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IDENTIFICATION OF TRACE ORGANIC COMPOUNDS IN DIMETHYL SULPHOXIDE SOLUTION USING HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY AND GAS CHROMATOGRAPHY–MASS SPECTROMETRY

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SUMMARY

The use of dimethyl sulphoxide (DMSO) as a solvent causes difficulties in the analysis of trace organics in complex mixtures by gas chromatography (GC) and gas chromatography–mass spectrometry (GC–MS). The high boiling point of DMSO causes problems in the concentration of trace organics. A semi-preparative high-performance liquid chromatographic (HPLC) separation procedure with gradient elution was employed to provide a means of solvent exchange for the analysis of organic mixtures in DMSO. This method was demonstrated using a DMSO solution of an extract of airborne particulate matter. After HPLC separation, a number of polynuclear aromatic hydrocarbons and their derivatives were identified by GC–MS and GC analysis.

INTRODUCTION

Dimethyl sulphoxide (DMSO) is a very popular solvent and its use in solvent partitioning separations has been reported[1]. DMSO is preferred as a solvent in many biochemical tests owing to its inertness. Recently, a short-term toxicity test using human blood leukocytes and high-resolution two-dimensional electrophoresis (HR2DE) was developed to evaluate directly the effects of environmental organic pollutants on human health[2]. In this test, the organic pollutants are first dissolved in DMSO.

This toxicity test was applied to an organic extract of airborne particulate matter in Oslo, and the analysis of the components of the same extract was undertaken in Waterloo. Although DMSO is a desirable solvent in the HR2DE test, its high boiling point (190°C) caused problems in chemical analysis.

Most organic compounds adsorbed on airborne particulates are present in very low concentrations. To raise the amounts of organic compounds to the detection limit of the analytical method used, a pre-concentration step is needed and solvent

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reduction is most frequently employed. Normally, the solvent reduction is first performed by rotary evaporation in a water-bath at *ca.* 50°C under aspirator vacuum. After being transferred into a Reacti-Vial, a volume of sample solution less than 100 μl is finally achieved by blowing a gentle stream of a high-purity inert gas across the top of the vial[3]. However, this procedure is not suitable for concentration of a sample solution with a high-boiling solvent such as DMSO. First, the temperature needed for the evaporation of DMSO could cause many other compounds to evaporate or decompose. Second, the use of an inert gas stream to reduce the volume of DMSO solution is not feasible because of the length of time that would be required. Further, a large amount of DMSO in the sample solution produces a broad solvent peak in gas chromatographic (GC) analysis, thus interfering with the analysis. Replacement of DMSO and reconstitution with another solvent having a low boiling point prior to detailed analysis is required for this study.

A high-performance liquid chromatographic (HPLC) technique has been employed in separations and analyses of trace organic compounds in various environmental samples, including drinking water[4], diesel exhaust particulates[5,6], municipal incinerator fly-ash[7] and fish samples[8]. About 50 polycyclic aromatic hydrocarbons (PAHs) have been identified in airborne particulate samples after HPLC separation of the extract mixtures[9–13].

In this study, an HPLC procedure with a semi-preparative normal-phase column and a ternary solvent gradient elution programme was employed for the solvent exchange of DMSO and fractionation of organic compounds in a complex mixture. This was demonstrated using a DMSO solution of an airborne particulate extract obtained in Oslo, Norway. The DMSO solvent and a large amount of hydrocarbons were separated from polycyclic aromatic compounds (PACs) by the HPLC procedure. Subsequently, the trace organic components in the solution with a new solvent were effectively concentrated. A number of PACs, many of which could not be seen in the DMSO solution, were identified in the extract of airborne particulates by gas chromatographic–mass spectrometric (GC–MS) analysis and GC analysis. Impurities generated from the sampling equipment were clearly isolated and identified.

EXPERIMENTAL

Reagents and standard chemicals

The solvents used were "distilled in glass", UV grade, from Caledon Laboratories. Most PAH standards used for compound identification were purchased from Aldrich (Montreal, P.Q., Canada) or Chem. Service (West Chester, PA, U.S.A.) and their purities were 95–99%.

