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Determination of anthropogenic and biogenic organic compounds on airborne particles: flash chromatographic fractionation and capillary gas chromatographic analysis

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ABSTRACT

n-Alkanes, polycyclic aromatic hydrocarbons, *n*-alkanals, 2-alkanones and *n*-alkanols were efficiently separated from alkanoic acids and then fractionated by flash chromatography on a silica gel column. These compounds were determined by capillary gas chromatography with flame ionization and/or mass spectrometric detection in the selected ion monitoring mode. The recoveries obtained for the whole analytical procedure were 82–91% for *n*-alkanes, 68–78% for polycyclic aromatic hydrocarbons, 70–75% for *n*-alkanals and 2-alkanones, 73–76% for *n*-alkanols and 80–84% for alkanoic acids. This analytical protocol was suitable for the determination of more than 140 compounds on aeolian particles collected on glass-fibre filters.

INTRODUCTION

The chemical composition of the lower troposphere in urban and non-urban environments is controlled, to a significant extent, by the marine and terrestrial biosphere and also the emission of various anthropogenic chemicals. Among these anthropogenic and biogenic compounds, many organic species are found, including a variety of naturally produced and synthetic organic compounds [1]. Long-chain *n*-alkanes, *n*-alkanols, *n*-alkanals, 2-alkanones, *n*-alkanoic acids, *n*-alkanoic acid salts, α,ω-dicarboxylic acids (or higher plant origin and/or photooxidation products of anthropogenic cyclic alkenes and biogenic unsaturated fatty acids), polycyclic aromatic hydrocarbons (PAHs) and chlorinated hydrocarbons from anthropogenic sources have been detected in urban, rural and in remote marine aerosols [2–8]. The study of the chemical composition of the atmosphere is of major importance not only because the anthropogenic compounds often represent a serious potential hazard to human health, but also because the atmosphere constitutes a "conveyor belt" for biogenic and anthropogenic compounds to the ocean. Atmospheric transport, and the relative importance of the aeolian input of continental material to the ocean, are subjects to intense research. Consequently, the reliable determination of organic compounds, which can be used as molecular markers, in air particulates is very important.

Some analytical methods [1,9] for the determination of organic compounds on airborne particles have been reported. The total organic extract is methylated to produce the corresponding fatty acid esters and then the compounds are separated by column liquid chromatography [9] into a non-polar fraction (aliphatic), a semi-polar fraction (aromatic) and a third fraction containing the polar compounds. The

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same separation has also been achieved by using, instead of liquid column chromatography, a thin-layer chromatographic system [1]. Taking into consideration that the concentrations of various polar compounds often differ greatly from one another, we would expect problems if, after fractionation, they are found in the same fraction.

In this paper we present a method in which acids are first separated from neutral compounds by using a liquid chromatographic column containing specially prepared silica gel, and then the neutral compounds are fractionated by silica gel flash chromatography into very distinct non-polar, semi-polar and polar compound fractions. This method is very sensitive and selective, and allows the use of capillary gas chromatography with flame ionization detection (GC–FID) as a reliable identification and quantification method. A comparison of GC–FID with capillary gas chromatographic–mass spectrometric analysis in the selected ion monitoring mode (GC–MS-SIM) is also presented.

EXPERIMENTAL

Materials

All solvents were of Pestanal grade from Riedel-de Haën (Seelze, Germany). Standard compounds were purchased from Ehrenstorfer (Augsburg, Germany). *n*-Alkanals were prepared by oxidation of the corresponding alcohols [10]. Silica gel (70–230 and 230–400 mesh) was obtained from Merck (Darmstadt, Germany). Soxhlet cartridges were supplied by Schleicher and Schüll (Dassel, Germany). Glass-fibre filters were purchased from Whatman (Maidstone, UK).

All materials used (silica gel, glass- and cotton-wool, paper filters, anhydrous sodium sulphate, etc.) were Soxhlet extracted overnight and kept dry until use. Glass-fibre filters were extracted with methylene chloride for 72 h. Every 24 h a new portion of methylene chloride was used for the extraction. The extracted and dried glass-fibre filters were kept in a dedicated clean glass container with silica gel to avoid contamination and humidity.

Fractionation, derivatization and identification

The standard compounds, about 100 ng each, dissolved in methylene chloride, were applied on a glass-fibre filter (their concentration corresponds to an air concentration of 40 pg/m^3) and the methylene chloride was evaporated. The compounds were extracted from the filters, which has been cut into small pieces, in a flask by refluxing methylene chloride for 20 h. The extracts were vacuum evaporated and separated into individual compound classes. The alkanoic acids were separated from neutral compounds by using a McCarthy–Dutie column [11]. The alkanoic acids (fraction F I) were methylated with boron trifluoride etherate–methanol (1:2).

