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FAST QUANTITATIVE ANALYSIS OF ORGANIC COMPOUNDS IN AIRBORNE PARTICULATE MATTER BY GAS CHROMATOGRAPHY WITH SELECTIVE MASS SPECTROMETRIC DETECTION

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SUMMARY

A method is described for the quantitative determination of the major organic constituents of airborne particulate matter. Organic compounds are isolated from the aerosol by Soxhlet extraction with benzene and methanol. Quantification is performed by the internal standard technique using a mass chromatographic approach. Results obtained for parallel samples of suspended matter demonstrate that the precision of the proposed method is within 10%. Sensitivity has been sacrified in order to allow the quick determination of about 60 organic compounds within 48 h after sampling.

INTRODUCTION

Quantitative analysis of organic compounds in aerosols is rather complex. After the collection of airborne particulate matter, the samples are usually run through several extraction and separation steps before quantification. During these manipulations losses of products occur. Therefore, simplification of this procedure is required.

For samples of aerosol extracts, quantitative analysis by gas chromatography (GC) alone is almost impossible because of the limited resolution of gas chromatographic columns. Therefore, column and thin-layer chromatography have been used for the separation of different classes of organic compounds. Methods are described in the literature for the quantitative analysis of aliphatic and polyaromatic hydrocarbons[1–3]. Polyaromatic hydrocarbons can be determined by spectrophotometric or spectrofluorimetric methods[4,5]. Thin-layer chromatography allows the separation of the individual polyaromatic hydrocarbons[6,7]. The method is time consuming and subject to losses, but is very sensitive. Only a few polyaromatic hydrocarbons can be separated completely and can be determined without interferences.

This article describes the determination of all of the major organic compounds after gas chromatographic separation combined with selective mass spectrometric detection (GC–MS). A major advantage here is the injection of a crude sample extract on to the GC column. Selective ion monitoring is performed with the aid of files containing complete mass spectral information for the sample (about 1000 mass

spectra). A reduction in analysis time has been achieved at the expense of a reasonable loss of sensitivity. For the determination of trace compounds, a preliminary separation into neutral, acidic and basic compounds results in simplification of the analysis. Losses occurring during this separation have been determined[8]. The qualitative composition of an urban aerosol extract has been described previously[9].

EXPERIMENTAL

Airborne particulate matter was sampled by filtration over glass-fibre filters mounted in a high-volume sampler as described by Dams and Heindryckx[10]. The simultaneous collection of "identical" particulate matter requires two high-volume samplers separated by 3 m.

Extraction of the samples was performed in a Soxhlet apparatus (capacity, 100 ml; cycletime, 6 min). Quantitative yields were obtained by successive extractions with 200 ml of benzene (4 h) and with 200 ml of methanol for another 4 h (ref. 8). The crude extract was evaporated under vacuum at low temperature (40°) and then redissolved in diethyl ether. The use of methanol as solvent is reflected in the appearance of both inorganic and organic compounds in the extract. The inorganic compounds were eliminated by extraction with water. Losses of organic products into the water layer were shown to be negligible. Correction factors have been determined for the separation into the neutral, acidic and basic fractions[8]. A slightly modified scheme, originally proposed by Hueper *et al.*[11], was followed here. All of the extractions were repeated five times with 1 *N* sodium hydroxide or hydrochloric acid.

Mass chromatographic determinations were performed on a Finnigan 3100 GC–MS system coupled to the 6000 data system. A 3-m 4% Dexsil-300 column was used. Typical runs were begun at 120° and temperature was programmed to 280° at 4°/min where it remained for another 15 min. 2 min after injection of the sample, cyclic scanning of the mass spectrometer from *m/e* 50 to *m/e* 400 was begun with a 3-sec cycletime. The data obtained were stored on a disk for future elaboration.

The quantification began with the generation of mass chromatograms for specific ion masses. A typical mass chromatogram peak contained an average of 15 information points. Areas from mass chromatographic peaks were integrated using the 6000 data system software. Mass chromatograms for specific ion masses of several internal standards were also generated and integrated. Ratios of the peak areas of the unknown and the internal standard were calculated. Calibration graphs were obtained by the injection of standard mixtures after addition of the same quantity of internal standard. Ratios of peak areas were plotted against the amount of product present in the standard mixtures.

RESULTS AND DISCUSSION

Sampling and extraction of airborne particulate matter

Sampling of airborne particulate matter was performed over $\geqslant$24-h periods. This corresponds to *ca.* 1000 m^3 of air. The total weight of the suspended particles varies with the quality of the sampled air. Normal values are *ca.* 50–100 mg for 24-h samples taken in city residential areas. Comparable samples taken in the Andes (Chacaltaya, Bolivia; altitude, 5200 m) showed a ten times lower loading of particles.

