Gas chromatographic–mass spectrometric characterization of polycyclic aromatic hydrocarbon mixtures in polluted coastal sediments

Lourdes Canton

Department of Applied Chemistry, College of Chemistry, University of the Basque Country, P.O. Box 1072, 20080-Donostia (Spain)

Joan O. Grimalt*

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

ABSTRACT

A gas chromatographic–mass spectrometric (GC–MS) study of the polycyclic aromatic hydrocarbon (PAH) composition of a series of 72 marine sediments collected from the Guipuzcoan Coast (Bay of Biscay, Spain) showed three end-member distributions, one related to pyrolytic soot contributions (type A), another to combined paper mill effluents and soot inputs (type B) and the third to petrogenic residues (type C). The detailed composition of each of these end-member mixtures is given. Further examination of the PAH extracts by GC–negative ion chemical ionization MS illustrated several previously unreported selectivity effects such as enhancement of the parent PAHs eluting with longer retention times and the increased response factor of the alkyl homologues corresponding to the m/z 252, 276 and 302 hydrocarbons.

INTRODUCTION

Many polycyclic aromatic hydrocarbons (PAHs) are carcinogenic, mutagenic and/or co-carcinogenic [1,2]. These features and the fact that these toxic species are spread extensively in the environment have led to PAH monitoring being a priority task in many health risk assessment studies.

Among other environments, PAHs commonly occur in polluted coastal areas [3–7] as a result of intentional or accidental oil spillages, combustion of fossil fuels, waste discharges, automobile exhausts, forest fires, etc. The evaluation of the impact of these pollutants on marine life requires the assessment of concentrations and the recognition of their sources. In this respect, sediments are particularly useful for the identification of the predominant contributions because they act as pollutant sinks and provide an integrated picture of the events taking place in the water column. Thus, the analysis of these sedimentary mixtures of PAHs allows the characterization of the chronic inputs into the areas of concern and their corresponding sources.

Many techniques have been used for the analysis of environmental samples for PAHs, but no reported method separates and resolves adequately the entire PAH fraction on a microgram scale from samples that contain a very large excess of non-hydrocarbons. Gas chromatography (GC) coupled with mass spectrometry (GC–MS) is the technique that has provided the most conclusive and detailed data, and has been applied to the study of the composition of standard PAH mixtures such as coal extracts [8–10] and atmospheric particulates [11–15]. PAHs in sediments have been comparatively less studied and less information is available on the PAH mixtures defining the input sources in this environmental compartment.

We have performed an extensive study of the hy-

drocarbon pollutants along the Guipuzcoan Coast (Bay of Biscay, Spain). Among other aspects, this study encompassed the determination of PAH distributions corresponding to sediments collected in front of the discharge sites of six rivers (Bidasoa, Oria, Oyarzun, Urumea, Urola and Deba) along radials encompassing three water depths (10, 20 and 50 m) and four replicates (July 1986, November 1986, February 1987 and May 1987). The resulting PAH sedimentary mixtures were analysed by GC using different detectors and by GC–MS, which allowed the characterization of diverse end members corresponding to very dominant single pollutant inputs. The detailed composition of these sedimentary end members is described is this paper.

In addition to the usual electron impact mode (EI), GC–MS analyses of selected samples were performed using negative-ion chemical ionization (NICI), which provided several interesting selectivity effects. The usefulness of NICI for the description of sedimentary PAHs is also considered.

EXPERIMENTAL

Materials

Pestipur-grade *n*-hexane and methanol were purchased from SDS (Peypin, France), Resi-analyzed grade dichloromethane from Baker (Phillipsburg, NJ, USA), analytical-reagent grade acetone from Carlo Erba (Milan, Italy), analytical-reagent grade hydrochloric acid (25%), neutral silica gel (Kieselgel 40, 70–230 mesh), alumina (aluminium oxide 90 active, 70–230 mesh) and copper from Merck (Darmstadt,Germany), potassium hydroxide from Fluka (Buchs, Switzerland) and Soxhlet thimbles from Schleicher and Schüll (Dassel, Germany).

Potassium hydroxide was cleaned by sonication in dichloromethane Silica gel, alumina and the Soxhlet thimbles were extracted with dichloromethane–methanol (2:1, v/v) in a Soxhlet apparatus for 24 h. After solvent evaporation, the silica and 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. Copper was activated with two rinses with 10% (w/w) hydrochloric acid (5 min each) and prepared for sample desulphurization by a series of successive rinses using Milli-Q-grade water, acetone and *n*-hexane (two rinses with each).

