

Gas chromatographic screening of organic compounds in urban aerosols

Selectivity effects in semi-polar columns

Merce Aceves

Environmental Control Service, Entitat Metropolitana de Barcelona, Carrer 62, 420 Edifici A Zona Franca, 08004 Barcelona, Catalonia (Spain)

Joan O. Grimalt*

Department of Environmental Chemistry (CID-CSIC), Jordi Girona 18, 08034 Barcelona, Catalonia (Spain)

ABSTRACT

A gas chromatographic–mass spectrometric study of aerosols collected in Barcelona allowed the identification of the major sources of airborne organic matter in an urban environment. The extracts were separated by column chromatography into three fractions encompassing aliphatic hydrocarbons, aromatic hydrocarbons plus semi-polar compounds and polar products. The overall procedure allowed the identification of 108 molecular species that were grouped according to their precursors. The study also allowed the characterization of significant changes in the elution order of linear and polycyclic molecules of similar retention using different semi-polar capillary columns such as DB-5, SE-52, CP-Sil 8 CB, SE-54 and HP-5.

INTRODUCTION

The emission of pollutants to the atmosphere often involves the direct, uncontrolled exposure of large populations to toxic substances, representing the environmental process of highest potential hazard to human health. This is especially relevant in urban areas where the proximity between humans and pollutant sources is closest. In this respect, the aerosol composition of *n*-alkanes and polycyclic aromatic hydrocarbons (PAHs) has sometimes been described [1–3], but the more polar products should also be considered because they may have significant health implications [4].

Since 1985 we have regularly monitored the composition of solvent extractable compounds in the aerosol of Barcelona (Spain) using methods based on gas chromatography (GC) and GC coupled with

mass spectrometry (GC–MS). This regular sampling and analysis has afforded a detailed knowledge of the major lipid atmospheric particulates of the city. In this study, standard GC traces corresponding to the central area of Barcelona, the most densely populated area, are reported and their composition is interpreted in terms of predominant input sources. These GC distributions provide reference patterns for comparison with those obtained in other cities.

However, the use of different capillary columns involves significant changes in the relative retentions of several major compounds. These selectivity changes are produced even among semi-polar stationary phase columns (5% phenyl–95% methyl type) which are reported to be equivalent in commercial catalogues. The study included, therefore, a comparison of five semi-polar columns (Table I)

TABLE I
SEMI-POLAR CAPILLARY COLUMNS COMPARED IN THIS STUDY

Column	Stationary phase ^a	Dimensions (m × mm I.D.)	Film thickness (μm)	Manufacturer
DB-5	5% Phenyl- 95% methyl	30 × 0.25	0.2	J & W Scientific, Folsom, CA, USA
SE-52 (cross-bond)	5% Diphenyl- 95% dimethyl	25 × 0.32	0.1–0.15	Carlo Erba, Milan, Italy
CP-Sil 8 CB	5% Phenyl- 95% dimethyl	25 × 0.25	0.13	Chrompack, Middelburg, Netherlands
SE-54 (cross-bond)	1% Vinyl- 5% diphenyl- 94% dimethyl	25 × 0.32	0.1–0.15	Carlo Erba
HP-5 (Ultra-2)	5% Diphenyl- 95% dimethyl	25 × 0.2	0.11	Hewlett-Packard, Palo Alto, CA, USA

^a As defined by the manufacturer.

with regard to the differences in their relative retention of dominant aerosol components.

EXPERIMENTAL

Materials

Pestipur-grade dichloromethane was purchased from Mallinckrodt (Paris, KY, USA). Chromatography quality *n*-hexane, methanol, isooctane, neutral silica gel (Kieselgel 40, 70–230 mesh) and alumina (aluminium oxide 90 active, 70–230 mesh) were from Merck (Darmstadt, Germany). The Soxhlet cartridges were from Schleicher and Schüll (Dassel, Germany). The glass microfibre filters were purchased from Whatman (Maidstone, UK).

The silica gel, the alumina and the Soxhlet cartridges were extracted with dichloromethane–methanol (2:1, v/v) in a Soxhlet apparatus for 24 h. After solvent evaporation, the silica and the alumina were heated for 12 h at 120 and 350°C, respectively. A total of 5% (w/w) of Milli-Q-grade water was then added to the chromatographic adsorbents for deactivation. The glass-fibre filters were kiln-fired for 12 h at 400°C and weighed prior to sampling.

The purity of the solvents was checked by concentrating under vacuum 100 ml of solvent to 10 μl for GC analysis. Blank requirements were as follows: splitless injection of 2 μl should result in chro-

matograms with no unresolved GC envelope and only a few peaks, representing up to 1 ng in terms of their flame ionization detector response. This threshold, under the above dilution factor, is equivalent to less than 0.02 ng/m³ when referred to 100 ml of solvent used for the extraction of one third of a filter that corresponds to 1000 m³ of air.

