

# Identification by gas chromatography–electron-capture detection and gas chromatography–mass spectrometry of the ozonation products in wastewater from dicofol and tetradifon manufacturing

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## ABSTRACT

In this work, a first step has been made in the characterization of the organic pollutants found in the residual water from the production of dicofol and tetradifon pesticides. Two techniques of sample concentration, liquid–liquid and solid–liquid extraction, for nineteen organochlorine compounds are compared. The extracts obtained were analysed using gas chromatography with electron-capture detection and gas chromatography with mass spectrometry; a total of 58 organic compounds were identified. The behaviour of the effluent was also studied using degradation techniques (treatment with ozone in a basic medium), whereby a large number of substances were removed. In all cases, the chemical structures of the molecules involved in the ozonation were determined.

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## INTRODUCTION

The production of pesticides [1,2] generates effluents of wastewater which contain residues of raw materials, intermediary products of reactions and the final products themselves. Their effects on the receptor medium, when they are known, can limit the uses of the water [3].

The application of corrective means which eliminate or minimize this type of pollution requires first the characterization of the effluent. In addition to the pollution global indicator parameters [total or-

ganic carbon (TOC) and chemical oxygen demand (COD)], the various chemical species responsible for the toxic nature of the effluents [4,5] are determined. Thus, the 76/464/EEC Directive [6] contains a list of substances or groups of substances which are to be subjected to regulation in forthcoming Directives, limiting the maximum quantity of effluent and the quality objectives for surface water.

The techniques normally used for the analysis of wastewater are based on prior treatment of the sample for the extraction and concentration of the organic pollutants [7] and subsequent separation by

gas chromatography (GC) with identification of the various components by mass spectrometry (MS) [8].

The application of degradation treatments of a physical-chemical nature (chloration and ozonation) for the purification of this type of wastewater may generate new chemical substances which modify the toxic nature of effluents, leading to induced pollution [9,10].

This report presents the results obtained in the characterization of the wastewater effluents from the production of dicofol and tetradifon from a plant located in the Ebro Valley. Various sample concentration techniques were tested (liquid-liquid and solid-liquid extraction), and the reliability of the final method chosen was examined. The substances were identified by GC-MS.

Ozonation treatment in basic medium is also applied to the effluents, the chemical structures of the compounds which are completely oxidized are established, and the new chemical species generated are determined [11].

## EXPERIMENTAL

### *Reagents*

The complete series of chlorobenzenes, dicofol, tetradifon, DDTs and their metabolites supplied by Cromlab (Barcelona, Spain) were used; the solvents used were hexane, 2,2,4-trimethylpentane, acetone, ethyl acetate and dichloromethane of Mallinckrodt (Paris, KY, USA); Florisil and anhydrous sodium sulphate reagent were supplied by Merck (Darmstadt, Germany); the cartridges used were Sep-Pak C<sub>18</sub> cartridges from Waters Millipore (Milford, MA, USA); N-55 nitrogen and N-50 helium were supplied by S.E.O. (Zaragoza, Spain).

The organic solvents used were of special grade for pesticide analysis.

### *Sample*

The wastewater used in this study came from an industry situated in Aragon, Spain, which produces the organochlorine pesticides dicofol and tetradifon.

### *Instrumentation*

An HP5890 gas chromatograph equipped with an electron-capture detector and a splitless injector was used in this work. The column was an HP-5 5%

diphenyl and 95% dimethylpolysiloxane column of 25 m length supplied by Hewlett Packard (Avondale, PA, USA); a Varian 3300 gas chromatograph supplied by Varian (Walnut Creek, CA, USA) and connected to an ITD Finnigan Mat 800 mass spectrometer supplied by Finnigan MAT (San Jose, CA, USA) was used; the computer data system was an Acer 915T from Acer Computer (Dusseldorf, Germany); the rotating evaporator was a Heildoph VV2011 supplied by Heildoph-Elektro (Kelheim, Germany); a Fischer Model 501 ozonizer supplied by Labor- und Verfahrenstechnik (Germany) was employed; the TOC-total carbon (TC) analyser was an Astro 1850 from Astro (Houston, TX, USA).