Results given in this paper are expressed in μg of compound per 1000 m^3 of air or μg of compound per gram of particulate matter (ppm weight). The reproducibility of sampling was checked by the collection of "identical" particulate matter using two parallel sampling units. Although there was a difference in the volume of air sampled and consequently in the weight of collected particulate matter, very similar concentrations of organic compounds were found. In view of the wide range of vapour pressures of the identified compounds, evaporation of the products during sampling cannot be excluded[12,13]. Corrections for these losses will involve gas-phase sampling in conjunction with particulates sampling, a technique under study in this laboratory.

Extraction of the organic compounds using a Soxhlet extractor was checked. Extraction times should be at least 8 h in order to yield quantitative recovery. Earlier data show the advantage of the successive extraction with benzene and methanol[8].

Specific ion masses for quantitative analysis

Ion masses for quantification of organic products in aerosols by mass chroma-

TABLE I

COMPOUNDS IDENTIFIED IN THE NEUTRAL FRACTION

Compound	*Mol. weight*	*Retention time**	*Kováts' index (RI)*	*m/e for quantification*		*Possible interferences***
				Unknown	*Internal standard*	
n-Hexadecane	226	9.12	1600	85	77	
n-Heptadecane	240	11.32	1700	85	77	
n-Octadecane	254	13.51	1800	85	77	
n-Nonaedcane	268	15.70	1900	85	77	
n-Eicosane	282	17.83	2000	85	77	
n-Heneicosane	296	20.03	2100	85	77	
n-Docosane	310	22.04	2200	85	77	
n-Tricosane	324	24.11	2300	85	77	
n-Tetracosane	338	26.07	2400	85	77	
n-Pentacosane	352	27.97	2500	85	77	
n-Hexacosane	366	29.80	2600	85	77	
n-Heptacosane	380	31.58	2700	85	77	
n-Octacosane	394	33.36	2800	85	77	
n-Nonacosane	408	34.96	2900	85	77	
n-Triacontane	422	36.62	3000	85	77	
n-Hentriacontane	436	38.22	3100	85	77	
n-Dotriacontane	450	39.76	3200	85	77	
n-Tritriacontane	464	41.53	3300	85	77	
Diethyl phthalate	222	10.37	1657	149 or 222	211	
Diisobutyl phthalate	278	16.06	1917	149 or 223	211	
Di-*sec*.-butyl phthalate	278	17.18	1970	149 or 223	211	
Di-*n*-butyl phthalate	278	18.25	2019	149 or 223	211	
Benzyl butyl phthalate	312	26.13	2403	149 or 206	211	
Di-2-ethylhexyl phthalate	390	29.63	2591	149 or 279	211 or 306	
Naphthalene	128	3.08	—	128	186	
Biphenyl	154	5.75	—	154	186	
Phenanthrene and anthracene	178	15.52	1892	178	186 or 211	

(Continued on p. 256)

TABLE I *(continued)*

Compound	*Mol. weight*	*Retention time**	*Kováts' index (RI)*	*m/e for quantification*		*Possible interferences***
				Unknown	*Internal standard*	
Fluoranthene	202	22.10	2203	202	211	
Pyrene	202	23.23	2258	202	211	
Benzo[*a*]fluorene	216	25.06	2349	216	211	
Benzo[*c*]fluorene	216	25.42	2367	216	211	
Benzo[*g,h,i*]fluoranthene	226	29.21	2568	226	211 or 240	benzo[*c*]-phenanthrene
Benzo[*c*]phenanthrene	228	28.68	2539	228	211 or 240	
Benz[*a*]anthracene and chrysene	228	30.28	2627	228	211 or 240	
$\beta\beta'$-Binaphthyl	254	33.48	2808	254	211 or 240	
Benzo[*k*]fluoranthene and benzo[*b*]fluoranthene	252	36.38	2986	252	211 or 240 or 306	
Benzo[*a*]pyrene and benzo[*e*]pyrene	252	37.86	3078	252	211 or 240 or 306	perylene
Perylene	252	38.45	3115	252	211 or 240 or 306	benzo[*a*]- and benzo-[*e*]pyrene
Methylphenanthrene and methylanthracene	192	18.55	2033	192	211	
Ethylphenanthrene	206	20.80	2138	206	211	ethylanthracene
Ethylanthracene	206	21.33	2165	206	211	ethylphenanthrene
Methylfluoranthene and methylpyrene	216	25.54	2425	216	211 or 240	
Methylbenz[*a*]anthracene and methylchrysene	242	32.65	2760	242	211 or 240 or 306	
Methylbenzo[*k*]- and methylbenzo*b*[-]fluoranthene	266	38.75	3134	266	211 or 240 or 306	
Methylbenzo[*a*]- and methylbenzo[*e*]-pyrene	266	39.99	3213	266	211 or 240 or 306	
Dihydrobenzo[*c*]fluorene	218	22.93	2243	218	211 or 240	
Hexahydrochrysene	234	28.68	2539	234	211 or 240	
Dihydrobenzo[*c*]phenanthrene	230	28.62	2436	230	211 or 240	
Dihydrobenz[*a*]anthracene and dihydrochrysene	230	29.92	2607	230	211 or 240	
Benzo[*a*]carbazol	217	30.57	2643	217	211	
Benzo[*c*]carbazol	217	31.94	2720	217	211	
Anthraquinone	208	19.97	2097	208	211	
7*H*-Benz[*d,e*]anthracene-7-one	230	32.82	2770	230	211	

