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# Potential Formation of Bromophenols in Barcelona's Tap Water Due to Daily Salt Mine Discharges and Occasional Phenol Spills

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The presence of phenol and chlorinated phenols in drinking water has been shown to affect both taste and odour and to cause negative effects on health (Kozak 1979). The priority pollutants list issued by E.P.A. includes eleven of these compounds as suspected carcinogens. Many authors have published their results on chlorinated phenols but little attention has been focussed on the presence of bromophenols. Rook (1974) has demonstrated the presence of volatile brominated organic compounds when bromide is present, due to chlorination according to the following reaction: $HOCl + Br^- \longrightarrow HOBr + Cl^-$. Similarly, brominated phenols might be formed during chlorination in the water works. Sweetman et al (1980a) reported the production of bromophenols resulting from the chlorination of distilled water containing bromide ion and phenol; recently Watanabe et al. (1984) observed the same effect by addition of bromide to wastewater. Bean et al. (1980b) identified brominated compounds in marine water and Kuehl et al. (1978a) in fish.

More than 3 million inhabitants in the area of Barcelona (N.E. of Spain) drink water taken from Llobregat river. Quality of this raw water is strongly influenced by high contents of bromide coming from salt mines located in the upper course of the river. Levels of bromide range from 1 mg/l to 3,5 mg/l during 1979-1983. Brominated THM's in Barcelona's tap water in this period, were the most predominant species reaching levels as high as 714 µg/l (Ventura and Rivera 1985). Phenol and phenolic compounds are usually found in raw water in the ppb range but occasional spills may increase the phenol content up to parts per million. Levels of phenol ranged from 0,1 mg/l to 6 mg/l for the same period. This study shows the possibility of formation of bromophenols during normal chlorination conditions at Barcelona's water works plant.

## MATERIALS AND METHODS

Many analytical methods for the determination of phenolic compounds in water using HPLC (Realini 1981a; Kung-Chao and Suatoni 1982) or GC techniques have been published (Coutts et al.

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1979; Fogelqvist et al. 1980; Renberg 1981b). The procedures for isolation include liquid-liquid extraction (Realini 1981a; Coutts 1979); concentration by anion-exchange resins (Chriswell 1975) or $C_{18}$ cartridges (Renberg 1981c). Many phenolic compounds are amenable to gas chromatographic analyses either as free phenols (Giger and Schaffner 1981d) or derivatized as acetates (Coutts 1979), pentafluorobenzylates (Kawahara 1968), heptafluorobutyrates (Lamparski and Nestrick 1978b) or pentafluorobenzoylates (Renberg 1981b). In this work, analyses have been carried out using liquid-liquid extraction and derivatization of phenols with pentafluorobenzoyl chloride according to the method described by Renberg (1981b). Gas chromatographic peaks have been identified by their retention time and their spectra by GC-MS. Also mass fragmentograms with significant peaks were obtained.

Solvent used -isooctane- (Fluka, Buchs, Switzerland) was HPLC quality. Potassium hydroxide and sodium bicarbonate were of analytical grade (Panreac, Spain). Derivatizing agent pentafluorobenzoylchloride (99%) was purchased to Fluka. the standards, phenol (99%) (C.Erba, Italy). 2 and 4 bromophenols, (95% and 99%), 2,4 and 2,6 dibromophenols (95% and 97%) and 2,4,6-tribromophenols (98%) were Fluka. These standards were used without further purification.

A Konik-2000 has chromatograph equipped with a $^{63}Ni$ electron capture detector (Tracor 560) was used. The column was 25 m x 0,25 mm SE-30 fused silica. Gas chromatographic conditions were as follows: $H_2$ carrier gas 0,6 atm. $N_2$ as make-up 67 ml/min. Injector and detector 250°C and 330°C respectively. Temperature program 65°C to 300°C at 8°C/min. A MS9 VG updated mass spectrometer connected to a Konik 2000 gas chromatograph and VG 11-250 data system was used. Chromatographic conditions as described above using He as carrier gas at 1 ml/min. The mass spectrometer operated in EI mode at 4 sec/scan time and 1000 of resolution.

Studies were performed using raw water from Llobregat river, in order to evaluate the formation of bromophenols varying a) $Cl_2$ dose/phenol relationship. b) bromide ion contents of raw water and c) analyses of real samples along the river course.

