



ELSEVIER

Journal of Chromatography A, 733 (1996) 511–522

JOURNAL OF
CHROMATOGRAPHY A

Wastewater from the manufacture of rubber vulcanization accelerators: characterization, downstream monitoring and chemical treatment

A. Puig^{a,*}, P. Ormad^b, P. Roche^b, J. Sarasa^b, E. Gimeno^b, J.L. Ovelleiro^b

^a*Confederación Hidrográfica del Ebro, Po. de Sagasta 24–28, 50006 Zaragoza, Spain*

^b*Department of Chemical Engineering and Environmental Technology, University of Zaragoza, Pza. San Francisco s/n, 50009 Zaragoza, Spain*

Abstract

The content of wastewater resulting from the manufacture of rubber antioxidants and accelerators by a factory situated in the Ebro basin (Spain) has been determined using gas chromatography–mass spectrometry (GC–MS) and gas chromatography–flame ionization detection (GC–FID). The change in the pollutants was studied in the riverbed via two modules which continuously gathered pollutants on various solid supports (activated carbon and XAD-2 resins). These modules were located in Bocal Station, lying a further 100 km downstream from the factory, and from the Zaragoza water supply. Forty-six different compounds were identified at Bocal Station, the majority resulting from the production of rubber additives. Due to the immunity of different waste substances, and to the toxic nature of some, we studied their reaction when subjected to techniques of chemical oxidation using ozone.

Keywords: Water analysis; Rubber additives; Antioxidants; Vulcanization accelerators

1. Introduction

In Spain, the quality control of water from the River Ebro is assigned by the Government to the Confederación Hidrográfica del Ebro. This body controls 85 550 km² of the Ebro basin. One of the control networks consists of a series of modules which gather organic pollutants from the raw water. These modules continuously pump from the riverbed an unchanging flow of 2 l/h to various solid supports (activated carbon, XAD-2 resins). By means of solvent extraction from the supports, followed by concentration of

the eluate, a concentration factor–related to the raw water–of approximately 10⁶ is obtained. This method provides a composite sample corresponding to the 30-day period of the test. The chemical analysis of the extract is performed by gas chromatography with mass spectrometry (GC–MS) [1,2].

This work presents the results obtained in the study of micropollutants at Bocal Station, the starting point of a canal that supplies Zaragoza, a town with 600 000 inhabitants. It is also used for agricultural irrigation. This technique has allowed the identification of 46 compounds. The greater part involved 2-mercaptobenzothiazole derivatives which were detected in the content of

* Corresponding author.

wastewater resulting from the production of rubber additives. These pollutants were also detected in the water supply of Zaragoza, lying a further 180 km from the factory. This kind of study is new in the Ebro basin. These modules allows us to know the real water quality of the River Ebro and the water supply of Zaragoza. Finally, they indicate the origin of the greater part of the pollutants identified. All this is possible due to the high concentration levels which can be reached. It was necessary to locate the industrial effluent that produced this kind of pollution. The dumping site was found 100 km upstream from the sample site. Once discovered, we analyzed the wastewater from the factory. Due to the stability of the different waste substances (they resist the wastewater treatment in the factory, the water supply disinfection process, and remain intact in the river), we subjected the partially treated effluent from the factory to a treatment of chemical oxidation using ozone in order to remove the waste substances. Many studies have been carried out regarding ozonation of laboratory samples done with a standard or a mixture of different standards. But there is less information available regarding the ozonation of wastewater collected from factories. In these kinds of samples, synergic effects between pollutants or matrix effects are often unforeseeable, and they can affect both non-specific parameters and by-products. The values of pH, chemical oxygen demand (COD), total organic carbon (TOC) and biotoxicity were determined. The compounds removed by-products, and those whose concentration was increased or decreased were identified by GC-MS. This study was completed with a bibliographic revision of toxicity (LD_{50} on rats, rabbits, LC_{50} , . . .), EEC Directive 464/76/EEC [3] and Priority Pollutants List, USEPA [4].

2. Experimental

2.1. Sampling and storage

1. For analysis of the precise samples by liquid-liquid extraction and bioluminescence test, amber glass bottles fitted with TFE-lined

screw caps were used. One litre of wastewater for chemical oxygen demand (COD) and total organic carbon (TOC) analysis was collected in glass bottles and preserved by acidification to pH 2 using concentrated H_2SO_4 .

2. The average river and tap samples were obtained by means of continuous sampling procedures via two modules installed in the riverbed and in the water supply. This allowed us to study average monthly water samples. The modules continuously gathered pollutants by passing 1300 l of water through two columns of granular activated carbon (Merck 2514) and Amberlite XAD-2 resins (Rohm and Haas) for one month.

2.2. Sample preparation

2.2.1. Liquid-liquid extraction

One litre of wastewater from the factory was analyzed according to EPA method 625 [5]. The acid fraction was derivatized using 3 ml of BF_3 -MeOH (Merck). Sample preparation for ozonated and chlorinated wastewater analysis was done according to the same procedure.

2.2.2. Granular activated carbon extract

Organic extracts were desorbed with CH_2Cl_2 (Carlo Erba Analyticals for the analysis of pesticides residue) by Soxhlet extraction. The eluate was concentrated and then redissolved with diethylether (Merck-pro analysis). The ether-soluble compounds were fractionated in base + neutrals (B + N) and acids (A). The acid fraction was derivatized using 3 ml of BF_3 -MeOH.

2.2.3. XAD-2 extract

XAD-2 Amberlite (Rohm and Haas) was previously treated to remove impurities. The desorption of organic compounds was carried out by eluting diethylether, which was sucked into the column and came into contact with the polymer for 10 min. The ethereal extracts were fractionated as described above.

2.2.4. Ecotoxicity

Samples collected for ecotoxicity were previously adjusted to pH 7 and salt content to 2% by NaCl (Carlo Erba Analyticals).

