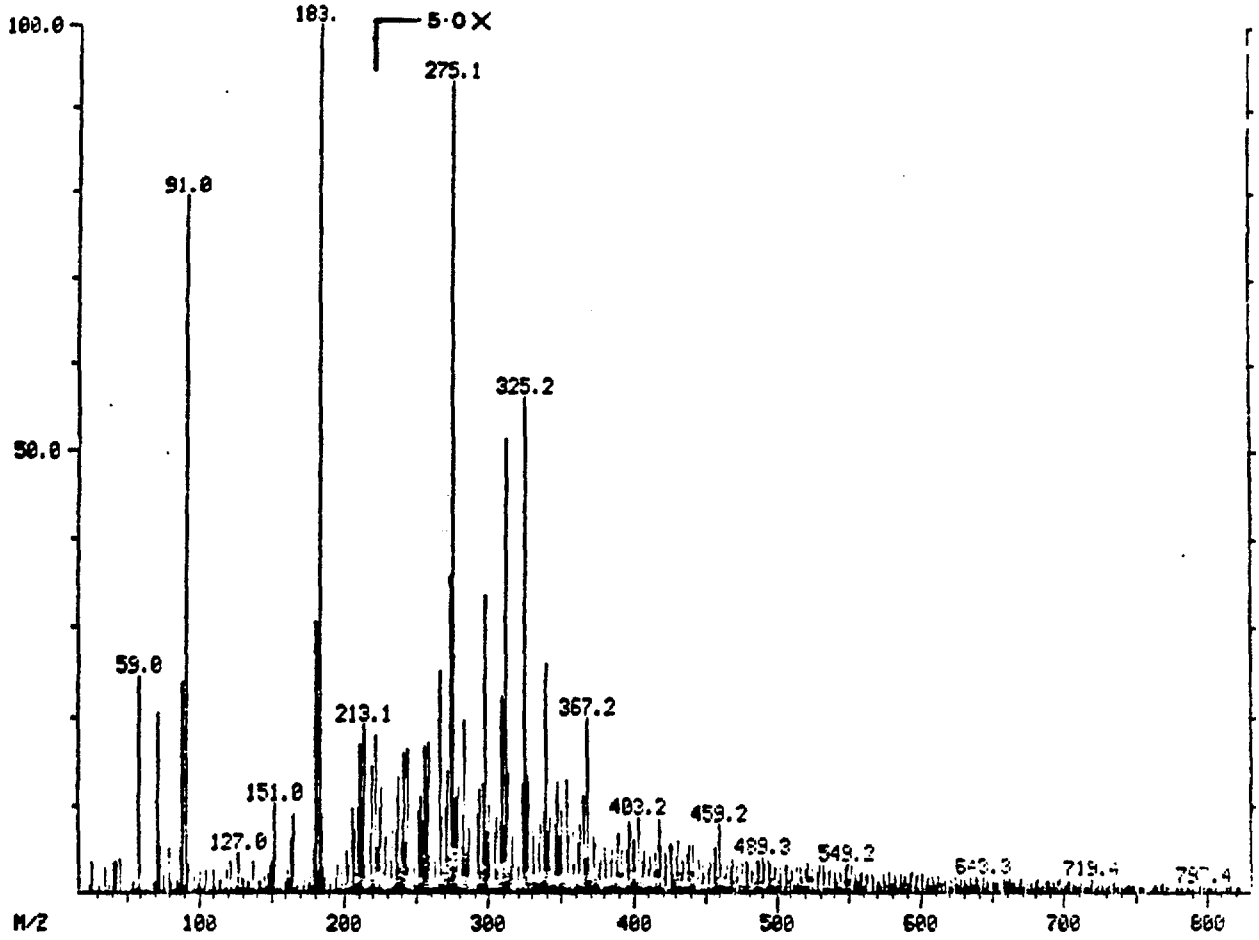
Figure 38. FAB negative ion mass spectra of 4-dodecylphenylsulphonate (DPS)

