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COMPUTERIZED GAS CHROMATOGRAPHIC-MASS SPECTROMETRIC ANALYSIS OF POLYCYCLIC AROMATIC HYDROCARBONS IN ENVIRONMENTAL SAMPLES

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SUMMARY

Substantial progress has been made in the last few years in the development of a rapid method for determining polycyclic aromatic hydrocarbons (PAH) in environmental samples. The three-step method consists of (i) a preliminary separation of PAH by solvent and/or column chromatography, (ii) identification by a combination of gas chromatography with quadrupole mass spectrometry and computer, and (iii) measurement by computerized gas chromatography using internal standards. Samples of industrial effluents, coke oven emissions, coal tar and airborne particulates have been investigated. The efficiencies of different gas chromatographic columns were evaluated during these investigations.

INTRODUCTION

During the past two decades, this laboratory has mounted a major effort to improve the methodology of polycyclic aromatic hydrocarbons (PAH) measurements and to establish the range of concentrations which are present in environmental samples^{1,2}. A number of different methods have been developed, all of which involved a combination of techniques such as solvent extraction, column chromatography, ultraviolet (UV) absorption and fluorescence spectrophotometry. These methods are generally somewhat complex, unit analytical time is excessive, and because of the complexity and slow analytical turn around there is a premium upon operator skill, experience and dedication.

Three years ago, we initiated a programme to develop a rapid and reliable approach to PAH analyses. The practical usefulness of the gas chromatograph-mass spectrometer-data processor combination has been well demonstrated in the analysis of air samples³. More than seventy important PAH, having from two to seven rings, were separated and identified in this work. Since then, a number of papers have been published dealing with the application of gas chromatography (GC), GC-UV and GC-mass spectrometry (MS)⁴⁻⁹.

We can start with the established baseline of the GC-MS-data processor method and its successful application to airborne particulates using Dexsil 300 col-

umns. A logical extension of the study was to evaluate various liquid phases for improved GC resolution. These analytical approaches have also been adapted to the measurement of PAH in various environmental samples, with the same reliability as for airborne particulates.

EXPERIMENTAL

A Perkin-Elmer Model 990 gas chromatograph with flame ionization detector (FID) was used for the quantitative measurement of the individual PAH compounds. Interfaced with the chromatograph, a Perkin Elmer PEP-1 data system measures the relative retention times (*RRT*) and calculates response factors (*RF*). In addition to the Dexsil 300 columns used previously³, packed columns of Dexsil 400 and 410 were evaluated. Operating conditions are summarized in Table I. Columns were conditioned at 350° for 24 h; Dexsil 400 required an additional period of conditioning before it performed in a stable manner. The GC-MS system used in this work consisted of a Finnigan Model 9500 gas chromatograph, a Model 1015D quadrupole mass spectrometer and a Model 6000 data system. This system has been demonstrated to be well suited to the routine analysis of air pollutants^{10,11} and the quadrupole instrument has a number of advantages over the magnetic scanning which was used in our previous work³.

TABLE I
CHROMATOGRAPHIC OPERATING CONDITIONS FOR THE PACKED COLUMN

| | |
|--------------------------------|---|
| Detector | FID |
| Detector temperature | 300° |
| Liquid sample volume | 0.5-10 μ l |
| Sample injector temperature | 325° |
| Column | 12 ft. \times 0.125 in. O.D., stainless steel, packed with 6% Dexsil 300, 400 or 410 on 80-100 mesh Chromosorb W HP |
| Carrier gas (helium) flow-rate | 40 ml/min |
| Initial temperature | 165° held for 2 min |
| Programmed temperature | 4°/min |
| Final temperature | 295° held for 50 min |
| Recorder attenuation | 160 and 640 |

For the present investigation, the mass range of the mass spectrometer was initially calibrated by FC-43, perfluorobutylamine, a compound supplied by Finnigan (Sunnyvale, Calif., U.S.A.). Once the instrument had been properly calibrated, the mass range did not alter over the experimental period. Each day a sensitivity check was made, using a sample of decafluorotriphenylphosphine (DFTPP) provided by the mass spectrometric group of the Methods Development and Quality Assurance Research Laboratory, NERC, EPA, Cincinnati, Ohio, U.S.A.^{12,13}. If sensibility degradation is found, this may generally be attributed to rod contamination, the effect of which is most pronounced in the ion abundances of high-mass ions.

The spectrum of DFTPP, having a base peak of *m/e* 198 and key fragments of *m/e* 275, 442 and 443, is convenient for the ion abundance calibration of the high-mass region in which many environmental compounds, including PAH, have their molecular and many fragment ions.

When the quadrupole mass spectrometer operating parameters had been established to give the normal ion abundances for DFTPP, a solution (0.5–0.7 μ l) of sample was injected into the gas chromatograph. The column elution fractions and helium carrier pass into a glass single jet separator and on into the ion volume of the mass spectrometer. The various processes occurring in the Finnigan mass spectrometer during operation have been described¹⁴. Ions which have been filtered by the rods according to their molecular weights pass through the quadrupole field to the ion detector. The ion current is amplified, gated, and then plotted against the spectrum scan time base. This output is stored on a magnetic disc via a computer interface. The ion abundance chromatogram of the GC effluent was acquired by scanning a mass range from 30–350 a.m.u., with a total scanning time of 1 sec. The dialogue required for mass spectrometer control, data acquisition and obtaining the plot are given by a push button and/or teletype command¹⁴. At the end of the GC run, the computer is used to plot a reconstructed gas chromatogram of total ion amplitude *versus* the spectrum number (ion abundance chromatogram). Identification of these chromatographic peaks can be accomplished by plotting the mass spectrum of a specified peak, or by generating a limited mass plot chromatogram obtained under computer control by searching through the collected spectra and identifying spectra containing ions with a specific m/e value.