2.3. Analytical instrumentation and conditions

2.3.1. GC–MS

Gas chromatographic–mass spectrometry analyses were carried out on a Finnigan MAT ITD Model 800 (San José, CA, USA) directly interfaced to a Varian 3300 (Sunnyvale, CA, USA) capillary gas chromatograph. The concentrated samples or the concentrated blanks were injected into a (30 m, 0.25 μm , 0.24 mm) DB-5 fused-silica capillary column (J&W Scientific, Folsom, CA, USA). The temperature program was 60°C (1 min) to 280°C at 4°C/min with a final hold time of 15 min. The carrier gas at 30 cm/s linear velocity was helium 99.999%. The injection temperature was 250°C. To obtain mass spectra the samples were analyzed by electron ionization (EI). The conditions were as follows: ionization energy, 70 eV; scan mode, full scan, 50–450 u, 1 scan s^{-1} ; and transfer line temperature, 250°C. GC–FID was performed on a Hewlett-Packard 5890 gas chromatograph equipped with a FID detector. A 30 m, 0.25 μm film thickness, 0.25 mm DB-WAX fused-silica capillary column (D&W Scientific, Folsom, CA, USA) was temperature programmed from 60°C (1 min) to 120°C (3 min) at a rate of 25°C/min, then until 250°C at a rate of 4°C/min. The carrier gas was helium 99.999%, and nitrogen was used as make-up. TOC was determined with an OI Analytical Mode 700 TOC (College Station, Texas, USA). The acute toxicity of the samples was measured with the help of the bioluminescence test with *photobacterium phosphoreum*; a Lumistox Dr Lange (Düsseldorf, Germany) was used to measure the development of light emission in order to determine the EC_{50} value (EC_{50} means the concentration of wastewater which causes 50% inhibition). COD was measured according to method 5220.B [5].

2.3.2. Quantitation

Concentration of individual pollutants was obtained by the external standard method. A gas chromatogram of the standard solution is shown in Fig. 1. Semiquantitative estimates for compounds without the available external standard were obtained by peak area comparisons of the

internal standards (d10-anthracene for GC–MS) to those of the analytes.

2.4. Wastewater chemical oxidation

The ozonation experiments were carried out in a Fisher Model 501 Ozonizer supplied by Labor und Verfahrenstechnik (Germany). Ozone was generated by passing purified oxygen through the samples. The generated ozone was brought into contact with the wastewater in a closed reactor equipped with a porous glass diffuser. In total, 1512 l of wastewater–initial pH 5.8–adjusted to pH 11.5 was ozonated by bubbling 3.375 g of ozone through with a 50 min contact time. The excess of O_3 was measured by passing the gas through a water trap containing potassium iodide (2% KI). The resulting solution was then titrated with standard sodium thiosulphate according to standard methods [5]. The applied ozone dosage was considered to be the difference between influent and effluent ozone concentrations, and it was calculated as 2203 mg/l.

3. Results and discussion

3.1. Results of the analysis of the wastewater of the rubber additives manufacturing plant

The partially treated effluent was analyzed 15 times over a three-year period. A typical gas chromatogram of the effluent is given in Fig. 2. The compounds identified and the average concentration of the most important substances are listed in Table 1. Compounds are classified into four different groups. The benzothiazole group is formed of all compounds which have the heterocyclic ring of benzothiazole in their molecular formula. These are the organic contaminants found in greatest abundance and originate in the manufacture of rubber accelerators like 2-mercaptobenzothiazole and benzothiazolesulfenamides. The aniline group is formed from the aromatic compounds with aniline in their molecular structure. Aniline and N-methylaniline are used as raw materials in the manufacture of the 2-mercaptobenzothiazole and 2,2,4-trimethyl-1,2-dihydroquinoline (TMDQ) polymer, which is