All organic solvents were distilled on a 1-m packed column (Raschig) equivalent to twelve theoretical plates, with a reflux ratio of 12:1. 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 2.5 μl should result in chromatograms with no unresolved GC envelope and only very 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 0.08 ng/g when referred to 30 g of sediment.

Sampling, extraction and fractionation

Surface sediments were taken by gravity coring from the R/V Elorrio and stored at −20°C in the dark. The upper 3 cm were cut prior to analysis and Soxhlet extracted with 150 ml of dichloromethane–methanol (2:1) for 36 h. The extract was vacuum evaporated to 2 ml and hydrolysed overnight with 35 ml of 6% potassium hydroxide–methanol. The neutral fraction was recovered with *n*-hexane (3 × 30 ml) and desulphurized with activated copper. The volume of this fraction was again vacuum evaporated to 0.5 ml and fractionated by column chromatography according to previously established methods [16]. A column filled with 8 g each of 5% water-deactivated alumina (top) and silica (bottom) was used. The PAHs were collected in a third fraction of 40 ml of dichloromethane–*n*-hexane (20:80) after elution with 20 ml of *n*-hexane (first fraction) and dichloromethane in *n*-hexane (10:90) (second fraction). These PAH fractions were vacuum and nitrogen concentrated almost to dryness and the residues were dissolved in *n*-hexane.

Instrumental analysis

All samples were analysed by GC with a Perkin-Elmer Model 8310 instrument equipped with a split–splitless injector and with flame ionization detection (FID). The separation was carried out on a 30 m × 0.32 mm I.D. SPB-5 (film thickness 0.25 μm) fused-silica capillary column (Supelco, Bellefonte, PA, USA). Injections were made in the splitless mode (split valve closed for 48 s; hot needle technique) with the column held at 60°, then heated to 300°C at 6°C/min. The carrier gas was hydrogen (0.5 m/s linear velocity). The injector and detector were maintained at 300 and 330°C, respectively. Ni-

trogen was used as make-up gas (30 ml/min). The detector gas flows were hydrogen 30 ml/min and air 300 ml/min.

Selected samples were analysed by GC with a Hewlett-Packard Model 5890A chromatograph equipped with a split–splitless injector and with electron-capture detection (ECD). The chromatographic conditions were the same as described above except that helium was used as the carrier gas.

Selected samples were also analysed by GC–MS using a Hewlett-Packard Model 5995 instrument coupled with an HP-300 data system. The mass spectrometer temperatures were as follows: transfer line, 300°C; ion source, 200°C; and analyser, 230°C. Data were acquired in the electron impact (EI) mode (70 eV), scanning from 50 to 650 mass units at 1 s per decade. Helium was used as the carrier gas and the other chromatographic conditions were the same as described above.

Alternatively, some samples were analyzed by GC–MS using a Hewlett-Packard Model 5998A instrument coupled with an HP-300 data system. Negative ions were recorded in the chemical ionization mode (NICI) [reagent gas methane, 1.5 Torr (199.98 Pa)]. The mass spectrometer temperatures were as follows: transfer line, 300°C; ion source 150°C; and analyser 130°C. The scan mode and chromatographic conditions were the same as described for GC–EI-MS.

Quantification

Compound identification was based on the GC–MS data and on co-injection with authentic standards. The predominant hydrocarbons were measured from the GC profiles using an external standard containing phenanthrene, anthracene, fluoranthene, benz[a]anthracene, retene, benzo[a]pyrene, perylene, indeno[1,2,3-cd]pyrene, benzo[ghi]perylene, dibenzo[a,h]anthracene and coronene. The unresolved complex mixture (UCM) of PAHs was integrated with a digital planimeter connected to a Hewlett-Packard Model 86 microprocessor and quantified according to the average response factor of phenanthrene, fluoranthene, benzo[a]pyrene and benzo[ghi]perylene. Samples and standards were repeatedly injected until less than 3–5% dispersion in the area measurements was obtained.

RESULTS AND DISCUSSION

Identification of PAH sources

Three main end-member PAH distributions were found in the sediments corresponding to the 72 samples considered in this study. Their composition is represented in Fig. 1 by the corresponding GC–MS total ion current traces. Table I gives the list of the peaks indentified in these samples and Table II shows the concentrations of the predominant PAHs.

