

Gas chromatographic–mass spectrometric characterization of volatile organic compounds in Barcelona tap water

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ABSTRACT

Barcelona's tap water is supplied by the Llobregat and Ter rivers, which have significant differences in raw water quality. Volatile organic compounds (VOCs) from Barcelona tap water were isolated by closed-loop stripping analysis (CLSA) and identified and determined by gas chromatography–mass spectrometry. The results showed that the Ter river gives the better quality tap water. VOCs, in particular solvents, phosphates, hydrocarbons, C₃ and C₄ alkylbenzenes and surfactant-related compounds such as C₁₀–C₁₃ alkylbenzenes and non-ionic compounds such as polyethoxylated nonylphenols and their brominated derivatives are present at the ppb level. The last two types of compounds have not previously been reported using the CLSA technique.

INTRODUCTION

The presence of disagreeable taste and odour compounds in drinking water is frequently the source of complaints from consumers. The nature of these substances is often unknown, their identification is difficult owing to low concentrations and above all the attribution of a specific taste or odour to one or more of the compounds present in water can be almost impossible. Biological sources of tastes and odours in raw water can be associated with actinomycetes [1,2], algal blooms of cyanobacteria [3–6] or other algae, bacteria and fungi [7,8]. Anthropogenic origins of tastes and odours from dispersed chronic pollution in urban areas, municipal and industrial wastewater effluents, waste disposals and miscellaneous sources are frequently described in the literature [9,10]. Moreover, these compounds can also be produced during the chemical treatment of water such as chlorination [11,12] or ozonization [12,13], or created in the distribution

systems by disinfectant residues, emissions from pipe and reservoir coatings [14–16] or from biological sources [7,8].

Isolation of these compounds has been carried out by different techniques (*e.g.*, liquid–liquid extraction, steam distillation, resin adsorption). Closed loop stripping analysis (CLSA) according to the procedure described by Grob [17] has proved particularly suitable for the analysis of volatile organic compounds (VOCs) at ppt (ng/l) levels in different types of water [18–20]. This is the detection odour threshold of some of the well known taste and odour compounds identified in water (geosmin, 2,3,6-trichloroanisole, 2-methylisoborneol, etc.).

This paper reports the identification of VOCs by gas chromatography–mass spectrometry (GC–MS) in raw and tap water from the Llobregat and Ter rivers. The analytical results together with those obtained by flavour profile analysis (FPA) by trained panel tasters can establish the products responsible for taste and odour compounds present in tap water and lead to appropriate preventive and corrective measures.

EXPERIMENTAL

Geographical situation

The Llobregat and Ter rivers each supply about half of the water to Barcelona city (N.E. Spain) and its surroundings (3.2 million inhabitants). The Llobregat river is extremely polluted, bearing effluents from various industries including textile, salt works, surfactants and domestic wastewaters. Industrial and municipal wastewaters are discharged with little purification. The water works plant is situated 7 km far from the mouth receiving all these discharges. The Ter river receives effluents from textile and tannery industries before reaching a three-reservoir system. From there, another water works plant receives the water through a pipeline of 60 km length and, after treatment, it is pumped to Barcelona through another pipeline (40 km).

Sampling

Raw water from the Llobregat river entering the water works plant and drinking water from the Llobregat and Ter rivers were collected within the city in 1-l amber-glass bottles and stored at 4°C before analysis (usually within 2 h). Samples were analysed once per week from September 1989 to March 1990.

Concentration of volatile organic compounds

Analyses were carried out in a commercial CLSA apparatus (Brechtbüler, Zürich, Switzerland) according the method developed by Grob [17]. We used 1.5- and 5.0-mg activated carbon filters for tap and raw water samples, respectively. Water samples (1 l) were spiked with 1-chloroalkanes (C₆, C₁₀, C₁₂, C₁₆ and C₁₈) to give a final concentration of 400 ng/l of each compound for tap water and 800 ng/l for raw water samples.