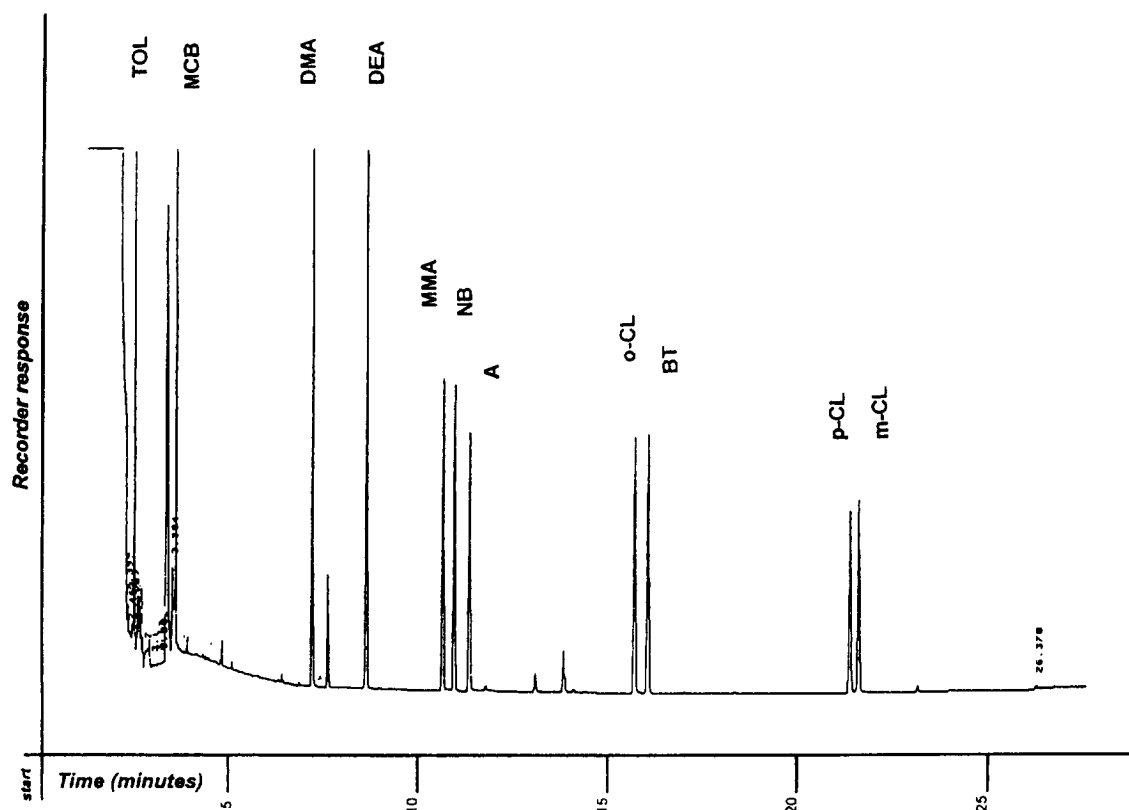


Fig. 1. Gas chromatogram of the standard solution, flame ionization detector. Peaks: TOL: toluene; MCB: monochlorobenzene; DMA: dimethylaniline; DEA: diethylaniline; MMA: monomethylaniline; NB: nitrobenzene; A: aniline; o-CL: *o*-chloroaniline; BT: benzothiazole; p-CL: *p*-chloroaniline; m-CL: *m*-chloroaniline. The GC conditions are given in the text.

used as rubber antioxidant. The other groups are other aromatics and nitrogen compounds. Toluene is used as a solvent for final product extraction. Several of the substances listed in Table 1 are toxic. Monochlorobenzene, toluene, chloroanilines and dichloroanilines appear in the toxic substances list [3,4]. The compounds found in this plant partially treated effluent in high quantities are benzothiazole (20 ppm), 2-mercaptobenzothiazole (1.1 ppm), aniline (5.6 ppm) and *N*-methylaniline (2.6 ppm). Benzothiazole has a mouse LD₅₀ of 900 mg/kg (oral) [6], 100 mg/kg (intraperitoneal) and 95 mg/kg intravenous [6]. 2-Mercaptobenzothiazole has an approximate fatal concentration of 2 mg/l in 48 h [7] and a LD₅₀ (in the rat by oral injection) of 100 mg/kg [6]. Aniline is included in 'Appendix IX List' [8]. With regard to its permissible concentration in

water, no criteria have been established, but the EPA has suggested an ambient limit in water of 262 µg/l based on health effects [7]. Finally, *N*-methylaniline has a oral man LDLo of 280 mg/kg [6].

3.2. Result of the analysis at Bocal Station and water supply

Compounds found at Bocal Station (concentration factor ca. 10⁶) are described in Table 2. Total ionization plot of the activated carbon extract from Bocal Station, B+N fraction, is given in Fig. 3. The compounds found in the two fractions, acid and base + neutral, are compiled in a single list. The unidentified compounds are named by indicating the most intense *m/z* fragments of their mass spectrum. Compounds are

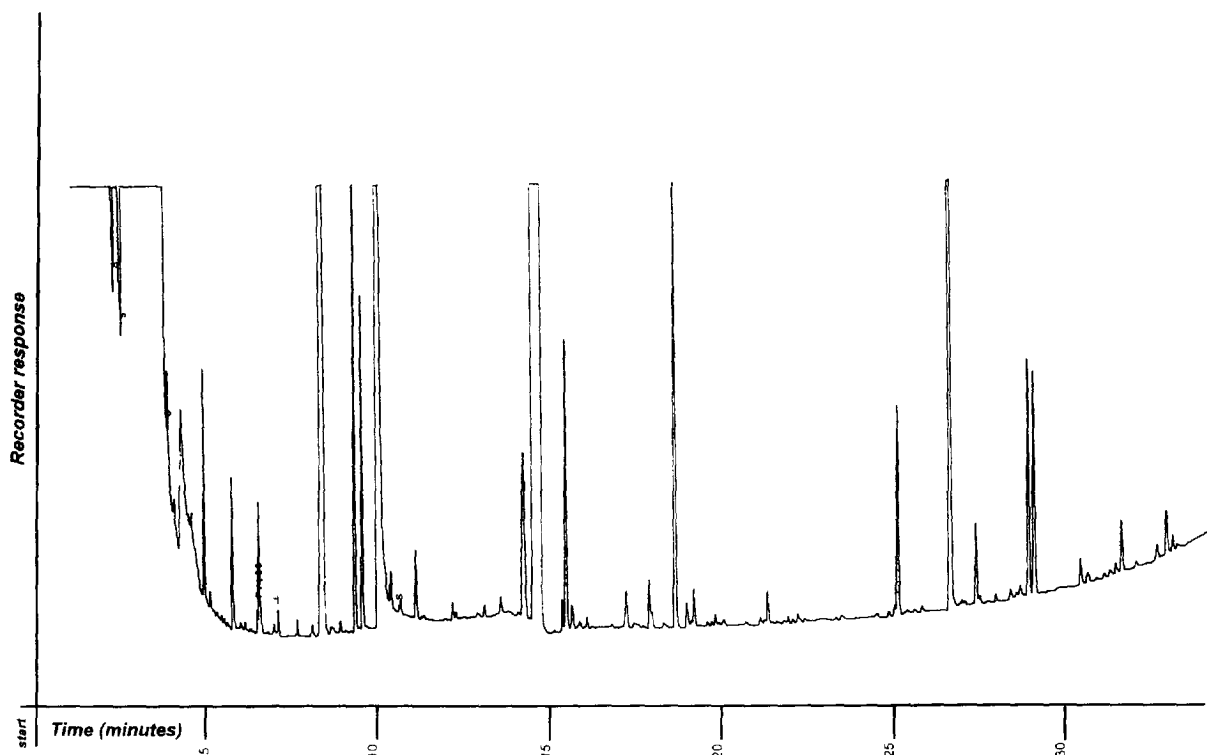


Fig. 2. Typical gas chromatogram of the effluent, B + N fraction, flame ionization detector. The GC conditions are given in the text.