The airborne particulate sample, investigated in the previous work, was used for the evaluation of the resolution of columns prepared with Dexsil 400 or 410. The procedures for sample preparation have been documented³.

Of the various samples investigated, one is a sample of coal tar, and another is a filter sample on which coal tar volatile material had been collected by drawing air through the filter. Four samples from coke oven sources in the steel industry were investigated. Two of these samples were taken on glass fibre filters and two were taken on 0.8- μ m porosity silver membrane filters. Samples were extracted for 24 h in Soxhlet extractors with spectrograde cyclohexane. The extracts were concentrated and injected into the GC-MS and GC-FID systems.

A sample of wood preservative sludge was investigated for the possible presence of PAH. This material was extracted for 24 h in a separatory funnel using methylene chloride as the extracting solvent, the funnel being mounted in a mechanical shaker. The methylene chloride phase was concentrated two-fold and injected into the GC-MS system for qualitative identification and into the GC-FID system for quantitative determination.

The procedures for determining GC parameters of PAH reference materials which are available, estimating *RRT* and *RF* values for unavailable PAH compounds and obtaining mass spectra for each GC effluent peak and primary PAH references of known purity, are given in the previous paper³. Fluoranthene has again been selected as the internal reference for both *RRT* and *RF* due to its presence in all samples and its elution from the GC column as a pure isolated compound. The GC-MS instrumental data are summarized in Table II.

All apparatuses and reagents used in the experiments were tested by GC-FID analyses of a pure cyclohexane extract to ensure freedom from PAH residue contamination. Spectral-grade methylene chloride and cyclohexane were used to make all standard and sample solutions. The 10- μ l syringes manufactured by Hamilton were used for injections.

TABLE II
FINNIGAN INSTRUMENTAL DATA

| | |
|---------------------------------------|---|
| <i>Gas chromatography</i> | |
| Column | 5 ft. × 2 mm I.D., packed with 3% OV-1 on 80-100 mesh Gas-Chrom Q |
| Carrier gas (helium) flow-rate | 20 ml/min |
| Inlet pressure | 40 p.s.i.g. |
| Column temperature | 165-290° |
| Programmed temperature | 4°/min |
| Sensitivity | 10 ⁻⁷ |
| Sample size | 1.0 μl |
| <i>Mass spectrometry</i> | |
| Filament current | 500 μA |
| Electron energy | 70 eV |
| Mass range | 35-350 a.m.u. |
| Operating pressure | 5 × 10 ⁻⁶ torr |
| Scanning speed | 1 sec |
| Maximum standard deviation of spectra | 5% |

RESULTS

GC parameters of the PAH reference materials, as measured on the Dexsil 300 packed column, have been given in the previous paper³. These reference materials were tested on Dexsil 400 and 410 packed columns and very small differences were found in *RRT* and *RF* values for the three column materials. The gas chromatograms for the airborne particulate sample are given in Figs. 1-3. All GC patterns are similar although very much less sample was used for the 400 and 410 columns. These columns show some significant improvements in GC resolution. For example, in Figs. 2 and 3, benz[*a*]anthracene (BaA, peak No. 29) is resolved from chrysene (No. 30). Likewise, benzo[*e*]pyrene (BeP, No. 44) is resolved from benzo[*a*]pyrene (BaP, No. 45). There is no obvious difference in resolution between the Dexsil 400 and 410 packed columns. The computer-reconstructed gas chromatogram of the airborne coal tar volatiles is shown in Fig. 4 and the mass chromatograms for ion fragments of *m/e* 228, 252 and 276, are represented in Fig. 5. The presence of C₁₉H₁₀, C₂₀H₁₂ and C₂₂H₁₂ isomeric PAH is thus confirmed in the samples. Figs. 6-9 give some of the mass spectra obtained from the sample. The number at the right side of the graph indicates the percentage of the ion abundance of that GC effluent peak in the total ion intensity of the chromatogram. Each spectrum has been corrected by eliminating the background contribution. Compounds in these figures either had not been previously reported or had been tentatively identified without confirmation³. Some of these compounds are considered to be carcinogenic¹⁵.

Figs. 10 and 11 illustrate the gas chromatograms of the coal tar and airborne emissions as given by a Dexsil 300 column, while Tables III and IV give the results. In passing, it may be appropriate to mention that there continue to be uncertainties about air filtration as a method of sampling for materials having appreciable vapor pressures¹⁶.