Sampling, extraction and fractionation

The air samples (1200 m³ and 50 m³/h) were taken with a High-Vol pumping system (CAV-P; MCV, Collbato, Spain) equipped with 20.3 × 25.4 cm glass microfibre filters (Whatman). After sampling the filters were frozen at –20°C until analysis in the laboratory. One third of each filter was Soxhlet extracted with 100 ml of dichloromethane for 24 h. The extract was vacuum and nitrogen evaporated until almost dryness and diluted to 0.5 ml with *n*-hexane, then fractionated by column chromatography according to previously established methods [5]. A column filled with 1 g each of 5% water-deactivated alumina (top) and silica (bottom) was used. The aliphatic hydrocarbons were obtained in the first fraction (4 ml of *n*-hexane), the aromatic hydrocarbons were collected in the second fraction (4 ml of 20% dichloromethane in *n*-hexane) and the polar compounds eluted in the third fraction (4 ml of 20% methanol in dichloromethane). These frac-

tions were vacuum and nitrogen concentrated almost to dryness and the residue was dissolved in isoctane.

Instrumental analysis

The samples were analysed by GC and GC-MS. These analyses were performed with a Carlo-Erba Model 5300 gas chromatograph equipped with a flame-ionization detector and with a Hewlett-Packard Model 5970 mass spectrometer provided with an HP-5994A data acquisition system. The GC analyses were performed with the capillary columns described in Table I. The oven temperature was programmed from 60 to 300°C at 6°C/min, and the injector and detector temperatures were set at 280 and 330°C, respectively. Hydrogen was used as carrier gas at 50 cm/s. The oven temperature programme for the GC-MS analyses was from 60 to 280°C at 6°C/min, the injector and transfer line temperatures were 280 and 300°C, respectively, and helium was used as the carrier gas at 50 cm/s. Data were acquired in the electron impact mode (70 eV), scanning from 40 to 600 mass units at 1 s per decade. In both instances the injector was in the splitless mode (1 µl; hot needle technique), the split valve being closed for 35 s.

Identification and quantification

Compound identification was based on the GC-MS data and on co-injection with authentic standards. Quantification was performed from the GC profiles using the external standard method. Samples and standards were repeatedly injected until less than 5% dispersion in the area measurements was observed. An external standard containing *n*-eicosane, *n*-tricosane, *n*-octacosane, *n*-dotriacontane and *n*-hexatriacontane was used for the alkane fraction and the aromatic hydrocarbons were determined with a standard containing phenanthrene, fluoranthene, pyrene, benzo[ghi]fluoranthene, benz[a]anthracene, chrysene, benzo[e]pyrene, dibenz[a,h]anthracene, benzo[ghi]perylene and coronene. These two standards were also used as test mixtures for the assessment of undesired column adsorption effects or sample discrimination in the injector. The polar compounds were determined with a standard containing coprostanol and *n*-octacosan-1-ol.

RESULTS AND DISCUSSION

The sampling site was located in Barcelona city centre, in a square (Plaça Molina) with heavy traffic. The High-Vol pump was situated 3 m above ground level and 100 m away from any vertical obstacle. The sampling periods were performed under conditions of atmospheric stability, in the absence of precipitation and with a wind speed of less than 4 m/s at 25 m above ground level.

Hydrocarbons and semi-polar lipids

The GC profile of the first column chromatographic fractions (Fig. 1 and Table II) is dominated

TABLE II
ALIPHATIC HYDROCARBONS IDENTIFIED IN THE PARTICULATE FRACTIONS OF THE AEROSOL SAMPLES COLLECTED IN BARCELONA CITY

No.	Compound	Diagnostic ions (<i>m/z</i>)	Average concentration (ng/m ³)
1	<i>n</i> -Pentadecane	212	
2	<i>n</i> -Hexadecane	226	
3	<i>n</i> -Heptadecane	240	1.3
4	Pristane	268	
5	<i>n</i> -Octadecane	254	2.0
6	Phytane	282	
7	<i>n</i> -Nonadecane	268	3.3
8	<i>n</i> -Eicosane	282	5.7
9	<i>n</i> -Heneicosane	296	8.9
10	<i>n</i> -Docosane	310	16
11	<i>n</i> -Tricosane	324	16
12	<i>n</i> -Tetracosane	338	16
13	<i>n</i> -Pentacosane	352	16
14	<i>n</i> -Hexacosane	366	16
15	<i>n</i> -Heptacosane	380	15
16	<i>n</i> -Octacosane	394	4.5
17	<i>n</i> -Nonacosane	408	10
18	<i>n</i> -Triacontane	422	3.5
19	17α(H),21β(H)-30-Norhopane	191	
20	<i>n</i> -Hentriacontene	434	
21	<i>n</i> -Hentriacontane	436	12
22	17α(H),21β(H)-Hopane	191	
23	<i>n</i> -Dotriacontene	448	
24	<i>n</i> -Dotriacontane	450	3.2
25	<i>n</i> -Tritriacontane	464	4.2
26	<i>n</i> -Tetracontane	478	0.97
27	<i>n</i> -Pentatriacontane	492	0.98
Total <i>n</i> -alkanes			160
Unresolved complex mixture			2400