classified into three classes set up in accordance with their frequency of appearance at this sample site of the river during the six months of this study. They are chronic compounds (C) if they appear in more than 80% of the analyzed samples; frequent compounds (F) if they appear with a frequency between 50% to 80%; and accidental compounds (A) when their frequency is below 50%. The percentage (expressed in %) of every organic substance in relation to the total of the compounds located is also indicated in Table 2. The table also indicates whether they are included in the EEC and USEPA list [3,4]. The asterisk that marks some of the compounds that were located indicates that they have been identified in the wastewater of the factory, which is located 100 km upstream from the sample site. It shows that they have come from its effluent. It is deduced from the results obtained in this analysis that 46.6% of the contamination produced by organic compounds at this sample site comes

from the production of rubber additives. The majority are benzothiazole; 2-benzothioazoisulfoxide derivatives; N-cyclohexyl-2-benzothiazole-sulfenamide; 2-methylthiobenzothiazole; 1,2-benzisothiazole, 3-methyl-, 2-methylbenzothiazole, etc. The results achieved by analyzing the extracts obtained from the XAD-2 resins are similar to those obtained with granular activated carbon.

Zaragoza city is supplied with water from the Canal Imperial de Aragon at Bocal Station. The disinfection treatment consists of perchlorination, coagulation with $Al_2(SO_4)_3$ and final chlorination. High levels of benzothiazole, in chronic form, were detected in the analysis of samples taken from the Zaragoza water supply. 1,2-Benzisothiazole, 3-methyl- and 2-methylbenzothiazole were also frequently detected. Finally, 2-methylthiobenzothiazole was detected in a more highly concentrated form.

From these analyses it can be deduced that the

Table 1
Compounds identified in industrial effluent

Compound	mg/l ^a	S.D. ^b
<i>Benzothiazole group</i>		
Benzothiazole	20	9.8
1,2-Benzisothiazole, 3-methyl	0.092 ^c	0.079
Benzothiazole, 2-methyl	0.024 ^c	0.048
Benzothiazole, 2-(methylthio)	1.104 ^c	1.272
2(3H)-Benzothiazolone	0.307	0.315
1,2-Benzisothiazole, 3-ol	u.c.	
Thiocyanic acid, (2-benzothiazoylthio) methyl ester	u.c.	
Benzothiazol, 2,2'-dithiobis	1.823	3.692
<i>Aniline group</i>		
Aniline	5.696	4.724
Aniline, N-methyl	2.690	7.589
Aniline, N,N-dimethyl	0.136	0.256
<i>o</i> -Chloroaniline	0.147	0.380
<i>m</i> -Chloroaniline	0.090	0.158
<i>p</i> -Chloroaniline	0.051	0.064
Σ Dichloroaniline	0.326	0.486
Aniline, N-(phenylmethylene)	u.c. ^d	
Aniline, <i>n</i> -chloro, <i>n</i> -methyl	u.c.	
Thiourea, N-phenyl-N'-(phenylmethyl)	u.c.	
Thiocyanic acid, <i>o</i> -anilinophenyl ester	u.c.	
<i>Other aromatics</i>		
Chlorobenzene (EEC, EPA) ^e	1.030	1.907
Toluene (EEC, EPA)	4.132	7.178
Benzene isothiocyanate	0.185 ^c	0.232
Benzoic acid, 4-methylamine	u.c.	
Benzene, [(methylthio)methyl]	u.c.	
Benzoic acid	u.c.	
Benzoic acid, 2-(methylthio)	u.c.	
Benzoic acid, 2-hydroxy-	u.c.	
Benzoic acid, 2-amine-	u.c.	
Benzoic acid, <i>n</i> -hydroxy- <i>n</i> '-methyl, methyl ester	u.c.	
<i>Nitrogen compounds</i>		
Cyclohexanamine, N,N'-methanetetraylbis-	u.c.	
Hydrazinecarboxamide, N,N-diphenyl	u.c.	
2,4-Imidazoledione, 3-methyl	u.c.	
Cyclohexylamine	u.c.	
1,2,3-Benzotrazin-4(1H)-one	u.c.	
4(1H)-Quinazoline, 2,3-dihydro-2-methyl-3-phenyl	u.c.	
TMDQ monomer	u.c.	

^a Average concentration.

^b Standard deviation.

^c Semiquantitative estimates (see text).

^d u.c. = unquantified compound.

^e EEC List of the 131 substances [3]; EPA Priority Pollutants List [4].