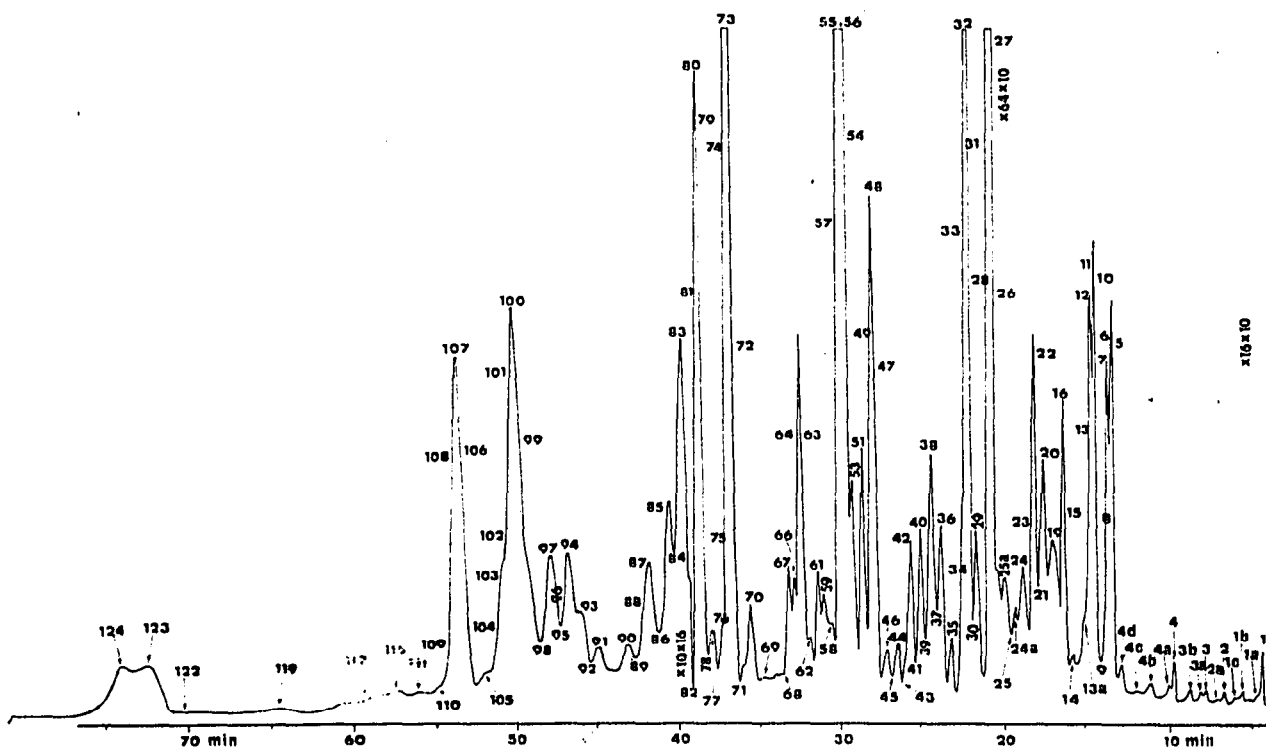


Fig. 1. Gas chromatogram of air sample on Dexsil 300 packed column (see ref. 3).

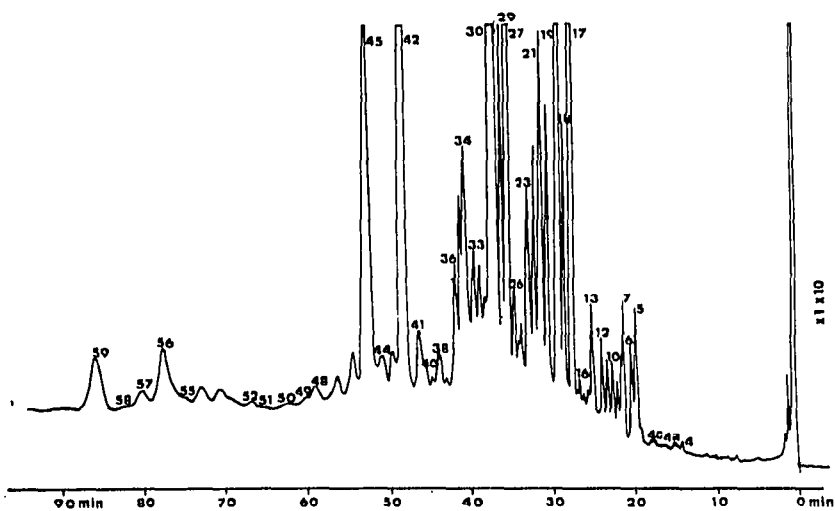


Fig. 2. Gas chromatogram of air sample on Dexsil 400 packed column. Peak numbers are arbitrarily assigned.

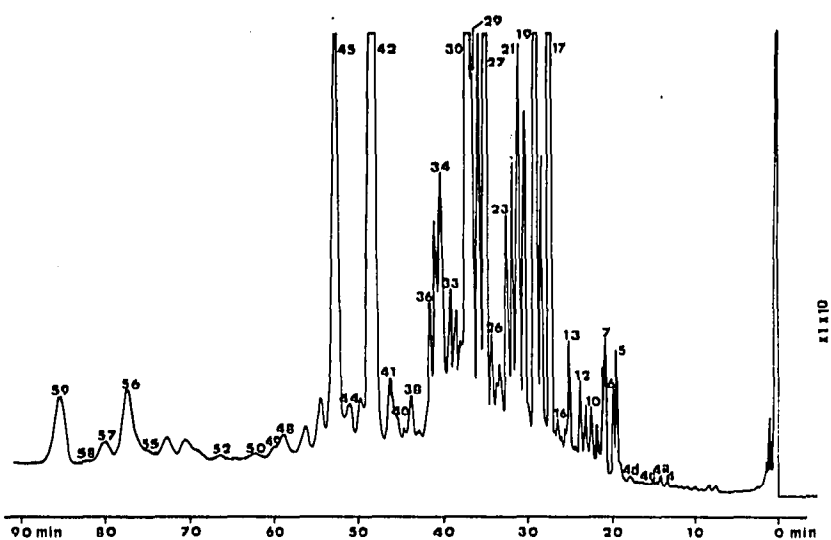


Fig. 3. Gas chromatogram of air sample on Dexsil 410 packed column. Peak numbers are arbitrarily assigned.