### *Liquid-liquid extraction [12]*

A 1-l volume of wastewater, pH 10 (6 M sodium hydroxide), was extracted with 3 × 60 ml of methylene chloride and the extracts were collected in a flask. They were concentrated in a rotating evaporator at 40°C until a final volume of approximately 3 ml was achieved. The extract was passed through a Pasteur column packed with Florisil and anhydrous sodium sulphate in the upper part. Previously, sodium sulphate and Florisil had been conditioned for 17 h at 150°C. The column was activated with 5 ml of isooctane (2,2,4-trimethylpentane) and a single fraction containing 10 ml of isooctane was collected. The extract was analysed using GC with electron-capture detection (ECD) and GC-MS. For a complete analysis of the series of chlorobenzenes, the solvent was replaced by hexane through drying with nitrogen.

### *Solid-liquid extraction [12]*

Extraction columns were small cartridges packed with octadecylsilane (C<sub>18</sub>). The solid phase was first conditioned with 5 ml of methanol, 10 ml of ultrapure water and 5 ml of methanol. A 1-l volume of residual water, pH 10 (6 M sodium hydroxide), was passed through the cartridge by continuous vacuum pump suction. A continuous nitrogen stream was passed through to dry the cartridge for 10 min. The final extracts were obtained through two separated fractions of hexane and then combined. In order to analyse dicofol, tetradifon, DDTs and their metabolites, the solvent was changed to isooctane; the hexane was dried with a nitrogen stream. The extract was analysed by GC ECD and by GC-MS.

*GC-ECD conditions*

Injection: 2  $\mu$ l; splitless: 0.8 s. Injection temperature: 250°C. Detection temperature: 350°C. Temperature programmes: chlorobenzenes, 60°C (1 min) up to 280°C at 4°C/min; dicofol, tetradifon, DDTs and their metabolites, 90°C (1 min) up to 170°C at 30°C/min, from 170°C up to 280°C at 2.5°C/min. Carrier gas: helium 30 cm<sup>3</sup>/s.

*GC-MS conditions*

Injection: 2  $\mu$ l; splitless: 0.8 s. Injection temperature: 250°C. Detection temperature: 350°C. Temperature programmes: chlorobenzenes, 60°C (1 min) up to 280°C at 5°C/min (0); dicofol, tetradifon, DDTs and their metabolites, 90°C (1 min) up to 150°C at 25°C/min, from 150°C up to 280°C at 3°C/min. Carrier gas: helium, 30 cm<sup>3</sup>/s. The identification of the compounds was carried out by National Bureau of Standards Library searching and the main substances were verified by comparison with reference standards.

*Calibration solutions*

Three calibration solutions of 0.1, 0.01 and 0.001

mg/l in hexane were prepared for the complete series of chlorobenzenes and in isooctane for dicofol, tetradifon and DDTs and their metabolites. Table I shows the mathematical expressions of the calibration curves using GC-ECD for the nineteen organochlorine compounds: *op'*-dicofol; *pp'*-dicofol; *o*-tetradifon; *p*-tetradifon; *o,p'*-1,1-dichloro-2,2-bis(4-chlorophenyl)ethylene (*op'*-DDE); *pp'*-DDE; *o,p'*-1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethane (*op'*-DDD); *pp'*-DDD; *op'*-DDT; *pp'*-DDT; 1,2-dichlorobenzene (1,2-DCB); 1,3-dichlorobenzene (1,3-DCB); 1,4-dichlorobenzene (1,4-DCB); 1,2,3-trichlorobenzene (1,2,3-TCB); 1,2,4-trichlorobenzene (1,2,4-TCB); 1,3,5-trichlorobenzene (1,3,5-TCB); tetrachlorobenzene (TetraCB); pentachlorobenzene (PCB); hexachlorobenzene (HCB).