Table 2

Compounds found at Bocal Station; acid and base + neutral fraction

	Compound	Occurrence ^a	% ^b
1	(*)Benzothiazole	C	17.538
2	(*) 2-Benzothiazoylsulfoxide derivate	A	10.667
3	Diisooctyl phthalate	A	8.018
4	Methoxyethyl phthalate	A	6.519
5	(*) 2-Benzothiazolesulfonamida, N-cyclohexyl	C	5.853
6	(*) Benzothiazole, 2-methylthio	C	4.936
7	Buthyl, 2-methylpropyl phthalate	A	4.334
8	Diethyl phthalate (EPA) ^c	A	3.606
9	2-Benzothiazolesulfonamida	A	2.889
10	Octadecanoic acid, octyl ester	F	2.722
11	Trichloroaniline	F	2.520
12	Trichloroacetic derivate	A	2.469
13	(*) 2-Benzothiazolesulfonamida, N-cyclohexyl isomer	A	1.946
14	Ethanol, <i>n</i> -chloro-, phosphate	A	1.705
15	Phosphorodithioic acid, O,O,S-trimethyl ester	C	1.494
16	Triisobutyl phosphate	F	1.130
17	Tributyl phosphate (EEC) ^d	F	1.082
18	(*) 255,191,150	F	0.815
19	2-Benzenesulfonamide, N-butyl	F	0.474
20	Benzene, trimethoxy	A	0.446
21	Camphorsulfonic acid	A	0.436
22	2,5-Furandione, 3-ethyl-4-methyl	C	0.368
23	Ethanol, <i>n</i> -chloro-, phosphate	A	0.350
24	Benzenepentanoic acid, beta-oxo, methyl ester	A	0.336
25	2-Butenedioic acid, 2-ethyl-3-methyl	A	0.316
26	Sulphur	C	0.290
27	Heptadecanoic acid, 16-methyl	C	0.284
28	(*) 1,2-Benzisothiazole, 3-methyl	F	0.205
29	2,5-Cyclohexanedione-1,4-dione, 2,6-bis (1,1-dimethyl ethyl)	F	0.188
30	1,2-Benzisothiazole, 3-OH	F	0.151
31	Benzaldehyde	C	0.146
32	(*) 1,2-Benzenedicarboxylic acid, 4-methyl	A	0.114
33	2(5H)-Furanone, 5,5-dimethyl	A	0.110
34	Benzoic acid, phenyl ester	A	0.109
35	Ethanone, 1-(methylphenyl)-	A	0.107
36	(*) 2-Mercaptobenzothiazole	F	0.103
37	Dimethyl phthalate (EPA) ^c	C	0.097
38	Heptanoic acid, 3,5-dimethyl	A	0.097
39	(*) Benzothiazol, 2-methyl	F	0.078
40	(*) Cyclohexylamine	A	0.077
41	Benzoic acid	F	0.076
42	<i>m</i> + <i>p</i> -Xyleno (EEC) ^d	F	0.060
43	ABC-3	C	0.058
44	(*) Toluene (EEC,EPA) ^{c,d}	F	0.056
45	Benzene, isocyano	F	0.052
46	(*) Aniline (traces)	A	0.014

(*) Compounds that have been identified in the wastewater of the factory.

^a C = Chronic compounds that appear in more than 80% of the analyzed samples; F = frequent compounds that appear with a frequency from 50% to 80%; A = accidental compounds with a frequency below 50%.^b Percentage of every organic substance in relation to the total of the compounds that were located (area percentage).^c EPA Priority Pollutant Lists [4].^d EEC List of the 131 substances [3].

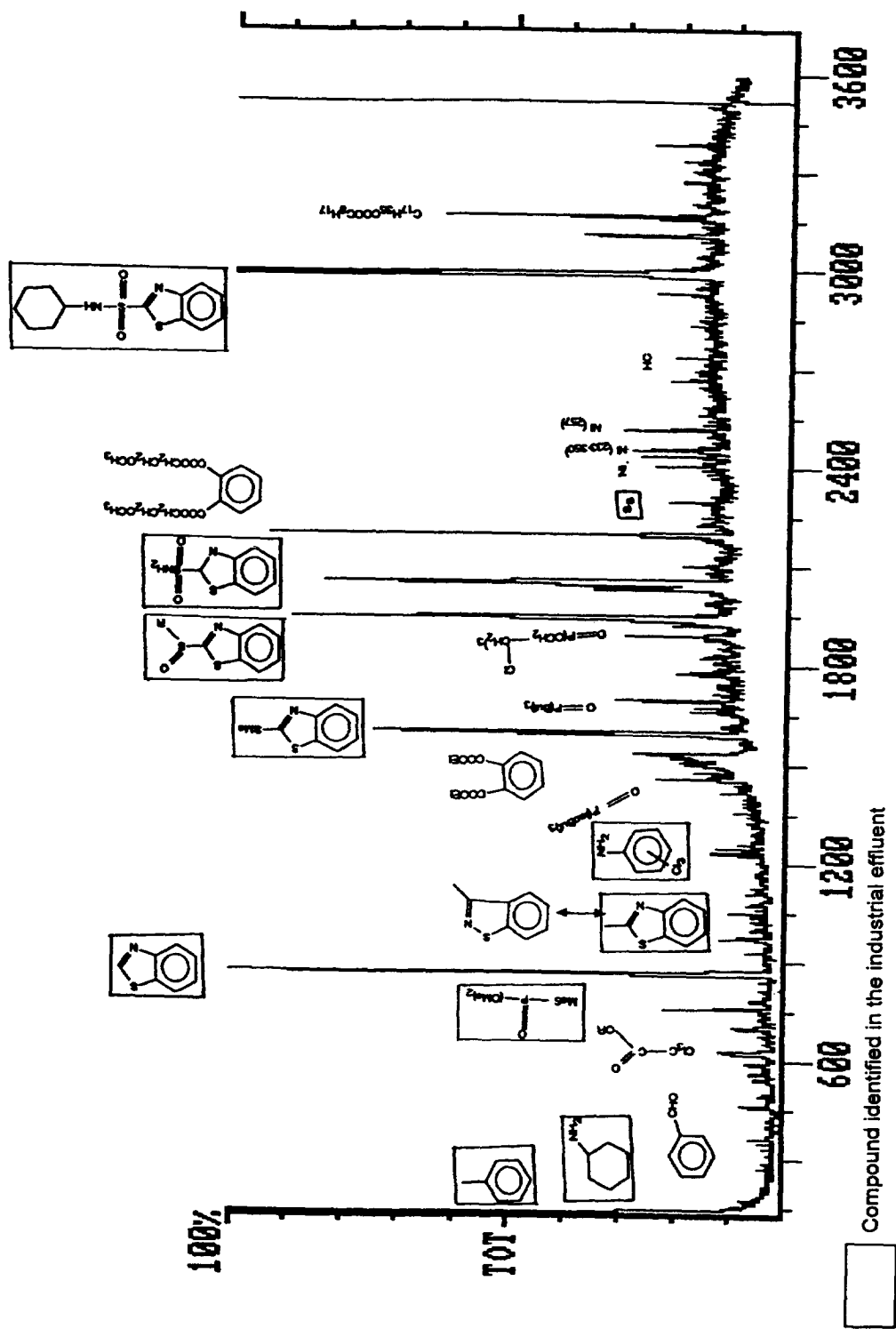


Fig. 3. Typical total ionization plot of the activated carbon extract from the Bocal Station, B + N fraction, ion trap detector. The GC conditions are given in the text.

compounds derived from benzothiazole in water have great stability. They are able to remain intact throughout the 100 km between the dumping site at the factory and the sample station, and along the 80 km to Zaragoza city. Moreover, they remain intact even after the purification process.