The samples were stripped for 2 h. Temperatures of 45 and 55–60°C were used for the sample water-bath and carbon filter, respectively. After stripping, the carbon filters were spiked with C₈ and C₁₄ 1-chloroalkanes at the same concentrations of the spiked water samples. The filters were then extracted with 20 µl of carbon disulphide (10 + 10 µl) for tap water and 40 µl of carbon disulphide (20 + 20 µl) for raw water samples.

GC and GC-MS parameters for CLSA extracts

A Carlo Erba (Milan, Italy) Model 5300 gas chromatograph equipped with a flame ionization detector was used. The column was a 50 m × 0.32 mm I.D. OV-1701 (Chrompack, Middelburg, The Netherlands) fused-silica capillary column of 0.2 µm film thickness fitted with a 1-m deactivated fused-silica capillary precolumn. Injections were 1 µl cold "on-column", using helium as carrier gas at a linear velocity of 30 cm/s. The temperature programme was from 28°C (held for 5 min) at 3°C/min to 280°C (held for 10 min). The detector was kept at 300°C. For GC-MS a VG TS-250 (VG Instruments, Manchester, U.K.) mass spectrometer was used. The chromatographic conditions were the same as described above. The operating conditions were as follows: ionization energy, 70 eV (electron impact mode); mass range, 40–400 u, scanned at 2 s per decade; and resolving power, 500. The ion source and interface temperatures were kept at 220 and 250°C, respectively.

RESULTS AND DISCUSSION

Evaluation of CLSA parameters

The influence of water temperature and stripping time is well documented [17, 21–25]. Recoveries of 1-chloroalkanes were determined over the water temperature range of 30–45°C and stripping times of 0.5–2 h, the carbon holder being 10°C above the temperature of the water-bath. A compromise between the analysis of large number of samples, stripping time and recovery of heavier compounds is required. We analysed real samples under different conditions and the nature of the compounds present in the CLSA extracts forced us to use a water temperature of 45°C and a stripping time of 2 h. Table I gives the recoveries obtained with 1-chloroalkanes and selected pollutants found in water with very different boiling points.

Analysis of raw and tap water

Figs. 1 and 2 show typical gas chromatograms of raw water from the Llobregat river entering the water works plant and of tap water. The main compounds identified (see Table II) were toluene, C₂–C₄ alkylbenzenes, which reflect petrogenic dumps, and C₁₀–C₁₃ alkylbenzenes (LABs), first identified in CLSA extracts, by Gómez-Belinchón and Albaiges [24], which are a complex mixture of isomers manufactured for the production of anionic surfactants of the linear

TABLE I

MEAN RECOVERIES OF 1-CHLOROALKANES AND SELECTED POLLUTANTS AFTER CLOSED-LOOP STRIPPING OF 1 l OF WATER

Results based on ten determinations for 1-chloroalkanes and seven for pollutants; *m*- and *p*-xylene were not separated.

| Compound | Recovery (%) | |
|---------------------------------------|-----------------|--------|
| | Mean \pm S.D. | Range |
| 1-Chlorohexane | 93 \pm 6 | 81-101 |
| 1-Chlorodecane | 99 \pm 3 | 97-105 |
| 1-Chlorododecane | 88 \pm 2 | 84-91 |
| 1-Chlorohexadecane | 82 \pm 4 | 74-87 |
| 1-Chlorooctadecane | 71 \pm 7 | 62-78 |
| Toluene | 54 \pm 9 | 51-66 |
| Ethylbenzene | 84 \pm 8 | 73-94 |
| <i>m</i> - + <i>p</i> -Xylene | 97 \pm 11 | 82-101 |
| Nonylphenols ($n = 0$) ^a | 78 \pm 10 | 61-97 |
| Methyl stearate | 64 \pm 5 | 60-70 |

^a n = Number of ethoxy units (all tables).

alkylbenzene sulphonate (LAS) type. These compounds have been considered by Eganhouse *et al.* [26] as molecular tracers of domestic wastes. A group of unprecedented anthropogenic pollutants were identified in CLSA extracts, namely polyethoxylated nonylphenol non-ionic surfactants. These compounds were identified with a degree of polyethoxylation $n = 0-3$ in raw water and their brominated derivatives ($n = 0-3$) in tap water. The presence of halogenated derivatives of non-ionic surfactants in tap water derives in this instance from water treatment and large amounts of bromide ions coming from salt-mine discharges in the upper course of the river [11,27].