The neutral compounds were further fractionated by flash chromatography on silica gel (Merck) (230–400 mesh, activated at 150°C for 3 h). The compound mixture was dissolved in *n*-hexane and applied to the top of a 30 × 0.7 cm I.D. column containing silica gel in *n*-hexane. Nitrogen pressure was used in order to obtain a flow-rate of 1.4 ml/min at the bottom of the column. The following solvent systems were used to elute the different compound classes: (1) 15 ml of *n*-hexane (fraction F II1, aliphatics), (2) 15 ml of toluene–*n*-hexane (9.4:5.6) (fraction F II2, PAHs) (3) 15 ml of *n*-hexane–methylene chloride (7.5:7.5) (fraction F II3, carbonyl compounds such as *n*-alkanals and 2-alkanones) and (4) 20 ml of ethyl acetate–*n*-hexane (8:12) (fraction F II4, *n*-alkanols). The extracted filters were treated with 0.1 *M* hydrochloric acid–methanol to protonate all fatty acid salts. The acidified filter was further extracted with *n*-hexane and the liberated fatty acids (fraction F III) were methylated as above.

n-Alkanols were derivatised to the corresponding acetates, as follows. The fraction containing the *n*-alkanols was evaporated to dryness under a gentle stream of nitrogen, 1 ml of pyridine and 1 ml of acetic anhydride were added and the reaction mixture was shaken vigorously for 10 min and allowed to stand overnight at room temperature. A few drops of 3 *M* hydrochloric acid were added to adjust the pH to 2–3, 20 ml of water were added and the mixture was extracted with 3 × 15 ml of *n*-hexane. The *n*-hexane phase was dried with sodium sulphate, filtered through a paper filter and evaporated in a rotary evaporator.

The individual fractions were spiked with internal standards (1-chlorohexadecane for *n*-alkanes, *n*-alkanals, 2-alkanones and *n*-alkanol acetates, hexamethylbenzene for PAHs and *n*-hexacosane for alkanoic acid methyl esters) for quantitative determinations.

Relative response factors, for both GC–FID and GC–MS-SIM, were calculated for 3–5 standard compounds, representing each compound class, of increasing molecular mass. Relative response factors for PAHs were calculated for each compound individually.

Control of procedural blanks were performed to assess possible contamination. The total blank mass never exceeded 2% of the individual sample extracts, except for the alkanoic acids fraction, where the maximum contamination represented 10% of the total fraction extract. The contaminants were characterized by GC–MS and comparison with standard mixtures. The most frequent contaminants were phthalate esters, *n*-alkanes ranging from C_{20} to C_{30} and alkanoic acids ranging from C_6 to C_{20}. All amounts given here were corrected by taking into consideration the application of the analytical methodology with standard compounds (column chromatographic performance and relative response factors in GC–FID and GC–MS-SIM).

Compound identification was performed by GC–MS and co-injection with authentic standard compounds or compound mixtures (PAHs).

GC–MS and GC–FID

GC–MS analyses were carried out on a Hewlett-Packard mass-selective detector with the appropriate data system. A Hewlett-Packard Model 5890 gas chromatograph, equipped with a Grob-type split–splitless injector, was directly coupled with the fused-silica capillary column (SE-54) (25 × 0.25 mm I.D.) to the ion source. Helium was used as the carrier gas with a back-pressure of 0.8 atm (1 atm = 101 325 Pa). The electron impact ionization conditions were ion energy 70 eV, ion source temperature 195°C, mass range *m/z* 35–590 or in the selected ion monitoring mode for quantitative determinations and electron multiplier voltage 1700–1800 V.

The GC–FID analyses were performed on a Hewlett-Packard Model 5890 gas chromatograph with a Hewlett-Packard Chemstation data system, equipped with the same fused-silica capillary column as above. Hydrogen was used as the carrier gas with a back-pressure of 1 atm. The chromatographic conditions were as follows: injector temperature, 270°C; detector temperature (FID), 290°C; temperature programme 1 (aliphatics, PAHs, *n*-alkanals, alkanoic acid methyl esters), 70°C (1 min), 70–150°C at 10°C/min, 150–290°C at 5°C/min, 290°C (30 min); temperature programme 2 (*n*-alkanol acetates), 80°C (2 min), 80–280°C at 4°C/min, 280°C (30 min). A 1-μl volume of each sample was injected, in the splitless mode (split closed for 30 s), and the hot needle technique was used.

Sampling of air particles and storage of glass-fibre filters

Particulate material was collected on a pre-extracted 20 × 25 cm glass-fibre filter, having a collection efficiency higher than 99% for particles with radius larger than 0.3 μm at the flow-rate of 90 m^3/h used. Filters were mounted in a high-volume air sampling system (Model GMWL-2000; General Metals Works, Cleves, OH, USA). Samples were collected for 24–36 hs (2500–3000 m^3 air sampled) on a 15-m high building situated in a urban coastal area of the Eastern Mediterranean (Heraklion, Island of Crete, Greece). The samples were stored frozen (−30°C) in precleaned glass flasks sealed with PTFE tape and covered with aluminium paper. Compound isolation from samples and determination were performed as described above.

RESULTS AND DISCUSSION

Table I gives the recoveries for each lipid class, with standard compounds used for the evaluation of extraction, separation and fractionation procedures.