3.3. Wastewater ozonation

3.3.1. Non-specific parameters

In Table 3 the values for pH, COD, TOC and EC_{50} of the wastewater before and after treatment with ozone are given. As can be deduced, the pH of the sample decreases at the end of the ozone treatment to 5.6, and the COD decreases by 32.93%. The TOC value remains practically constant. Bioluminescence with *photobacterium phosphoreum* was used to measure the acute toxicity of the waste. The EC_{50} of 4500 mg/l indicates the presence of a residue of high toxicity [9]. The ozonated sample was three times less toxic than the non-ozonated one, because the EC_{50} increased to 12 600 mg/l.

3.3.2. Waste compounds whose concentration decreases

Table 4 groups the substances identified in this study and the reduction (expressed in %) or increase of every compound after chemical treatment with ozone and chlorine. The new compounds formed after each treatment are given in Table 4. Both A and B + N fractions are listed in the same table. Total ionization plots of the ozonated and non-ozonated wastewater, B + N fraction, are given in Fig. 4.

As is known, ozone can oxidize organic compounds by two mechanisms [10–12]: direct re-

action or decomposition to OH radical, which in turn reacts with the organics. The direct ozone reactions are highly substrate-specific and depend on the nature of the molecules. The presence of substituting groups in the aromatic ring can lead to the formation of nucleophilic centres where ozone can attack more easily by electrophilic substitution. Therefore, ozone will attack more easily the aromatic compounds that contain an unshared pair of electrons on the atom connected to the ring [13]. In this category are NR_2 , NHR , NH_2 , OH , O^- , which are strongly activating groups, and SR , S^- , which are mildly activating. After ozonation, compounds like those listed in the aniline group are removed or their concentration has decreased more than 99%. Although $-Cl$ has a weak deactivating effect because it withdraws electron density from the ring and it also contains an unshared pair of electrons, the concentration of chlorobenzene is decreased by 92.79%. $-CH_3$ is an electron-donating group and has a moderate activating effect; the concentration of toluene is decreased by 90.79%. With regard to the benzothiazole group, after ozonation, the heterocyclic compounds like 2-benzothiazoleamine, benzothiazole, 2-(methylthio)- or 2-mercaptobenzothiazole with activating substituting groups are completely removed. The concentration of 2-methylbenzothiazole and 1,2-benzisothiazole, 3-methyl are decreased by 82.3% and 79.7%. The concentration of benzothiazole, without any substituting group, is decreased by 66%.

3.3.3. Waste compounds whose concentration increases and ozone by-products

Table 5 lists ozonation by-products. The percentage indicates the level of every substance in relation to the total of the compounds located. Ozone reacts with organics according to different mechanisms. Electrophilic substitution leads to hydroxylation of the aromatic ring and reaction with unsaturated and aromatic groups to form aldehydes, ketones and acids. Aldehydes are by-products of potential toxicological significance. They react straightforward [14] with amines to give imines, which are usually called Schiff bases. Imines with a hydrogen on the nitrogen spontaneously polymerize. Amines can be oxidized to

Table 3
Ozonation

Ozonation	Raw water	Ozonated
pH	11.5	5.6
TOC	560	574
COD	2010	1348
EC_{50}	4500	12 635

Non-specific parameters determined as mg/l.

Table 4
Ozonation results

Compound	% removed	Compound	% removed
<i>Benzothiazole group</i>		<i>Other aromatics</i>	
2-Benzothiazoleamine	-100	Benzoic acid 2-hydroxy-3-methyl, met ester	-100
Morpholine,4-(2-benzothiazoylthio)	-100	Chlorobenzene ^{a,b}	-92.79
Thiocyanic acid,(2-benzothiazoylthio)methyl ester	-100	Toluene ^{a,b}	-90.79
2(3H)-Benzothiazolethione, 3-methyl	-100	Benzene, isothiocyanate	-44.12
Benzothiazole, 2-(methylthio)	-100	Cyclohexanamine, N-(phenylmethylene)	-36.9
2-Mercapenzothiazole	-100	Benzene, methanol	+2765
Benzothiazole 2-(ethylthio)	-99.7	Benzoic acid	+45.41
2-Benzothiazoleamine, N-cyclohexyl	> -98	Phenol, trimethyl	-100
2(3H)-Benzothiazolone	-96.99	Phenol, 2,6-bis(1,1-dimethylethyl)-4-methyl	-100
1,2-Benzisothiazole, 3-methyl	-82.3	1,2,4-trichlorobenzene ^{a,b,c}	-100
Benzothiazole, 2-methyl	-79.7	Benzene, 1,1'-sulfonylbis-	-97.48
1,2-Benzisothiazole, 3-acetic acid	-74.6	Phthalate, bis(ethylhexyl)	-98.69
Benzothiazole	-66	Phthalate, butyl, 2-methylpropyl	-70.42
Benzothiazole-6-OH-2-methyl	-27.8	Dimethyl phthalate	-48.64
1,2-Benzisothiazole, 3-OH	+28.6	Phthalate, butyl, cyclohexyl	-2.45
<i>Aniline group</i>		<i>Nitrogen compounds</i>	
Benzenemethanamine N-(phenylmethyl)-	-100	Urea, N,N'-dicyclohexyl-	-100
Aniline, N,N'-(1,2-dimet)-1,2-(ethanediyldene)bis	-100	Thiourea, N,N'-dicyclohexyl	-100
Aniline, N-(phenylmethylene)	-100	2,2,4-Trimethyl, 1,2-dihydroquinoline (monomer)	-100
<i>o</i> -Chloroaniline ^{a,b}	-100	Cyclohexylamine, N,N'-methanetetra-bis-	-99.3
Guanidine, N,N',N''-triphenyl	-100	Thiocyanic acid, <i>o</i> -anilinephenyl ester	-93.99
Aniline, <i>n,n'</i> -dimethyl	-100	Quinoleine, 2,3,4-trimethyl, 1-oxide	-100
Aniline	-99.99	Hydrazine, 1,1-diethyl-2-propyl	-11.52
Aniline, N-methyl	-99.77	Carbamic compounds	-100
Aniline, N,N-dimethyl	-99.98	Mercaptane	-100
		1-H-Imidazole-2-methanol	+3065

Removed compounds as %, acid and base + neutral fraction.