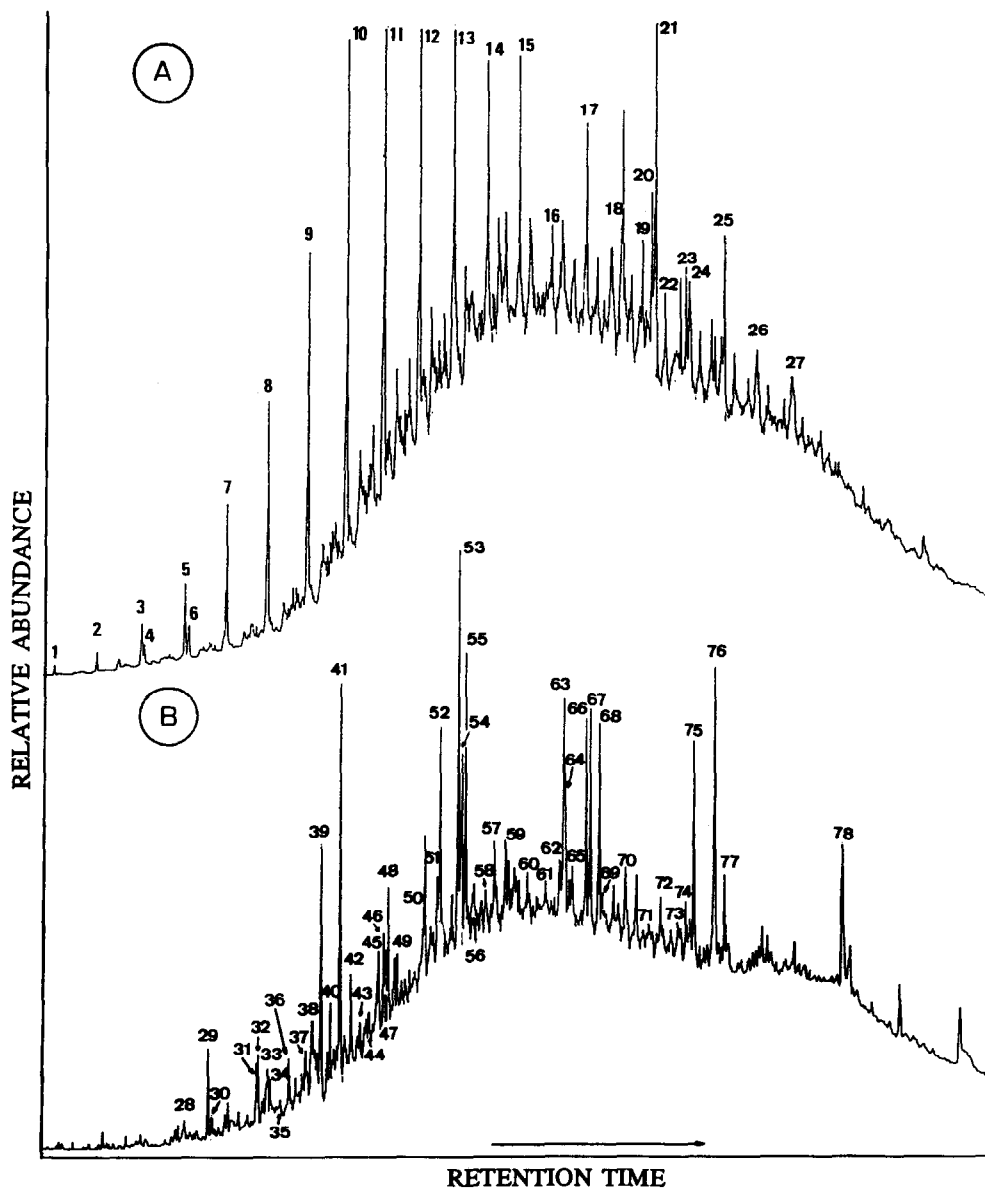


Fig. 1. GC profiles of the aliphatic and aromatic hydrocarbons present in the aerosols collected in Barcelona during winter. Column: CP-Sil 8 CB (See Table I). The numbered peaks refer to Tables II and III.

by *n*-alkane distributions ranging between C_{16} and C_{35} without odd-even carbon number predominance. Other characteristic resolved peaks in this GC trace encompass regular isoprenoids, pristane (4) and phytane (6), and olefins, *n*-hentriacontene (20) and *n*-dotriacontene (23). These compounds over-

lay an unresolved complex mixture (UCM) of hydrocarbons eluting over all the temperature range of the chromatogram. The *n*-alkanes without odd-even carbon number predominance occurring together with pristane and phytane, and an unresolved mixture of aliphatic hydrocarbons are char-

acteristic of petroleum residues and vehicular exhausts [6,7]. Similarly, the olefins are likely pyrolysis products in the vehicular combustion processes. Thus, pyrolysis naphtha produced by thermal cracking of naphtha contains large amounts of olefins and aromatics [8]. The presence of 17 α (H), 21 β (H)-hopanes is consistent with the petroleum-related origin of these hydrocarbon mixtures [6,9].