Sample collection and extraction

The DMSO solution of the airborne particulate extract was received from the Institute of Clinical Biochemistry, University of Oslo, Norway. The airborne particulate sample was collected in the centre of Oslo. A standard High-Volume (Hi-Vol) sampler equipped with glass-fibre filters and a polyurethane plug was used for the collection of airborne particulate. A 8250 m^3 volume of air was drawn through the sampler and 656 mg of particulate matter were then obtained on the filter. After collection, the filter was cut into small pieces and placed in a glass thimble of an

all-glass Soxhlet extractor. Purified acetone was used for the extraction. The extract was concentrated to a small volume and DMSO was then added as the major solvent. This DMSO solution of airborne particulate extract was first subjected to the HR2DE toxicity test in Oslo and then to the chemical characterization study in Waterloo, Canada. A DMSO solution of the extract of the glass-fibre filter and polyurethane plug from the particulate sampler was used as the blank for both the HR2DE test and the chemical analysis.

High-performance liquid chromatographic separation

Fractionation of the DMSO solution of the airborne particulate extract was performed with a Spectra-Physics SP-8000 HPLC system equipped with an SP-8400 UV–visible detector and an SP-4100 integrator. The monitoring wavelength was 254 nm. A normal phase, semi-preparative Spherisorb silica column (250 × 9.4 mm I.D.) (Terochem. Toronto, Canada) was used with a 140-μl sample loop.

A gradient elution programme with *n*-hexane, dichloromethane and acetonitrile was utilized to separate the DMSO solution of the airborne particulate extract into five fractions. The details of this elution programme have been published previously[7].

The DMSO sample was injected on to the HPLC column twice and the corresponding fractions obtained were combined. Each pooled fraction was first concentrated to about 10 ml in a round-bottomed flask by rotary evaporation under aspirator vacuum, and then transferred into a 25-ml pear-shaped flask and reduced to 1 ml by further evaporation under the same conditions. After transferring the fraction into a 1.0-ml calibrated Reacti-Vial, a final volume of 50 μl was achieved by gently blowing a stream of high-purity nitrogen across the top of the vial. The exception was HPLC fraction 5, where the final volume was 300 μl, owing to the elution of DMSO in that fraction. The concentrated fractions were stored in Reacti-Vials with PTFE-lined screw-caps in a freezer at −15°C. All HPLC fractions were analysed by GC–MS and high-resolution GC.

Prior to loading the sample, the HPLC system was cleaned by running a 60-minute gradient elution programme similar to the sample programme, and the sample loop was carefully cleaned with different solvents.

The DMSO solution of the extraction blank of sampling filter and plug underwent the same HPLC fractionation once, except that fractions 1 and 2 were combined in the collection, as were fractions 3 and 4.

Gas chromatographic–mass spectrometric analysis

Two GC–MS systems were used. A Finnegan Model 4021 was used at the Institute of Clinical Biochemistry, University of Oslo, Norway. This GC–MS system is equipped with an INCOS 2000 data system, capable of executing a modified probability based matching (PBM) search based on a library of 32 000 reference compounds. Electron-impact ionization was operated at 70 eV, and the mass analyser was scanned from 500 to 50 a.m.u. The chromatographic conditions were as follows: 30 m × 0.25 mm I.D. DB-5 fused-silica capillary column (FSCC) (J & W Scientific, Rancho Cardova, CA, U.S.A.); splitless injection; column temperature, programmed from 90 to 325°C at 4°C/min.

A Hewlett-Packard HP5992 GC–MS–data station system equipped with a lim-

ited special library of reference compounds was used at the University of Waterloo, Canada. An HP59916A glass capillary effluent splitter, interfacing the GC and MS instruments, allowed the carrier gas to enter the mass spectrometer at 0.5 ml/min. Electron-impact ionization at 70 eV was used, and the mass spectrometer was scanned from 500 to 50 a.m.u. at 300 a.m.u./sec. The chromatographic conditions were as follows: 30 m × 0.32 mm I.D. DB-5 FSCC; on-column injection; column temperature, programmed from 80 to 300°C at 6°C/min with initial 1 min and final 10 min isothermal periods. The flow-rate of helium carrier gas was 3 ml/min at room temperature.

Gas chromatographic analysis

GC analysis was conducted using a Hewlett-Packard HP5880A gas chromatograph equipped with a flame-ionization detector. A Hewlett-Packard cool on-column injector and the same column as used in GC–MS analysis were used on the HP5880A instrument. The GC conditions were as follows: injection port temperature, less than 50°C; column temperature, 80°C for 1 min, programmed to 300°C at 3°C/min, held at 300°C for 10 min; detector temperature, 350°C. The flow-rate of helium carrier gas was 3 ml/min at room temperature.