-x%: percentage of concentration reduction; +x%: concentration increase.

^a Included in EEC List of the 131 substances [3].

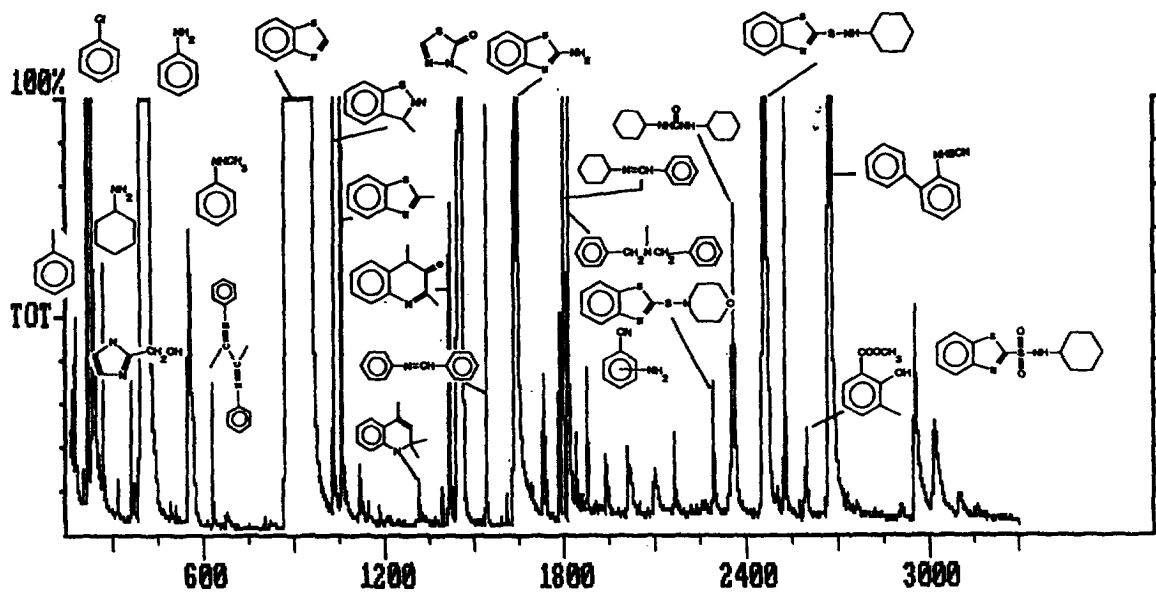
^b Priority Pollutant Lists [4].

^c Appears in 90/415/EEC Directive [15].

the corresponding nitro compounds in good yields with ozone. The waste substances found in the wastewater from the factory were aryl and alkyl amines, aromatics, olefins and sulphur compounds; therefore, all the reactions described above will occur. After ozonation, nitrobenzene was the most abundant by-product formed. It does not belong to the list of 131 EEC substances [3], but is defined by the USEPA as a hazardous substance and waste, and it is a priority pollutant. The permissible concentration in water to protect freshwater aquatic life is 27 mg/l on an acute

toxicity basis. Other new abundant compounds formed were methylamine; N-cyclopentylidene; 2-butenic acid, 3-methyl, methyl ester; azobenzene (orl-rat LD₅₀: 1000 mg/kg, ipr-mus LD₅₀: 500 mg/kg) [6], and azoxybenzene (orl-rat LD₅₀: 620 mg/kg and orl-mus LD₅₀: 515 mg/kg) [6]. The concentrations of benzoic acid (used as a food preservative) and benzenemethanol (LC₅₀ rat inhalation: 1000 ppm; 8 h) [6] were increased. Both of them are biodegradable. Only the concentration of 1,2-benzisothiazole, 3-OH from the benzothiazole group, increased slightly.

WASTEWATER



OZONATED WASTEWATER

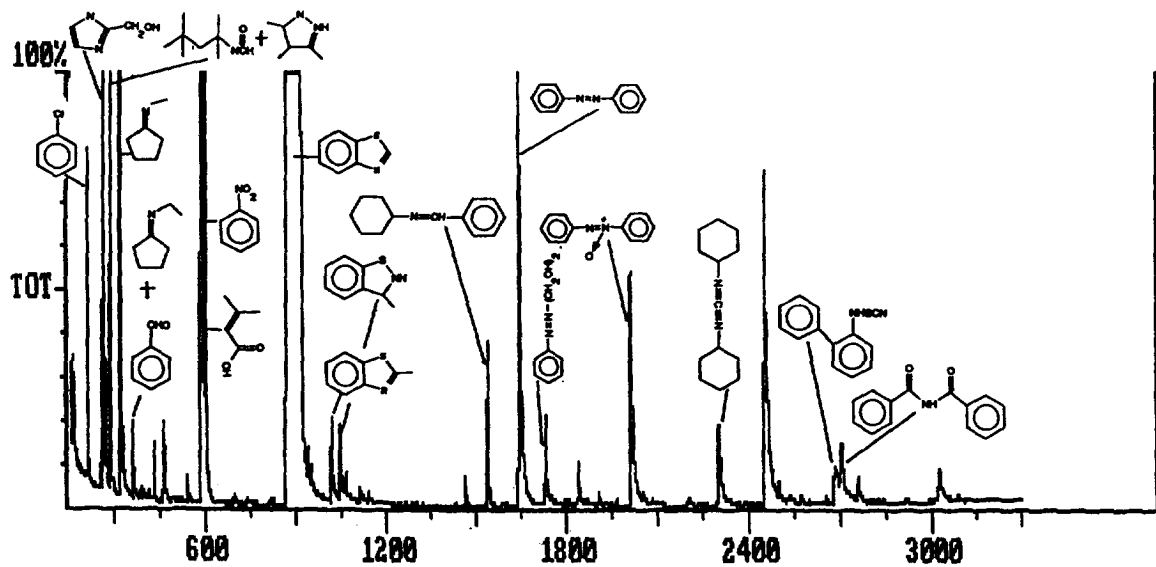


Fig. 4. Total ionization plot of the effluent and the ozonated effluent, B + N fraction, ion trap detector.