*Ozonation conditions*

The ozone used for the treatment of the water was produced with a silent electrical discharge of dry prefiltered oxygen. Ozonation was carried out using a closed reactor to which 1 l of residual water, pH 10 (6 M sodium hydroxide) was added [13]. The current of the apparatus was adjusted to 0.5 A. The excess ozone was retained by two bubblers containing 250 ml of a solution of 2% potassium iodide. The contact time was 50 min during which 78.3 l of oxygen generated 3.33 g of ozone which passed through the sample. By titration of the solutions from the bubblers with sodium thiosulphate and starch as an indicator, the dosage used in the ozonation of the water was calculated as 1.16 g/l.

TABLE I

MATHEMATICAL EXPRESSIONS OF THE CALIBRATION CURVES FOR DDTs, DICOFOL, TETRADIFON AND CHLOROBENZENES

Compound	Mathematic expressions <sup>a</sup>	r
<i>op'</i> -Dicofol	Area = 14733330.3C + 46659.8	0.999
<i>pp'</i> -Dicofol	Area = 8709932.0C + 89763.2	0.999
<i>op'</i> -DDE	Area = 48181442.2C - 28242.6	0.999
<i>pp'</i> -DDE	Area = 62275402.4C - 89143.9	0.999
<i>op'</i> -DDD	Area = 33769491.8C - 18921.6	0.999
<i>pp'</i> -DDD	Area = 36734977.5C - 19994.9	0.999
<i>op'</i> -DDT	Area = 12703593.9C - 24375.5	0.999
<i>pp'</i> -DDT	Area = 11256519.5C - 33764.9	0.999
<i>o</i> -Tetradifon	Area = 29116585.7C + 27735.9	0.999
<i>p</i> -Tetradifon	Area = 34870035.1C + 2322.6	0.999
1,3-DCB	Area = 6054631.1C + 18691.1	0.997
1,4-DCB	Area = 3134420.0C + 12291.8	0.994
1,2-DCB	Area = 5063608.6C + 9335.3	0.998
1,3,5-TCB	Area = 33837.4C + 78706.8	0.999
1,2,4-TCB	Area = 26428556.7C + 76516.7	0.999
1,2,3-TCB	Area = 37098350.1C + 96530.6	0.999
TetraCB	Area = 82147023.0C + 364742.8	0.999
PCB	Area = 68789759.8C + 55349.8	0.999
HCB	Area = 66630337.8C + 464278.8	0.995

<sup>a</sup> C = concentration in mg/l.

## RESULTS AND DISCUSSION

*Total recoveries by the proposed methods*

The nineteen organochlorine compounds were added to ultrapure water, adjusted to pH 10 with 6 M sodium hydroxide, in 30  $\mu$ g/l concentration in order to study the percentage recoveries achieved with the extraction techniques previously described and their later analysis by GC-ECD. Figs. 1 and 2 compare the percentage recoveries for the liquid-liquid and solid-liquid extraction techniques.

Neither of the techniques gave good results for the complete series of chlorobenzenes. A result is considered acceptable at around 80%. The best results were obtained with the DDTs and their metabolites with liquid-liquid extraction, these being in the range 89-129%.

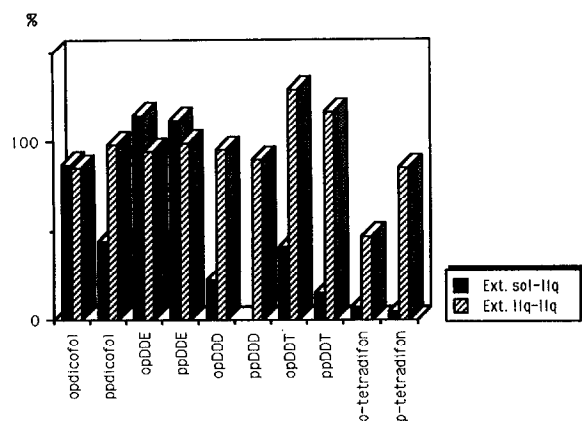


Fig. 1. Total recoveries of DDTs, dicofol and tetradifon.