Other commonly found anthropogenic pollutants are phthalates and phosphates (triisobutyl and tri-*n*-butyl), chlorinated solvents (tri- and tetrachloroethylene, trichlorobenzenes), alkanes and some miscellaneous compounds. Terpenes (menthol, borneol, camphor, limonene, α -pinene, etc.) are usually found at low concentrations relative to the most common compounds. They probably come from discharges from a flavour industry plant located on the banks of the river or alternatively have a natural origin. VOCs in raw and tap water from the Llobregat river are at the ppb ($\mu\text{g/l}$) level. Table III shows the concentrations of the most abundant pollutants in raw and tap water from the Llobregat river and in tap water from the Ter river.

The change in quality of raw water entering the water works plant on the Llobregat river is clearly influenced by spills of extremely diverse origin and is

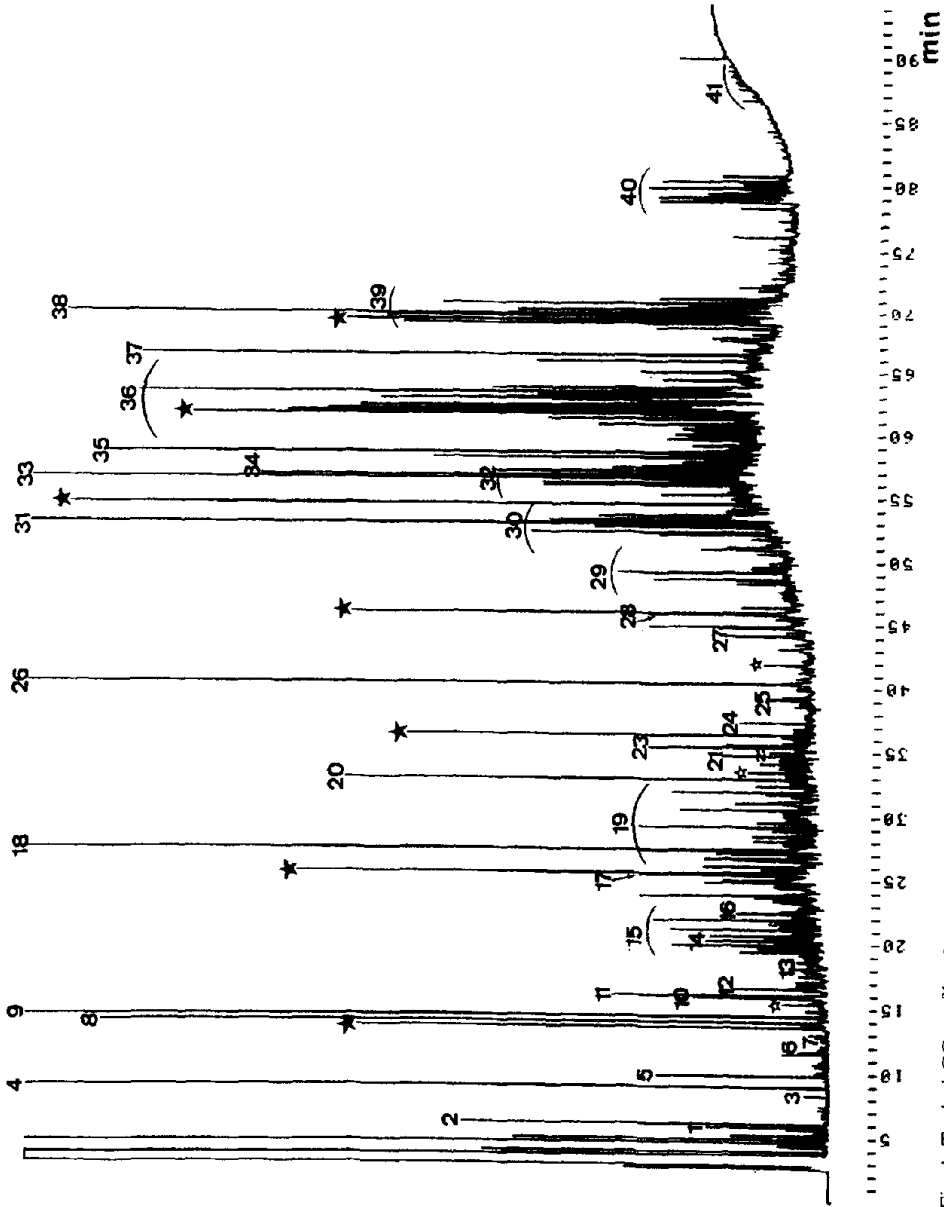


Fig. 1. Typical GC profile of raw water from the Llobregat river. ★ = Internal standards (1-chloroalkanes); ☆ = hydrocarbons.