Table 5
New ozonation by-products, acid and base + neutral fraction

Compound	%
Nitrobenzene ^a	28.72
Methylamine, N-cyclopentylidene	22.70
2-Butenoic acid, 3-methyl-, methyl ester	15.86
Azobenzene	13.68
Azoxybenzene	6.29
1H-Pyrazole, 4,5-dihydro-3,4,5-trimethyl	4.15
Aniline, 4-cyclohexyl	2.17
Phenol, 4-(phenylazo)	1.72
1,3-Cyclopentadiene, methyl	0.83
7-Oxabicyclo[4.1.0.]heptan-2-one	0.76
3-Isoxazolecarboxamide, 5-phenyl	0.71
Diazene, bis(4-nitrophenyl)	0.41
Benzoate, 3-buten-2-ol	0.39
1,2,3-Benzothiadiazole	0.25
Ethylcyclohexane	0.22
Benzoxazole	0.21
Benzene carbonothioic acid	0.19
Ph-CO-CO-CH ₂ -NOH	0.18
Ethanal,2,2'-phenylimino-bis	0.11
Benzamide, 3-amino-4-methoxy-N-phenyl	<0.08
Cyclohexanamine, N-butylidene	0.08
S-Triazolo[4,3-A]pyrazine, 3-ethyl-8-methyl	0.08
Benzene, 1-methyl-2-nitro	0.07
Phenol, 2-(2-benzothiazoyl)-	0.07
Diazene, (4-methylphenyl)phenyl	0.05
Pyridine, 3-ethyl-5-methyl-	0.05
Benzoic acid, 2-benzoylhydrazide	0.03
Diazene, (4-chlorophenyl)phenyl	0.02
1-Propanone, 2,-dimethyl-1-phenyl	0.02

^a EPA Priority Pollutant List [4].

4. Conclusions

By means of a sampling technique based on the adsorption and concentration of organic pollutants from the riverbed in the River Ebro (Spain), 46 different compounds have been identified. Sixteen of them are waste substances resulting from the manufacture of rubber additives. The majority are 2-MBT (2-mercaptobenzothiazole) derivatives with a heterocyclic ring in their molecular structure.

The industrial effluent from which this pollution originated is located 100 km upstream from the sample site. The wastewater analysis has allowed us to identify a total of 53 different waste substances.

After wastewater ozonation the COD decreased by 33%, and the TOC remained practi-

cally constant. Nevertheless, 2-MBT and its derivatives and most of the other waste substances were removed. The by-products formed in greatest abundance were: nitrobenzene; imine derivatives; 2-butenic acid, 3-methyl, methyl ester and azobenzene. After ozone treatment, the acute toxicity measured as EC₅₀ was three times less.

Acknowledgements

I would like to thank all the staff at the laboratory of Confederación Hidrográfica del Ebro.

References

- [1] J. Rivera, F. Ventura, J. Caixach, M. Torres and A. Figueras, *Int. J. Environ. Anal. Chem.*, 29 (1987) 15.
- [2] P. Van Rossum and R.G. Webb, *J. Chromatogr.*, 150 (1978) 381.
- [3] 76/464/EEC: Council Directive of May 1976 on pollution caused by certain dangerous substances discharged into the aquatic environment of the Community, Official Journal No. L 129, 18/05/76 p. 0023, Greek special edition, Vol. 01 P.138, Ch. 15.
- [4] U.S. EPA Priority Pollutant List, Clean Water Act of 1977, Federal Register, 44, 233, December 3, 1979.
- [5] L.S. Clesceri, A.E. Geenberg and R.R. Trussell (Editors), *Standard Methods for the Examination of Water and Wastewater*, American Public Health Association, Washington, DC, 17th. ed., 1989.
- [6] N.I. Sax, *Dangerous Properties of Industrial Materials*, Van Nostrand Reinhold, New York, 1984.
- [7] S. Sitting (Editor), *Handbook of Toxic and Hazardous Chemicals*, Noyes Publications, Park Ridge, NJ, 1981.
- [8] Appendix IX List, Promulgated by the US EPA under authority of the Solid Waste Disposal Act of 1965 and the Resource Conservation and Recovery Act (RCRA) of 1976, Federal Register, 52, 131, July 9, 1987.
- [9] Orden Ministerial de 13 de Octubre de 1989, BOE no. 270, 10-XI-1989.
- [10] R. Andreozzi, A. Insola, V. Caprio and M.G. D'Amore, *Water Res.*, 25 (1991) 655.
- [11] F.J. Benitez, J. Bertrán-Heredia and T. González, *Water Res.*, 25 (1991) 1345.
- [12] N. Doré, B. Merlet, B. Legube and J.Ph. Croue. *Ozone Sci. Eng.*, 10 (1988) 153.
- [13] M.P. Ormad, J. Sarasa, A. Puig, M.C. Martínez, N. Cebrián, M.S. Mutuberría and J.L. Ovelleiro, *J. Chromatogr.*, 607 (1992) 311.
- [14] J. March, *Advanced Organic Chemistry: Reactions, Mechanisms and Structures*, Wiley, New York, Fourth ed., 1992, Ch. 11, p. 507.
- [15] 90/415/EEC Directive, Official Community Journal No. L219 14/08/90.