The GC traces of the aromatic hydrocarbon fractions (Fig. 1 and Table III) are dominated by parent PAHs, namely fluoranthene (39), pyrene (41), benzo[ghi]fluoranthene (52), 4(H)-cyclopenta[cd]pyrene (53), benz[a]anthracene (54), chrysene/triphenylene (55), benzo[fluoranthene]s (63–65), benzopyrenes (66,67), indeno[1,2,3-cd]pyrene (74), benzo[ghi]perylene (76) and coronene (78). The abundance of catacondensed structures and the predominance of parent hydrocarbons over alkylated homologues indicate that these distributions of resolved compounds are of pyrolytic origin [10,11].

Further assessment of processes determining the

composition of these hydrocarbons can be obtained from the consideration of some concentration ratios. Thus, the fluoranthene/(fluoranthene + pyrene) ratio, 0.40, approaches that reported for exhausts of gasoline-fuelled vehicles [12]. The indeno[1,2,3-cd]pyrene/(indeno[1,2,3-cd]pyrene + benzo[ghi]perylene) ratio, 0.45, corresponds to coal combustion emissions [13,14]. The benzo[e]pyrene/(benzo[e]pyrene + benzo[a]pyrene) ratio, 0.47, also reflects pyrolytic emissions related to coal use.

An important UCM is found in addition to these resolved compounds. This mixture is related to petrogenic sources such as that observed in the aliphatic hydrocarbon chromatograms. In fact, the "baseline humps" from the GC traces in Figs. 1 and 3 merely reflect the fractionation of the same UCM by the column chromatographic method selected for this study. These petrogenic inputs are also represented by some minor resolved compounds such as the alkylated phenanthrenes and chrysenes/triphenylenes.

The occurrence of some aromatic hydrocarbons such as retene (47), a compound characteristic of coniferous vegetation [15], is related to higher plant inputs. Squalene (68) is another biogenic product that is usually representative of microorganism contributions [16].

Squalene, often a major peak in the chromatograms of the semi-polar fraction, is a compound exhibiting a high column dependence of its retention indices. This is illustrated in Table IV, where the relative retention indices of this unsaturated hydrocarbon and those of benzo[a]pyrene and benzo[e]pyrene are shown. These indices were calculated according to the PAH series of naphthalene, phenanthrene, chrysene and picene for better reproducibility [17]. Squalene elutes before benzo[e]pyrene in the DB-5 column. In the SE-52 column it elutes between the two benzopyrenes and may co-elute with benzo[a]pyrene in columns of this type with lower efficiency. Finally, squalene elutes after benzo[a]pyrene in the CP-Sil 8 CB, SE-54 and HP-5 columns. GC traces corresponding to the elution time windows of the benzofluoranthene, benzopyrene and squalene peaks are illustrated in Fig. 2.

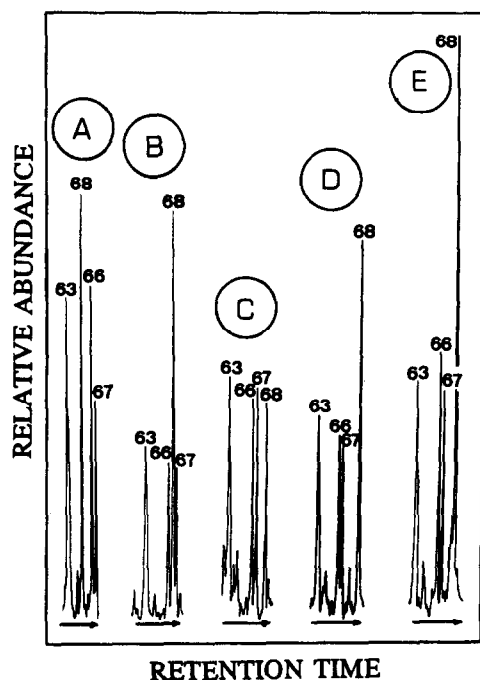


Fig. 2. GC profiles showing the elution order of benzofluoranthenes, squalene and benzopyrenes in the semi-polar capillary columns described in Table I: (A) DB-5; (B) SE-52; (C) CP-Sil 8 CB; (D) SE-54; (E) HP-5. Peak numbers refer to Table III.