Sample A is a sediment collected in May 1987 at a water depth of 10 m in the Deba transect. Its PAH distribution is that most abundantly found on the Guipuzcoan coast. Phenanthrene, fluoranthene, py-
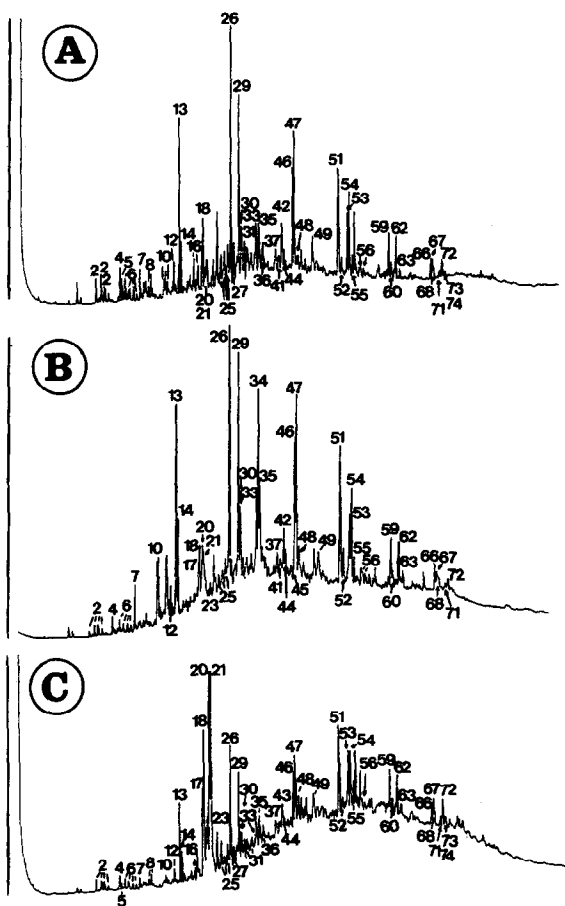

Fig. 1. Total ion current GC–EI-MS traces of the three end-member PAH mixtures identified in the sediments from the Guipuzcoan coast. The numbered peaks are identified in Table I.

TABLE I

POLYCYCLIC AROMATIC HYDROCARBONS IDENTIFIED IN THE SEDIMENTS COLLECTED FROM THE GUIPUZ-COAN COAST

No.	Compound	No.	Compound
1	Ionene	41	Benzo[b]naphtho[2,1-d]thiophene
2	Dimethylnaphthalene	42	Benzo[ghi]fluoranthene
3	Acenaphthylene	43	Benzo[c]phenanthrene
4	Acenaphthene	44	Benzo[b]naphtho[1,2-d]thiophene
5	Dibenzofuran	45	Benzo[b]naphtho[2,3-d]thiophene
6	Trimethylnaphthalene	46	Benz[a]anthracene
7	Fluorene	47	Chrysene/triphenylene
8	Methyldibenzofuran	48	Benzo[a]carbazole
9	Tetramethylnaphthalene	49	Methyl-228
10	Methylfluorene	50	Dimethyl-228
11	Dimethyldibenzofuran	51	Benzo[b/j/k]fluoranthene
12	Dibenzothiophene	52	Benzo[a]fluoranthene
13	Phenanthrene	53	Benzo[e]pyrene
14	Anthracene	54	Benzo[a]pyrene
15	Dimethylfluorene	55	Perylene
16	Methyldibenzothiophene	56	Methyl-252
17	3-Methylphenanthrene	57	Dibenz[a,j]anthracene
18	2-Methylphenanthrene	58	Dimethyl-252
19	4H-Cyclopenta[def]phenanthrene	59	Indeno[1,2,3-cd]pyrene
20	4/9-Methylphenanthrene	60	Dibenz[a,h]anthracene/pentaphene
21	1-Methylphenanthrene	61	Benzo[b]chrysene
22	Dimethyldibenzothiophene	62	Benzo[ghi]perylene
23	4,5-Dihydropyrene	63	Anthanthrene
24	Ethylphenanthrene	64	Methyl-276
25	Dimethylphenanthrene	65	Dimethyl-276
26	Fluoranthene	66	Dibenzo[e,l]pyrene
27	Trimethyldibenzothiophene	67	Naphtho[1,2-a]pyrene
28	Benzoxanthene	68	Naphtho[2,3-a]pyrene
29	Pyrene	69	Coronene
30	Benzo[b]naphtho[2,3-d]furan	70	Naphtho[1,2-e]pyrene
31	Trimethylphenanthrene	71	Dibenzo[a,e]fluoranthene
32	Methyl-202	72	Dibenzo[a,f]fluoranthene
33	Benzo[a]fluorene	73	Dibenzo[a,j]fluoranthene
34	Retene	74	Dibenzo[a,k]fluoranthene
35	Benzo[b]fluorene	75	Dibenzo[a,l]fluoranthene
36	Ethylmethyl-4H-cyclopenta[def]phenanthrene	76	Dibenzo[b,e]fluoranthene
37	Dimethyl-202	77	Methyl-302
38	11H-Benzo[a]fluoren-11-one	78	Dimethyl-302
39	7H-Benzo[c]fluoren-7-one	79	m/z 326
40	11H-Benzo[b]-fluoren-11-one	80	m/z 328