* In minutes on Dexsil 300 column (4%; length, 3 m).

** Due to incomplete resolution on the GC column.

TABLE II

COMPOUNDS IDENTIFIED IN THE ACIDIC FRACTION

Compound	*Mol. weight of derivatized product*	*Retention time (min)*	*RI*	*m/e for quantification*		*Possible interferences*
				Unknown	*Internal standard*	
Lauric acid	214	7.58	1200	74	77	
Myristic acid	242	11.91	1400	74	77	
Pentadecanoic acid	256	14.22	1500	74	77	
Palmitic acid	270	16.41	1600	74	77	deuterated methylester
Heptadecanoic acid	284	18.60	1700	74	77	
Oleic acid	296	20.15	1772	74	77	stearic acid
Stearic acid	298	20.74	1800	74	77	oleic acid
Nonadecanoic acid	312	22.87	1900	74	77	
Eicosanoic acid	326	24.89	2000	74	77	
Heneicosanoic acid	340	26.90	2100	74	77	
Docosanoic acid	354	28.80	2200	74	77	
Tricosanoic acid	368	30.69	2300	74	77	
Tetracosanoic acid	382	32.47	2400	74	77	
Pentacosanoic acid	396	34.19	2500	74	77	
Hexacosanoic acid	410	35.91	2600	74	77	
Phthalic acid	194	7.05	—	194 or 163	211	
Terephthalic acid	194	7.88	1207	194 or 163	211	isophthalic acid
Isophthalic acid	194	8.30	1217	194 or 163	211	terephthalic acid
Methylphthalic acid	208	9.78	1251	208 or 177	211	methylphthalic acid
4-Hydroxybenzoic acid	166	4.86	—	166 or 135	211	
3,4-Dihydroxybenzoic acid	196	9.89	1254	196 or 165	211	
Naphthalenecarboxylic acid	186	11.55	1292	186	211	
Phenanthrenecarboxylic acid	236	24.35	1973	236	211 211	
Hydroxyphenanthrene and hydroxyanthracene	208	21.74	1847	208	211	
Hydroxypyrene	232	28.38	2178	232	211	
Tetrachlorophenol	244	8.59	1223	244	211	
Pentachlorophenol	278	13.21	1456	278	211	

tography were chosen on the basis of three factors: selectivity, sensitivity and absence of interferences. Less selective ions can be used for the determination of some compounds provided that their retention times are sufficiently different. This shows the importance of using GC columns having high separation efficiencies. Tables I–III show the ion masses chosen for each compound together with their retention times and Kováts' indices (RI). Available internal standards are also mentioned.

Possible interferences have been identified. They occur when two compounds are not resolved completely on the GC column and one of them contributes to the ion mass chosen for quantification of the other. For the neutral and basic fractions