A typical gas chromatogram of a methylated carboxylic acid fraction (F I) of an urban aerosol extract is presented in Fig. 1A. In Fig. 1B is shown a combined ion chromatogram for *m/z* 97, 111 and 112 (specific ions for ω-oxo- and α,ω-dicarboxylic acids [8]) of the same

TABLE I

RECOVERIES (TRIPLICATE MEASUREMENTS) FOR EACH LIPID CLASS, WITH STANDARD COMPOUNDS

Compound class	Recovery (%)	
	A[a]	B[b]
n-Alkanes		
n-$C_{19}H_{40}$	91.5 ± 1.5	78.4 ± 0.6
n-$C_{26}H_{54}$	82.0 ± 2.0	76.3 ± 1.0
PAHs		
Phenanthrene	78.0 ± 1.0	76.6 ± 2.0
Benzo[*a*]anthracene	68.5 ± 1.5	65.8 ± 0.2
n-Alkanals		
n-$C_{22}H_{44}O$	74.3 ± 1.0	71.4 ± 1.5
n-$C_{26}H_{52}O$	71.5 ± 1.5	67.2 ± 1.0
n-Alkanols[c]		
n-$C_{16}H_{33}OH$	76.1 ± 1.0	70.6 ± 2.3
n-$C_{22}H_{45}OH$	73.3 ± 1.0	68.4 ± 1.0
n-Alkanoic acid[c]		82.0 ± 2.0
n-$C_{18}H_{36}O_2$		

[a] After filter extraction and flash chromatography.

[b] After filter extraction and McCarthy–Dutie column.

[c] After derivatization.

methylated acidic fraction. In Fig. 2A is shown a representative GC–FID profile of an aliphatic hydrocarbon fraction (F II1), of the same aerosol sample as above, and Fig. 2B shows the ion chromatogram of the same fraction for the ion of *m/z* 191 (representative for the hopanes). Fig. 3A shows a typical GC–FID trace for a PAH fraction (F II2). The same fraction analysed by GC–MS-SIM (only molecular ions of the compounds of interest were selected) is presented in Fig. 3B. In Fig. 4 are given GC–FID traces for (A) *n*-alkanals and 2-alkanones (F II3) and (B) *n*-alkanols (F II4, as acetates), identified in the same as for the above aerosol extract.

In Table II are summarized the quantitative results of the analyses of airborne particles collected in the sampling area.

The recoveries obtained fro the representative standard compounds are generally higher if the McCarthy–Dutie column for the separation of acidic fraction is not used. When used, the corresponding recoveries are lower but still satisfactory if we consider the small amount (about 10 ng for each compound or 4 pg/m^3 if we take into consideration the sampling volume) of the compounds applied on the filter and the efficiency of fractionation. The efficiency of fractionation becomes obvious when the GC–FID traces of all fractions are examined (Figs. 1A, 2A, 3A and 4A and B). We obtained a reliable fractionation of the different compound classes, namely complete separation of the non-polar aliphatic fraction (Fig. 2A) from the semi-polar PAH fraction (Fig. 3A). Also carbonyl compounds, such as alkanals and alkanones (Fig. 4A), were cleanly separated from the more polar alkanols (Fig. 4B). The McCarthy–Dutie column proved to lead to very efficient separations of alkanoic acids from the neutral lipids (Fig. 1A). When larger amounts of standard compounds (1–10 μg) were applied on the glass-fibre filters, the recoveries obtained were 5–10% higher than those shown in Table I.

In Table II are given the concentration ranges measured for each compound class in the samples collected. These concentration ranges differ appreciably in the polar compounds, such as alkanoic acids, *n*-alkanols, *n*-alkanals and 2-alkanones. Whenever these compounds were collected in the same fraction and then derivatized, determination of compounds of lower concentration was very difficult. This may be one of the reasons why in most published studies *n*-alkanals and 2-alkanones are generally only tentatively identified, and rarely quantified.

The results of the analysis of the above fractions by GC–MS-SIM mode, shown in Figs. 1B, 2B and 3B, indicate that greater specificity can be obtained for some compound classes. We used the SIM mode, as being more specific, to determine the ω-oxo- and α,ω-dicarboxylic acids (Fig. 1B), although this could be also done by GC–FID . The SIM technique was very useful in detecting some molecular markers, such as hopanes in the aliphatic fraction (Fig. 2B), which are difficult to determine with FID alone. Especially for the PAH fraction, by eliminating the possible interferences from other compound classes, this technique gives a better resolved chromatogram (Fig. 3B) than the corresponding