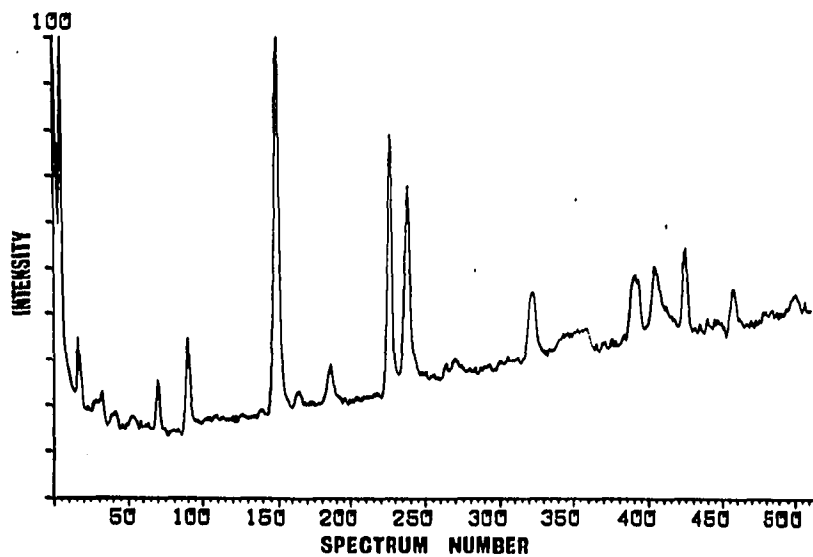


Fig. 4. Computer-reconstructed gas chromatogram of airborne coal tar volatile sample on OV-1.

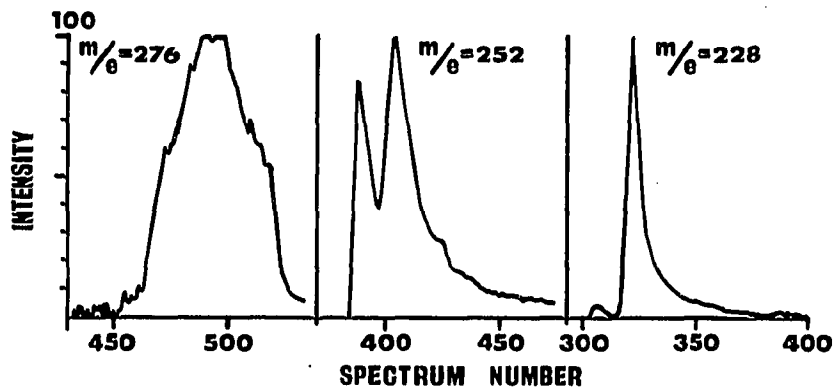


Fig. 5. Mass chromatogram of coal tar volatile sample.



Fig. 6. Mass spectrum of GC effluent peak No. 149 of coal tar volatile sample.

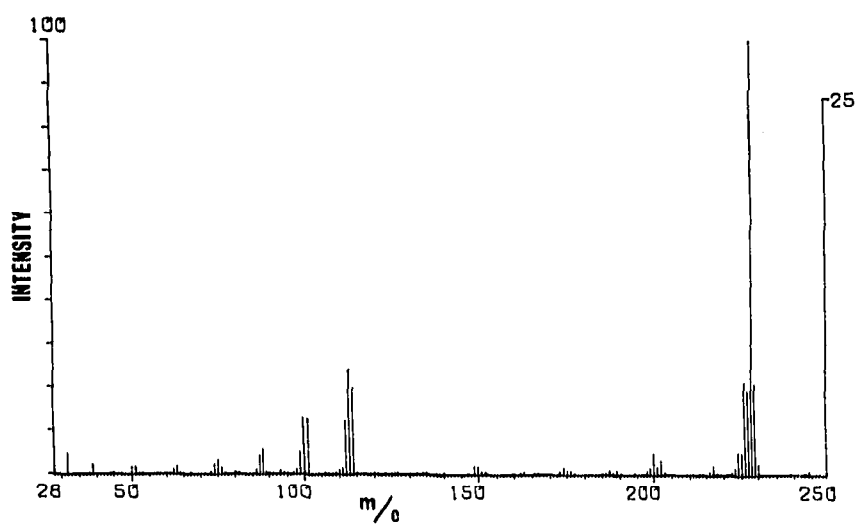


Fig. 7. Mass spectrum of GC effluent peak No. 238 of coal tar volatile sample.

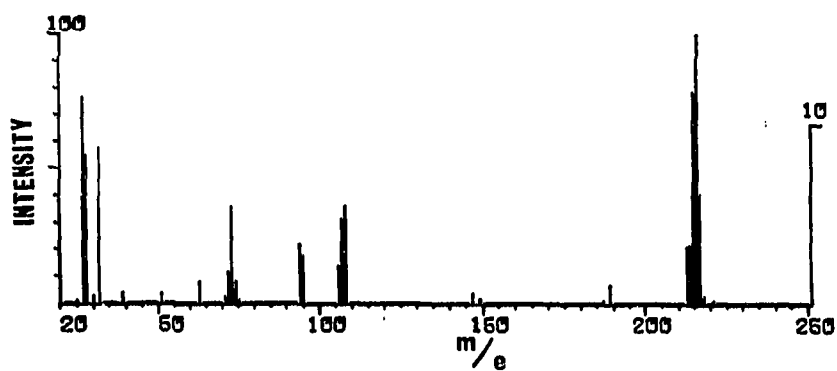


Fig. 8. Mass spectrum of GC effluent peak No. 270 of coal tar volatile sample.