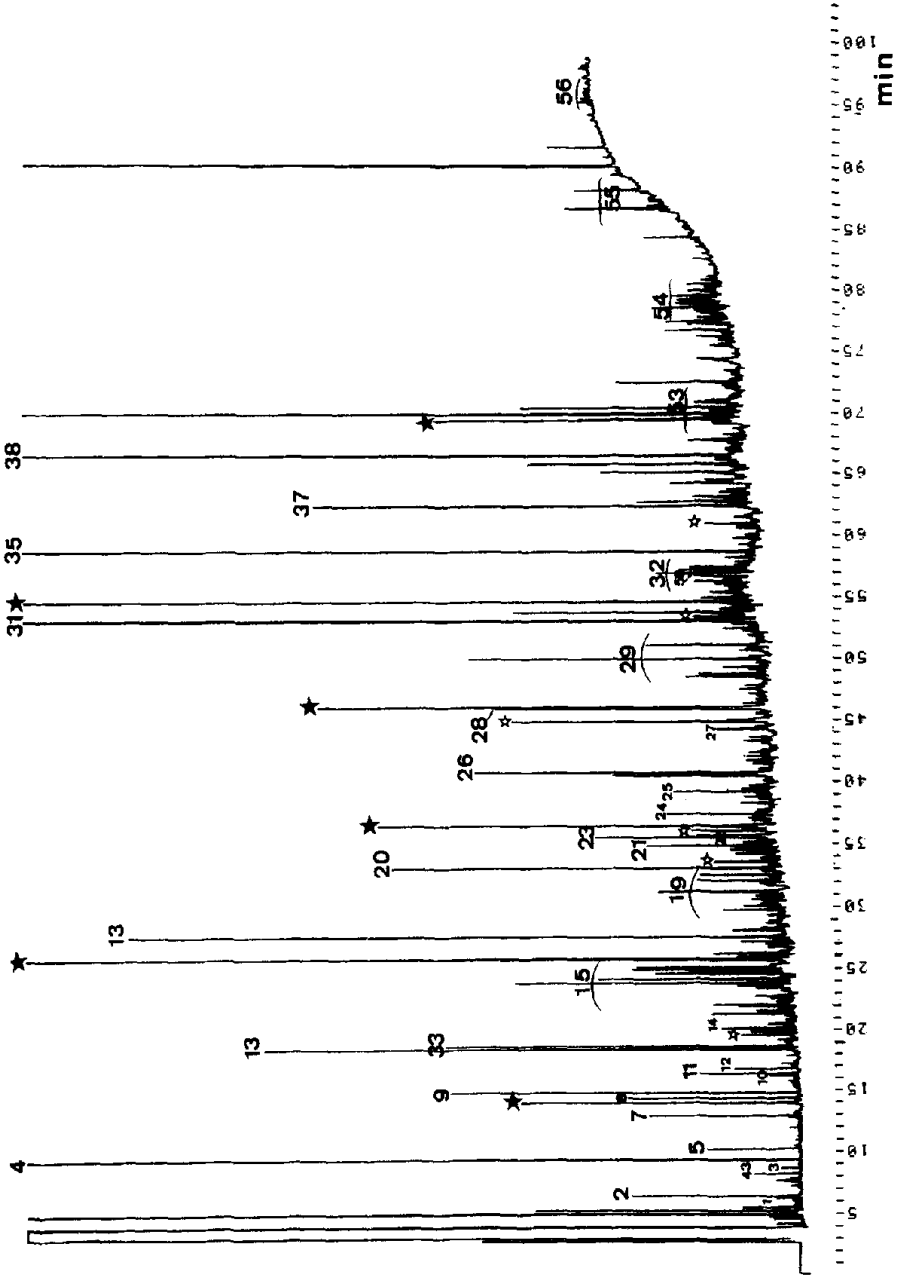


Fig. 2. GC profile of tap water from the Llobregat river.

TABLE II

VOLATILE ORGANIC COMPOUNDS IDENTIFIED IN RAW AND TAP WATER FROM LLOBREGAT AND TER RIVERS

Numbers refer to peaks on figures.

| No. | Compound ^a | No. | Compound ^a |
|-----|--------------------------------|-----|--|
| 1 | Heptane | 31 | Triisobutyl phosphate |
| 2 | Benzene | 32 | C ₁₂ -Alkylbenzenes |
| 3 | Trichloroethylene | 33 | 1,1'-Methylene(oxibismethylene)-bisbenzene |
| 4 | Toluene | | n.i. |
| 5 | Perchloroethylene | 34 | n.i. |
| 6 | 1,1,2-Trichloroethane | 35 | Tri- <i>n</i> -butyl phosphate |
| 7 | Dibromochloromethane | 36 | Nonylphenols (<i>n</i> = 0) |
| 8 | Ethylbenzene | 37 | Diiso butyl phthalate |
| 9 | <i>m</i> + <i>p</i> -Xylene | 38 | Di- <i>n</i> -butyl phthalate |
| 10 | α -Pinene | 39 | Nonylphenols (<i>n</i> = 1) |
| 11 | <i>o</i> -Xylene | 40 | Nonylphenols (<i>n</i> = 2) |
| 12 | Styrene | 41 | Nonylphenols (<i>n</i> = 3) |
| 13 | Bromoform | 42 | n.i. |