TABLE III

COMPOUNDS IDENTIFIED IN THE BASIC FRACTION

Compound	*Mol. weight*	*Retention time (min)*	*RI*	*m/e for quantification*		*Possible interferences*
				Unknown	*Internal standard*	
Isoquinoline	129	4.62	—	129	186, 211	—
Methylquinoline	143	5.27	—	143	186, 211	—
Acridine	179	16.47	1936	179	186, 211	179*
Benzo[*x*]quinolines	179	17.18	1970	179	186, 211	179
Phenanthridine	179	19.43	2073	179	186, 211	—
Methylacridines	193	17.24	1972	193	211	—
Methylphenanthridines	193	18.43	2027	193	211	—
Methylbenzoquinolines	193	19.43	2073	193	211	193
(6 isomers)	193	20.15	2106	193	211	193
	193	21.92	2194	193	211	193
	193	22.63	2229	193	211	—
Azafluoranthenes	203	22.87	2240	203	211	—
and azapyrenes	203	23.82	2286	203	211	—
	203	24.77	2334	203	211	203
	203	25.06	2349	203	211	203
Azabenzo[*x*]fluorenes,	217	26.01	2397	217	211	217
methylazapyrenes	217	26.60	2428	217	211	217
and methylazafluoranthenes	217	27.79	2491	217	211	—
Benzacridines,	229	29.33	2574	229	211, 240	—
benzophenanthridines	229	30.45	2637	229	211, 240	—
and dibenzoquinolines	229	32.11	2730	229	211, 240	243
Methylbenzacridines	243	31.34	2687	243	211, 240	243
Methylbenzophenanthridines	243	32.05	2726	243	211, 240	243
Methyldibenzoquinolines	243	32.88	2773	243	211, 240	243
	243	33.24	2793	243	211, 240	243
Azabenzopyrenes and	253	35.91	2957	253	211,240,306	253
azabenzofluoranthenes	253	36.44	2989	253	211,240,306	253, 253
(7 isomers)	253	36.79	3011	253	211,240,306	253
	253	37.74	3070	253	211,240,306	253
	253	38.22	3100	253	211,240,306	253
	253	39.34	3173	253	211,240,306	—
	253	40.05	3216	253	211,240,306	—
Dibenz[*a,h*]acridine	279	43.13	—	279	211,240,306	—
Dibenz[*a,j*]acridine	279	43.96	—	279	211,240,306	—

* Other isomers having the same molecular weight.

overlap can occur when the distance between two peaks is less than 40 RI units. For the acidic fraction the level is 35 RI units.

Neutral fraction. The aliphatic hydrocarbon series was determined by generating the mass chromatogram for $m/e = 85$ ($C_6H_{13}^+$). Although the peak at $m/e = 71$ was more sensitive than that at $m/e = 85$, this mass was discarded because of frequent interferences. Higher masses were discarded because of lower sensitivity. From Table I it is evident that no interferences were present in the determination at $m/e = 85$. The use of a selective ion of low mass always increases the chance of overlapping of compounds. Therefore retention times, band withs and the appearance of the mass spectra must be checked before analysis is attempted. The generation of the peak at $m/e =$

149 allows the determination of phthalic acid esters in a very sensitive way (base peak). Diethyl phthalate can be measured selectively at $m/e = 222$ (molecular ion), dibutyl phthalates at $m/e = 223$, benzylbutyl phthalate at $m/e = 206$ and dioctyl phthalates at $m/e = 279$. The high concentrations of phthalic acid esters in natural samples often overload the mass chromatogram at $m/e = 149$. Quantification at ion masses of low intensity ($m/e = 222$, 223, 206 and 279) is preferred over dilution of the sample since this will also decrease the sensitivity for other products.

Polyaromatic hydrocarbons were quantified as their corresponding molecular ions (base peak). It is a very sensitive and specific technique. No interferences occur because of the high m/e values of the chosen ions. Sometimes isomers could not be separated completely by the GC column. In these cases products were measured together. Fig. 1 shows a combination of mass chromatograms for molecular ions of polyaromatic hydrocarbons. Here a 6-m Dexsil column (4% on Gas Chrom Q, 100–120 mesh) was used. For quantitative determinations, the column length was limited to 3 m in order to shorten the analysis time.

Acidic fraction. Before analysis, the acidic fraction was derivatized by reaction with an excess of diazomethane solution in diethyl ether. Consequently, carboxylic acid functions are converted into methyl esters and phenolic functions into methyl ethers. Generation of the mass chromatogram at $m/e = 74$ (base peak), corresponding to the MacLafferty rearrangement of methyl esters, allows quantification. The deuterated methyl ester of palmitic acid was used as internal standard; its MacLafferty rearrangement ion yields $m/e = 77$. Trace amounts of undeuterated methyl ester led to a correction at $m/e = 74$ for palmitic acid. Normally this correction is *ca.* 0.1%. Other products found in the acidic fraction were measured at either the molecular ion or at $(M-31)^+$, corresponding to the loss of the OCH_3 fragment.

No interferences were observed for these products. Under the conditions used, oleic and stearic acid were resolved up to 10% of the peak height, so they can be measured separately with sufficient accuracy. Isophthalic and terephthalic acid were not separated and have to be measured together.