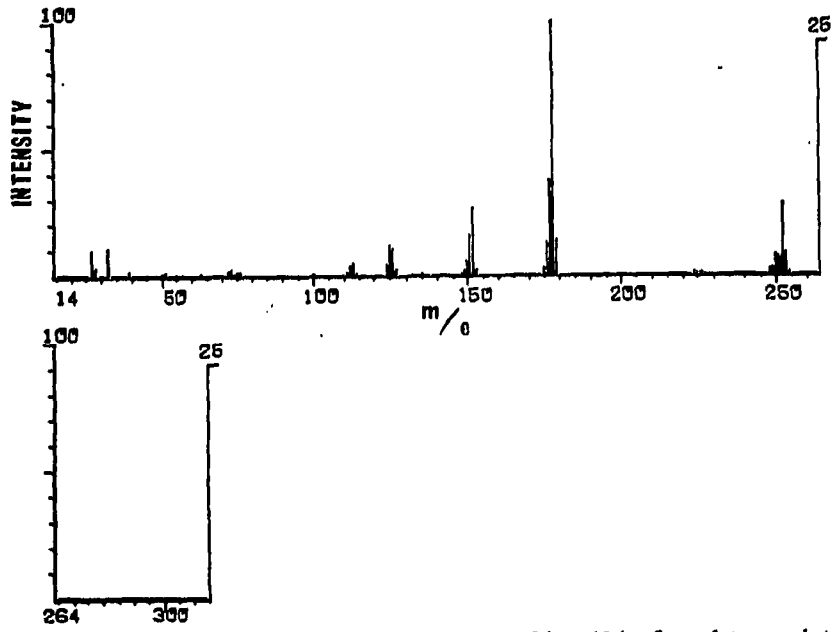


Fig. 9. Mass spectrum of GC effluent peak No. 404 of coal tar volatile sample.

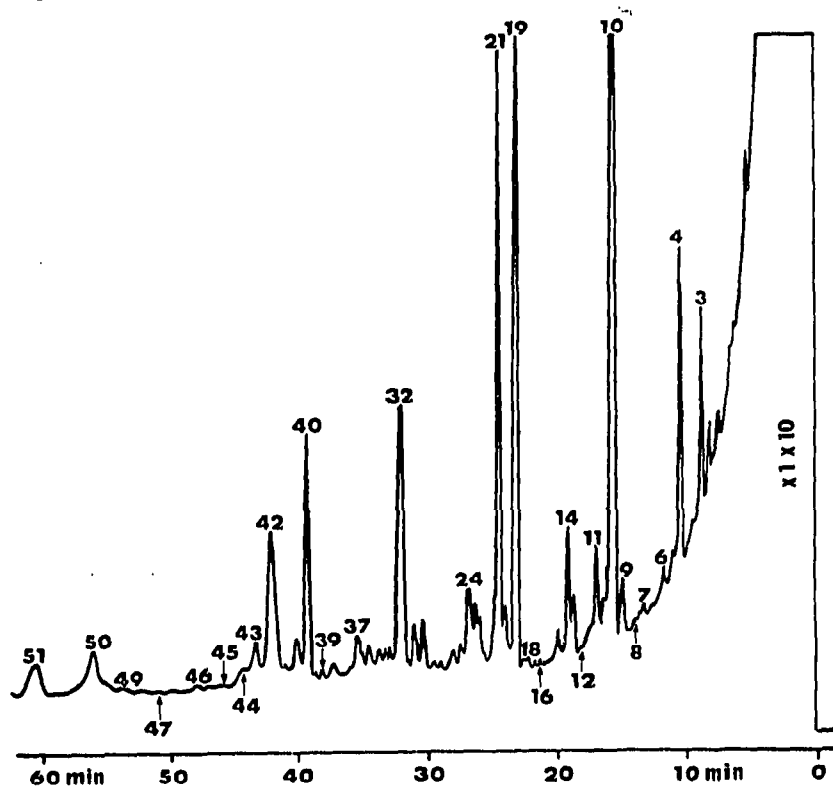


Fig. 10. Gas chromatogram of coal tar on Dexsil 300 packed column.

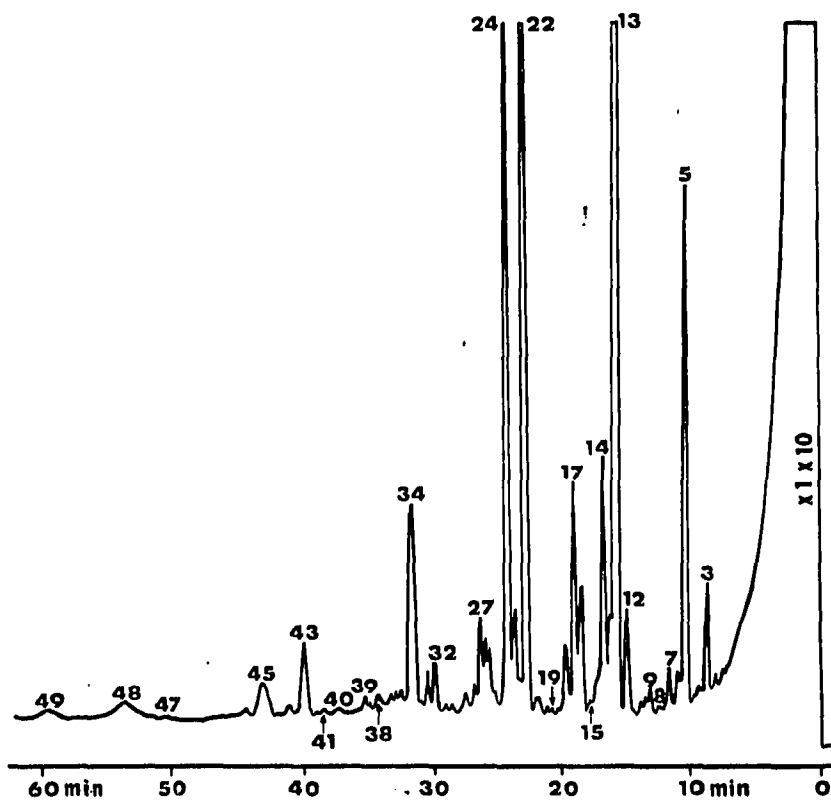


Fig. 11. Gas chromatogram of airborne coal tar sample on Dexsil 300 packed column.