| 14 | 1-Chloro- <i>m</i> -toluene | 43 | Dichlorobromomethane |
| 15 | C ₃ -Alkylbenzenes | 44 | n.i. |
| 16 | 2-Chloropyridine | 45 | Limonene |
| 17 | 2-Ethylhexanol | 46 | Dihydro(1-hydroxy)indene |
| 18 | 1,4-Dichlorobenzene | 47 | Unidentified siloxane |
| 19 | C ₄ -Alkylbenzenes | 48 | Unidentified terpene |
| 20 | 1,3,5-Trichlorobenzene | 49 | Unidentified terpene |
| 21 | Menthol | 50 | Camphor |
| 22 | Borneol | 51 | Unidentified terpene |
| 23 | 1,2,4-Trichlorobenzene | 52 | Unidentified terpene |
| 24 | Dimethylcyclohexanol | 53 | Brominated nonylphenols (<i>n</i> = 0) |
| 25 | Borneol acetate | 54 | Brominated nonylphenols (<i>n</i> = 1) |
| 26 | Tetradecane | 55 | Brominated nonylphenols (<i>n</i> = 2) |
| 27 | Biphenyl | 56 | Brominated nonylphenols (<i>n</i> = 3) |
| 28 | n.i. | 57 | 1-Bromohexane |
| 29 | C ₁₀ -Alkylbenzenes | | |
| 30 | C ₁₁ -Alkylbenzenes | | |

^a n.i. = Not identified.

reflected in the wide range of concentrations found. Fig. 3 shows as an example the chromatogram of a spill of gasoil in the Llobregat river.