Basic fraction. All of the products found in the basic fraction were identified as nitrogen-containing polyaromatic hydrocarbons[9]. The generation of the mass chromatograms at the corresponding molecular ions permits the determination of these compounds. For many products, a high number of isomers were present. Overlap between isomers occurred frequently and the isomers had to be measured together. Fig. 2 shows mass chromatograms for the basic fraction (6-m Dexsil column).

Choise of internal standards. Table IV gives a summary of the internal standards used in this work. For triphenylbenzene or the deuterated polyaromatics, the molecular ions were chosen. Doubly charged molecular ions of the deuterated polyaromatics can also be used. Sometimes the ion M^{2+} of deuterated pyrene ($m/e = 106$) was used. Generation of the rearrangement ion at $m/e = 77$ yielded good results for the deuterated methyl ester of palmitic acid. The selective m/e value taken as the internal standard should be as close as possible to the selective mass of the unknown in order to avoid the influence of fluctuating instrumental parameters, *e.g.*, mass discrimination. Experiments have shown the advantage of using an internal standard which has a comparable retention index to that of the unknown.

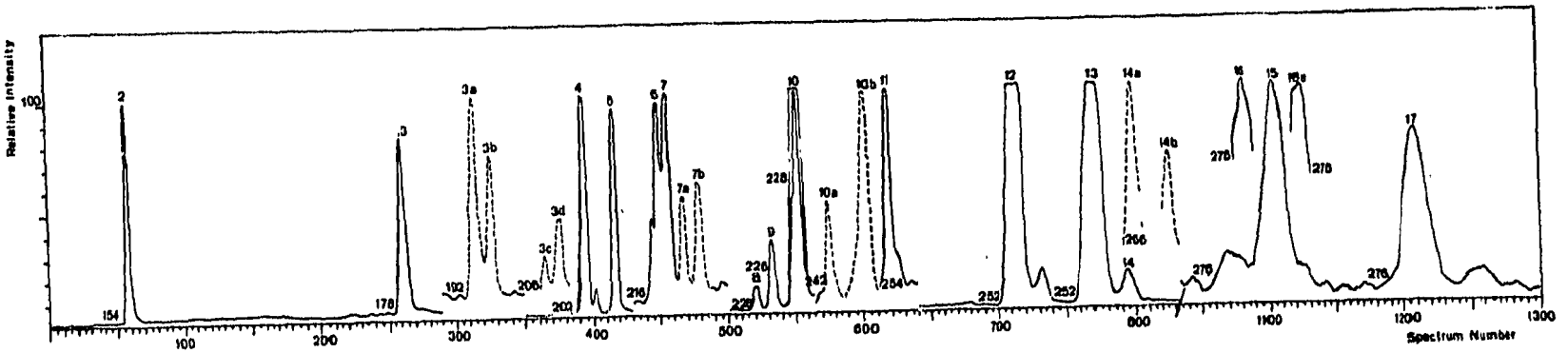

Fig. 1. Mass chromatograms for polyaromatic hydrocarbons. Peaks: 2 = biphenyl; 3 = phenanthrene, anthracene; 3a = methylphenanthrene; 3b = methylanthracene; 3c = ethylphenanthrene; 3d = ethylanthracene; 4 = fluoranthene; 5 = pyrene; 6 = benzo[*a*]fluorene; 7 = benzo[*c*]fluorene; 7a = methylfluoranthene; 7b = methylpyrene; 8 = benzo[*c*]phenanthrene; 9 = benzo[*g,h,i*]fluoranthene; 10 = benz[*a*]anthracene, chrysene; 10a = methylbenz[*a*]anthracene; 10b = methylchrysene; 11 = $\beta\beta'$-binaphthyl; 12 = benzo[*k*]fluoranthene, benzo[*b*]fluoranthene; 13 = benzo[*a*]pyrene, benzo[*e*]pyrene; 14 = perylene; 14a = methylbenzo[*k/b*]fluoranthene; 14b = methylbenzo[*a/e*]pyrene; 15 = benzo[*b*]chrysene, *o*-phenylenepyrene; 16 = dibenzanthracenes; 16a = picene, benzo[*c*]tetraphene; 17 = benzo[*g,h,i*]perylene, anthanthrene.