Polar compounds

The major compounds in the GC profiles of the polar fractions are phthalates, fatty acids and alco-

TABLE III

AROMATIC HYDROCARBONS AND SEMI-POLAR COMPOUNDS IDENTIFIED IN THE PARTICULATE FRACTIONS OF THE AEROSOL SAMPLES COLLECTED IN BARCELONA

No.	Compound	Diagnostic ions (<i>m/z</i>)	Average concentration (ng/m ³)
28	Dibenzothiophene	184	
29	Phenanthrene	178	2.6
30	Anthracene	178	0.96
31	3-Methylphenanthrene	192	
32	2-Methylphenanthrene	192	
33	4/9-Methylphenanthrene	192	
34	1-Methylphenanthrene	192	
35	Methyl hexadecanoate	270	
36	4H-Methylcyclopenta[<i>def</i>]phenanthrene	204	
37	Dimethyl-178	206	
38	Dimethyl-178	206	
39	Fluoranthene	202	10
40	Acephenanthrylene	202	
41	Pyrene	202	15
42	Methyl octadecanoate	298	
43	Trimethyl-178	220	
44	Trimethyl-178	220	
45	8/7-Methylpyrene	216	
46	Benzo[<i>a</i>]fluorene	216	
47	Retene	234	
48	Benzo[<i>b</i>]fluorene	216	
49	1-Methylpyrene	216	
50	Dimethyl-202	230	
51	Benzo[<i>b</i>]naphtho[2,1- <i>d</i>]thiophene	234	
52	Benzo[<i>ghi</i>]fluoranthene	226	12
53	4(H)-Cyclopenta[<i>cd</i>]pyrene	226	23
54	Benz[<i>a</i>]anthracene	228	8.8
55	Chrysene/triphenylene	228	16
56	Methyl-234	248	
57	Methyl-234	248	
58	<i>n</i> -Octyl hexadecanoate	112	
59	Methylchrysene	242	
60	Methyl-226	240	
61	Binaphthyl	254	
62	<i>n</i> -Octyl octadecanoate	112	
63	Benzo[<i>b,j</i>]fluoranthene	252	27
64	Benzo[<i>k</i>]fluoranthene	252	
65	Benzo[<i>a</i>]fluoranthene	252	
66	Benzo[<i>e</i>]pyrene	252	19
67	Benzo[<i>a</i>]pyrene	252	22
68	Squalene	410	
69	Perylene	252	
70	Quaterphenyl	306	
71	Methyl-252	266	
72	Methylene-252	264	
73	Dibenzonaphthothiophene	284	
74	Indeno[7,1,2,3- <i>cdef</i>]chrysene	276	
75	Indeno[1,2,3- <i>cd</i>]pyrene	276	24
76	Benzo[<i>ghi</i>]perylene	276	29
77	Anthantrene	276	
78	Coronene	300	10
Total HAP			220
Unresolved aromatic hydrocarbons			1800

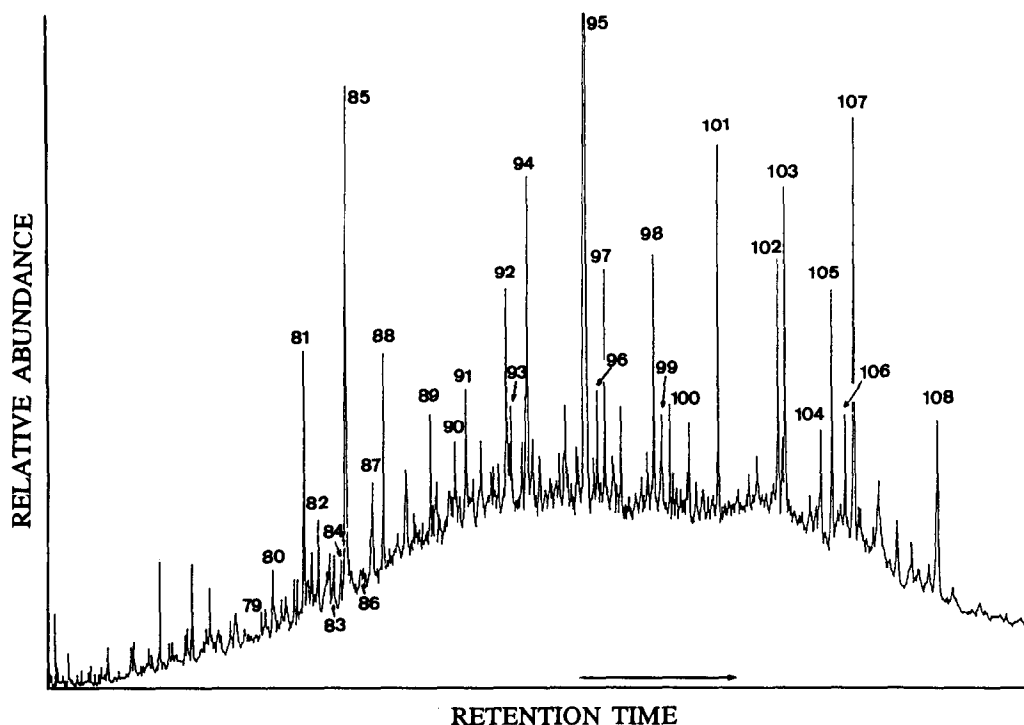


Fig. 3. Representative GC profile of the TMS-derivatized polar compounds present in the winter aerosols of Barcelona. Column: DB-5 (see Table I). The numbered peaks refer to Table V.