### Wastewater ozonation

The wastewater was examined before and after ozonation. The TOC and COD of ozonized and non-ozonized samples were analysed and were reduced by 95 and 99%, respectively. Two 1-l portions of ozonized and non-ozonized water were extracted with  $C_{18}$  cartridges and analysed using GC-ECD and GC-MS.

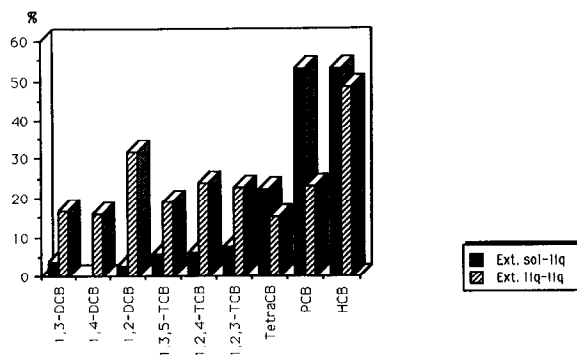


Fig. 2. Total recoveries of chlorobenzenes.

### GC-ECD analysis

Figs. 3 and 4 show chromatograms of non-treated and treated water extracts, respectively, indicating clearly the positive effect of the ozone treatment. The reduction of the nineteen organochlorine compounds determined by the previous methods is presented in Figs. 5 and 6.

### GC-MS analysis

A total of 58 organic compounds were identified in the wastewater using GC-MS; 17 of these appear

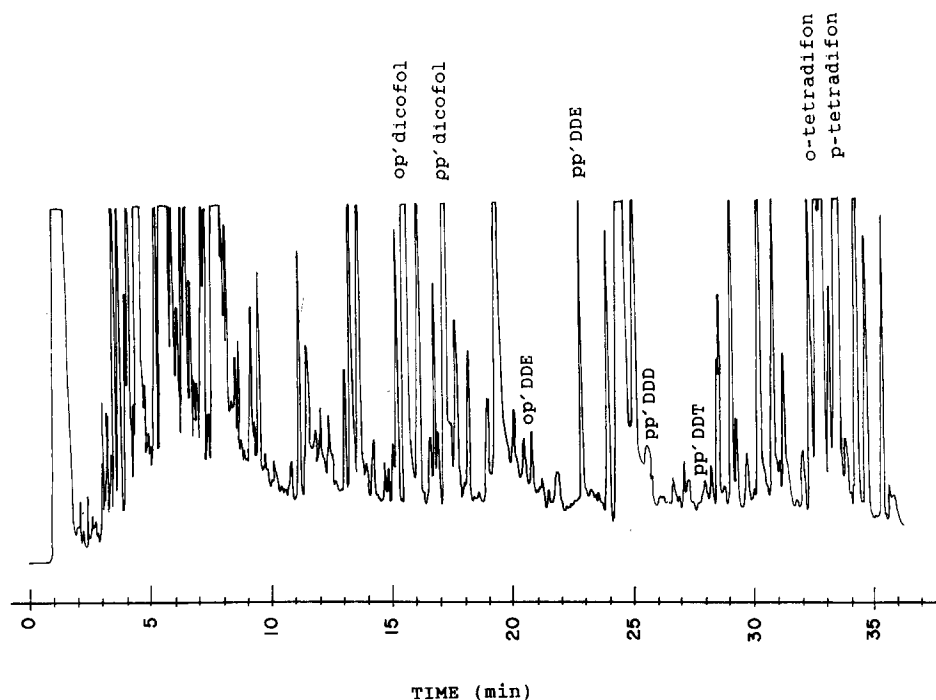


Fig. 3. ECD gas chromatogram for non-ozonated effluent.