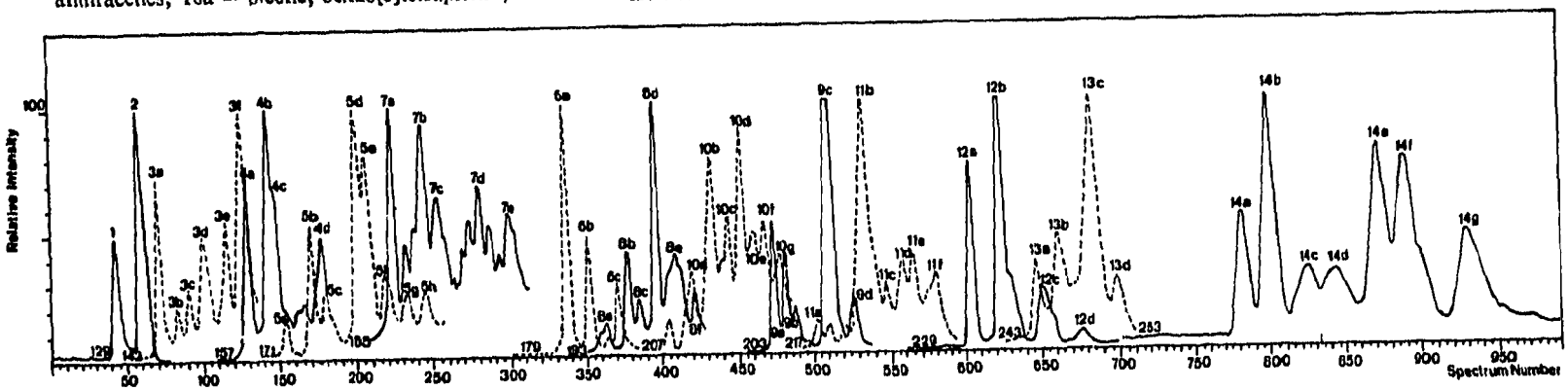

Fig. 2. Mass chromatograms for nitrogen-containing polyaromatic hydrocarbons. Peaks: 1 = quinoline; 2 = isoquinoline; 3 = methyl(iso)quinolines; 4 = dimethyl(iso)quinolines; 5 = trimethyl(iso)quinolines; 6 = acridine, phenanthridine and benzo(iso)quinolines; 7 = tetramethyl(iso)quinolines; 8 = methylacridines, methylphenanthridines and methylbenzo(iso)quinolines; 9 = azafluoranthenes and azapyrenes; 10 = dimethylacridines, dimethylphenanthridines and dimethylbenzo(iso)quinolines; 11 = azabenzofluorenes, methylazapyrenes and methylazafluoranthenes; 12 = azabenz[*a*]anthracenes, azachrysenes and dibenzo(iso)quinolines; 13 = methylbenzacridines, methylbenzophenanthridines and methyldibenzo(iso)quinolines; 14 = azabenzopyrenes and azabenzofluoranthenes.

TABLE IV

INTERNAL STANDARDS USED

Compound	*Mol. weight*	*RI**	*RI***	*m/e values used*
Triphenylbenzene	306	3016	—	306
Deuterated anthracene	186***	1892	—	186
Deuterated pyrene	211***	2258	1903	211, 106
Deuterated chrysene	240***	2627	—	240
Palmitic acid deuterated methyl ester	273	1942	1597	77

* Relative to aliphatic hydrocarbon series.

** Relative to fatty acid methyl ester series.

*** Maximum intensity values for the distributions obtained after an exchange reaction with deuterium chloride and aluminium chloride.

Determination of calibration graphs

Reproducibility of peak-area ratios. Multiple analysis of standard samples by mass chromatography yielded relative standard deviations of $\leqslant 5\%$ for peak ratios of the unknowns to the internal standards. For the fatty acid series, where a deuterated homologue was used as the internal standard, the peak ratios for masses 74/77 showed a relative standard deviation of 3%. The same value was found for masses 85/77 in the hydrocarbon series.

Plotting calibration graphs. Instrumental parameters of a quadrupole mass spectrometer are time-dependent. Experiments showed the need for injection of standard mixtures and natural samples during the same day. One GC run required *ca.* 1.30 h. Generation of mass chromatograms, checking of retention indices and integration was performed within 30 min. Thus, the number of injections in one day is limited to about five. At first, experiments were performed using five standard mixtures of different concentrations. Peak ratios were calculated and plotted against the quantities of products by use of linear regression.

The concentration ranges where linearity holds are dependent on the nature of the products. Table V shows the concentration ranges for all of the classes of products. Typical correlation coefficients varied between 0.99 and 1.00, showing the good linearity of the experimental graphs. The slopes (k) of the graphs were calculated by linear regression. Typical relative standard deviations for these slopes (s_k) are 5%. This results in a relative standard deviation of 10% for quantities read on the abscissa.

