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Gas chromatographic screening of organic compounds in urban aerosols

II. Changes in hydrocarbon composition during storage

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ABSTRACT

Gas chromatographic and gas chromatographic–mass spectrometric analyses of inadequately stored filters and hydrocarbon extracts of urban aerosols have shown the occurrence of microbially mediated transformation processes giving rise to hydrocarbon patterns different from the original composition of the samples. In all cases, a strong decrease in the concentration of the unresolved complex mixture of hydrocarbons is observed. The modifications also involve the formation of mixtures of C_{29}–C_{34} iso- and anteisoalkanes and modal distributions of C_{15}–C_{20} n-alkanes with no even/odd carbon number preference in vials and filters, respectively. These n-alkane distributions may even dominate the chromatographic profiles of the aliphatic hydrocarbon fractions corresponding to long-term stored filters. Decay of the polycyclic aromatic hydrocarbons of lower stability, *e.g.* 4(H)-cyclopenta[*cd*]pyrene and benzo[*a*]pyrene, is also observed in the filters. These *de novo*-produced n-alkane and iso- and anteisoalkane distributions occur at the initial stages of transformation, providing a useful tool for the detection of this type of post-sampling process.

INTRODUCTION

Very little attention has been paid to modifications of hydrocarbon composition in environmental samples after storage. In general, there is a wide consensus that the samples should be deep frozen (*ca.* −20°C) immediately after collection, taking stringent precautions to prevent external contamination. However, the information available on possible changes in composition under these storage conditions, or when they are not fulfilled, is very limited. Furthermore, the

few studies described in the literature only concern sedimentary materials [1,2]. To the best of our knowledge post-sampling transformations of organic constituents in stored aerosol samples have not been reported.

These aspects are relevant in monitoring studies, in which samples may be regularly collected at distant places, and in some cases the filters may not be stored deep frozen immediately after collection. A correct evaluation of the analytical results corresponding to these cases requires the availability of safety criteria based on knowledge of the changes in composition that may be produced under these accidental circumstances. On the other hand, an additional activi-

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ty of many of these monitoring studies is the storage of representative samples to keep a record of the temporal evolution of the environment of interest. These deep-frozen filters may provide information in subsequent additional studies. Examples of retrospective investigations based on the materials kept in these archives are available in the literature, e.g. asthma epidemics studies [3,4], but again reference data on possible storage-related modifications are needed for a correct interpretation of the results.

Since 1985 we have regularly monitored the composition of solvent-extractable compounds in the air from Barcelona (Catalonia, Spain) using methods based on gas chromatography (GC) and GC coupled to mass spectrometry (MS). As described in the previous study of the present series [5], this regular sampling and analysis affords a detailed knowledge of the distributions of the major lipids among the atmospheric particulates of the city. Aliquots of the filters analysed were stored at $-20°C$ to provide a temporal record for subsequent investigations.

In the course of some retrospective studies, comparison of the hydrocarbon composition (aliphatics and aromatics) in filter aliquots analysed after sampling or after long storage times showed that major transformations occurred in cases of accidental storage at ambient temperature. In addition to these, changes were also observed in the vials in which the hydrocarbon fractions were stored, and in this case the transformation could occur even in deep-frozen conditions. Interestingly, the modifications produced in the filters or vials were rather uniform, leading to well-defined hydrocarbon patterns. These patterns were very different from the original distributions. However, they could easily be confused with real atmospheric mixtures.

The hydrocarbon patterns generated in these post-sampling transformations are described in the present study. They are compared with the original mixtures and the main features for their recognition are discussed. These results provide evidence of post-sampling transformation reactions as possible modifiers of the original molecular composition in aerosols.

EXPERIMENTAL

Materials

Pestipur-grade dichloromethane was purchased from Mallinckrodt (Paris, TX, 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 & Schürl (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) 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 chromatograms with no unresolved GC envelope and only 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 pg/m^3 when referred to 100 ml of solvent used for the extraction of one-third of a filter that corresponds to 1000 m^3 of air sample.