Based on the work of Lee and Vassilaros[14], a user-developed Basic programme stored in the GC microprocessor terminal allowed the calculation of the retention indices of PAHs in the sample injected[7]. These retention indices of PAHs and their derivatives were used to facilitate the identification of these compounds.

RESULTS AND DISCUSSION

After applying the conventional concentration procedure to the DMSO sample, the DMSO solution of the airborne particulate extract was injected on to the GC column. The gas chromatogram obtained is shown in Fig. 1. A very large solvent peak identified as DMSO is observed. The exact mechanism of elution of DMSO at such a low GC temperature (*ca.* 90°C) is not well understood, but the high boiling point of DMSO seems to cause it to elute gradually, resulting in a broad solvent peak. This tailing peak of DMSO covers some of the earlier peaks and is partly responsible for the heavy background in the gas chromatogram. Injection of a larger volume of sample solution was not feasible because of the background problem. From the gas chromatogram containing a few poorly resolved peaks, little information regarding the sample composition can be obtained.

The HPLC separation procedure provided an effective means of reconstituting the sample solution with other solvents having low boiling points. Among the five HPLC fractions collected, the major solvents in fractions 1–4 are either *n*-hexane or dichloromethane, which are the mobile phases in the HPLC separation. *n*-Hexane and dichloromethane have such low boiling points that the volumes of fractions 1–4 were easily reduced to 50 μl using the conventional concentration method previously described. DMSO eluted in fraction 5, and was therefore completely isolated from the other four fractions.

The components in fractions 1–4 were *ca.* 6 times more concentrated than they were in the DMSO solution. The gas chromatograms of fractions 1, 2 and 3 are illustrated in Figs. 2a, 3a and b, respectively. Fig. 2b shows the gas chromatogram of fraction 5, where a broad peak of DMSO can be observed.

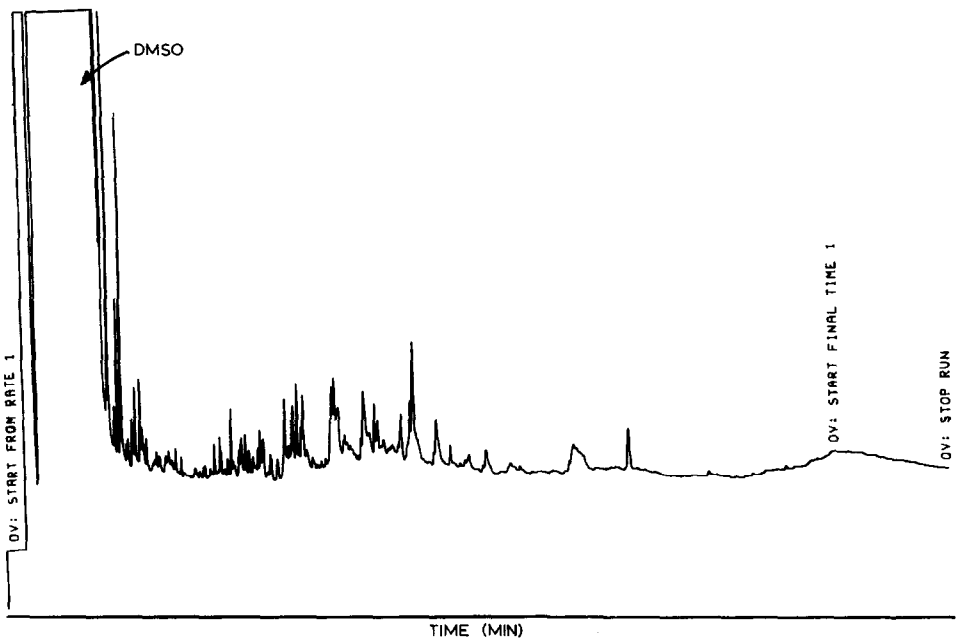

Fig. 1. Gas chromatogram of concentrated DMSO solution of Oslo airborne particulate extract. Chromatographic conditions: 30 m × 0.32 mm I.D. DB-5 fused-silica column; temperature, 80°C for 1 min, programmed to 300°C at 3°C/min.

According to our previous study[7], this HPLC separation was designed to separate organic compounds into different classes based on their relative polarities. The major components in each fraction were as follows: aliphatic hydrocarbons in fraction 1, PACs distributed among fractions 2–4 and more polar components in fraction 5. As a number of PACs have been linked with direct and indirect mutagenicity, fractions 2–4 are of great interest in the detailed analysis. In this procedure the interference of DMSO has been essentially eliminated.