rene, benz[a]anthracene, chrysene + triphenylene, benzofluoranthenes, benzo[a]pyrene, benzo[e]pyrene, indeno[1,2,3-cd]pyrene and benzo[ghi]perylene constitute the predominant compounds. The abundance of catacondensed structures and the predominance of parent hydrocarbons over alkylated homologues indicate a pyrolytic origin [17,18]. In principle, this origin may include a wide range of sources such as soots from car emissions, power plants, wood and coal combustion products and coal tars. The assignment of a few of these specific sources to the composition of type A sediments requires a more detailed comparison of the PAH distributions.

The PAH mixtures from car emissions and urban aerosols exhibit a high proportion of cyclopenta-

TABLE II

CONCENTRATIONS OF THE PREDOMINANT POLYCYCLIC AROMATIC HYDROCARBONS IN THE MODEL SEDIMENTARY ENVIRONMENTS CORRESPONDING TO FIG. 1

No.	Compound	Concentration (ng/g)		
		Sample type[a]		
		A	B	C
13	Phenanthrene	57	71	20
14	Anthracene	17	24	6
17	3-Methylphenanthrene	17	8	22
18	2-Methylphenanthrene	25	13	40
20	4/9-Methylphenanthrene	5	13	100
21	1-Methylphenanthrene	5	11	100
26	Fluoranthene	93	100	30
29	Pyrene	67	87	25
30	Benzo[b]naphtho[2,3-d]furan	17	22	4
33	Benzo[a]fluorene	16	27	6
34	Retene	1	76	1
35	Benzo[b]fluorene	16	33	7
46	Benz[a]anthracene	28	54	15
47	Chrysene + triphenylene	50	65	19
51	Benzo[b/j/k]fluoranthene	39	87	33
52	Benzo[a]fluoranthene	6	16	1.5
53	Benzo[e]pyrene	22	41	18
54	Benzo[a]pyrene	30	60	19
55	Perylene	6	14	8
59	Indeno[1,2,3-cd]pyrene	18	38	16
62	Benzo[ghi]perylene	18	35	17
	Unresolved complex mixture of PAH	1000	2700	10 000

[a] See text.

[cd]pyrene and a high benzo[a]pyrene to benzo[e]pyrene ratio [19,20], two features that are not observed in sample A. However, these differences have a limited assignment value because benzo[a]pyrene and, particularly, cyclopenta[cd]pyrene are unstable in the environment [21,22]. Other more stable features of the PAHs produced by traffic activities involve the predominance of pyrene vs. fluoranthene and benzo[ghi]perylene vs. indeno[1,2,3-cd]pyrene. type A sediments exhibit an inverse relationship between these m/z 202 PAHs and almost the same amount of benzo[ghi]perylene and indeno[1,2,3-cd]pyrene, which establishes a significant difference between the PAH distributions of these sediments and possible crude oil combustion or traffic sources.

The fluoranthene to pyrene and the indeno[1,2,3-cd]pyrene to benzo[ghi]perylene ratios of sample A are similar to those found in the PAH mixtures of coal tars and coal soots [9,23–26]. A close look at the m/z 226 and 228 homologues allows a more precise source characterization. Thus, benz[a]anthracene predominates over chrysene + triphenylene in coal tars whereas, as observed in sample A, chrysene + triphenylene is more abundant in coal soots. The predominant m/z 226 PAH in this sample is benzo[ghi]fluoranthene, which is also in agreement with the coal soot distributions. Conversely, the major m/z 226 aromatic hydrocarbon in the coal tars is cyclopenta[cd]pyrene, a compound that is below the detection limit in type A sediments.