Sampling, extraction and fractionation

The air samples (1200 m^3 and 50 m^3/h) were taken with a High-Vol pumping system (CAV-P; MCV, Collbato, Catalonia, Spain) equipped with 20.3 × 25.4 cm glass microfibre filters (catalogue No. 1820866 Whatman, Maidstone, UK). 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 dry and diluted to 0.5 ml with n-hexane. Then, it was

fractionated by column chromatography according to previously established methods [6]. These methods were scaled down to suitable amounts of solvents and packings according to the small lipid content of the filters. 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) and the aromatic hydrocarbons were collected in the second fraction (4 ml of 20% dichloromethane in n-hexane). These fractions were vacuum and nitrogen concentrated until almost dry and redissolved with isooctane.

Instrumental analysis

The samples were analysed by GC and GC–MS. These analyses were performed, respectively, with a Carlo-Erba 5300 system equipped with a flame ionization detector, and with a Hewlett-Packard 5970 system provided with an HP-5994A data aquisition system. A 30 m × 0.25 mm I.D. DB-5 (film thickness 0.2 μm) fused-silica capillary column (J&W Scientific, Folsom, CA, USA) was used in all cases. The GC analyses were performed with an oven temperature programme of 60–300°C at 6°C/min, injector and detector temperatures of 280 and 330°C, respectively, and hydrogen as carrier gas (50 cm/s). The oven temperature programme for the GC–MS analyses was from 60 to 280°C at 6°C/min, injector and transfer line temperatures were 280 and 300°C, respectively, and helium was the carrier gas (50 cm/s). Data were acquired in the electron impact (EI) mode (70 eV), scanning from 40 to 600 mass units at 1 s per decade. In both cases the injector was in the splitless mode (1 μl, hot needle technique), the split valve being closed for 35 s.

RESULTS AND DISCUSSION

Glass-fibre filters

As indicated above, the changes in composition observed in the filters stored at ambient temperature exhibit rather uniform trends leading to characteristic GC profiles. These profiles are illustrated in Fig. 1, in which the aliphatic
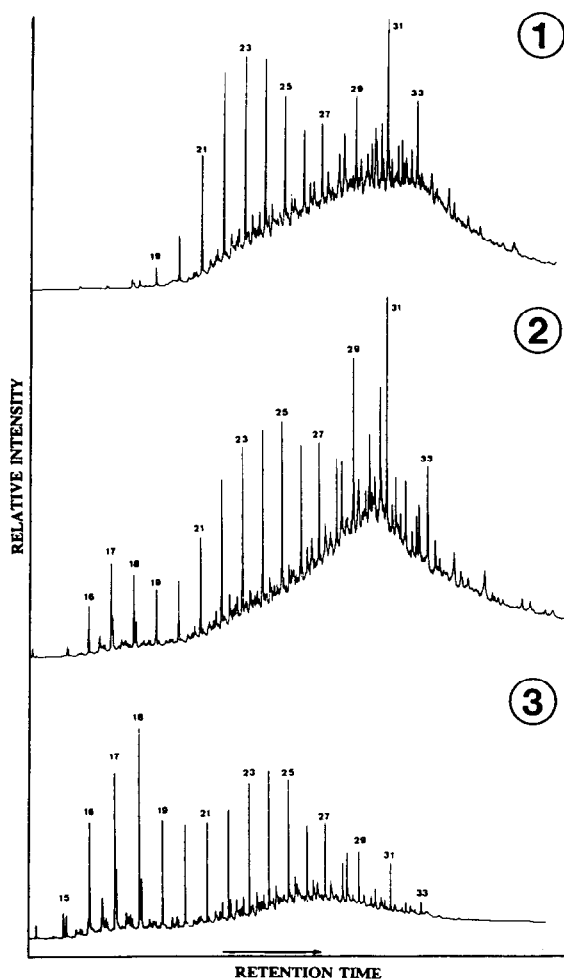

Fig. 1. GC profiles of the aliphatic hydrocarbon mixtures corresponding to three glass-fibre filter aliquots analysed (1) a few days after deep-frozen storage, (2) after 1 year and (3) after 2 years of ambient temperature storage. Peak numbers refer to n-alkane carbon number. Pr = Pristane; Ph = phytane.

hydrocarbon composition of filter aliquots analysed a few days after collection and after 1 and 2 years of storage at ambient temperature are compared.