The presence of a large amount of hydrocarbons in the Oslo airborne particulate sample is another factor causing the heavy background and poor peak resolution shown in Fig. 1. The interference of hydrocarbons was also removed by eluting them into fraction 1. Fig. 2a illustrates the characteristic GC trace of the hydrocarbons in fraction 1. A series of normal alkanes is observed. Those hydrocarbons contain up to 30 or more carbon atoms and cover a wide range of boiling points.

After being separated from DMSO and hydrocarbons, the concentrated fractions 2–4 yielded good chromatograms with well resolved and sharp peaks. This resolution makes compound identification by GC–MS and GC analyses possible.

The details of the compound identification procedure have been described previously[7]. The preliminary identification was based on the mass spectra data of the sample components. The retention index data obtained from the high-resolution GC analysis of the sample provided complementary information for the identification. Other published information was used to facilitate the identification[9–13,15–17].

The major compounds identified in fraction 2 of the Oslo airborne particulate

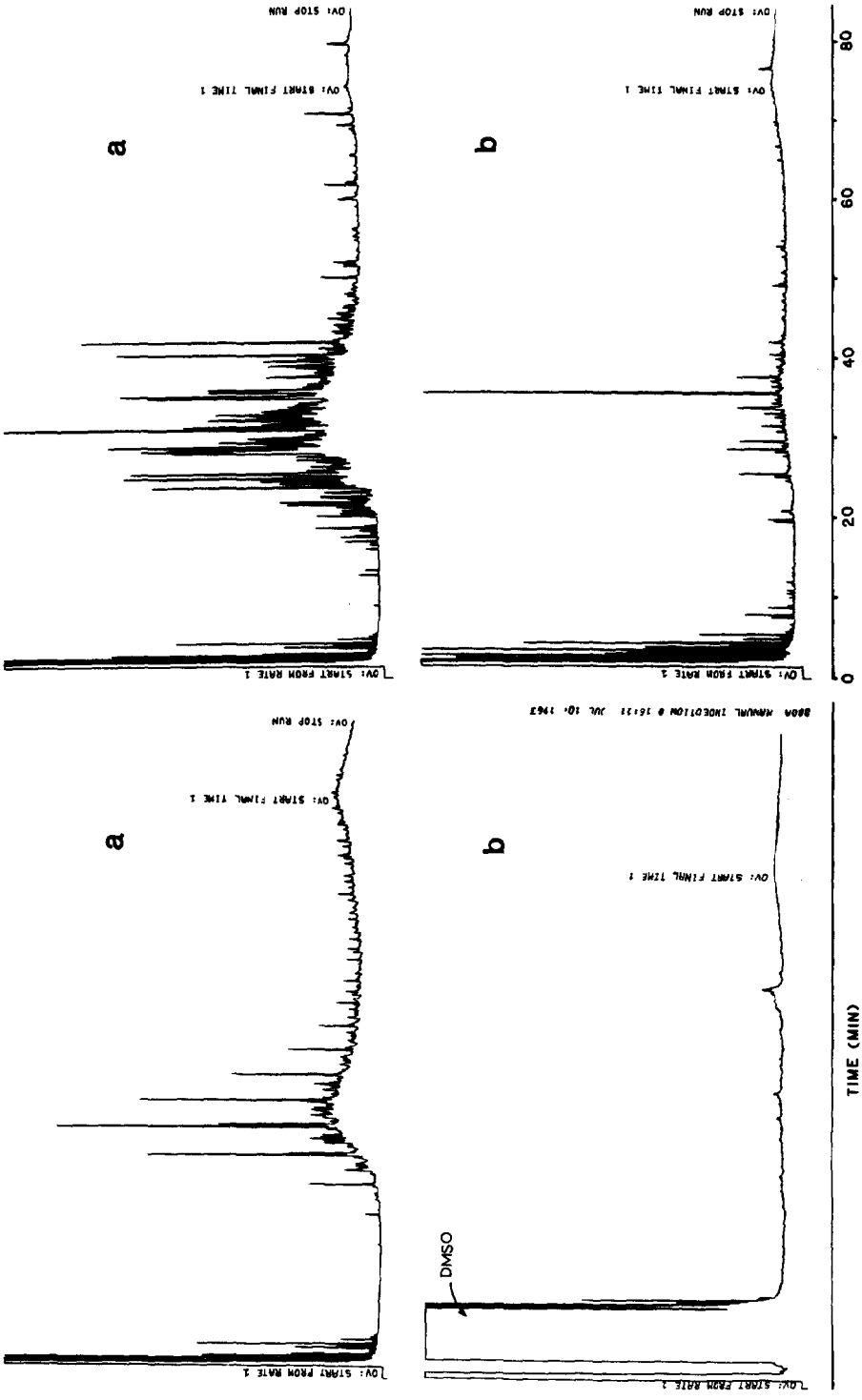

Fig. 2. Gas chromatograms of HPLC fractions of Oslo airborne particulate extract. (a) Fraction 1; (b) fraction 5. GC conditions as in Fig. 1.

Fig. 3. Gas chromatograms of HPLC fractions of Oslo airborne particulate extract. (a) Fraction 2; (b) fraction 3. GC conditions as in Fig. 1.

TABLE I

COMPOUNDS IDENTIFIED IN FRACTION 2 OF OSLO AIRBORNE PARTICULATE EXTRACT

No.	*Compound*	*Molecular weight*	*Retention time (min)*	*Retention index (standard deviation)*	*Published retention index**	*Method of identification***
1	2-Methylnaphthalene	142	12.81	217.00 (0.16)	218.14	a, b, c, d
2	1-Methylnaphthalene	142	13.44	219.83 (0.16)	221.04	a, b
3	1,2-Dihydroacenaphthylene	154	16.05	231.65 (0.13)		a
4	Biphenyl	154	16.58	234.05 (0.13)	233.96	a, b, d
5	1- or 2-ethylnaphthalene	156	17.00	235.93 (0.13)	236	a, b