a Ozonated DPS



m/z	identification
325.2	4-dodecylphenylsulphonate anionic component

b Ozonated Blank



c Unozonated DPS

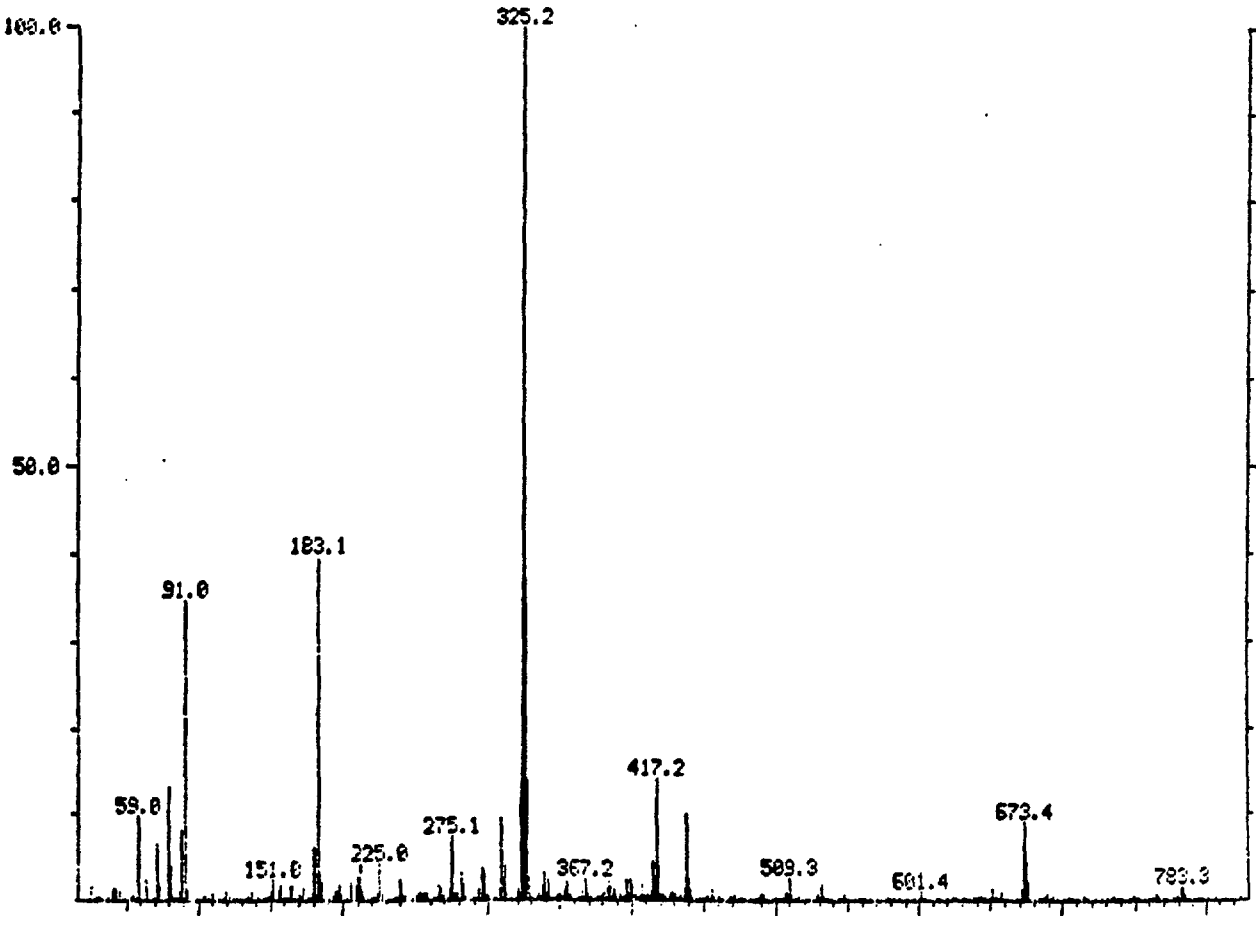