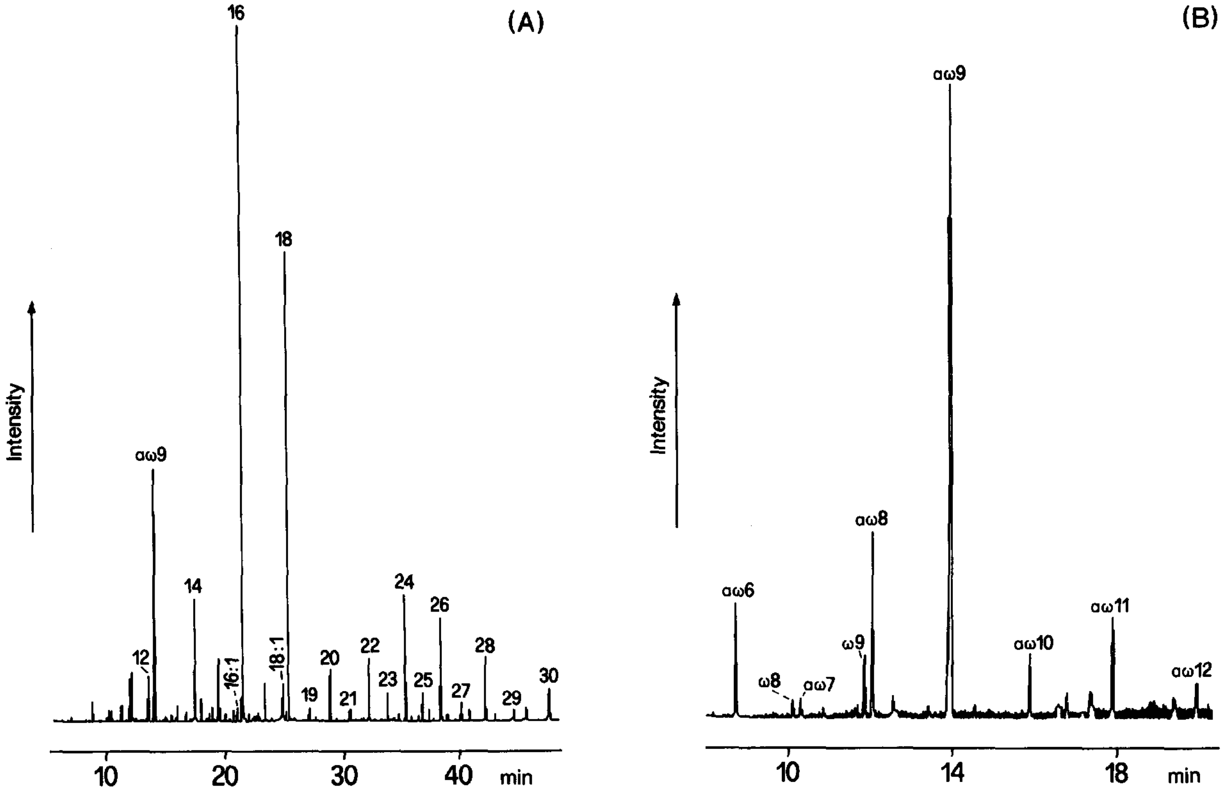

Fig. 1. (A) GC–FID trace of methylated alkanoic acid fraction (F I) identified in an urban aerosol (city of Heraklion); (B) selected ion (*m/z* 97, 111 and 112) GC–MS trace of the same fraction, specific for the α,ω-dicarboxylic (αω 6, 7, 8, 9, 10, 11, 12) and ω-oxocarboxylic (ω 8, 9) acids. Numbers on the peaks indicate the carbon number for each homologue.

FID trace (Fig. 3A). The GC–MS-SIM technique for the analysis of F I (carboxylic acids, selected ion *m/z* 74), F II3 (selected ions *m/z* 82 and 96 for *n*-alkanals and *m/z* 58 for 2-alkanones) and F II4 (selected ions *m/z* 61, 83 and 97), because of the efficiency of fractionation, did not offer any clear advantage over the FID technique.

Carboxylic compound fraction (F I)

The chromatographic profile of this fraction (Fig. 1A) shows that the compounds present range from C_{10} to C_{32}. The compound distribution, characterized by a strong even-to-odd carbon preference index (CPI) (Table II), indicates a definite biogenic origin of these compounds. The homologues of $<C_{20}$ are attributed to microbial sources, while those of $>C_{20}$ show a more pronounced plant origin [1].

In all samples analysed in this study, a series of α,ω-dicarboxylic acids and ω-oxocarboxylic acids were determined. It has been proposed that these compounds are photooxidation products of cyclic alkenes [12] and of unsaturated fatty acids [8]. The C_5 and C_6 homologues are formed by the oxidation of cyclic alkenes, whereas the C_8 and C_9 homologues, which are the most abundant, are formed by the photooxidation of unsaturated carboxylic acids such as oleic ($C_{18:1}$) and linoleic ($C_{18:2}$) acid. The latter compounds were either absent or found in very low concentrations in all the samples examined. It is interesting that the highest α,ω-dicarboxylic acid concentrations (summer), and at the same time the lowest concentrations of their precursors (oleic and linoleic acids), were related to high ozone concentrations (160 $\mu g/m^3$) determined in the sampling area [8].