6	2-Methylbiphenyl	168	17.58	238.55 (0.12)	238.77	a, b
7	Dimethylnaphthalene	156	17.70	239.11 (0.13)		a
8	1,3-Dimethylnaphthalene	156	17.95	240.23 (0.12)	240.25	a, b
9	Dimethylnaphthalene	156	18.17	241.23 (0.12)	240	a
10	Dimethylnaphthalene	156	18.33	241.95 (0.11)	240	a
11	Acenaphthylene	152	18.69	243.59 (0.11)	244.63	a, b
12	(2-Propenyl)naphthalene or methylbiphenyl	168	20.09	249.89 (0.12)		a
13	(2-Propenyl)naphthalene or methylbiphenyl	168	20.21	250.44 (0.09)		a
14	C_3-Naphthalene	170	20.54	251.95 (0.10)		a, d
15	C_3-Naphthalene	170	20.90	253.58 (0.11)		a
16	C_2-Biphenyl	182	20.90	253.58 (0.11)		a
17	3- or 4-methylbiphenyl	168	21.12	254.56 (0.09)	254	a, b
18	C_2-Bisbenzene	182	21.30	255.30 (0.10)		a
19	C_3-Naphthalene	170	21.59	256.78 (0.09)		a
20	C_2-Biphenyl	182	21.75	257.42 (0.08)		a
21	C_2-Biphenyl	182	22.36	260.19 (0.08)		a
22	C_3-Naphthalene	170	22.55	261.06 (0.06)		a
23	C_3-Naphthalene	170	22.64	261.44 (0.07)		a
24	2,3,6-Trimethylnaphthalene	170	23.18	263.87 (0.10)	263.31	a, b
25	2,3,5-Trimethylnaphthalene	170	23.60	265.81 (0.06)	265.90	a, b
26	Fluorene	166	23.88	267.04 (0.08)	268.17	a, b, c, d
27	C_2-Biphenyl	182	24.18	268.37 (0.08)		a
28	C_2-Biphenyl	182	24.33	269.07 (0.06)		a
29	Methylbiphenyl	168	24.58	270.21 (0.08)		a, b
30	3,3'-Dimethylbiphenyl	182	24.71	270.79 (0.06)	271.87	a
31	C_3-Bisbenzene	196	25.10	272.56 (0.06)		a
32	C_4-Naphthalene	184	25.25	273.28 (0.04)		a
33	C_3-Bisbenzene	196	25.49	274.37 (0.04)		a
34	C_3-(Bisbenzene/biphenyl)	196	25.64	275.02 (0.04)		a
35	Methoxyfluorene	196	25.87	276.04 (0.06)		a, d
36	Methoxyfluorene	196	26.02	276.76 (0.04)		a, d
37	C_4-Naphthalene	184	26.66	279.57 (0.08)		a
38	C_4-Naphthalene	184	27.27	282.37 (0.04)		a
39	Methoxyfluorene	196	27.71	284.39 (0.03)		a
40	C_4-Naphthalene	184	27.86	285.08 (0.02)		a
41	C_3-Biphenyl	196	28.03	285.76 (0.06)		a
42	Methylfluorene	180	28.20	286.60 (0.06)		a
43	Methylfluorene	180	28.28	286.94 (0.05)		a
44	Methylfluorene	180	28.38	287.40 (0.02)		a
45	Methylfluorene	180	28.51	287.99 (0.04)	288.21	a, b