The GC profile of the aliquot analysed after collection is dominated by a bimodal n-alkane distribution ranging between the C_{19} and C_{33} homologues with no even/odd carbon number predominance in the first mode (C_{19}–C_{27}) and with odd-to-even carbon number predominance in the second mode (C_{27}–C_{33}). These n-alkanes

overlie an important unresolved complex mixture (UCM) of hydrocarbons, which constitutes one of the most distinct features of this type of sample. Two types of sources are represented in this aliphatic hydrocarbon fraction, the first modal distribution of n-alkanes and the UCM correspond to petrogenic residues and vehicular exhausts [7,8], and the n-alkanes defining the second mode originate from higher plant waxes [9].

The filter aliquot stored at ambient temperature for 2 years exhibits a very distinct hydrocarbon composition (Fig. 1). An additional modal distribution of C_{15}–C_{20} n-alkanes is now present and dominates the whole GC profile. This distribution of shorter chain length homologues exhibits no even/odd carbon number preference and occurs together with pristane and phytane. The other major change concerns the practical disappearance of the UCM. The aliquot corresponding to 1 year of storage at ambient temperature represents an intermediate situation in which the C_{15}–C_{20} n-alkane mode is present but not dominant and a considerable UCM can still be observed. In quantitative terms, the n-alkanes in the aliquots corresponding to 1 and 2 years of storage represent about 70 and 50% of those present in the original mixture.

The modal n-alkane distribution eluting in the C_{15}–C_{20} range has not been observed in any of the aerosol samples collected in Barcelona and stored in deep-frozen conditions [5]. In fact, it may rarely be found in high proportion in aerosols because these lower-molecular-mass hydrocarbons are usually associated to the gas phase [10]. This type of distribution is characteristic of microbial inputs [11,12], and its occurrence may be indicative of microbially mediated post-sampling transformations. Microbial reworking of hydrocarbon mixtures during storage has also been observed in sediment samples although other n-alkane distributions were produced [1,2].

The other distinct feature of the filter samples stored at ambient temperature is the large decrease in UCM. This transformation contrasts with the biodegradation trends observed in many natural sedimentary environments where micro-

bial activity is reflected in n-alkane removal and the preservation of the UCM [13–15].

The changes in aromatic hydrocarbon content of these filter aliquots are illustrated in Fig. 2 by comparison of the GC profiles corresponding to analyses performed after collection and after 1 year of ambient temperature storage. The hydrocarbon mixtures displayed in Fig. 2A are characteristic of those found in the atmosphere of Barcelona [5]; the abundance of catacondensed structures and the predominance of parent over alkylated homologues are indicative of pyrolytic
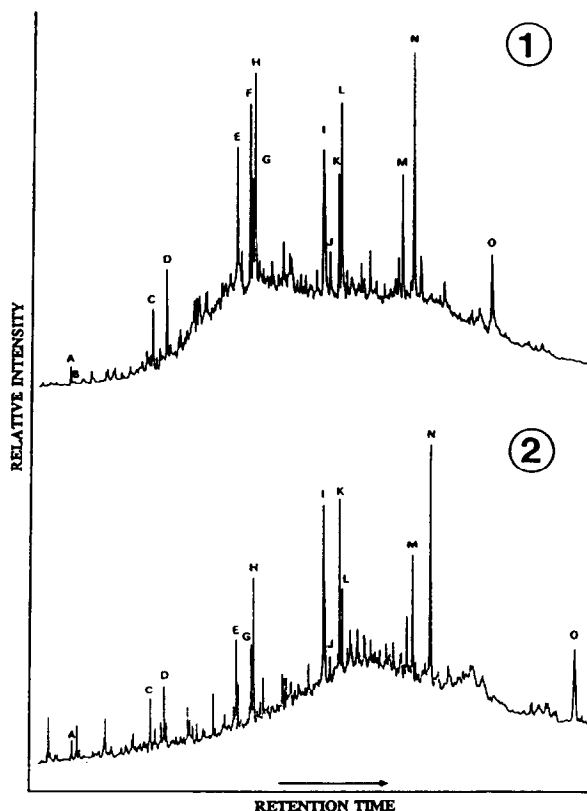