Phenol (6 mg/l) was added to a raw water containing bromide (1,6 mg/l not added) and chlorinated at different doses. Contact time was established to 24 hr. The $Cl_2$ dose/phenol ratio was 1:1, 2:1, 4:1, 7:1 and 10:1.

To raw water containing 1 mg/l of bromide, phenol (6 mg/l) was added and chlorinated at 12 mg/l. To the same raw water, KBr was added to ensure a bromide concentration of 3.5 mg/l. The same amount of phenol and $Cl_2$ dose were used. The contact time in both cases was 24 hr.

Real samples along the river course were analyzed. Neither phenol nor bromide were added. Samples were chlorinated at 12 mg/l, the common chlorine dose at Barcelona's water works plant.

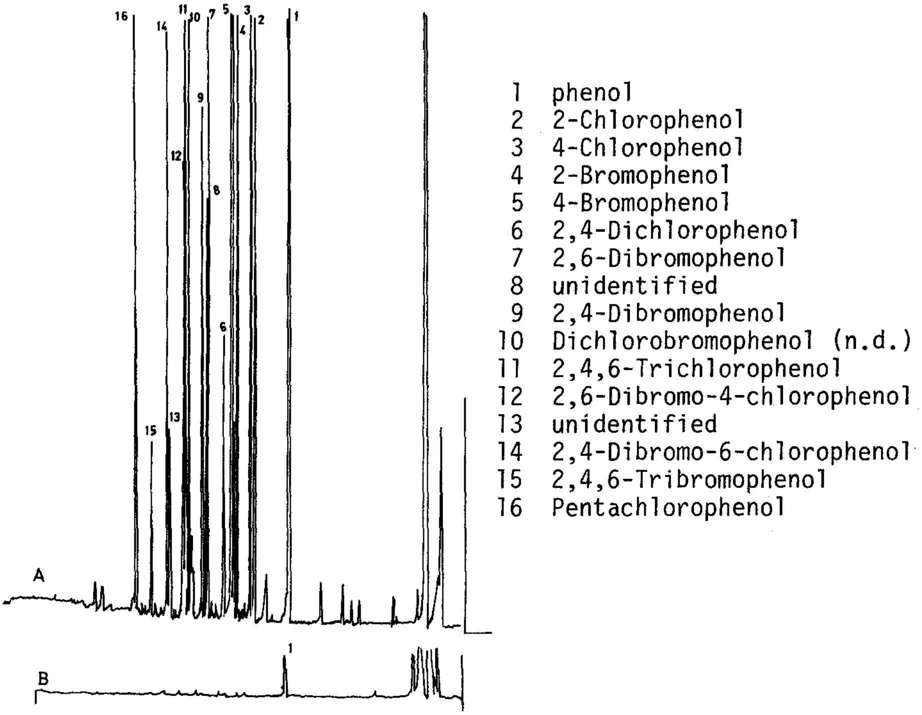

Figure 1. Influence of $Cl_2$ dose/phenol relationship. A) ratio 4:1 B) ratio 10:1. GC conditions described in the text.