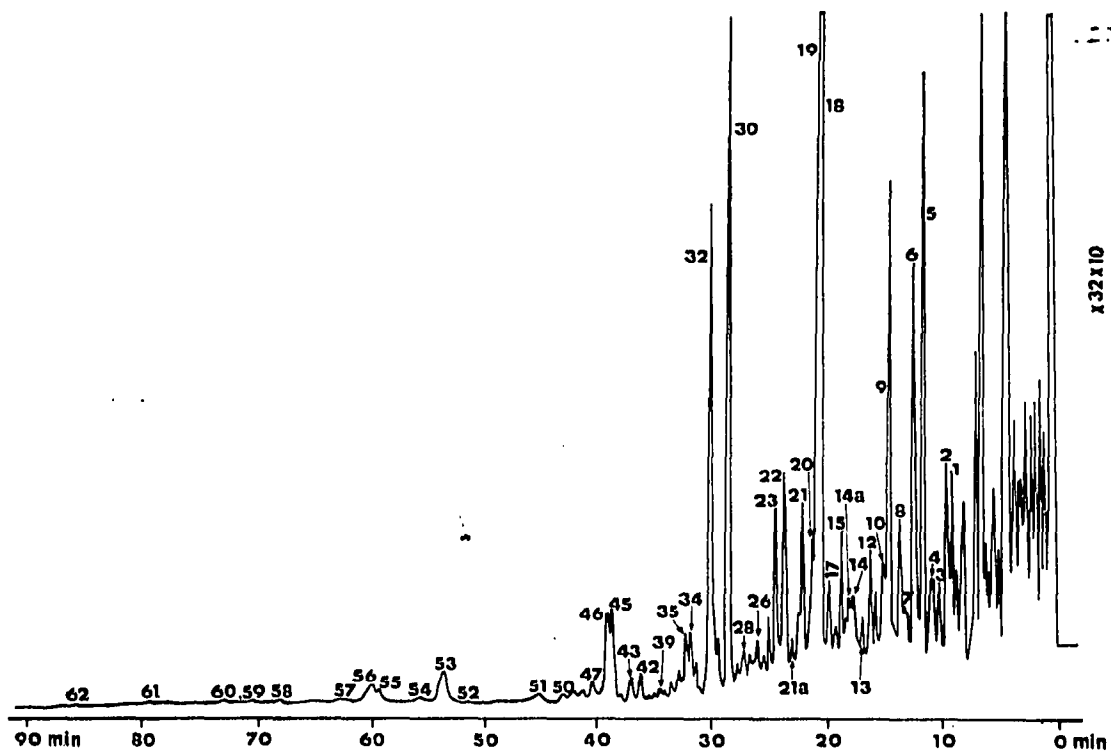


Fig. 12. Gas chromatogram of wood preservative sludge on Dexsil 400 column.

TABLE III
PAH CONCENTRATION IN AIRBORNE COAL TAR EMISSIONS

Sample size: 10 μ l. Calibration with fluoranthene; specific response, 0.3265 μ g/unit area. Determination by comparison with primary standard compound of known purity with respect to relative retention time and mass spectrum. See ref. 3. 9.68 m³ of air was drawn through the filter. GC column: Dexsil 300, packed.

| Peak No. | Compound | Concentration | |
|--------------|---|-----------------|---------------------------------------|
| | | mg/g of samples | μ g/m ³ of air sampled |
| 1 | Biphenyl | 0.29 | 10 |
| 2 | Methylbiphenyl | 0.29 | 10 |
| 3, 4 | Benzindene | 1.44 | 51 |
| 5 | Fluorene | 2.41 | 85 |
| 6, 7 | Dihydrophenanthrene and dihydroanthracene | 0.68 | 24 |
| 8, 9, 10, 11 | Methylfluorenes | 0.74 | 26 |
| 12, 13 | Phenanthrene and anthracene | 142.90 | 5020 |
| 14 | Acridine | 8.44 | 297 |
| 15, 16 | Methylphenanthrene and methylanthracene | 2.18 | 77 |
| 17, 18 | Ethylphenanthrene and ethylanthracene | 3.88 | 136 |
| 19 | Octahydrofluoranthene | 0.15 | 5 |
| 20 | Octahydropyrene | 0.15 | 5 |
| 21 | Dihydrofluoranthene and dihydropyrene | 0.15 | 5 |
| 22 | Fluoranthene | 144.85 | 5090 |
| 23 | Dihydrobenzofluorenes | 8.85 | 311 |
| 24 | Pyrene | 105.47 | 3705 |
| 25, 26, 27 | Benzofluorenes | 24.53 | 862 |
| 28 | Methylfluoranthenes | 3.91 | 137 |
| 29 | Methylpyrenes | 3.88 | 136 |
| 30, 31 | Trimethylfluoranthene and trimethylpyrene | 1.29 | 45 |
| 32 | Benzo[ghi]fluoranthene | 3.29 | 115 |
| 33 | Dihydrobenz[a]anthracene, dihydrochrysene and dihydrotriphenylene | 2.65 | 93 |
| 34 | Benz[a]anthracene, chrysene and triphenylene | 45.74 | 1607 |
| 35, 36, 37 | Dihydromethylbenz[a]anthracene, chrysene and triphenylene | 0.50 | 18 |
| 38, 39 | Methylbenz[a]anthracene, methylchrysene and methyltriphenylene | 4.26 | 150 |
| 40 | Dimethylbenz[a]anthracene, chrysene and triphenylene | 0.41 | 15 |
| 41 | Benzo[j]fluoranthene | 0.12 | 4 |
| 43 | Benzo[k]fluoranthene | 9.96 | 350 |
| 44 | Methylbenzo[k]fluoranthene and methylbenzo[j]-fluoranthene | 2.47 | 88 |
| 45 | Benzo[a]pyrene and benzo[e]pyrene | 13.83 | 486 |
| 46 | Methylbenzo[a]pyrene and methylbenzo[e]pyrene | 2.15 | 76 |
| 47 | Dibenzanthracene | 0.41 | 14 |
| 48 | Benzo[b]chrysene and o-phenylenepyrene | 3.88 | 137 |
| 49 | Benzo[ghi]perylene and anthanthrene | 2.62 | 92 |