hols (Fig. 3 and Table V). Phthalates are in fact the predominant constituents in all instances. These compounds are found world-wide in soils [18] and waters [19], reflecting the widespread use of plasticizers. Di-*n*-octyl phthalate (95) is the major homo-

TABLE IV

RETENTION INDICES OF BENZO[*e*]PYRENE, BENZO[*a*]PYRENE AND SQUALENE IN THE SEMI-POLAR COLUMNS LISTED IN TABLE I

Retention indices relative to the PAH scale [17].

Column	Benzo[<i>e</i>]pyrene	Benzo[<i>a</i>]pyrene	Squalene
DB-5	451.1	452.3	446.9
SE-52	452.7	456.4	454.9
CP-Sil 8 CB	449.4	451.0	454.3
SE-54	453.1	454.3	462.4
HP-5	452.4	454.5	459.4

logue; its presence is concurrent with other *n*-octyl esters identified in these samples such as di-*n*-octyl hexanedioate (94), a major compound in fraction 3, and *n*-octyl hexadecanoate (58) and octadecanoate (62), in fraction 2.

n-Alkan-1-ols and sterols constitute the second major group of polar compounds. The *n*-alkan-1-ols encompass a distribution of even-carbon-numbered homologues ranging between C₁₆ and C₃₂ in which the C₂₈–C₃₂ mode is predominant. This type of distribution is characteristic of contributions from higher plant waxes [20]. The sterols constitute a mixture of C₂₇–C₂₉ compounds dominated by 24-ethylcholest-5-en-3 β -ol (107) in which cholest-5-en-3 β -ol (103), 24-methylcholest-5-en-3 β -ol (104) and 24-ethylcholest-5,22-dien-3 β -ol (105) are other major species. This composition is also representative of inputs from higher plant materials [21,22] which in some cases may be introduced anthropogenically [4].

TABLE V

POLAR COMPOUNDS IDENTIFIED IN THE PARTICULATE FRACTIONS OF THE AEROSOL SAMPLES COLLECTED IN BARCELONA

No.	Compound	Diagnostic ions (<i>m/z</i>)	Average concentration (ng/m ³)
79	9H-Fluoren-9-one	180	
80	<i>n</i> -Tetradecanoic acid ^a	285	
81	Diisobutyl phthalate	149	
82	1H-Phenalen-1-one	180	
83	<i>n</i> -Pentadecanoic acid	299	
84	<i>n</i> -Hexadecan-1-ol ^a	299	
85	Di- <i>n</i> -butyl phthalate	149	
86	9,10-Anthracenedione	180	
87	<i>n</i> -Hexadecenoic acid	311	3.8
88	<i>n</i> -Hexadecanoic acid	313	7.1
89	<i>n</i> -Octadecan-1-ol	327	
90	<i>n</i> -Octadecenoic acid	339	3.8
91	<i>n</i> -Octadecanoic acid	341	4.7
92	Benzyl butyl phthalate	149	
93	Methyl dehydroabietate	239	
94	Dioctyl hexanedioate	370	
95	Di- <i>n</i> -octyl phthalate	149	
96	1- <i>n</i> -Hexadecenoylglycerol ^a	369	
97	1- <i>n</i> -Hexadecanoylglycerol	371	
98	<i>n</i> -Tetracosan-1-ol	412	9.5
99	1- <i>n</i> -Octadecenoylglycerol	397	
100	1- <i>n</i> -Octadecanoylglycerol	399	
101	<i>n</i> -Hexacosan-1-ol	440	12
102	<i>n</i> -Octacosan-1-ol	468	9.5
103	Cholest-5-en-3 β -ol	129	16
104	24-Methylcholest-5-en-3 β -ol	129	4.0
105	24-Ethylcholesta-5,22-dien-3 β -ol	484	11
106	<i>n</i> -Triacontan-1-ol	496	5.0
107	24-Ethylcholest-5-en-3 β -ol	129	19
108	<i>n</i> -Dotriacontan-1-ol	524	9.8

^a Acids and alcohols analysed as trimethylsilyl ether derivatives.

The fatty acids constitute another major group of solvent-extractable compounds present in these aerosol fractions. They constitute distributions of even-carbon-numbered C₁₄–C₁₈ saturated straight-chain homologues occurring together with *n*-hexadecenoic (87) and *n*-octadecenoic (90) acids. The presence of these fatty acid mixtures in atmospheric samples is generally attributed to inputs from microorganisms [23]. These fatty acids are present in unbound form. However, the saturated and unsaturated C₁₆ and C₁₈ *n*-alkanoic homologues, the major free fatty acids, show a similar composition

to that of the monoacylglycerols. This parallelism is in agreement with their presumed microorganism origin and suggest that the free fatty acids may have originated from hydrolysis of these monoglycerides. However, inputs related to decomposition of di- or triglycerides cannot be excluded because the analytical methods used in this study were not aimed at their identification.