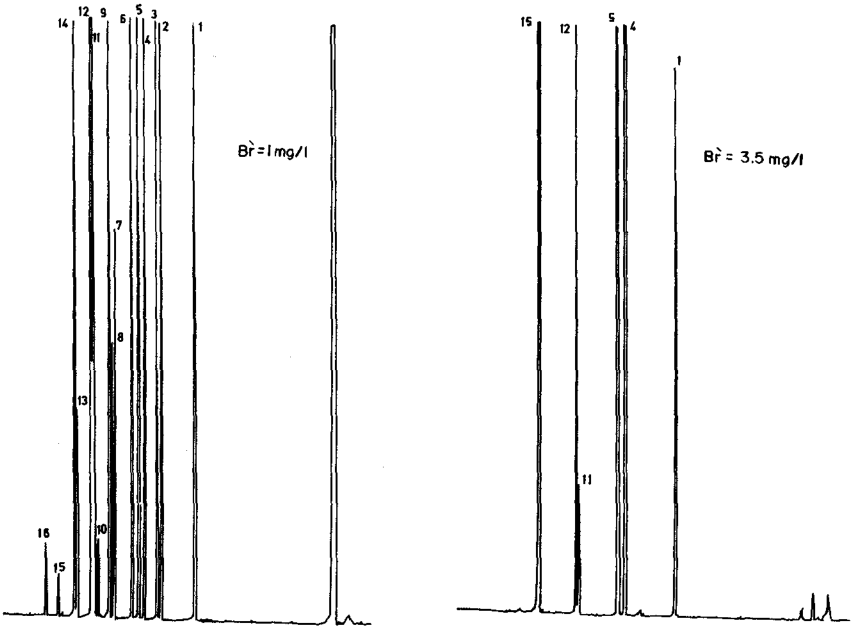

Figure 2. Variation of bromide contents in raw water (Phenol added 6 mg/l, $Cl_2$ dose 12 mg/l).

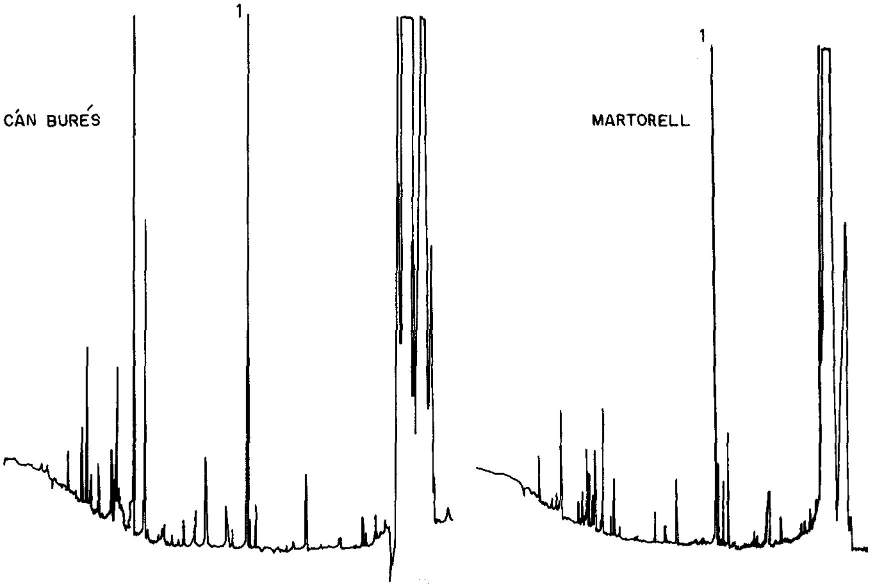

Figure 3. Analyses of two samples collected along the river course.

RESULTS AND DISCUSSION

Chlorine dose plays an important role in the formation of brominated phenols. If the chlorine dose/phenol ratio is less than 4:1, halogenated phenols (chlorinated, brominated and mixed) are formed. This is in agreement with Burtschell et al. (1959). The maximum amount of brominated phenols were obtained at this ratio. When the relationship is changed to values higher than 4:1 (7:1 or 10:1) ring cleavage of phenol was observed. The ratio at which phenol cleavage began appearing depended on the nature of raw water and chlorine consuming substances. Eisenhauer (1968b) and Masschelein (1969) identified fumaric and maleic acids (HOOC-CH=CH-COOH), tartaric acid (HOOC-CHOH-CHOH-COOH), oxalic acid (HOOC-COOH), glyoxylic acid (HOOC-CHO), glyolic acid (HOCH -COOH), cis-muconic acid (HOOC-CH=CH-CH=CH-COOH), formic acid (HCOOH), glyoxal (OHC-CHO) and CO as the main oxidation products of phenol. Figure 1 shows the influence of $Cl_2$ dose/phenol relationship in the production of bromophenols.

Figure 2 shows how the variation of bromide in raw water affects. An increase in bromide content tended to increase the bromination of the phenolic ring to 2,4,6-tribromophenol, with the formation of mono and dibrominated derivatives. A dramatic decrease of chlorinated phenols was observed.