Sample B corresponds to a sediment collected in July 1986 at a water depth of 50 m in the Oyarzun transect. The PAH distributions of samples A and B are similar but the high proportion of retene in the latter represents a very distinct feature. Retene is usually a transformation product of diterpenoids

with an abietane skeleton, particularly dehydro-abietic acid. In aquatic environments, the presence of large amounts of retene and dehydroabietic acid may be indicative of effluents from kraft paper milling processes [27,28]. This applies to the Oyarzun River, which contains several paper industries near the mouth. The PAH distributions of the sediments located in front of this river are therefore indicative of paper mill effluents and soot contributions.

Sample C corresponds to a sediment collected in February 1987 at a water depth of 20 m in the Oria transect. Its PAH distribution strongly contrasts with those of samples A and B by the predominance of methylphenanthrenes and the high UCM. These two features are indicative of petrogenic inputs [29,30]. In this respect, the vehicular emissions are characterized by alkylphenanthrene distributions maximized at the C_1 homologues [18]. The predominance of 4/9- and 1- methylpenanthrenes over the 3- and 2-methyl isomers is probably indicative of partial biodegradation of these crude oil residues

[31]. In addition to these petrogenic hydrocarbons, the pyrolytic PAH pattern described in sample A also occurs as a minor contribution in type C sediments.

Electron impact vs. GC–MS negative-ion chemical ionization

The PAH composition of the predominant type A sediments has been investigated in more detail using GC–NICI-MS. Fig. 2 displays the gas chromatographic profiles obtained by FID, ECD and MS in the EI and NICI modes from the PAH fraction of a sediment sample collected in July 1986 at a water depth of 20 m in the Bidasoa transect. As expected, the strongest contrast is observed between the FID and ECD traces. In fact, the ECD profile corresponds to a series of brominated compounds that also elute with the PAH in the column fractionation procedure of the sample extracts. These brominated compounds are also detected in the NICI trace.
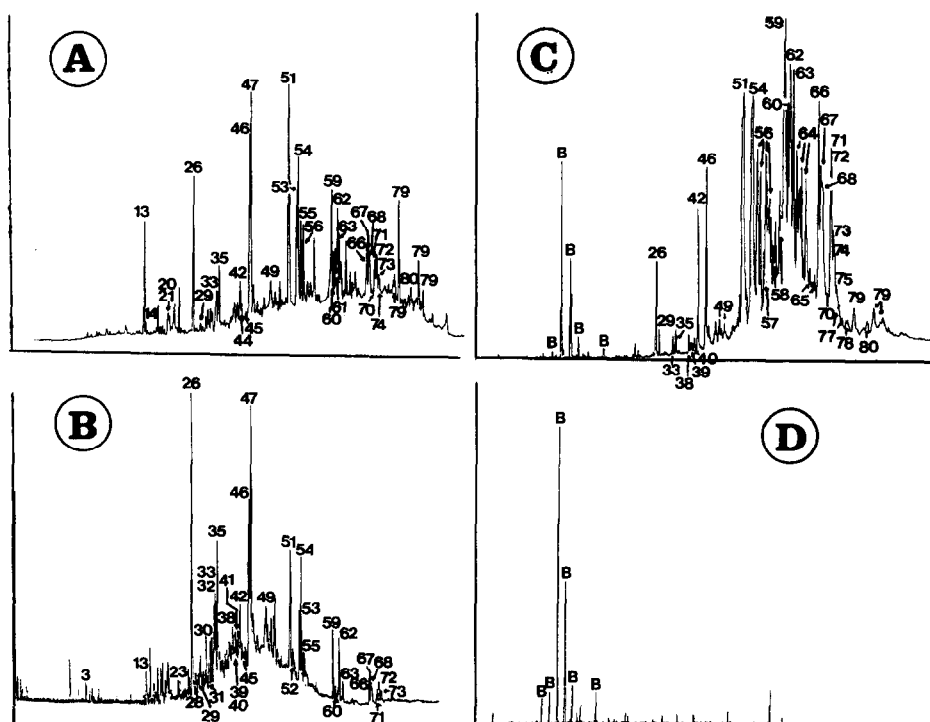

Fig. 2. GC profiles of a type A PAH sedimentary mixture recorded with (A) flame ionization detection, (B) electron impact and (C) negative-ion chemical ionization mass spectrometry and (D) electron-capture detection. The numbered peaks are identified in Table I. B refers to a series of brominated compounds.