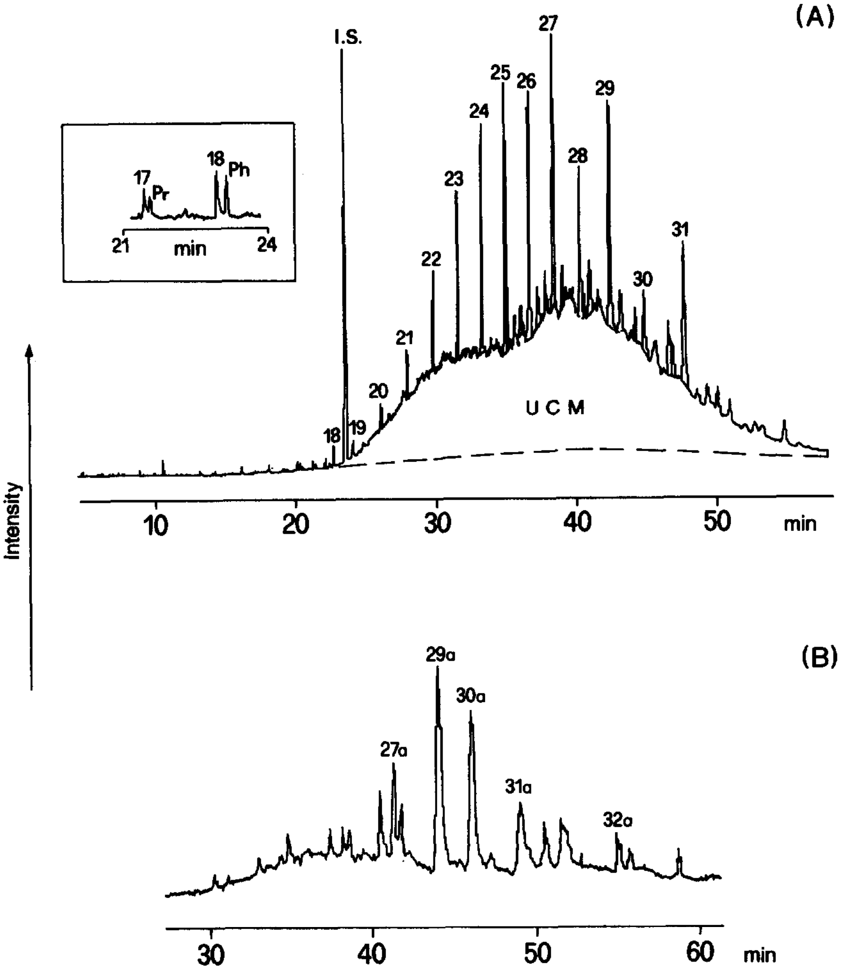

Fig. 2. (A) GC–FID trace of the aliphatic hydrocarbon fraction (F II1) present in airborne particles collected in Heraklion. UCM = unresolved complex mixture; Pr = pristane; Ph = phytane. (B) Ion chromatogram (*m/z* 191) of the same fraction, specific for the 17α(H),21β(H)-hopanes. The numbers on the peaks indicate the carbon number of each homologue.

Aliphatic hydrocarbon fraction (F II1)

All gas chromatograms of the aliphatic fraction (Fig. 2A) exhibited an envelope of an unresolved complex mixture (UCM) of branched and cyclic hydrocarbons. Such traces are characteristic of petroleum residues. The carbon preference index (CPI), a measure of carbon number predominance in a homologous compound series, is a useful estimate of the relative contributions of biogenic *versus* anthropogenic sources. The *n*-alkanes of plant waxes show a pronounced odd carbon number predominance, or CPI > 1, while fossil fuel hydrocarbons exhibit CPI ≤ 1. In these aerosol samples the *n*-alkanes ranged from about C_{11} to C_{33} and had CPI varying from 0.6 to 1.3. Those *n*-alkanes in the range C_{22}–C_{33} had CPI values between 1.4 and 1.6. The homologues above C_{25} in all the samples, maximizing at C_{25}, C_{29} and C_{27}, suggest predominant vascular plant wax alkane inputs. Most of the oils contained isoprenoid hydrocarbons such as pristane (Pr) and phytane (Ph) and some molecular markers such as hopanes and steranes [13]. Pristane, phytane and hopanes were present in all the samples analysed. The ratio of unresolved complex mixture to the total