In contrast with these distributions, the occurrence of methyl dehydroabietate (93) is representative of contributions from coniferous vegetation. This compound can be transformed into retene by

TABLE VI

RETENTION INDICES OF THE MAJOR *n*-ALKAN-1-OLS AND STEROLS IN THE SEMI-POLAR COLUMNS LISTED IN TABLE IRetention indices relative to *n*-alkan-1-ols.

Column	<i>n</i> -Octacosan-1-ol	Cholest-5-en-3 β -ol	<i>n</i> -Tridecan-1-ol	β -Sitosterol
DB-5	2800.0	2819.7	3000.0	3020.3
SE-52	2800.0	2803.6	3000.0	2998.2
CP Sil 8 CB	2800.0	2776.9	3000.0	2974.1
SE-54	2800.0	2782.5	3000.0	2985.3
HP-5	2800.0	2774.4	3000.0	2969.1

photochemical oxidation in the atmosphere [15], a hydrocarbon that has also been identified (47 in Table III).

Important changes in relative retention are again observed when analysing the polar fraction with different capillary columns. These changes again concern the elution order of linear and polycyclic molecules, namely the *n*-alkan-1-ols and the sterols (see Table VI and Fig. 4). Thus, in the DB-5 column, the trimethylsilyl (TMS) ethers of *n*-octacosan-1-ol and *n*-triacontan-1-ol elute before than the

TMS ethers of cholest-5-en-3 β -ol and β -sitosterol, respectively, whereas in the CP-Sil 8 CB, SE-54 and HP-5 columns the elution order is the reverse. The TMS ethers of these *n*-alkan-1-ols and sterols co-elute in the SE-52 column. These selectivity effects parallel, in fact, the elution order changes observed in fraction 2 and define three groups of columns, corresponding to early (DB-5), intermediate (SE-52) or late (CP-Sil 8 CB, SE-54, HP-5) elution of the linear compounds in relation to the polycyclic molecules.

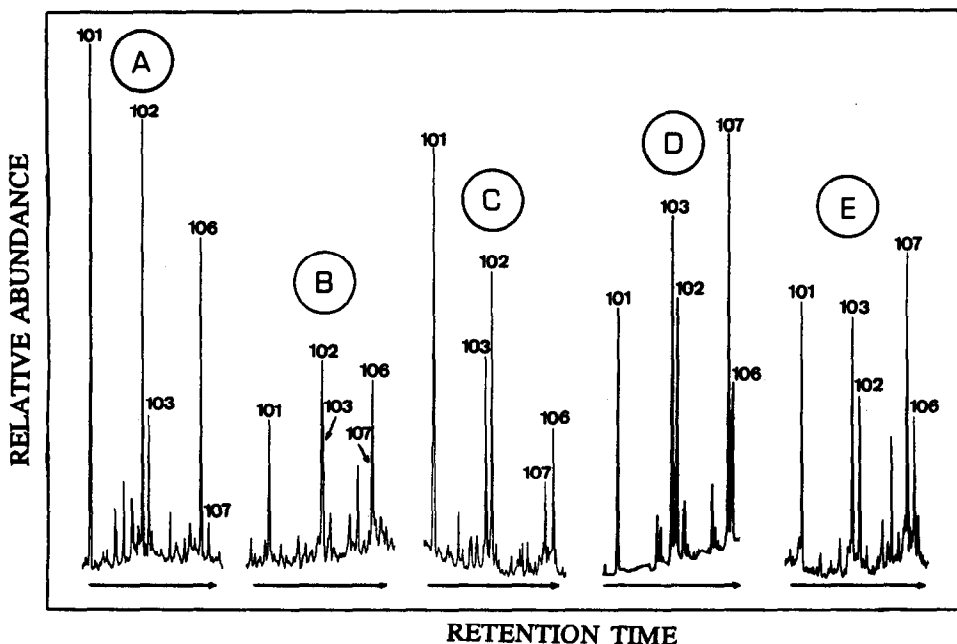


Fig. 4. GC profiles showing the elution order of the TMS ether derivatives of *n*-alkan-1-ols and Δ^5 -sterols in the semi-polar columns described in Table I. (A)–(E) as in Fig. 2. Peak numbers refer to Table V.

CONCLUSIONS

Petrogenic hydrocarbons are the dominant products in the GC profiles of the solvent-extractable organic fractions from large and small airborne particles collected in urban areas. They are essentially represented by an UCM of hydrocarbons, *n*-alkanes with no odd-even carbon number predominance, 17 α (H),21 β (H)-hopanes, and parent and alkylated phenanthrenes and chrysenes/triphenylenes. Pyrolytic products, namely parent PAHs eluting between fluorene and coronene, constitute the second major quantitative group of molecules that can be recognized in these chromatographic traces. The third major group of anthropogenic compounds is related to the plastiziers, being constituted by phthalates and related esters.