(*Continued on p. 380*)

TABLE I *(continued)*

No.	*Compound*	*Molecular weight*	*Retention time (min)*	*Retention index (Standard deviation)*	*Published retention index**	*Method of identification***
46	C_4-(Bisbenzene/biphenyl)	210	28.51	287.99 (0.04)		a
47	C_4-(Bisbenzene/biphenyl)	210	28.92	289.81 (0.04)		a
48	C_4-(Bisbenzene/biphenyl)	210	29.14	290.84 (0.05)		a
49	C_4-(Bisbenzene/biphenyl)	210	29.38	291.90 (0.04)		a
50	C_4-(Bisbenzene/biphenyl)	196	29.51	292.47 (0.04)		a
51	C_4-(Bisbenzene/biphenyl)	210	29.71	293.42 (0.05)		a
52	Dibenzothiophene	184	30.01	294.74 (0.03)	295.81	a, b, c
53	Phenanthrene	178	31.17	300.00 (0.00)	300.00	a, b, c, d
54	Anthracene	178	31.44	301.26 (0.01)	301.69	a, b, c, d
55	C_5-(Bisbenzene/biphenyl)	224	31.76	302.86 (0.05)		a
56	C_2-Fluorene	194	31.87	303.27 (0.01)		a
57	C_5-(Bisbenzene/biphenyl)	224	32.42	305.82 (0.07)		a
58	C_2-Fluorene	194	32.65	306.99 (0.01)		a
59	C_2-Fluorene	194	32.74	307.43 (0.01)		a
60	C_2-Fluorene	194	32.74	308.38 (0.03)		a
61	C_5-Bisbenzene	224	33.04	308.87 (0.03)		a
62	C_5-(Bisbenzene/biphenyl)	224	33.34	310.22 (0.05)		a
63	Methyldibenzothiophene	198	33.49	310.96 (0.01)		a
64	C_2-Fluorene	194	33.67	311.84 (0.03)		a
65	Phenylnaphthalene	204	34.04	313.55 (0.04)	315.19	a, b
66	Methyldibenzothiophene	198	34.64	315.53 (0.01)		a
67	3-Methylphenanthrene	192	35.17	318.90 (0.01)	319.46	a, b, d
68	2-Methylphenanthrene	192	35.36	319.80 (0.03)	320.17	a, b
69	2-Methylanthracene	192	35.64	321.12 (0.01)	321.57	a, b, c, d
70	4*H*-Cyclopenta[*def*]phenanthrene	190	35.86	322.15 (0.01)	322.08	a, b, d
71	9-Methylphenanthrene	192	36.01	322.86 (0.02)	323.06	a, b
72	4- or 1-methyl(phenanthrene/anthracene)	192	36.17	323.61 (0.02)	323	a, b
73	Methylpropenendiylbisbenzene	208	36.50	325.19 (0.02)		a
74	Methylpropenendiylbisbenzene	208	36.70	326.14 (0.03)		a
75	C_2-Dibenzothiophene	212	36.88	326.99 (0.03)		a
76	C_2-Dibenzothiophene	212	37.43	329.58 (0.03)		a
77	1- or 2-phenylnaphthalene	204	37.80	331.35 (0.02)	332	a, b, d
78	1- or 2-phenylnaphthalene	204	38.32	333.79 (0.03)	332	a, b, d
79	Methylpropenendiylbisbenzene	208	38.53	334.79 (0.03)		a
80	C_2-(Phenanthrene/anthracene)	206	38.65	335.35 (0.03)	337–339	a, b
81	C_2-(Phenanthrene/anthracene)	206	38.92	336.60 (0.02)		a, b
82	C_2-(Phenanthrene/anthracene)	206	39.20	337.92 (0.02)		a, b
83	C_2-(Phenanthrene/anthracene)	206	39.80	340.79 (0.02)		a, b
84	C_2-(Phenanthrene/anthracene)	206	39.98	341.63 (0.02)		a
85	C_2-(Phenanthrene/anthracene)	206	40.17	342.52 (0.02)		a
86	C_2-(Phenanthrene/anthracene)	206	40.40	343.57 (0.05)		a
87	Fluoranthene	202	40.58	344.43 (0.01)		a, b, c, d
88	Methylphenylnaphthalene	218	41.43	348.45 (0.02)		a, d
89	Pyrene	202	42.19	352.09 (0.02)	351.22	a, b, c, d
90	Methylphenylnaphthalene	218	42.48	353.48 (0.05)		a, d
91	C_3-(Phenanthrene/anthracene)	220	43.36	357.62 (0.04)		a
92	C_3-(Phenanthrene/anthracene)	220	43.59	358.66 (0.04)	359.91	a, b
93	C_3-(Phenanthrene/anthracene)	220	44.14	361.33 (0.04)		a

