



# Identification of organic compounds migrating from polyethylene pipelines into drinking water

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## Abstract

A study of the diffusion of organic additives from four polyethylene (PE) materials into drinking water was conducted. Various structures of organic chemicals were identified in the water extracts by means of gas chromatography–mass spectrometry analysis. Most of them presented a basic common structure characterised by a phenolic ring typically substituted with hindered alkyl groups in positions 2 and 6 on the aromatic ring. The structures attributed to some of the chemicals have been confirmed using commercial or purposely synthesised standards. Unprocessed granules of raw PE were also analysed, in order to investigate the origin of the chemicals detected in the water samples. Consequently, the presence of some of the compounds was attributed to impurities or by-products of typical phenolic additives used as antioxidants in pipeline production. Finally, the occurrence of the identified chemicals was tested under field conditions, i.e. in water samples from newly installed pipelines in a distribution system. Here, the presence of three of the compounds identified *in vitro* was detected. © 2002 Elsevier Science Ltd. All rights reserved.

**Keywords:** GC–MS analysis; Organic additives; Polyethylene; Alkylphenols; Irganox; Pipes; Drinking water

## 1. Introduction

Old pipes used to supply drinking water are often being replaced with pipes manufactured from polymer materials. Various types of polyethylene (PE) and polyvinylchloride (PVC) are used presently, although the trend is to select PE materials rather than PVC materials [1].

The polymer materials contain a variety of organic and inorganic additives in order to improve the material's durability, the manufacturing, and handling during installation, as well as to modify the colour. The additives used include the following: antioxidants and other stabilisers, lubricants, softeners and colouring agents [2]. Since the pipes are expected to last over 100 years in the ground, stringent quality requirements regarding mechanical strength must be fulfilled by the

manufacturers. While good mechanical properties of the pipes are fundamental, the possibility that toxic organic compounds from the pipes may leach into the drinking water, resulting in contamination must be considered as well. Such leaching could occur directly, by diffusion of chemicals into the water, or indirectly, for example, metabolites from biological growth in a biofilm on the interior surface of the pipes being released into the water. Thus, a situation could arise where high-quality water leaving water works is contaminated before reaching the consumer.

A number of papers have been published regarding chemical analyses of additives used in polymeric material production [3–5]. However, there has been little research concerned with the identification of additives diffusing into drinking water from pipes. Some of the latter research includes: (i) monitoring of a few target hazardous chemicals [6]; (ii) identification of those compounds responsible for the alteration of the organoleptic properties of drinking water [7]; and (iii) measurement of the non-volatile organic compounds

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(NVOC) released into the drinking water [8]. Knowledge of the chemistry of those organic chemicals with the potential to migrate into drinking water is lacking.

In the present project, an extraction and identification of the organic chemicals migrating from a PE pipeline into water was undertaken. Four different PE pipe materials available on the Danish market were tested. Furthermore, the presence of some of the identified chemicals was investigated under field conditions, i.e. in water samples from newly installed pipes in a distribution system. Finally, in order to understand the origin of the degraded additives detected in water, as well as the chemistry of these additives, unprocessed PE granules were investigated.

This paper will present the details of the diffusion test, the liquid–liquid extraction, and the gas chromatography–mass spectrometry (GC–MS) analysis methods set-up. The results of the identification study will also be presented. Furthermore, a comparison of the laboratory results, and results obtained from in situ drinking water samples will be reported.

## 2. Materials and methods

### 2.1. Samples

Four different PE material pipes (A, B, C and D) were employed as samples during the laboratory study. Sample A consisted of cross-linked polyethylene (PEX); samples B and D are made of medium-density polyethylene (PEM); and sample C consisted of low-density polyethylene (PEL). The four sample types are representative of pipe materials commonly used in drinking water distribution systems. Pipe pieces had lengths of 1 m, and the following internal diameters: A, 10 mm; B, 28 mm; C, 31 mm; D, 25 mm. All samples used in this study were obtained directly from the manufacturers and, prior to analysis, were packed in aluminium foil and stored in paper bags. Small granules (diameter about 5 mm) of the raw PE material used in the industrial production of pipe B were also supplied by the manufacturer.