Fig. 2. GC profiles of the aromatic hydrocarbon mixtures corresponding to glass-fibre filter aliquots analysed (1) after a few days of deep-frozen storage and (2) after 1 year of ambient temperature storage. Lettered peaks are as follows: A = phenanthrene; B = anthracene; C = fluoranthene; D = pyrene; E = benzo[ghi]fluoranthene; F = 4(H)-cyclopenta-[cd]pyrene; G = benz[a]anthracene; H = chrysene/triphenylene; I = benzo[b/j]fluoranthene; J = benzo[a]fluoranthene; K = benzo[e]pyrene; L = benzo[a]pyrene; M = indeno[1,2,3-cd]pyrene; N = benzo[ghi]perylene; O = coronene.

origins [16,17]. The main differences between the two profiles (Fig. 2A and B) concern the disappearance of 4(H)-cyclopenta[cd]pyrene and the decrease in benzo[a]pyrene in the aliquot stored at ambient temperature. The lower concentration of these two compounds is likely to reflect their lower stability, especially in the case of 4(H)-cyclopenta[cd]pyrene [18,19]. In atmospheres with a high content of reactive gases such as O_3 or NO_x these compounds may even be degraded on the filter surface during collection [20,21]. However, extended degradation of aromatic hydrocarbons also involves the decay of benz[a]anthracene with respect to chrysene [18,22], which is not observed in the GC profiles of Fig. 2.

Vials

The post-sampling changes in composition of aliphatic hydrocarbons observed in the vials also lead to characteristic GC profiles which are different from those observed in the filters.

These profiles are illustrated in Fig. 3, in which the aliphatic hydrocarbons from two Barcelona sampling stations, Molina and Poble Nou, are compared with the distributions found in the same vials after 1 year of storage at ambient temperature. The chromatograms corresponding to long-term stored vials exhibit the same pattern, irrespective of the differences in composition of the original mixture. As described for the filters, the UCM has disappeared but now no modal profile of low-carbon-number n-alkanes is generated. Conversely, the final mixture of this type of transformations contains a distribution of C_{23}–C_{37} n-alkanes with low odd-to-even carbon number predominance and a distribution of C_{29}–C_{34} iso- and anteisoalkanes. In quantitative terms, the total n-alkanes in the vials stored at ambient temperature represent between 60 and 80% of those in the original mixture.