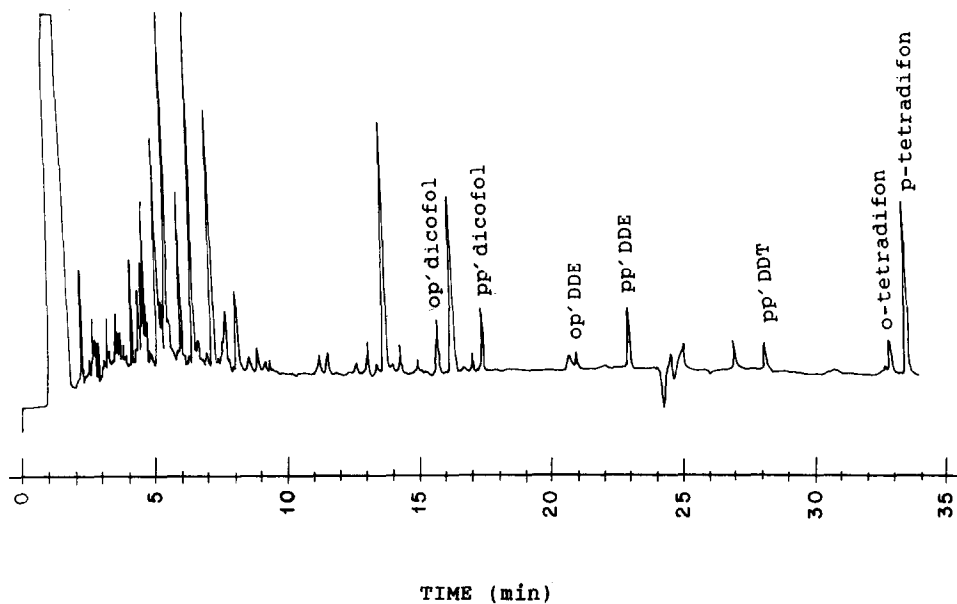


Fig. 4. ECD gas chromatogram for ozonated effluent.

in the group of substances susceptible to the figure in list I of the 74/464/EEC Directive. After ozonation, 46 organic compounds were identified, 8 of which appear in the above-mentioned group. In the ozonation process, 35 substances were removed (Fig. 7), 23 new products were formed (Fig. 8) and 23 others remained unchanged (Fig. 9), *i.e.* they

were already present in the polluted water and not derived from ozonation or other degradation steps.

Only the least reactive compounds resist treatment. Ozonation leads to a significant decrease in aromatic compounds together with a slight increase in polar compounds.

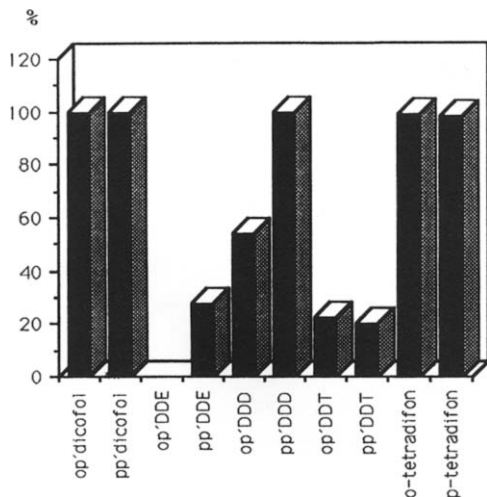


Fig. 5. Reduction (%) of DDTs, dicofol and tetradifon after ozonation treatment.

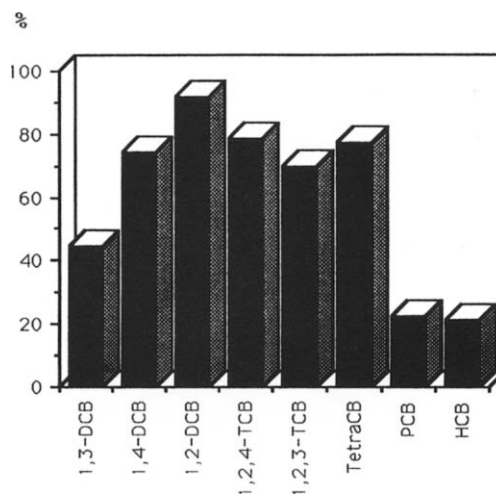


Fig. 6. Reduction (%) of chlorobenzenes after ozonation treatment.