Samples of the polymer additives Irganox 1035, Irganox 1010 and, Irganox 1076 were supplied by Ciba-Geigy (Denmark). The following standards were supplied by Merck, Fluka and Acros: 4-ethyl phenol, 4-*tert*-butyl phenol, 2,4-di-*tert*-butyl phenol, 2,6-di-*tert*-butyl-*p*-benzoquinone and 3,5-di-*tert*-butyl-4-hydroxy benzaldehyde. The following chemicals were obtained by organic synthesis: 3,5-di-*tert*-butyl-4-hydroxy acetophenone, 3-(3,5-di-*tert*-butyl-4-hydroxy-phenyl) propionic acid, 3-(3,5-di-*tert*-butyl-4-hydroxy-phenyl) methyl propanoate. The commercial chemicals and additives were used without any purification. Structures of the

chemicals cited in this paper are reported in Figs. 2 and 4.

In situ water samples were collected from newly installed PEX pipes (corresponding to sample A in our laboratory study) in a drinking water distribution system. Water samples were collected after a contact time of 60 h at a temperature of approximately 20°C.

### 2.2. Additive migration test

During the migration test, the inner surface of a sample was brought into contact with test water (Milli Q water) for 7 days at a temperature of  $23 \pm 2^\circ\text{C}$ . The pipe surface area to water volume ranged from 13 to  $43\text{ dm}^{-1}$ . Prior to the migration test, the pipe samples were filled with test water for 24 h, flushed with tap water for 60 min and finally rinsed with test water for 2 min. Immediately after this pre-treatment, the pipes were filled with fresh test water and capped with brass stoppers at both ends. At the end of the test period, the test water was removed and subsequently extracted with an organic solvent. The organic extracts were analysed by GC. Each polymeric material was tested in triplicate. Blank migration and extraction tests were also performed. Blank samples were created by placing brass stoppers in glass bottles, immersing the stoppers in test water and sealing the bottles with Teflon caps.

### 2.3. Liquid–liquid extraction method

Prior to the extraction of leached water, 100  $\mu\text{L}$  of an internal standard (IS) solution (2-naphthol, 50 ppm in pentane) was spiked into the water. The resulting water solution was shaken for approximately 1 min. The leached water was then transferred into a separating funnel and 15 mL of chloroform (SupraSolv Merck) was added. The resulting solution was shaken manually for approximately 3 min. The organic phase was stored in a glass flask and the water phase was re-extracted with 15 mL of fresh chloroform. The two organic fractions were unified. The volume of the organic solution was reduced to approximately 100  $\mu\text{L}$  under a gentle nitrogen stream (approximately 50 min). The concentrated extracts were stored in a refrigerator at  $-14^\circ\text{C}$  until analysis. The mean IS extraction recovery, determined on six consecutive extractions, was 99.2% with a standard deviation of  $\pm 13.7$ .

### 2.4. Identification of additives

The identification of the organic compounds extracted from the leached water was performed by GC coupled with a mass spectrometry detector (GC–MS). Electron impact (EI) spectra were obtained on a Hewlett-Packard 6890 GC coupled with a Hewlett-Packard 5973 MS. The carrier gas was helium at a constant flow of

1.2 mL min<sup>-1</sup>. One microlitre of solution was injected in the split-splitless mode (the split was opened after 30 s) into the injection port at a temperature of 280°C. The MS scan range was from 20 *m/z* to 650 *m/z* (full scan) 3.6 times every second under an electron impact condition of 70 eV. Employing a capillary column (Hewlett-Packard, HP-MS5 30 m, 0.25 mm i.d., 0.25 mm film thickness) the oven temperature was held at 45°C for 1 min, raised by 5°C min<sup>-1</sup> to 300°C, and then held at 300°C for 10 min. Part of the identification of the extracted compounds was made using the reference spectra held in the library NBS 75 K (NIST HS Chem Station Library.)

### 3. Results and discussion

Fig. 1 shows a typical total ion chromatogram (TIC) of the water extract. The extraction and the analysis conditions were appropriate for a good peak resolution and IS recovery.

A variable number of peaks (between 20 and 30) of different intensities were detected, during the GC–MS analysis of the water samples which were in contact with the four polymeric-pipe samples. Some peaks, however, were both present and dominant in all four samples. The following results concern only ten of these peaks, i.e. ten compounds, refer to Table 1. The compounds in Table 1 are enumerated in order of chromatographic elution.