The distributions of C_{29}–C_{34} iso- and anteisoalkanes also exhibit a uniform pattern that is shown in Fig. 4 by enhancement of the GC–MS
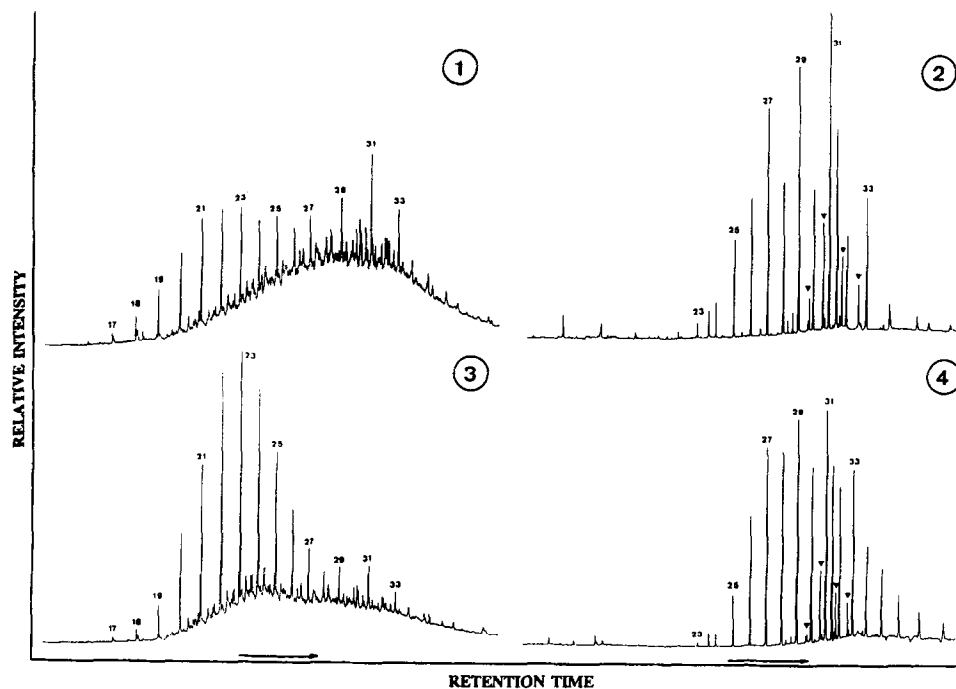

Fig. 3. GC profiles of the aliphatic hydrocarbon extracts from Molina (1 and 2) and Poble Nou (3 and 4) sampling stations stored in vials kept at −20°C (1 and 3) or ambient (2 and 4) temperature. Peak numbers refer to n-alkane carbon number. ▼ = Iso- and anteisoalkanes.
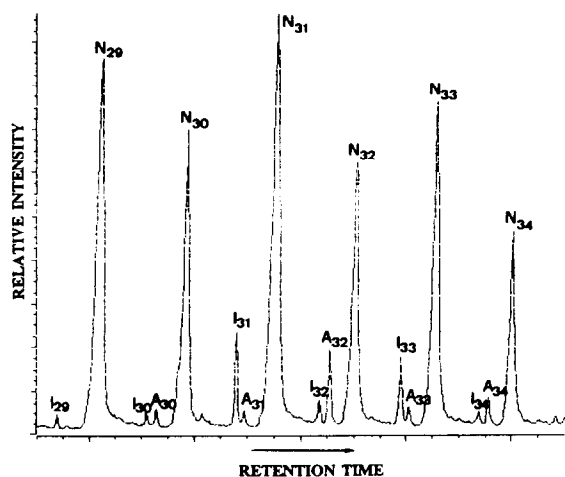
Fig. 4. Enhanced GC–MS total-ion current profile showing the composition of the C_{29}–C_{34} iso- and anteisoalkanes produced in the vials during storage. Peak numbers refer to carbon number.

total-ion trace. Representative mass spectra of iso and anteiso homologues are displayed in Fig. 5. The isoalkanes are recognized by their intense
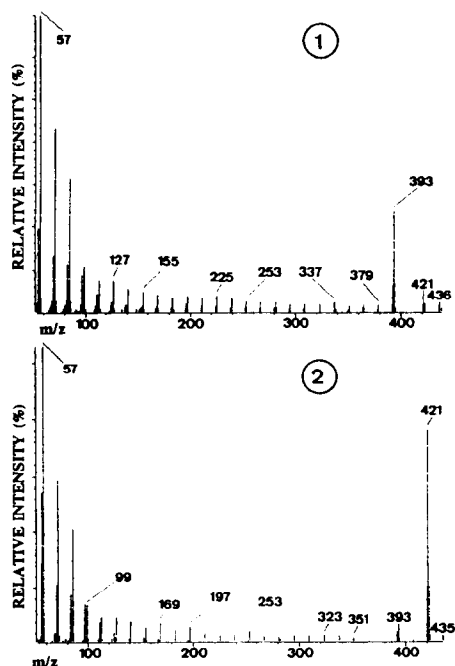

Fig. 5. Mass spectra of (1) isohentriacontane and (2) anteisodotriacontane.