The PAH composition is represented by the FID, EI and NICI traces. The FID and EI profiles show the closest similarity and NICI selectivity enhances the compounds eluting at higher retention times. These NICI-selective effects are also important at the level of isomeric mixtures. As described previously [32,33], Fig. 2 shows a strong enhancement of benzo[a]pyrene vs. benzo[e]pyrene and of benz-[a]anthracene vs. chrysene + triphenylene and a high sensitivity for benzo[ghi]fluoranthene. NICI is also very sensitive to many nitrogen-containing PAHs [34,35]. The absence of these heteroatomic hydrocarbons in the GC–MS profile displayed in Fig. 2 indicates that these compounds are not very significant in the PAH fractions isolated from these pyrolytic type A sediments.

In addition to these previously described selectivity features, further high-molecular-weight enhancement effects have been observed in this study. Thus, the m/z 302 compounds appear as one of the most prominent group of peaks in the NICI trace whereas these compounds are usually detected as minor peaks in the FID and GC–EI-MS traces of the PAH extracts [10]. These effects also allow the determination of the GC–MS profiles of isomeric mixtures of high molecular weight, such as the m/z 326 and 328 PAHs. To date, the identification of these hydrocarbons in environmental samples has

been performed by direct probe introduction MS in the EI mode [11,36].

The higher NICI response factor for high-molecular-weight PAHs also includes the alkylated homologues. This effect is illustrated in Fig. 3 by means of the mass fragment ions corresponding to the m/z 252, 276 and 302 series. The study of the alkylated series of these PAHs is difficult because they are essentially produced in combustion processes which, at the same time, give rise to distributions with a strong predominance of parent vs. alkylated homologues. As shown in Fig. 3, sensitive and selective methods such as GC–NICI-MS appear to be the most suitable techniques for their structural elucidation.

CONCLUSIONS

Three main end-member PAH distributions have been identified by GC–EI-MS analysis of the sediments of the Guipuzcoan coast. The type A mixtures correspond to pyrolytic soot contributions and are characterized by the predominance of phenanthrene, fluoranthene, pyrene, benz[a]anthracene, chrysene + triphenylene, benzofluoranthenes, benzo[a]pyrene, benzo[e]pyrene, indeno[1,2,3-cd]pyrene and benzo[ghi]perylene. The type B sediments exhibit distributions with a high proportion of retene in addition to the above-described pyrolytic PAHs. Finally, the type C mixtures are predominated by methylphenanthrenes and contain a high UCM that is found together with a minor proportion of pyrolytic PAHs. The analysis by GC–NICI-MS of some type A samples revealed selectivity effects not reported in previous studies. These include the enhancement of the parent PAHs eluting with longer retention times, such as the m/z 302, 326 and 328 isomers, and an increased response factor of the alkylated PAHs corresponding to m/z 252, 276 and 302.
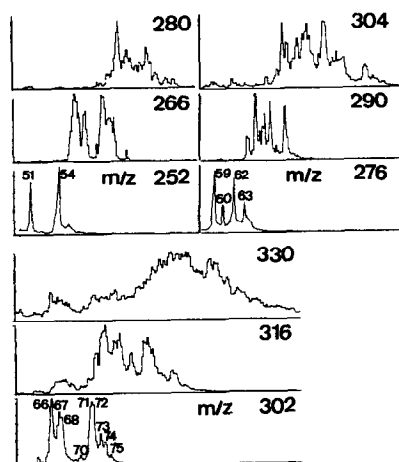
Fig. 3. Representative negative-ion chemical ionization mass fragmentograms of a type A PAH sedimentary distribution. The numbered peaks are identified in Table I.