Fig. 12 is the gas chromatogram of an aqueous extract of wood preservative sludge and the corresponding data are listed in Table V. This effluent contained very high concentrations of PAH, toxic to marine life. It is also to be noted that the extract contains a number of aliphatic and low-molecular-weight compounds. The strong

TABLE IV

PAH CONCENTRATION IN COAL TAR

Sample size: 7 μ l. Calibration and determination, as in Table III. GC column: Dextsil 300, packed.

| Peak No. | Compound | Concentration mg/g of sample |
|------------|--|---------------------------------|
| 1 | Biphenyl | 2.72 |
| 2 | Methylbiphenyl | 3.61 |
| 3 | Benzindene | 18.44 |
| 4 | Fluorene | 27.39 |
| 5, 6 | Dihydrophenanthrene and dihydroanthracene | 1.99 |
| 7, 8 | Methylfluorenes | 3.12 |
| 9, 10 | Phenanthrene and anthracene | 81.07 |
| 11 | Acridine | 9.18 |
| 12, 13 | Methylphenanthrene and methylanthracene | 2.53 |
| 14, 15 | Ethylphenanthrene and ethylanthracene | 4.36 |
| 16 | Octahydrofluoranthene | 0.23 |
| 17 | Octahdropyrene | 0.21 |
| 18 | Dihydrofluoranthene and dihydropyrene | 1.05 |
| 19 | Fluoranthene | 54.28 |
| 20 | Dihydrobenzofluorenes | 5.26 |
| 21 | Pyrene | 46.50 |
| 22, 23, 24 | Benzo[<i>a</i>]fluorenes | 20.13 |
| 25 | Methylfluoranthenes | 2.25 |
| 26 | Methylpyrene | 2.06 |
| 27, 28 | Trimethylfluoranthene and trimethylpyrene | 0.66 |
| 29 | Benzo[<i>ghi</i>]fluoranthene | 4.40 |
| 30 | Dihydrobenz[<i>a</i>]anthracene, dihydrochrysene and dihydrotriphenylene | 3.87 |
| 32 | Benz[<i>a</i>]anthracene, chrysene and triphenylene | 42.66 |
| 33, 34, 35 | Dihydromethylbenz[<i>a</i>]anthracene, chrysene and triphenylene | 2.12 |
| 36, 37 | Methylbenz[<i>a</i>]anthracene methylchrysene and methyltriphenylene | 11.04 |
| 38 | Dimethylbenz[<i>a</i>]anthracene, chrysene and triphenylene | 1.87 |
| 39 | Benzo[<i>j</i>]fluoranthene | 0.73 |
| 40 | Benzo[<i>k</i>]fluoranthene | 32.54 |
| 41 | Methylbenzo[<i>k</i>]fluoranthene and methylbenzo[<i>j</i>]fluoranthene | 7.43 |
| 42 | Benzo[<i>a</i>]pyrene and benzo[<i>e</i>]pyrene | 33.13 |
| 43 | Methylbenzo[<i>a</i>]pyrene and methylbenzo[<i>e</i>]pyrene | 8.76 |
| 44 | Perylene | 3.51 |
| 45 | <i>o</i> -Phenylenefluoranthene | 0.52 |
| 46 | Dimethylbenzo[<i>k</i>]fluoranthene, dimethylbenzo[<i>a</i>]pyrene and dimethylbenzo[<i>e</i>]pyrene | 2.42 |
| 47, 48, 49 | Dibenzanthracenes | 2.13 |
| 50 | Benzo[<i>b</i>]chrysene and <i>o</i> -phenylenepyrene | 22.79 |
| 51 | Benzo[<i>ghi</i>]perylene and anthanthrene | 17.94 |

smell of the sample is characteristic of phenolic and other oxygenated materials. Most of these compounds were eluted from the GC column before biphenyl, the first polycyclic to appear in the elution sequence. However, peaks 2 and 5 in Fig. 12 also show the presence of heterocyclics. The retention times of PAH on the column were longer than in other samples because of the presence of these aliphatic and oxygenated compounds.

Figs. 13-16 illustrate gas chromatograms from coke oven sources and the

TABLE V

PAH CONCENTRATION IN WOOD PRESERVATIVE SLUDGE

Sample size: 1 μ l. For calibration and determination, see Table III. GC column: Dexsil 400, packed.