Analyses of real samples showed that in normal conditions, brominated phenols are not present in chlorinated raw water from Llobregat river. This is due to several reasons, mainly to low phenol level and strong chlorination conditions used in the water

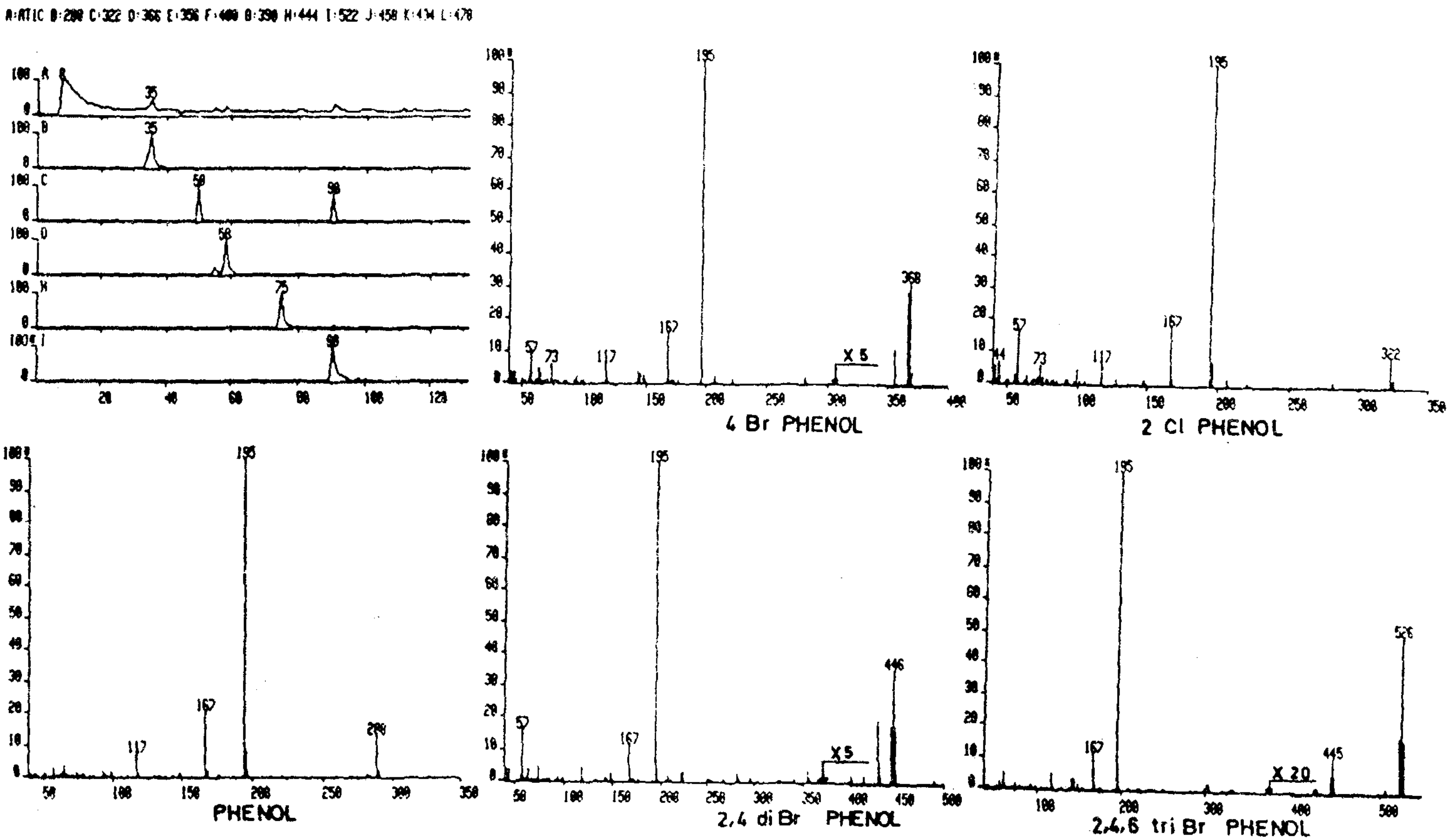

Fig. 4 Mass spectra of some pentafluorobenzoylhalogenated phenols found in the samples of figure 2.

The identification of brominated phenols were confirmed by GC-MS. The peak base of pentafluorobenzoylated phenols is 195 due to $(C_6F_5CO)^+$ with a very small molecular peak. Mass spectra of some phenols found in the samples of figure 2 are provided. The molecular peak was magnified in some cases to reveal the unknown compound (see Fig 4).

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