TABLE I *(continued)*

No.	*Compound*	*Molecular weight*	*Retention time (min)*	*Retention index (standard deviation)*	*Published retention index**	*Method of identification***
94	Methyl(fluoranthene/pyrene)	216	44.42	362.59 (0.03)		a, d
95	Methyl(fluoranthene/pyrene)	216	45.03	365.53 (0.07)		a
96	Benzo[*a*]fluorene	216	45.24	366.44 (0.01)	366.74	a, b, d
97	Benzo[*b*]fluorene	216	45.93	369.70 (0.03)	369.39	a, b, d
98	Methyl(fluoranthene/pyrene)	216	46.83	373.99 (0.03)	373.55	a, b, d
99	Benzo[*ghi*]fluoranthene	226	50.36	390.63 (0.02)	389.60	a, b, d
100	Benz[*a*]anthracene	228	51.82	397.55 (0.05)	396.38	a, b, d
101	Chrysene or triphenylene	228	52.04	398.59 (0.04)	400.00	a, b, d
102	Chrysene or triphenylene	228	52.34	400.00 (0.02)	400.00	a, b, c, d
103	Benzo[*e*]pyrene	252	62.04	452.85 (0.09)	450.73	a, b, c, d
104	Benzo[*a*]pyrene	252	62.36	454.42 (0.07)	453.22	a, b, c, d
105	*p*-Quaterphenyl	306	65.75	472.80 (0.08)	472.81	a, b, d
106	Dibenzanthracene	278	69.57	493.83 (0.15)	495.01	b, c, d
107	Benzo[*ghi*]perylene	276	70.98	501.59 (0.16)	501.32	b, d
108	Coronene	300	79.83	549.65 (0.30)		d

* Obtained from ref. 14.

** a, Identified by mass spectra; b, identified by retention indices in ref. 14; c, identified by standard compound injected; d, can be found in refs. 9–13 and 15–17.

extract are PAHs and their alkyl-substituted derivatives. Several sulphur-containing PAHs were also found in this sample. Table I lists the compounds identified in fraction 2 and their retention indices. These retention indices were determined from triplicate injections and have an average standard deviation of 0.06. Published retention indices are also listed for comparison, and small differences from the values obtained in this study can be seen. This has been discussed previously[7].

Numerous isomers were found in the Oslo airborne particulate sample. In some instances, the retention indices permit the differentiation of various isomers, because many isomers have similar mass spectra but different retention indices. In Table I, isomers such as 2- and 1-methylnaphthalene, phenanthrene and anthracene, pyrene and fluoranthene, and benzo[*a*]pyrene and benzo[*e*]pyrene can be distinguished. However, in other instances, positive identification of isomers was not possible owing to the presence of numerous possible isomers and the absence of auxiliary information. For some PAHs the alkyl substitution group, such as trimethyl or dimethylmethyl, cannot be distinguished solely on the basis on MS data. They are tentatively identified as C_3 parent compounds. A number of isomers of alkyl-substituted biphenyl and bisbenzene are present but they cannot be differentiated on the basis of data obtained from GC–MS and GC analyses. Compounds 46–51 in Table I, for example, are tentatively identified as C_4-(bisbenzene/biphenyl).