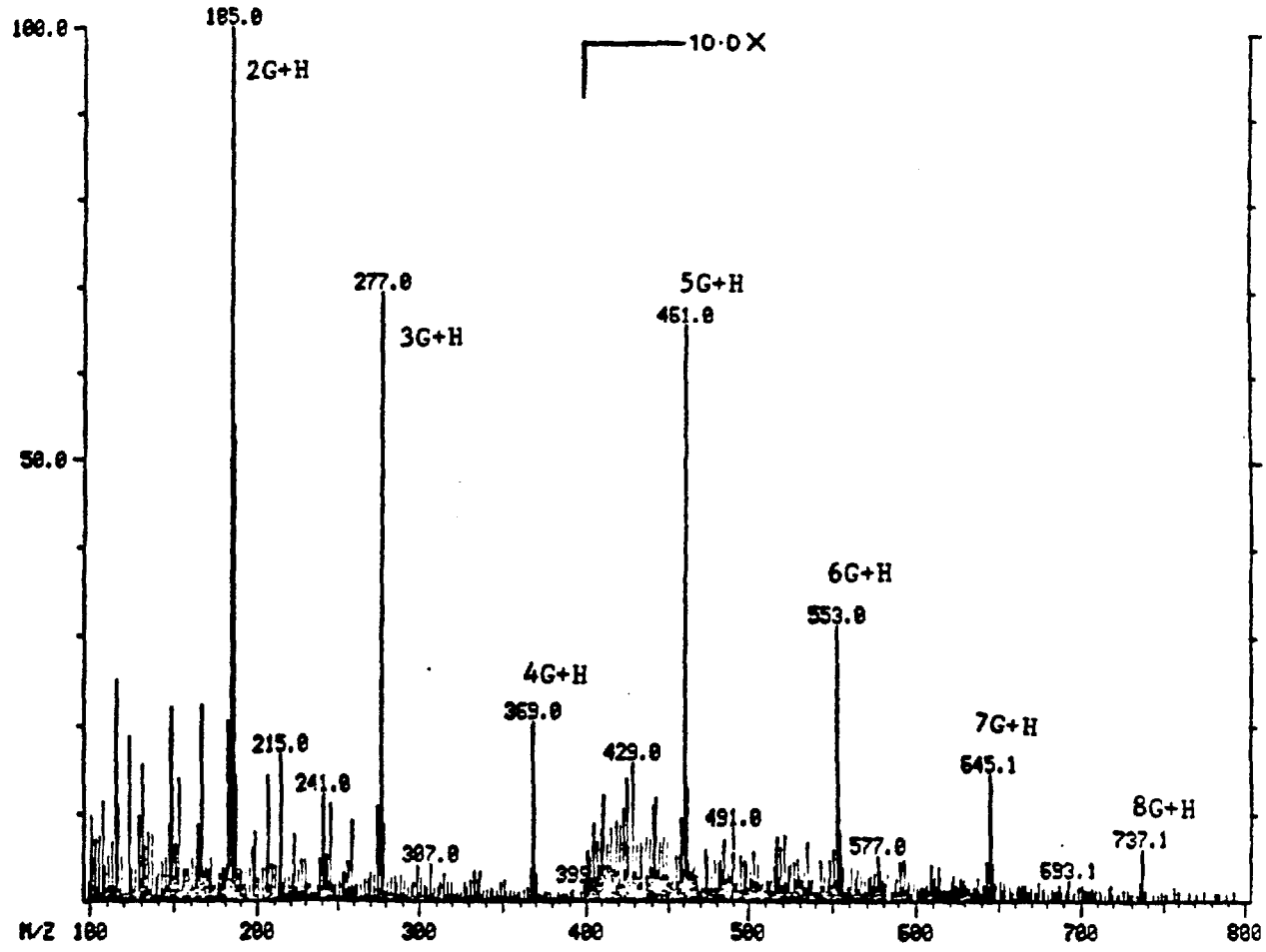
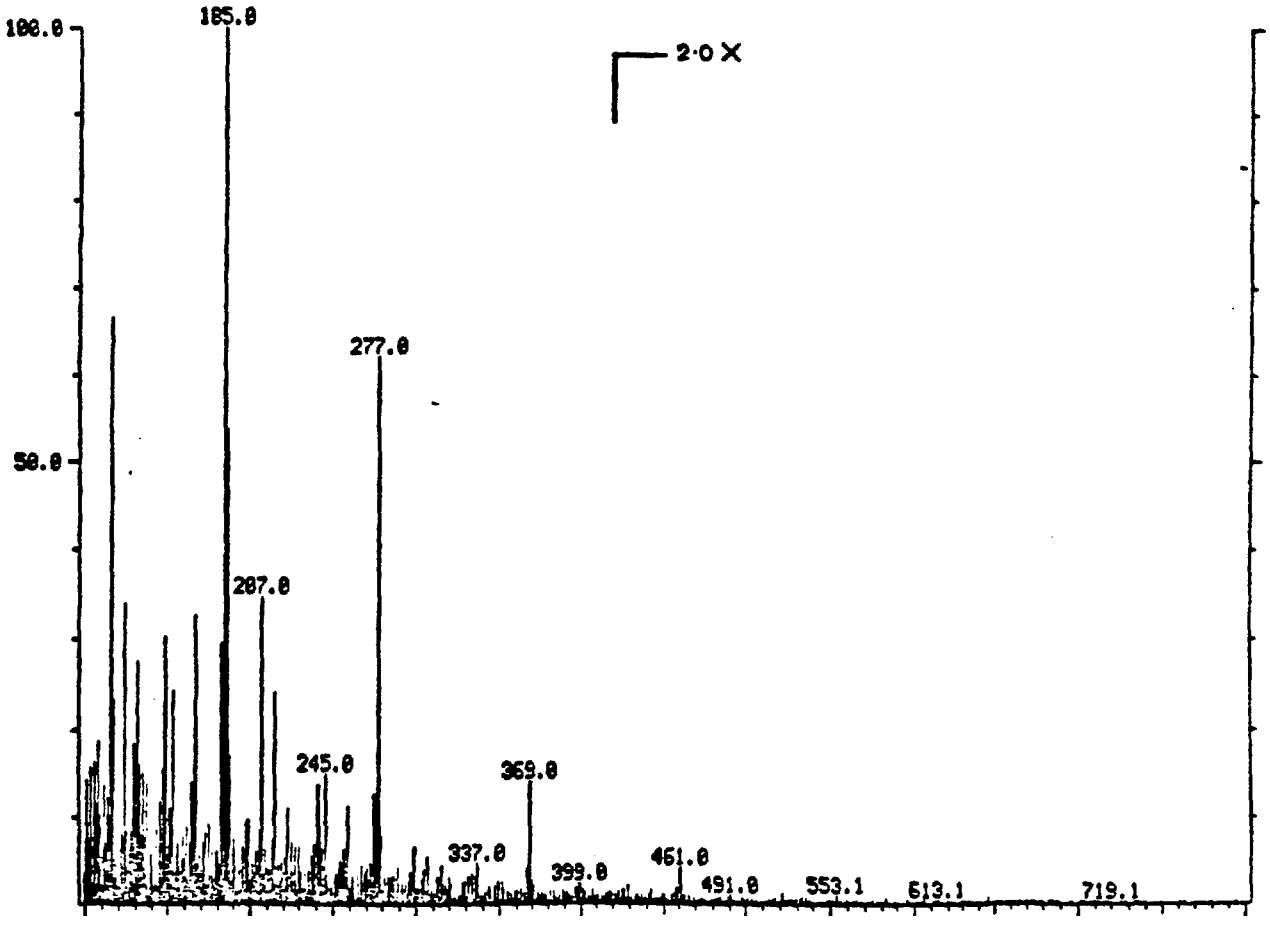