REFERENCES

1 M. J. Suess, *Sci. Total Environ.*, 6 (1976) 239.
2 L. Van Vaeck and A. Van Cauwenberghe, *Environ. Sci. Technol.*, 19 (1985) 707.
3 R. J. Law, *Mar. Pollut. Bull.*, 12 (1981) 153.
4 J. D. Smith and W. A. Maher, *Aust. J. Mar. Freshwater Res.*, 35 (1984) 119.
5 A. Saliot, C. Andrie, R. Ho and J. C. Marty, *Int. J. Environ. Anal. Chem.*, 22 (1985) 25.
6 P. D. Dunn and H. F. Stich, *J. Fish. Res. Board Can.*, 33 (1976) 2040.
7 I. Ramos, M. Fuentes, R. Mederos, J. O. Grimalt and J. Albaigés, *Mar. Pollut. Bull.*, 20 (1989) 262.
8 W. J. Simonsick, Jr., and R. A. Hites, *Anal. Chem.*, 56 (1984) 2749.
9 S. A. Wise, B. A. Benner, G. D. Byrd, S. N. Chesler, R. E. Rebbert and M. M. Schantz, *Anal. Chem.*, 60 (1988) 887.
10 S. A. Wise, B. A. Benner, H. Liu, G. D. Byrd and A. Colmsjo, *Anal. Chem.*, 60 (1988) 630.
11 T. Romanowski, W. Funcke, J. Konig and E. Balfanz, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 4 (1981) 209.
12 U. R. Stenberg and T. E. Alsberg, *Anal.Chem.*, 53 (1981) 2067.
13 T. Ramdahl, G. Becher and A. Bjorseth, *Environ. Sci. Technol.*, 16 (1982) 861.
14 M. Oehme, *Anal. Chem.*, 55 (1983) 2290.
15 H. Stray, A. Mikalsen, B. Sonsterud and M. Oehme, *J. Chromatogr.*, 349 (1985) 331.
16 M. Aceves, J. O. Grimalt, J. Albaigés, F. Broto, L. Comellas and M. Gassiot, *J. Chromatogr.*, 436 (1988) 503.
17 R. E. LaFlamme and R. A. Hites, *Geochim. Cosmochim. Acta*, 42 (1978) 289.
18 B. R. T. Simoneit, *Int. J. Environ. Anal. Chem.*, 22 (1985) 203.
19 A. Rosell, J. O. Grimalt, M. G. Rosell, X. Guardino and J. Albaigés, *Fresenius' J. Anal. Chem.*, 339 (1991) 689.
20 G. Grimmer, J. Jacob, K-W. Naujack and G. Dettbarn, *Fresenius' Z. Anal. Chem.*, 309 (1981) 13.
21 R. M. Kamens, Z. Guo, J. N. Fulcher and D. A. Bell, *Environ. Sci. Technol.*, 22 (1988) 103.
22 T. Nielsen, *Atmos. Environ.*, 22 (1988) 2249.
23 G. Grimmer, J. Jacob, K.-W. Naujack and G. Dettbarn, *Anal. Chem.*, 55 (1983) 892.
24 G. Grimmer, J. Jacob, G. Dettbarn and K.-W. Naujack, *Fresenius' Z. Anal. Chem.*, 322 (1985) 595.
25 R. C. Lao, R. S. Thomas and J. L. Monkman, *J. Chromatogr.*, 112 (1975) 681.
26 E.-A. Ratajczak, E. Ahland, G. Grimmer and G. Dettbarn, *Staub Reinhalt. Luft*, 44 (1984) 505.
27 M. F. Fox, in L. H. Keith (Editor), *Identification and Analysis of Organic Pollutants in Water*, Ann Arbor Sci. Publ., Ann Arbor, MI, 1976, p. 641.
28 L. H. Keith, in L. H. Keith (Editor), *Identification and Analysis of Organic Pollutants in Water*, Ann Arbor Sci. Publ., Ann Arbor, MI, 1976, p. 671.
29 W. W. Youngblood and M. Blumer, *Geochim. Cosmochim. Acta*, 39 (1975) 1303.
30 J. W. Farrington and B. W. Tripp, *Geochim. Cosmochim. Acta*, 41 (1977) 1627.
31 J. M. Bayona, J. Albaigés, A. M. Solanas, R. Parés, P. Garrigues and M. Ewald, *Int. J. Environ. Anal. Chem.*, 23 (1986) 289.
32 L. R. Hilpert, G. D. Byrd and C. R. Vogt, *Anal. Chem.*, 56 (1984) 1842.
33 M. Oehme, *Anal. Chem.*, 55 (1983) 2290.
34 M. Oehme, *Chemospere*, 14 (1985) 1285.
35 J. M. Bayona, D. Barceló and J. Albaigés, *Biomed. Environ. Mass Spectrom.*, 16 (1988) 461.
36 W. Giger and M. Blumer, *Anal. Chem.*, 46 (1974) 1663.