$M - C_3H_7$ mass fragment and their distinct $M - CH_3$ peak [23]. The anteisoalkanes exhibit an intense $M - C_2H_5$ fragment together with a characteristic $M - C_4H_9$ ion [24]. Not even traces of these compounds are observed when GC analysis is performed a few days after separation of the aliphatic hydrocarbon fractions by the column chromatography procedure described in the Experimental section.

All these modifications suggest that microbial reworking is again at the origin of the transformation process. In this respect, the occurrence in aquatic environments of distributions of iso- and anteisoalkane homologues with carbon number higher than C_{22} has been attributed to
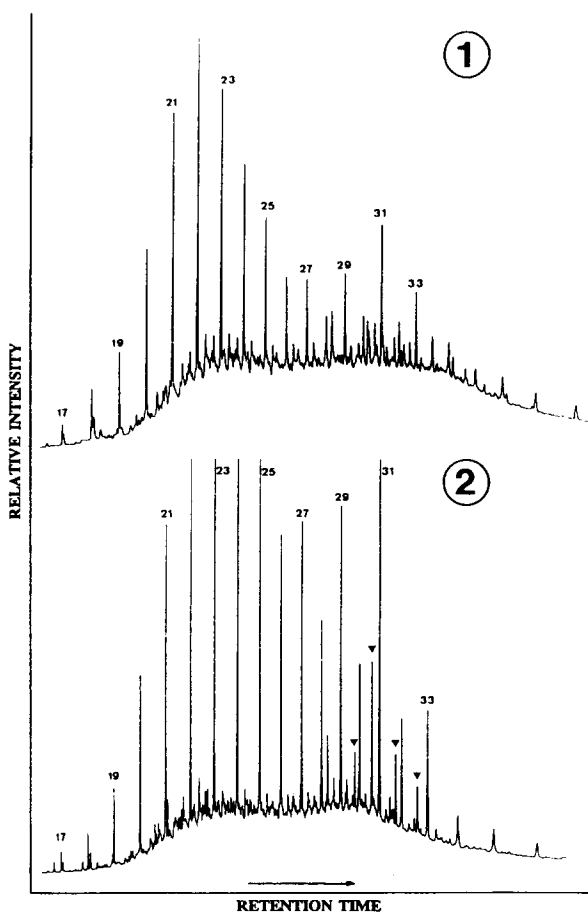

Fig. 6. GC profiles of aliphatic hydrocarbon fractions analysed (1) after separation by column chromatography and (2) after 1 year of storage at −20°C. Peak numbers refer to n-alkane carbon number. ▼ = Iso- and anteisoalkanes.

microbial reworking of petrogenic hydrocarbon mixtures [15,25].

These C_{29}–C_{34} iso- and anteisoalkanes are useful for the early identification of post-sampling changes because they may be detected at initial stages of the reworking process. This is illustrated in Fig. 6, in which the GC profiles corresponding to one aliphatic hydrocarbon fraction analysed after column chromatography isolation and after 1 year of storage at −20°C are shown. The general composition of n-alkanes has not been modified substantially, but these branched alkanes may already be identified. It is not the purpose of the present study to ascertain whether or not the differences between these two chromatographic traces correspond to processes effectively occurring at −20°C. It cannot be excluded that this sample was taken out of the freezer for very short periods. The aspect to be emphasized is the availability of two series of hydrocarbons indicative of changes in composition during storage that can be identified at early stages of transformation.

CONCLUSIONS

Major changes in the hydrocarbon composition of aerosol samples are observed in filter particulates and vial-contained extracts when the conditions of deep-frozen storage are not fulfilled. The modifications follow rather uniform trends, involving a strong depletion of the UCM and the generation of new distributions of straight-chain or branched alkanes, which suggests that the processes are mediated by the activity of microorganisms.

In the filters, a new distribution of C_{15}–C_{20} n-alkanes with no even/odd carbon number preference is produced. This distribution may dominate the GC profile of the hydrocarbon extract and is already observed at the initial stages of ambient temperature transformations. The polycyclic aromatic hydrocarbon mixtures of these filters exhibit a decrease of the less stable compounds such as the disappearance of 4(H)-cyclopenta[cd]pyrene and the decay of benzo-[a]pyrene.