TABLE V

CONCENTRATION RANGES FOR DIFFERENT CLASSES OF ORGANIC COMPOUNDS

Compounds	*Amount of product (μg) in solution for 24-h samples*
Aliphatic hydrocarbons	0–1000
Polyaromatic hydrocarbons	0– 100
Phthalic acid esters	0–1000
Fatty acid esters	0–1000
Carboxylic acids	0– 100
Phenolic acids	0– 100
Nitrogen-containing polyaromatics	0– 100

TABLE VI

QUANTITATIVE RESULTS FOR THE NEUTRAL FRACTION

Sample 1: volume, 2616 m^3; load, 124.7 μg. Sample 2: volume, 1944 m^3; load, 116.5 mg.

Compound	*First determination (ppm weight)**		*Second determination (ppm weight)*		*Average*
	Sample 1	*Sample 2*	*Sample 1*	*Sample 2*	
n-Heptadecane	20	30	24	30	26
n-Octadecane	16	15	20	26	19
n-Nonadecane	18	27	28	30	26
n-Eicosane	10	8.6	24	20	16
n-Heneicosane	8.0	8.6	16	13	11
n-Docosane	12	8.6	20	20	15
n-Tricosane	22	19	36	30	27
n-Tetracosane	40	40	51	50	45
n-Pentacosane	60	58	76	77	68
n-Hexacosane	79	77	82	82	80
n-Heptacosane	104	99	96	110	102
n-Octacosane	88	67	76	70	75
n-Nonacosane	112	108	124	142	122
n-Triacontane	52	34	52	47	46
n-Hentriacontane	76	63	76	76	73
n-Dotriacontane	32	30	52	34	37
Diethyl phthalate	116	99	80	84	95
Diisobutyl phthalate	702	665	521	712	650
Di-*sec*.-butyl phthalate	98	116	80	116	103
Di-*n*-butyl phthalate	1147	1240	1090	1313	1198
Di-2-ethylhexyl phthalate	617	437	738	515	577
Phenánthrene and anthracene	15	14	15	15	15
Fluoranthene	24	23	27	29	26
Pyrene	21	20	24	21	22
Benzo[*a*]fluorene and benzo[*c*]fluorene	22	21	31	26	25
Benz[*a*]anthracene and chrysene	210	220	280	240	238
Benzo[*k*]fluoranthene and benzo[*b*]fluoranthene	460	500	480	520	490
Benzo[*a*]pyrene, benzo[*e*]pyrene and perylene	360	390	380	400	383
Methylphenanthrene and methylanthracene	11	10	11	11	11
Methylfluoranthene and methylpyrene	9.6	6.9	6.1	8.3	7.7
Anthraquinone	20	17	23	22	21
7*H*-Benz[*d*,*e*]anthracene-7-one	143**	44**	12	15	—

* Corresponds to 1 μg per gram of aerosol.

** Values is in error owing to an artifact.

For the quantification of natural samples, the number of injections of standard mixtures was reduced. Because all of the graphs were known to intersect at the origin, good results were obtained by injection of only two standard mixtures. In this way, three different natural samples could be measured within one day. Graphical comparison showed that the standard deviations were comparable to those obtained using five data points.

TABLE VII

QUANTITATIVE RESULTS FOR THE ACIDIC FRACTION

For samples see Table VI.

Compound	*First determination (ppm weight)*		*Second determination (ppm weight)*		*Average*
	Sample 1	*Sample 2*	*Sample 1*	*Sample 2*	
Lauric acid	260	270	230	250	253
Myristic acid	150	130	140	130	138
Pentadecanoic acid	38	35	47	35	39
Palmitic acid	710	650	690	650	675
Heptadecanoic acid	39	41	22	59	40
Stearic acid	570	540	550	530	548
Nonadecanoic acid	23	25	34	25	27
Eicosanoic acid	91	86	100	86	91
Heneicosanoic acid	23	20	35	25	26
Docosanoic acid	160	140	150	130	145
Tricosanoic acid	86	92	64	69	78
Pentachlorophenol	120	120	100	90	108

Quantitative determinations

The results are presented in Tables VI–VIII. Two 48-h samples were collected in the same period (January 7th to 9th, 1976) in a typical city residential area. The sampling volumes and loading of both filters are given in Table VI. A first determination was performed immediately after collection, the second determination being made after 1 month. The samples were stored in a refrigerator and protected against light between determinations. The results are corrected for losses due to the extraction and separation procedure by use of correction factors determined earlier[8]. The results indicate the reproducibility of both the sampling procedure and the analytical method. Although the volumes and loading of the samples were different, they yielded similar concentrations of organic compounds.