Figure 39. FAB positive ion mass spectra of nonylphenyl ethoxylate (NP7)

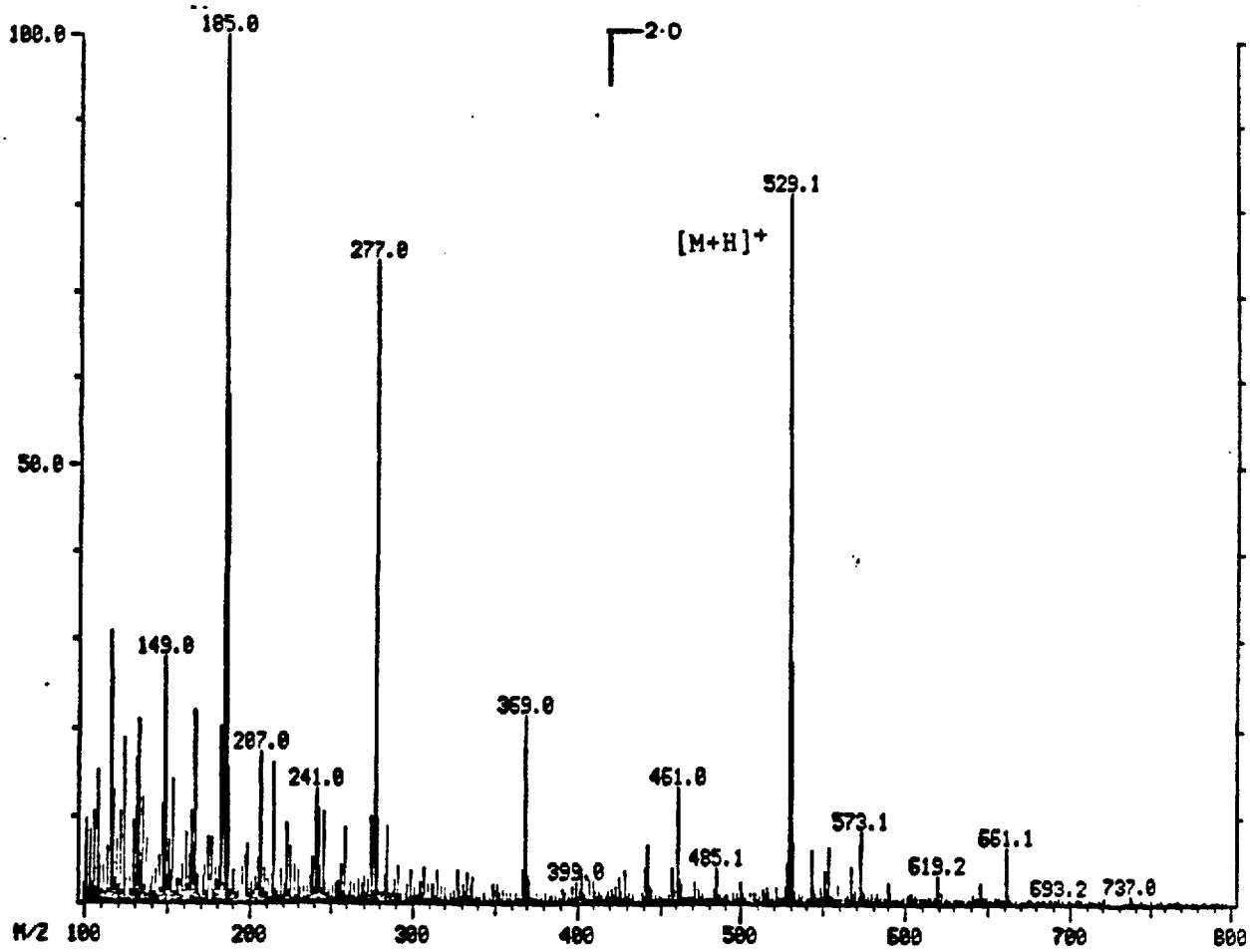
a Ozonated NP7



b Ozonated Blank



c Unozonated NP7



m/z	identifcation
529.1	nonylphenyl ethoxylate (NP7) $[M+H]^+$ ion

Figure 40. The reaction of ozone with (a) hexadec-9-enoic and (b) octadecan-9,12-dienoic acids.