During the mass spectra interpretation, the structural identification of “unknown” chemicals was initially accomplished either by comparison with spectra reported in the literature and in the MS library, or by interpreting the fragmentation pattern of the mass

spectra. Once a more precise theory regarding the chemistry of the “unknown” compounds was formulated, the structure attributed to a particular chemical was confirmed by recording chromatograms and the MS spectra of standards. Thus, the structure attributed to a detected compound was considered to be a positive identification whenever both the GC retention time and the mass spectra of pure standards matched with the two corresponding parameters of the unknown compound. Some of the standards were commercially available: those, which were not, were synthesised. To date, not all of the ten compounds in Table 1 have been positively identified. A structure was tentatively attributed to peak V based on an interpretation of the mass spectra fragmentation pattern. While a structure was tentatively attributed to peak VIII based on comparisons with a

Table 1

List of the most abundant organic compounds found in water which was in contact with various polymeric pipe samples (for nos. refer to Fig. 2)

No.	A (PEX)	B (PEM)	C (PEL)	D (PEM)	In situ samples
I			✓		
II		✓	✓	✓	
III			✓	✓	
IV		✓		✓	
V		✓	✓	✓	
VI	✓	✓	✓	✓	✓
VII	✓	✓	✓	✓	✓
VIII	✓	✓	✓	✓	✓
IX		✓	✓	✓	
X		✓	✓	✓	

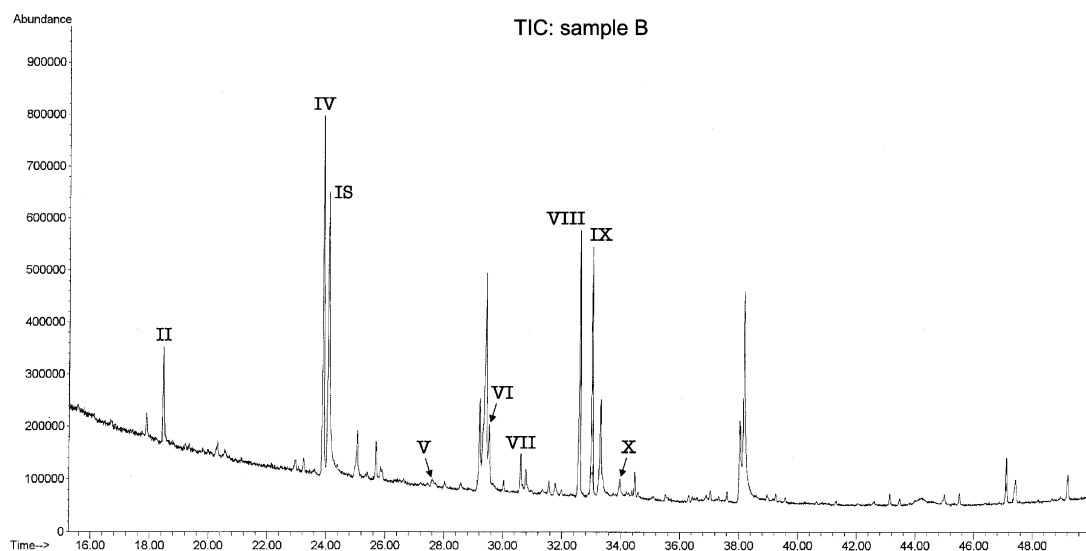
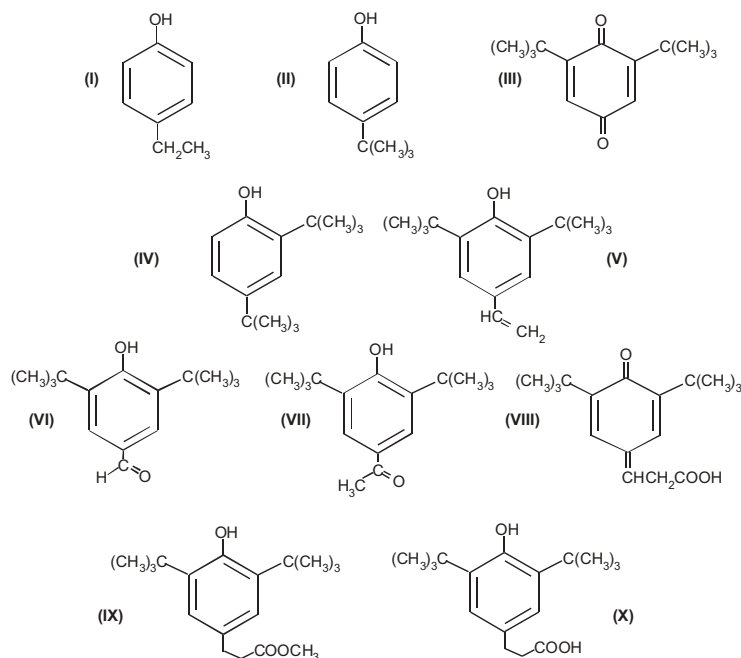