On the other hand, tap water from the Ter river (Fig. 4) is less influenced by spills because the three-reservoir system acts as a barrier for the transport of pollutants. Thus, tap water from the Ter river showed similar profiles throughout the study.

The main compounds identified are C₃-C₄ alkylbenzenes, solvents (toluene and trichlorobenzene) and non-ionic surfactants such as nonylphenols. The re-

TABLE III
 CONCENTRATIONS ($\mu\text{g/l}$) OF THE MOST ABUNDANT VOCs IN RAW AND TAP WATER OF BARCELONA
 Sampling period: September 1989–March 1990.

| Compound | Llobregat (raw) | | | Llobregat (tap) | | | Ter (tap) | | |
|--|-----------------|-----------|--------|-----------------|--------------------|--------|-----------|-----------|--------|
| | Mean | Range | Median | Mean | Range | Median | Mean | Range | Median |
| Benzene | 0.76 | 0.05–1.80 | 0.64 | nd ^c | nd | nd | nd | nd | nd |
| Toluene | 18.8 | 1.90–36.7 | 16.2 | 2.4 | 1.0–5.60 | 2.1 | 1.10 | 0.10–2.80 | 0.90 |
| Ethylbenzene | 0.86 | 0.49–12.0 | 0.69 | 0.2 | nd–0.36 | 0.2 | 0.03 | nd–0.05 | 0.04 |
| Perchloroethylene | 0.28 | 0.42–0.81 | 0.24 | 0.2 | nd–0.62 | 0.14 | 0.27 | nd–0.66 | 0.09 |
| Xylenes | 1.42 | 0.65–2.87 | 1.15 | 0.29 | 0.16–0.53 | 0.27 | 0.19 | 0.14–0.24 | 0.19 |
| 1,3,5-Trichlorobenzene | 1.70 | 0.33–4.50 | 1.10 | 0.67 | 0.02–1.40 | 0.56 | 0.45 | 0.20–0.80 | 0.60 |
| Σ Phosphates ^a | 7.80 | 2.20–15.0 | 6.70 | 6.90 | 3.10–18.0 | 5.80 | nd | nd | nd |
| Σ Phthalates ^b | 1.62 | 0.28–2.30 | 1.60 | 1.80 | nd–4.30 | 1.40 | nd | nd | nd |
| Σ Hydrocarbons ^c | 9.50 | 1.20–31.6 | 6.50 | 0.90 | 0.50–1.30 | 0.80 | 0.71 | 0.50–0.87 | 0.70 |
| C ₃ –C ₄ -Alkylbenzenes | 3.90 | 1.20–6.40 | 4.10 | 0.74 | 0.24–1.70 | 0.70 | 6.90 | 3.0–11.60 | 6.60 |
| Surfactant-related compounds: | | | | | | | | | |
| Σ C ₁₀ –C ₁₃ -Alkylbenzenes | 61.4 | nd–340 | 11.0 | | nd–tr ^e | | nd | nd | nd |
| Nonylphenols ($n = 0$) | 5.85 | nd–11.7 | 5.40 | tr | tr | | 0.04 | nd–0.14 | 0.10 |
| Nonylphenols ($n = 1$) | 1.83 | nd–4.80 | 1.50 | tr | tr | | 0.34 | nd–1.10 | 0.10 |
| Nonylphenols ($n = 2$) | 1.23 | nd–1.90 | 1.23 | tr | tr | | 0.12 | nd–0.25 | 0.07 |
| Nonylphenols ($n = 3$) | tr | tr | | tr | tr | | nd | nd | nd |
| Bromononylphenols ($n = 0$) | nd | nd | nd | tr | nd–0.24 | | nd | nd | nd |
| Bromononylphenols ($n = 1$) | nd | nd | nd | tr | nd–0.12 | | nd | nd | nd |
| Bromononylphenols ($n = 2$) | nd | nd | nd | tr | nd–0.05 | | nd | nd | nd |

^a Indicates triisobutyl + tri-*n*-butyl phosphates.

^b Indicates dimethyl + diethyl + diisobutyl + di-*n*-butyl phthalates.