Major compounds present in the analyzed samples were phthalic acid esters,

TABLE VIII

QUANTITATIVE RESULTS FOR THE BASIC FRACTION

For samples see Table VI.

Compound	*First determination (ppm weight)*		*Second determination (ppm weight)*		*Average*
	Sample 1	*Sample 2*	*Sample 1*	*Sample 2*	
Methylquinoline	14	15	13	—	14
Acridine and benzoquinolines	33	26	25	20	26
Phenanthridine	12	9.4	14	11	12
Benz[*x*]acridine	18	13	25	16	18
Benzo[*x*]phenanthridine	35	25	28	24	28
Dibenzo[*x*]quinoline	11	8.0	8.6	6.6	8.6
Dibenz[*x*]acridine	8.8	13	26*	13	—

* Value is in error owing to an artifact.

fatty acids and a few polyaromatic hydrocarbons. The relative quantities of polyaromatic hydrocarbons found in this study show a good correlation with earlier data[14]. The quantities of aliphatic hydrocarbons obtained seem rather low. Only a few products could be detected in the basic fraction in low concentrations. About 60 different organic compounds were determined with a relative standard deviation of $\leqslant 10\%$.

The detection limit was dependent on the selective ion mass chosen for quantification. Products determined by integration of base-peak ion masses (polyaromatics, phthalates, fatty acids and heterocyclic arenes) had a detection limit of *ca.* 1 ng on the column, which corresponds to an absolute quantity of *ca.* 100 ng in solution. Thus 1 ppm of a 100-mg sample of particulate matter can be determined. Measurements on fragment ions of lower intensity increased the detection limit to 5 ppm. For comparison, mass fragmentography of the same compounds (polyaromatic hydrocarbons) gives detection limits of 20 pg on the column. However, the number of channels that can be used for each analysis run is normally restricted (4–8).

CONCLUSION

The sensitivity of mass chromatography has been shown to be sufficient for the determination of all of the major organic compounds in 48-h samples of particulate matter. Typical relative standard deviations vary between 5 and 10%. The sample extracts need no complex separation procedure. The analysis time is considerably reduced considering the wealth of data produced. An advantage of the proposed method, relative to mass fragmentography, is that complete mass spectral information is kept on a disk and can be used whenever necessary. Qualitative analysis can be performed, and unexpected new products can be identified and determined using the same file. The proposed method should be applicable to similar analytical problems in pollution chemistry (water or sludge samples) or biochemistry whenever one can afford to trade off some sensitivity for the attainment of an overall picture of the sample composition. For air-pollution studies, it seems that a single ion mass chromatogram approach in combination with retention data is sufficient for quantitative determination free from interferences. However, this may not be the case for other types of samples.

REFERENCES

1 D. Brocco, V. Cantuti and G. P. Cartoni, *J. Chromatogr.*, 49 (1970) 66.
2 A. Raymond and G. Guiochon, *Environ. Sci. Technol.*, 8 (1974) 143.
3 T. R. Hauser and J. N. Pattison, *Environ. Sci. Technol.*, 6 (1972) 551.
4 W. Giger and M. Blumer, *Anal. Chem.*, 46 (1974) 1663.
5 R. C. Pierce and M. Katz, *Anal. Chem.*, 47 (1975) 1743.
6 E. Sawicki, T. W. Stanley, W. C. Elbert and J. D. Pfaff, *Anal. Chem.*, 36 (1964) 497.
7 G. M. Badger, J. K. Donnelly and T. M. Spotswood, *J. Chromatogr.*, 10 (1963) 397.
8 W. Cautreels and K. Van Cauwenberghe, *Water, Air Soil Pollut.*, 6 (1976) in press.
9 W. Cautreels and K. Van Cauwenberghe, *Atmos. Environ.*, 10 (1976) 447.
10 R. Dams and R. Heindryckx, *Atmos. Environ.*, 7 (1973) 313.
11 W. C. Hueper, P. Kotin, E. C. Tabor, W. W. Payne and E. Sawicki, *Arch. Pathol.*, 74 (1962) 89.
12 C. Pupp, R. C. Lao, J. J. Murray and R. F. Pottie, *Atmos. Environ.*, 8 (1974) 915.
13 H. Della Fiorentina, F. De Wiest and J. De Graeve, *Atmos. Environ.*, 9 (1975) 517.
14 R. C. Lao, R. S. Thomas, H. Oja and L. Dubois, *Anal. Chem.*, 45 (1973) 908.