Fig. 1. Typical GC–MS chromatogram of a water extract (sample B).



- (I) 4-ethyl phenol (P)  
 (II) 4-*tert*-butyl phenol (P)  
 (III) 2,6-di-*tert*-butyl-*p*-benzoquinone (P)  
 (IV) 2,4-di-*tert*-butyl phenol (p)  
 (V) 3,5-di-*tert*-butyl-4-hydroxy styrene (T)  
 (VI) 3,5-di-*tert*-butyl-4-hydroxy benzaldehyde (P)  
 (VII) 3,5-di-*tert*-butyl-4-hydroxy acetophenone (P)  
 (VIII) Cyclo hexa 1,4 dien, 1,5-bis (*tert*-butyl), 6-on,4-(2-carboxy-ethylidene) (T)  
 (IX) 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl) methyl propanoate (P)  
 (X) 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl) propanoic acid (P)

Fig. 2. Structures and names of the identified organic compounds. (P=positive identification, i.e. peak spectra matches with standard spectra. T=tentative identification, i.e. either the peak spectra matches with a data base spectra or by interpretation of the fragmentation pattern in the spectra.)

mass spectra previously reported in the literature [9]. Structures of the ten identified compounds are depicted in Fig. 2.

The EI mass spectrum of 2,6-di-*tert*-butyl-4-hydroxy acetophenone (VII, MW = 248 emu) is given in Fig. 3. The base peak is found at  $m/z$  233, corresponding to  $[M-CH_3]^+$ . This fragment loss is due to a  $\beta$ -cleavage on the aromatic ring: the methyl group involved in this fragmentation is one of the two *tert*-butyl groups [10]. The ion at  $m/z$  205 results from the loss of  $[M-C_3H_7]^+$ , corresponding to the loss of three methyl groups from the two *tert*-butyl groups. Except for compounds III and VIII, all the compounds identified in this work present spectra characterised by a base peak at  $[M-15]$  due to the loss of one methyl group, either from one of the *tert*-butyl groups or from the ethyl group (for compound I). The different fragmentation patterns in spectra III and VIII were attributed to the presence of oxidised substitutions in positions 1 and 4 on the aromatic ring.

It is well known that alkylphenols are used as antioxidant agents in polymer pipe production [2]. Thus, compounds I, II and IV were probably additives in the PE pipe production. The structures of the compounds III and V–X, are not, however, recognisable as typical antioxidant additives. Their basic chemical structure is characterised by a phenolic ring, substituted with hindered alkyl groups (typically *tert*-butyl substitutions in positions 2 and 6 on the aromatic ring), as well as an unsaturated, mostly oxygenated, substitution in position 4 on the aromatic ring. Since compounds II and V–X represent chemical structures similar to those of the well-known phenolic additives (e.g. Irganox-based additives with structures XI–XIV in Fig. 4), two hypotheses were made about the origin of these compounds. The first hypothesis was that these compounds were alteration or degradation products, produced from the original additives, during the extrusion step (200–250°C) in the pipe manufacturing process. The second hypothesis was

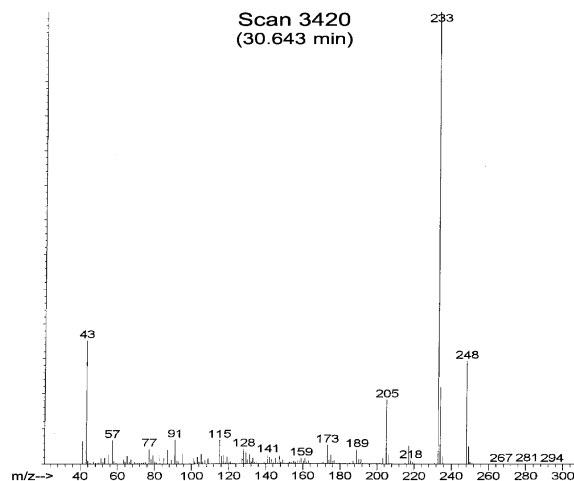


Fig. 3. EI mass spectrum of 3,5-di-*tert*-butyl-4-hydroxy acetophenone (VII).