Several oxygenated PAHs (oxy-PAHs) and nitrated PAHs (nitro-PAHs) are present in Oslo airborne particulate matter. The mass spectra obtained from fraction 3 are highly characteristic of oxy- and nitro-PAHs. Table II lists the compounds found in fraction 3. Not all compounds were identified owing to the shortage of auxiliary information on these kinds of compounds.

TABLE II

COMPOUNDS IDENTIFIED IN FRACTION 3 OF OSLO AIRBORNE PARTICULATE EXTRACT

No.	*Compound*	*Molecular weight*	*Retention time (min)*
1	Biphenylamine (impurity)	169	25.44
2	9-Fluorene	180	29.53
3	Unidentified nitro-PAH	191	30.80
4	Phenanthrone or anthrone	194	32.61
5	Unidentified oxy-PAH	226	33.75
6	Phenanthrone or anthrone	194	34.85
7	Unidentified nitro-PAH	251	35.64
8	Unidentified phthalate (bp*)	149	40.48
9	9,10-Anthraquinone	208	42.01
10	Unidentified aldehyde derivative of PAH	248	49.23

* bp, Base peak in mass spectra.

As previously described, an extract blank was obtained from the glass-fibre filter and polyurethane plug. Four major compounds were identified in the combined fractions 3 and 4 of the extract blank: biphenylamine, diisobutyl phthalate, di-*n*-butyl phthalate and bis(2-ethylhexyl)phthalate. Biphenylamine was also found in fraction 3 of the particulate sample, and the three phthalates were the predominant components in fraction 4. Therefore, we conclude that the major compounds, phthalates, found in fraction 4 of the Oslo airborne particulate extract were generated from the extract blank of the material used in the sample collection apparatus. No significant impurity was found in the combined fractions 1 and 2 of the extract blank. This established HPLC separation provides a good means of separating blank impurities when glass-fibre filters and a polymer plug are used. Usually the separation of these impurities from a complex mixture of sample components is difficult.

Good recoveries of 81–110% for some representative PAH, oxy-PAH and nitro-PAH standards with this HPLC separation procedure have been reported elsewhere[18].

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REFERENCES

1 M. L. Lee, M. V. Novotny and K. D. Bartle, *Analytical Chemistry of Polycyclic Aromatic Compounds*, Academic Press, Toronto, 1981.
2 E. Jellum, A. K. Thorsrud and F. W. Karasek, *Anal. Chem.*, 14 (1983) 2340.
3 F. W. Karasek, R. E. Clement and J. A. Sweetman, *Anal. Chem.*, 53 (1981) 1050A.
4 A. D. Thruston, *J. Chromatogr. Sci.*, 16 (1978) 254.
5 D. Schuetzle, F. S.-C. Lee and T. J. Prater, *Int. J. Environ. Anal. Chem.*, 9 (1981) 93.
6 H. Y. Tong, J. A. Sweetman and F. W. Karasek, *J. Chromatogr.*, 264 (1983) 231.
7 H. Y. Tong, D. L. Shore, F. W. Karasek, P. Helland and E. Jellum, *J. Chromatogr.*, 285 (1984) 423.

8 K. A. Niemann, W. C. Brumley, D. Firestone and J. A. Sphon, *Anal. Chem.*, 55 (1983) 1497.
9 W. C. Eisenberg, *J. Chromatogr. Sci.*, 16 (1978) 145.
10 J. Mueller and E. Kohbock, *Talanta*, 27 (1980) 673.
11 T. Romanowski, W. Funcke, J. Konig and E. Balfanz, *Anal. Chem.*, 54 (1982) 1285.
12 D. R. Choudhury and R. Bush, *Anal. Chem.*, 53 (1981) 1351.
13 T. Nielsen, *Anal. Chem.*, 55 (1983) 286.
14 M. L. Lee and D. L. Vassilaros, *Anal. Chem.*, 51 (1979) 768.
15 F. W. Karasek, D. W. Denney, K. W. Chan and R. E. Clement, *Anal. Chem.*, 50 (1978) 82.
16 A. Björseth, G. Lunde and A. Lindskog, *Atmos. Environ.*, 13 (1979) 45.
17 A. Björseth, *Anal. Chim. Acta*, 94 (1977) 21.
18 H. Y. Tong, J. A. Sweetman, F. W. Karasek, E. Jellum and A. K. Thorsrud, *J. Chromatogr.*, 312 (1984) 183.