^c Indicates C₁₀–C₂₀ hydrocarbons.

^d nd = Not detected.

^e tr = Trace ($\leq 0.05 \mu\text{g/l}$).

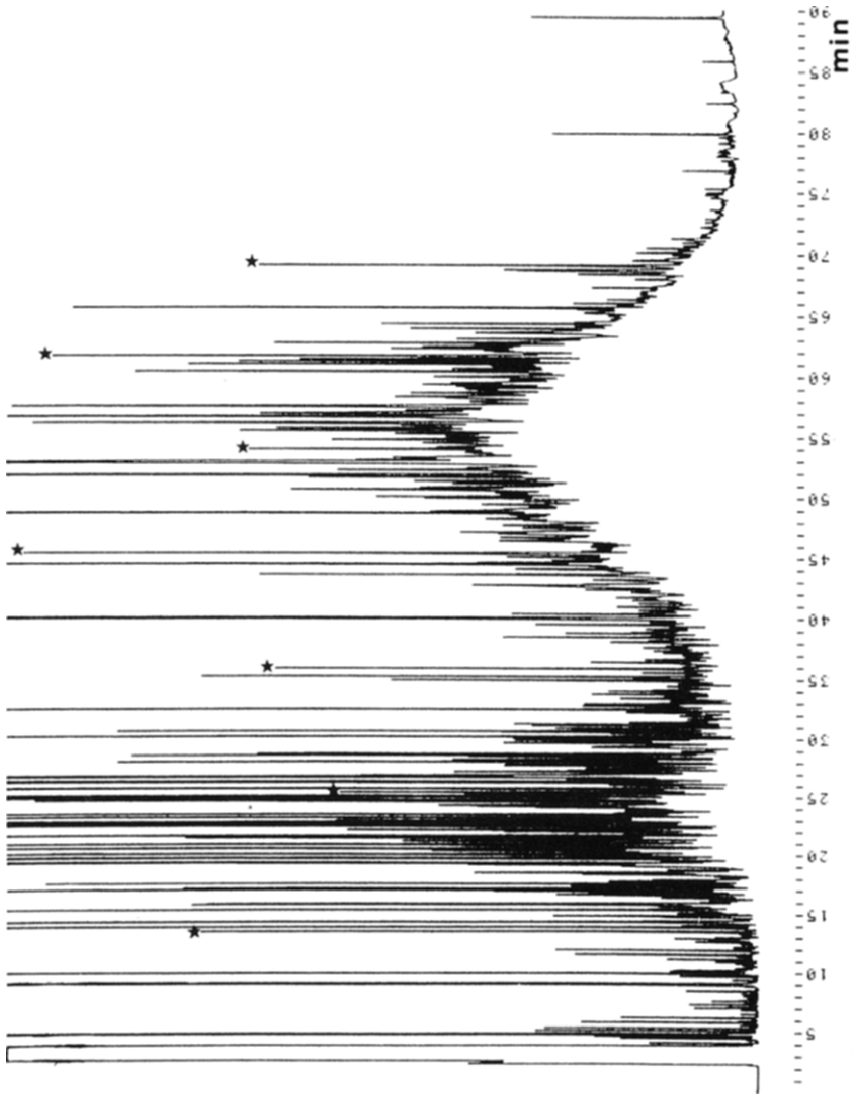


Fig. 3. A spill in the Llobregat river: GC profile of raw water entering the water works plant.