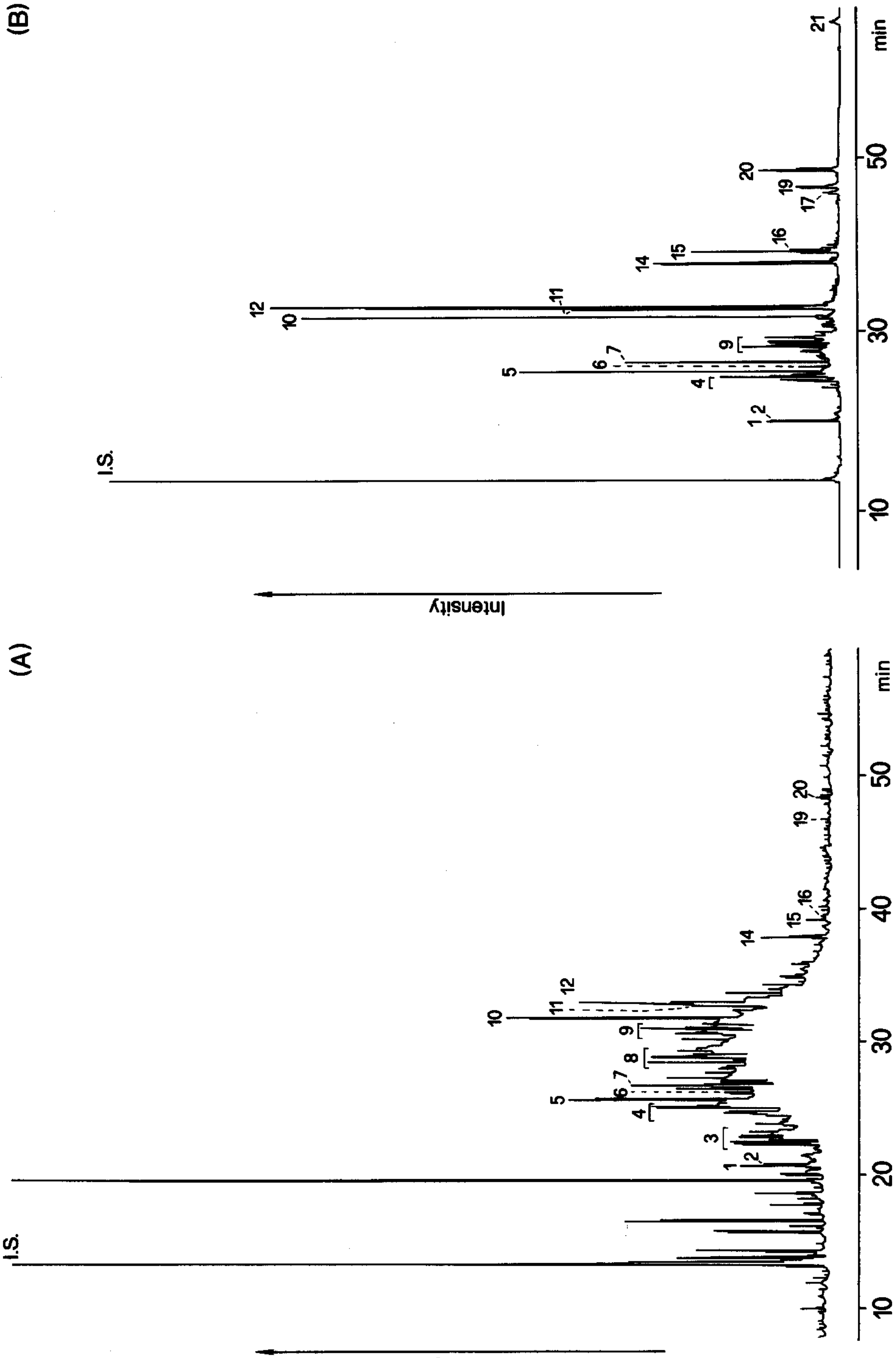

Fig. 3. (A) GC–FID trace of the PAH fraction (F II2) identified in an urban aerosol extract collected in Heraklion; (B) the same fraction analysed by GC–MS-SIM. The peak numbers are identified in Table III.