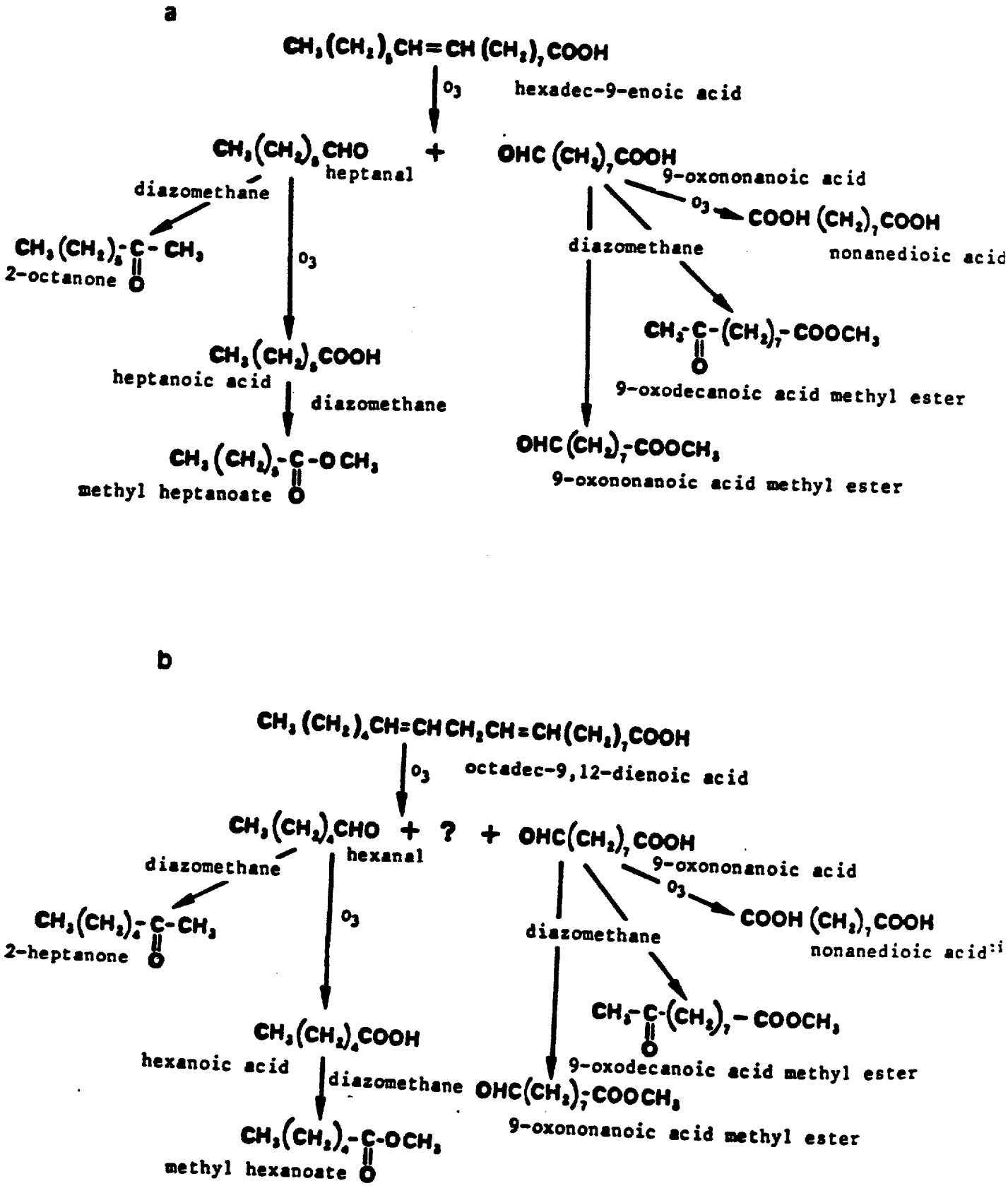
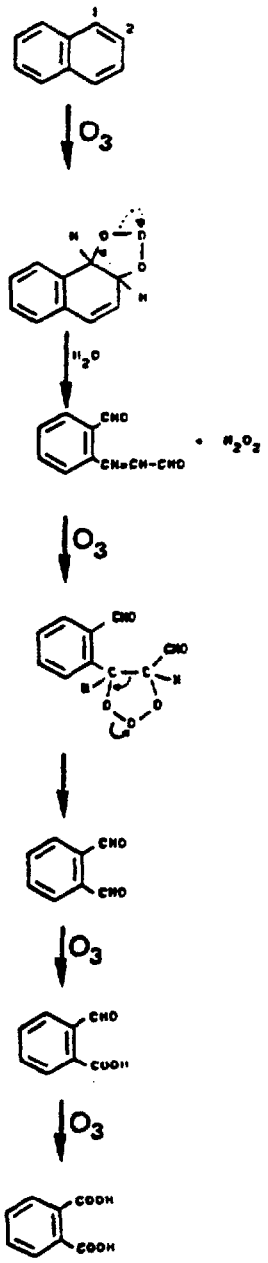


Figure 41 Electrophilic substitution reaction of ozone with naphthalene



APPENDIX

Production of 9-oxononanoic acid methyl ester and nonanedioic acid standards by nonaqueous ozonation

1.
Experimental

300 mg hexadec-9-enoic methyl ester in 250 ml of ehtyl acetate was reacted with approximately 50 mg ozone at -30°C. Iodine formation in trap 3 after the reaction vessel (containing 2% potassium iodide solution) indicated saturation of the reaction mixture with ozone and the end point of the reaction.

After removal from the cold bath, excess ozone was removed by addition of 60 ml 50% acetic acid and 200 mg KI. After 1 hour, the absence of ozone was indicated by the lack of further iodine formation upon addition of 2% potassium iodide solution. the reaction mixture was transferred to a separating funnel and 60 - 90 ml 0.1M thiosulphate added to remove the iodine formed.

Sodium bicarbonate (equivalent to 50 g) was added to achieve a pH 8-9. The aqueous layer was run off and re-extracted with 100 ml ethyl acetate. The ethyl acetate extracts were combined and dried by freezing out the water. The extract was subsequently filtered, an aliquot taken for TLC analysis and the remaining extract rotary evaporated to dryness. The resulting deposit was stored at -18°C.

2.
Thin layer chromatography (TLC) analysis

The products formed upon ozonation of hexadec-9-enoic methyl ester were separated by TLC. An aliquot of the deposit obtained (in the previous section) was applied to a silica plate and eluted with 50% ethyl acetate/ hexane.

3.
GC-MS analysis

GC-MS analysis of the extract prior to rotary evaporation (see section 1) revealed the presence of the following compounds:

9 oxononanoic acid methyl ester
nonandioic acid
heptanoic acid
heptanal

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