The largest group of biogenic products corresponds to higher plant lipids and constitute distributions of straight-chain and polycyclic molecules, including even-carbon-numbered *n*-alkan-1-ols, 24-ethylcholest-5-en-3 β -ol, retene and methyl dehydroabietate. Other biogenic sources leaving a fingerprint in these chromatograms are related to microbial contributions. They can be recognized by the distributions of predominant fatty acids and 1-*n*-alkanoyl and 1-*n*-alkenoyl glycerols.

Important changes in relative retention are observed on analysis of these organic compounds with different semi-polar columns. These changes essentially concern the elution order of linear vs. polycyclic molecules of similar retention and define three groups of columns. The first group, DB-5, corresponds to the elution of linear (squalene, C₂₈/C₃₀ *n*-alkan-1-ol TMS ethers) before polycyclic compounds (benzopyrenes, cholest-5-en-3 β -ol and β -sitosterol TMS ethers). The second (SE-52) represents an intermediate situation in which squalene elutes between benzo[*e*]pyrene and benzo[*a*]pyrene and the TMS ethers of the C₂₈/C₃₀ linear alcohols

co-elute with those of the C₂₇/C₂₉ Δ^5 -sterols. Finally, the third group (CP-Sil 8 CB, SE-54, HP-5) exhibits a reverse elution order.

REFERENCES

- 1 R. C. Pierce and M. Katz, *Environ. Sci. Technol.*, 19 (1975) 347.
- 2 L. Van Vaecck and K. Van Cauwenberghe, *Atmos. Environ.*, 12 (1978) 2229.
- 3 P. Pistikopoulos, H. M. Wortham, L. Gomes, S. Masclet-Beyne, E. Bon Nguyen, P. A. Masclet and G. Mouvier, *Atmos. Environ.*, 24A (1990) 2573.
- 4 M. Aceves, J. O. Grimalt, J. Sunyer, J. M. Anto and Ch. E. Reed, *J. Allergy Clin. Immunol.*, 88 (1991) 124.
- 5 M. Aceves, J. O. Grimalt, J. Albaiges, F. Broto, L. Comellas and M. Gassiot, *J. Chromatogr.*, 436 (1988) 503.
- 6 B. R. T. Simoneit, *Atmos. Environ.*, 18 (1984) 51.
- 7 C. V. Hampton, W. R. Pierson, D. Schuetzle and T. M. Harvey, *Environ. Sci. Technol.*, 17 (1983) 699.
- 8 J. Albaiges and X. Guardino, *Chromatographia*, 13 (1980) 755.
- 9 J. W. Farrington and P. A. Meyers, in G. Eglinton (Editor), *Environmental Chemistry*, Vol. 1, Chemical Society, London, 1975, p. 109.
- 10 R. E. LaFlamme and R. A. Hites, *Geochim. Cosmochim. Acta*, 42 (1978) 289.
- 11 B. R. T. Simoneit, *Int. J. Environ. Anal. Chem.*, 29 (1985) 203.
- 12 G. Grimmer and A. Hildebrandt, *Zentralbl. Bakteriol. Parasitenkd. Infektionskr. Hyg. Abt. 1: Orig. Reihe B*, 161 (1975) 104.
- 13 G. Grimmer, J. Jacob, K.-W. Naujack and G. Dettbarn, *Anal. Chem.*, 55 (1983) 892.
- 14 E.-A. Ratajczak, E. Ahland, G. Grimmer and G. Dettbarn, *Staub-Reinhalt. Luft*, 44 (1984) 505.
- 15 B. R. T. Simoneit and M. Mazurek, *Atmos. Environ.*, 16 (1982) 2139.
- 16 C. W. Bird and J. M. Lynch, *Chem. Soc. Rev.*, 3 (1971) 309.
- 17 M. L. Lee, D. L. Vassilaros, C. M. White and M. Novotny, *Anal. Chem.*, 51 (1979) 768.
- 18 D. J. Russel and B. McDuffie, *Int. J. Environ. Anal. Chem.*, 15 (1983) 165.
- 19 R. Ritsema, W. P. Cofino, P. C. M. Frintrop and U. A. Th. Brinkman, *Chemosphere*, 18 (1989) 2161.
- 20 G. Eglinton and R. Hamilton, *Science*, 156 (1967) 1322.
- 21 B. A. Knights, *Phytochemistry*, 7 (1968) 1707.
- 22 E. Kvant, *Acta Chem. Scand.*, 22 (1968) 2161.
- 23 B. R. T. Simoneit, R. E. Cox and L. J. Standley, *Atmos. Environ.*, 22 (1988) 983.