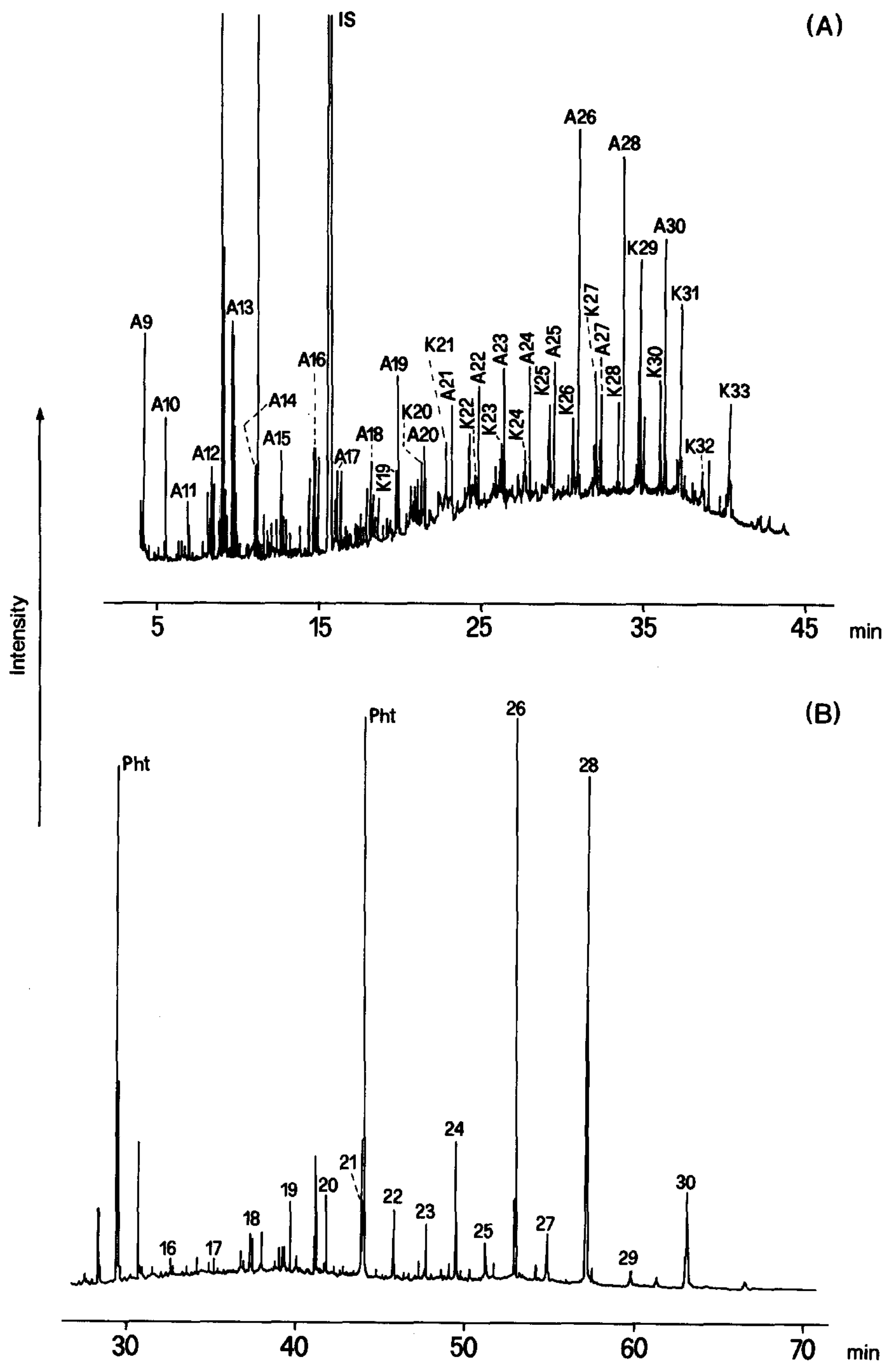

Fig. 4. (A) GC–FID trace of the *n*-alkanal and 2-alkanone fraction (F II3) present in Heraklion aerosol extract. The number of carbon atoms is indicated by A for the *n*-alkanal homologues and K for the 2-alkanone homologues. (B) GC–FID trace of the *n*-alkanol fraction (F II4) identified in an urban aerosol extract. The numbers on the peaks indicate the carbon number of each homologue identified; Pht: phthalate esters.

TABLE II

QUANTITATIVE RESULTS OF THE ANALYSES OF AIR PARTICLES COLLECTED IN THE SAMPLING AREA

CPI (carbon preference index), odd-to-even for *n*-alkanes and 2-alkanones and even-to-odd for *n*-alkanals, *n*-alkanols and *n*-alkanoic acids. Pr = pristane; Ph = phytane; UCM = unresolved complex mixture; TRA = total resolvable aliphatics; IP = indeno[1,2,3-*cd*]pyrene; BgP = benzo[*ghi*]perylene; BeP = benzo[*e*]pyrene; BaP = benzo[*a*]pyrene; MP = methylphenanthrenes; P = phenanthrene.

Compound class	Concentration range (ng/m^3)	CPI	C_{max}	Diagnostic ratio
Aliphatics				
C_{11}–C_{33}	76.6–323,1	0.6–1.3	C_{25}, C_{29}	
UCM	382.0–1277.0			
Pr	0.3–0.6			
Ph	0.2–0.9			
UCM/TRA				4.0–6.6
PAHs	8.8–48.4			
IP/BgP + IP				0.28–0.54
BeP/BeP + BaP				0.76–0.87
MP/P				1.3–8.6
n-Alkanals				
C_9–C_{32}	5.4–6.7	1.1–1.4	C_{26}, C_{28}	
C_{20}–C_{32}	3.6–4.6	1.5–2.3		
2-Alkanones				
C_{16}–C_{33}	1.8–2.6	1.1–1.8	C_{25}, C_{29}	
n-Alkanols				
C_{10}–C_{32}	17.2–100.7	6.6–11.9	C_{26}, C_{28}	
n-Alkanoic acids				
C_9–C_{32}	132.1–205.2	7.0–12.8	C_{16}	
n-Alkanoic acid salts				
C_{11}–C_{30}	39.4–48.9	2.2–4.8	C_{16}	
α,ω-Dicarboxylic acids				
C_6–C_{24}	19.2–45.8		C_9, C_8	
α,ω-Dicarboxylic acid salts				
C_6–C_{26}	16.8–35.0		C_9, C_8	

resolvable aliphatics (UCM/TRA, Table II) is consonant with an important anthropogenic contribution. Thus in the aliphatic fraction two main sources of compounds are reflected in the aeolian particulates of this coastal urban area: emmissions from higher plant waxes and petroleum residues.

Aromatic hydrocarbon fraction (F II2)

The gas chromatograms of the aromatic hydrocarbon fractions (Fig. 3A and B and Table III) contain mostly compounds of pyrolytic origin. In Table II are given the diagnostic ratios [4,9] (indeno[1,2,3-*cd*]pyrene)/(benzo[*ghi*]perylene + indeno[1,2,3-*cd*]pyrene) and (benzo[*e*]pyrene)/(benzo[*e*]pyrene + benzo[*a*]pyrene). These ratios should be interpreted with caution because the values obtained here cannot be attributed to specific sources with certainty. For example, the first ratio (0.28–0.54) indicates mixed combustion sources. The ratio values reported are 0.18 for cars, 0.37 for diesel fuel and 0.56 for coal [4]. The second ratio, between 0.76 and 0.87, corresponds to a faster decay of benzo[*a*]pyrene,