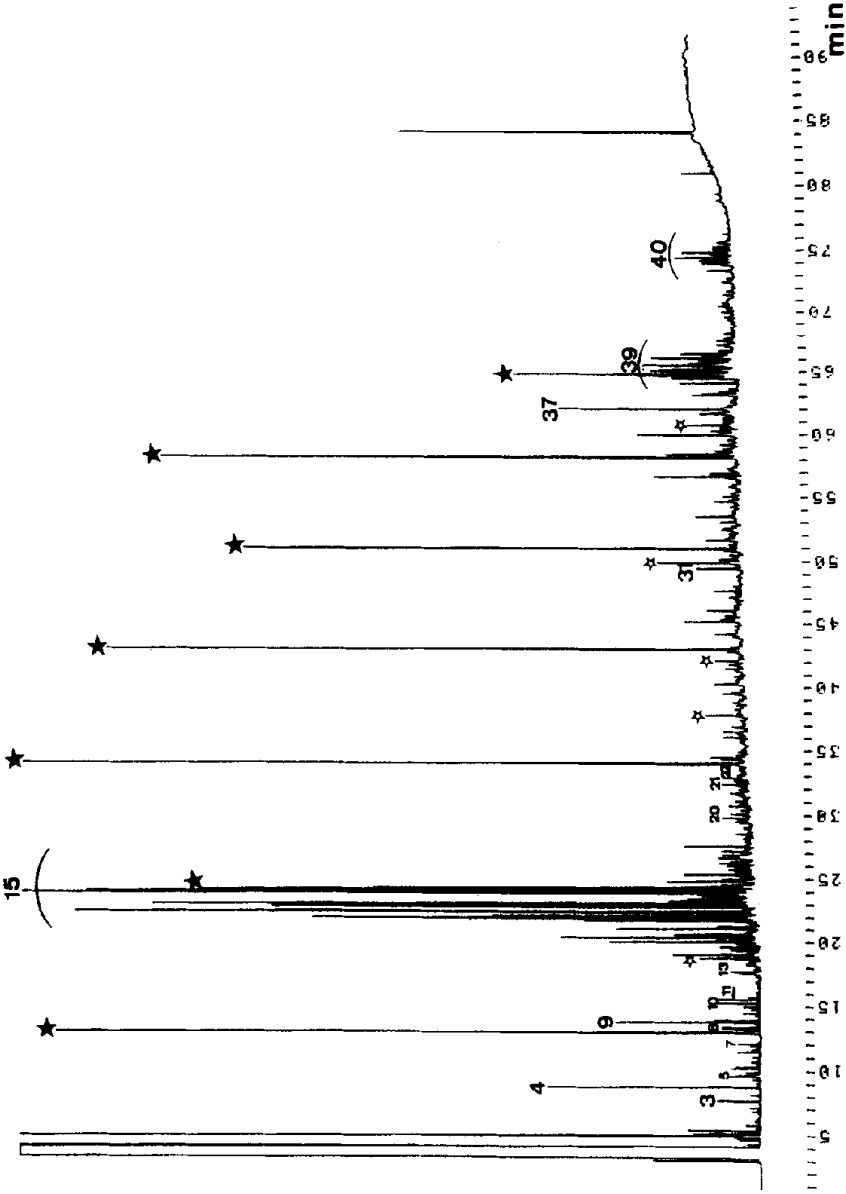


Fig. 4. Typical GC profile of tap water from the Ter river.

sults obtained are in accord with dumping from the tannery and textile industries, which are the main industrial activity on the banks of the Ter tributaries before reaching the reservoirs. The comparison of the chromatographic profiles of tap water from the Llobregat and Ter rivers shows the difference in drinking water quality from the two sources.

CONCLUSIONS

The CLSA technique is suitable for the analysis of VOCs in raw and tap water. The quality of tap water supplied depends on its origin. Thus raw water from the Llobregat river is influenced by its seasonal regime and dumps and spills of diverse origin. The compounds identified in this raw and tap water are solvents, phthalates, phosphates, hydrocarbons and C₃-C₄ alkylbenzenes. Other pollutants such as LABs and nonylphenols are related to textile and surfactant industries located on the banks of the river. The presence of brominated compounds (bromomethanes and bromononylphenols) in tap water is probably due to large amounts of bromide coming from salt-mine discharges. The median values of VOCs are at the ppb level, with significant variations in concentration ranges due to dumping. For tap water the median values are at the low ppb level.

On the other hand, tap water from the Ter river shows less variations in concentration ranges than that from the Llobregat river. Only the C₃ and C₄ alkylbenzene median values are at the ppb level. VOCs from the Ter river are related to surfactants and probably to the tannery industry.

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