In the vials, both the UCM and the lower carbon number n-alkanes are depleted, which

results in distributions of C_{29}–C_{34} n-alkanes with low odd-to-even carbon number preference. These distributions occur together with a characteristic mixture of C_{29}–C_{34} iso- and anteisoalkanes which is not present in the original hydrocarbon fractions and can be detected at the initial stages of transformation.

Early stages of post-sampling modifications of atmospheric hydrocarbons due to inadequate storage may therefore be detected by the presence of C_{15}–C_{20} n-alkanes with no even/odd carbon number preference in the filters and C_{29}–C_{34} iso- and anteisoalkanes in the vial-contained extracts.

REFERENCES

1 Y. Debyser, Geochim. Cosmochim. Acta, 39 (1975) 531.
2 J.O. Grimalt, E. Torras and J. Albaiges, Org. Geochem., 13 (1988) 741.
3 J.M. Anto, J. Sunyer, J.O. Grimalt, M. Aceves and Ch.E. Reed, N. Engl. J. Med., 321 (1989) 1128.
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 and J.O. Grimalt, J. Chromatogr., 607 (1992) 261.
6 M. Aceves, J.O. Grimalt, J. Albaiges, F. Broto, L. Comellas and M. Gassiot, J. Chromatogr., 436 (1988) 503.
7 B.R.T. Simoneit, Atmos. Environ., 18 (1984) 51.
8 C.V. Hampton, W.R. Pierson, D. Schuetzle and T.M. Harvey, Environ. Sci. Technol., 17 (1983) 699.
9 G. Eglinton and R. Hamilton, Science, 156 (1967) 1322.
10 A. Rosell, J.O. Grimalt, M.G. Rosell, X. Guardino and J. Albaiges, Fresenius' J. Anal. Chem., 339 (1991) 689.
11 J. Han and M. Calvin, Proc. Natl. Acad. Sci. U.S.A., 64 (1969) 436.
12 C.W. Bird and J.M. Lynch, Chem. Soc. Rev., 3 (1974) 309.
13 W. Giger, M. Reinhardt, C. Schaffner and W. Stumm, Environ. Sci. Technol., 8 (1974) 454.
14 S.C. Wakeham, Mar. Pollut. Bull., 7 (1976) 206.
15 I. Ramos, M. Fuentes, R. Mederos, J.O. Grimalt and J. Albaiges, Mar. Pollut. Bull., 20 (1989) 262.
16 R.E. LaFlamme and R.A. Hites, Geochim. Cosmochim. Acta, 42 (1978) 289.
17 B.R.T. Simoneit, Int. J. Environ. Anal. Chem., 29 (1985) 203.

18 R.M. Kamens, J.N. Fulcher and G. Zhishi, *Atmos. Environ.*, 20 (1986) 1579.

19 T. Nielsen, *Atmos. Environ.*, 22 (1988) 2249.

20 F.S.C. Lee, W.R. Pierson and J. Ezike, In A. Bjorseth and A.J. Dennis (Editors), *Polynuclear Aromatic Hydrocarbons: Chemical and Biological Effect*, Battelle Press, Columbus, OH, 1980, p. 543.

21 J. Peters and B. Seifert, *Atmos. Environ.*, 14 (1980) 117.

22 R.M. Kamens, Z. Guo, J.N. Fulcher and D.A. Bell, *Environ. Sci. Technol.*, 22 (1988) 103.

23 E.D. McCarthy and M. Calvin, *Tetrahedron*, 23 (1967) 2609.

24 R.B. Johns, T. Belsky, E.D. McCarthy, A.L. Burlingame, P. Haug, H.K. Schnoes, W. Richter and M. Calvin, *Geochim. Cosmochim. Acta*, 30 (1966) 1191.

25 G. Gassmann, *Mar. Pollut. Bull.*, 13 (1982) 309.