TABLE III

POLYCYCLIC AROMATIC HYDROCARBONS IDENTIFIED IN AN URBAN AEROSOL SAMPLE COLLECTED IN THE CITY OF HERAKLION

No.	Specific ion (m/z)	Compound
1	178	Phenanthrene
2	178	Anthracene
3	192	Methylphenanthrenes Methylanthracenes
4	206	Dimethyl-178
5	202	Fluoranthene
6	202	Acephenanthrylene
7	202	Pyrene
8	220	Trimethyl-178
9	216	Methylpyrene Benzo[*a*]fluorene
10	226	Cyclopenta[*cd*]pyrene
11	228	Benzo[*a*]anthracene
12	228	Chrysene/triphenylene
13	242	Methylchrysene
14	252	Benzo[*b,j,k*]fluoranthene
15	252	Benzo[*e*]pyrene
16	252	Benzo[*a*]pyrene
17	252	Perylene
18	276	Indeno[7,1,2,3-*cdef*]chrysene
19	276	Indeno[1,2,3-*cd*]pyrene
20	276	Benzo[*ghi*]perylene
21	300	Coronene

which indicates an origin from a more distant source. Petrogenic inputs also constitute important contributors of aromatic compounds in air particulates. The compositional difference, from combustion originates PAHs, is expressed as the relative abundance of total methylphenanthrenes to phenanthrene (MP/P). Values of MP/P measured in combustion mixtures are generally <1, whereas unburned, fossil PAH mixtures typically display a range of values from 2 to 8 [14]. In this study the MP/P values are between 1.3 and 8.6, thus indicating important unburned petrogenic inputs.

Carbonyl compound fraction (F II3)

n-Alkanals and 2-alkanones are the major compound classes dominating this fraction. Their concentration ranges are at least one order of magnitude lower than those of the other polar compounds, such as *n*-alkanols and alkanoic acids (Table II).

The *n*-alkanals, especially those $>C_{20}$, are of biogenic origin [15]. The chain length distribution of alkanals in the range C_{20}–C_{32} (Fig. 4A) is usually very similar to or identical with that of alkanols (Fig. 4B), suggesting a close relationship [15]. The CPI (even-to-odd) values for the alkanals (Table II), although >1, are not as high as expected for compounds of biogenic origin. The higher values found for these in the range C_{20}–C_{32} indicate more biogenic input, whereas the lower values of the homologues with lower carbon atoms number, C_9–C_{19}, indicate oxidation of alkanes as a possible origin [16].

2-Alkanones are considered to originate form *in situ* microbial formation from *n*-alkanes [17]. The homologue distribution and C_{max} (Fig. 4A) within the range C_{25}–C_{33} are very similar to those for the corresponding *n*-alkanes (Fig. 2A), supporting the above hypothesis.

Hydroxy compound fraction (F II4)

n-Alkanols constitute by far the most abundant compound class determined in this fraction. The homologues range from C_{11} to C_{33}, with a strong even carbon number preference (CPI 6.6–11.9) (Fig. 4B and Table II). This very strong even-to-odd carbon number predominance and the presence of major amounts of C_{26} and C_{28} suggest higher plant waxes as sources of these aerosol lipids. The homologues up to C_{20} are characteristic of vascular plant waxes [18], whereas those lower than C_{20} may originate from microbial sources [1]. The distributions obtained here are similar to those obtained in other areas, such as the north Pacific [19] or in many locations in the United States [1].

Alkanoic acid salt fraction (F III)

The alkanoic acid salts, ranging between C_{10} and C_{30}, show very similar GC profiles (Fig. 1A) and compound distributions to the free alkanoic acids. Their CPI values indicate a definite biogenic origin. The FAS fraction is dominated by the lower carbon number homologues, which are probably derived from a marine source, although a terrestrial plant wax source may be a minor contributor.

Unsaturated fatty acids were also detected but in lower concentrations than in those detected in the free carboxylic acid fraction. In contrast, ω-oxocarboxylic and α,ω-dicarboxylic acids were found in higher concentrations in the salt form than in the free acid form (Table II). Considering these two pieces of evidence, we conclude that in air particulate samples unsaturated fatty acids undergo faster degradation when in the salt than when in the free acid form.

CONCLUSIONS

We have established a procedure for the determination of biogenic and anthropogenic compounds in airborne particulates. This method consists of separation of the acidic compounds from the neutrals, followed by a flash chromatographic fractionation technique, which allows the complete separation of compound classes into distinct fractions. The fractions obtained can be easily analysed, qualitatively and quantitatively, by capillary gas chromatography with flame ionization detection. The GC–MS technique in the selected ion monitoring method was advantageous over the GC–FID technique for the analysis of PAHs and for the detection of some molecular markers such as hopanes and dicarboxylic acids. More than 140 organic compounds were determined in aeolian particulates from a coastal urban area, using this procedure. Petrogenic and pyrolytic hydrocarbons dominated the anthropogenic compounds, whereas the biogenic compounds consisted mainly of fatty acids and their salts, alkanols, alkanals and 2-alkanones.

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