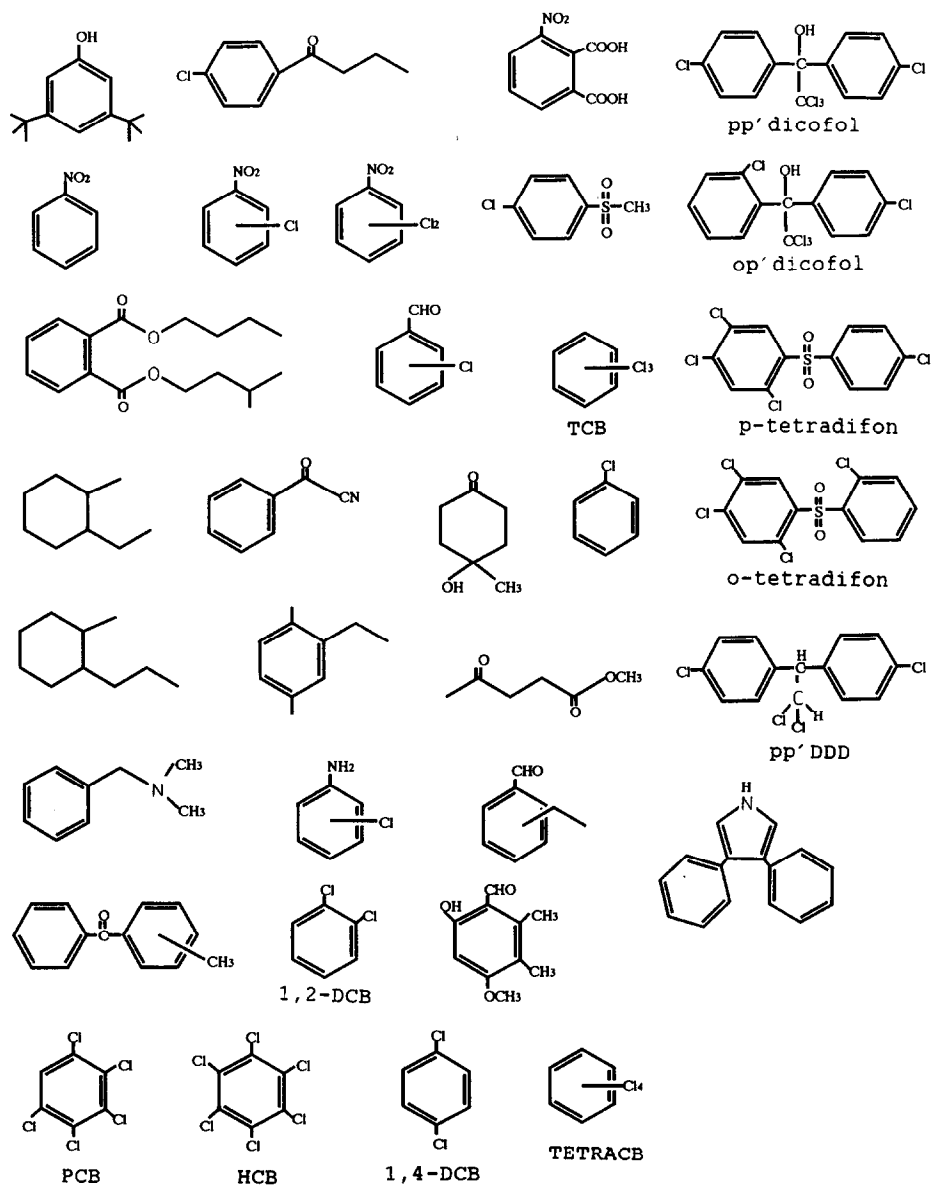


Fig. 7. Removed compounds after ozonation treatment.