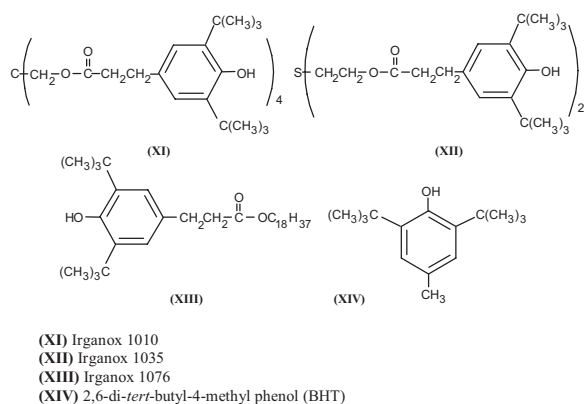


Fig. 4. Structures and names of some common polymer additives.

that these compounds were by-products or impurities resulting from the synthesis of pure phenolic additives.

In order to investigate the two hypotheses, migration and extraction tests were conducted on raw granular PE material used in the extrusion step. Furthermore, GC–MS analyses of some Irganox additives were performed in order to test their purity. Results of both the additives' purity tests and a migration test of PE granules are reported in Table 2.

Individual GC–MS runs of Irganox-based additives revealed a few impurities as indicated by small peaks, corresponding to additive by-products. Some of the small peak retention times and mass spectra matched perfectly with those of peaks V, VI, VIII, and IX. As reported in Table 2, compounds V, VI, VIII, and IX were also found in the unprocessed granules; thus, they could not originate from an alteration of additives during the pipe manufacturing process. Further investigations are required in order to determine whether

Table 2

List of the most abundant organic compounds found in polymer additives and in water in contact with unprocessed PE granules (for nos. refer to Figs. 2 and 4)

No.	Irganox 1035 (XII)	Irganox 1010 (XI)	Irganox 1076 (XIII)	PE granules (sample B)
I				
II				✓
III				
IV				✓
V	✓	✓		✓
VI	✓	✓		
VII				
VIII	✓	✓		✓
IX	✓	✓		✓
X				

compounds I, III, VII, and X originated from oxidation/degradation products formed during the production process.

To our knowledge, only a few of the identified structures have been previously reported in the literature, as being present in drinking water (e.g. III [11]). While no documentation regarding the occurrence of other compounds (e.g. VI, VII, and X) in drinking water could be found. This sparse scientific research suggests that the potential negative environmental impacts of PE pipes have been, to date, ignored. Therefore, it is important, in the future, that when additives for the manufacturing of polymeric pipes for drinking water supply systems are being selected, that both the environmental aspects of the additives are considered, as well as those of new compounds which may be present in the formulation of the PE as impurities of the main additives and/or which may be formed during the production process.

### 3.1. *In situ* drinking water samples

In order to confirm results found in the laboratory study, drinking water samples were collected *in situ* from a newly installed pipeline distribution system made of PEX material (sample A). Water samples were collected at two different points in the distribution system. As reported in Table 1, the three main compounds VI, VII, and VIII, detected in laboratory samples, were also present in the *in situ* water samples collected from the two sampling points.

## 4. Conclusion

The migration test conducted in this study has shown that the four PE pipe samples tested are capable of

releasing organic chemicals into drinking water. The number of chemicals detected in this study ranged from 20 to 30. Not all of them have been identified to date, although chemical structures were attributed to ten selected representative compounds. Eight of the ten structures were positively confirmed by means of commercial or purposely synthesised standards. Most of the compounds present a basic common structure characterised by a phenolic ring typically substituted with hindered alkyl groups in positions 2 and 6 on the aromatic ring. To our knowledge, few of the identified structures have previously been reported in the literature as being present in drinking water. Some of the compounds were likely impurities or by-products of typical phenolic additives employed as antioxidants in the pipeline production. Analysis of *in situ* water samples verified the presence of three of the identified compounds in actual drinking water samples.

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