| Peak No. | Compound | Concentration (g/l of raw sludge) |
|------------|---|--------------------------------------|
| 1 | Biphenyl | 3.64 |
| 3 | Octahydrophenanthrene and octahydroanthracene | 1.04 |
| 4 | Dihydrofluorene | 1.47 |
| 6, 7, 8 | Methylbiphenyls | 9.79 |
| 9, 10, 11 | Benzindene | 13.64 |
| 12, 13 | Fluorene | 6.61 |
| 14 | Dihydrophenanthrene | 1.33 |
| 14a | Dihydroanthracene | 1.18 |
| 15 | 2-Methylfluorene | 3.82 |
| 16 | 1-Methylfluorene | 0.37 |
| 17 | 9-Methylfluorene | 1.44 |
| 18 | Phenanthrene and anthracene | 15.30 |
| 19 | Benzoquinoline | 7.11 |
| 20 | Acridine | 3.47 |
| 21, 21a | Fluorene carbonitrile | 7.64 |
| 22 | Methylphenanthrene | 8.21 |
| 23 | Methylanthracene | 7.77 |
| 24, 25 | Ethylphenanthrene and dimethylphenanthrene | 2.39 |
| 26, 27 | Ethylanthracene and dimethylanthracene | 2.86 |
| 28 | Dihydrofluoranthene | 1.11 |
| 29 | Dihdropyrene | 1.60 |
| 30 | Fluoranthene | 26.47 |
| 31 | Dihydrofluorenes | 2.05 |
| 32 | Pyrene | 24.19 |
| 33 | Dihydrobenzofluorenes | 1.03 |
| 34 | Methylfluoranthene | 2.05 |
| 35 | Methylpyrene | 2.05 |
| 36 | Methylpyrene | 1.17 |
| 37, 38, 39 | Trimethylfluoranthene and trimethylpyrene | 1.66 |
| 40, 41 | Dihydrobenzo[<i>c</i>]phenanthrene | 0.44 |
| 42 | Benzo[<i>c</i>]phenanthrene | 0.87 |
| 43 | Benzo[<i>ghi</i>]fluoranthene | 0.91 |
| 44 | Dihydrobenz[<i>a</i>]anthracene and dihydrochrysene | 0.42 |
| 45 | Benz[<i>a</i>]anthracene | 5.18 |
| 46 | Chrysene and triphenylene | 5.03 |
| 47 | Dihydromethylbenz[<i>c</i>]anthracene, chrysene and triphenylene | 0.67 |
| 48 | Methylbenz[<i>c</i>]anthracene | 0.52 |
| 49 | Methyltriphenylene | 0.38 |
| 50 | Methylchrysene | 0.43 |
| 51 | Dimethylbenz[<i>a</i>]anthracene, chrysene and triphenylene | 1.12 |
| 52 | Benzo[<i>j</i>]fluoranthene | 0.31 |
| 53 | Benzo[<i>k</i>]fluoranthene and benzo[<i>b</i>]fluoranthene | 6.85 |
| 54 | Methylbenzo[<i>k</i>]fluoranthene and benzo[<i>b</i>]fluoranthene | 1.68 |
| 55 | Benzo[<i>e</i>]pyrene | 2.48 |
| 56 | Benzo[<i>a</i>]pyrene | 3.59 |
| 57 | Methylbenzo[<i>e</i>]pyrene and benzo[<i>a</i>]pyrene | 1.93 |
| 58 | Dimethylbenzo[<i>k</i>]fluoranthene, benzo[<i>e</i>]pyrene and benzo[<i>a</i>]pyrene | 0.20 |
| 59 | Dibenzanthracene | 0.07 |
| 60 | <i>o</i> -Phenylene-pyrene and benzo[<i>c</i>]chrysene | 0.05 |
| 61 | Benzo[<i>ghi</i>]perylene and anthanthrene | 0.07 |
| 62 | Methyl- <i>o</i> -phenylene-pyrene and benzo[<i>c</i>]chrysene | 0.04 |
| 63 | Methylbenzo[<i>ghi</i>]perylene and anthanthrene | 0.03 |

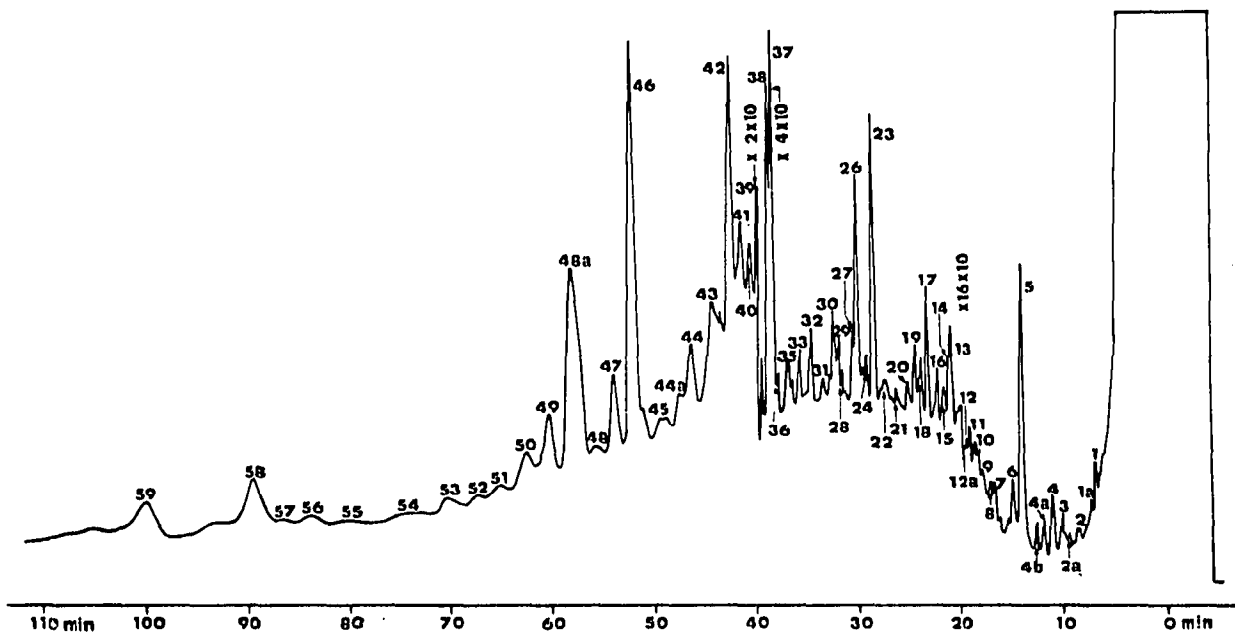


Fig. 13. Gas chromatogram of glass fibre filter No. 1 from coke oven source on Dexsil 400 packed column.

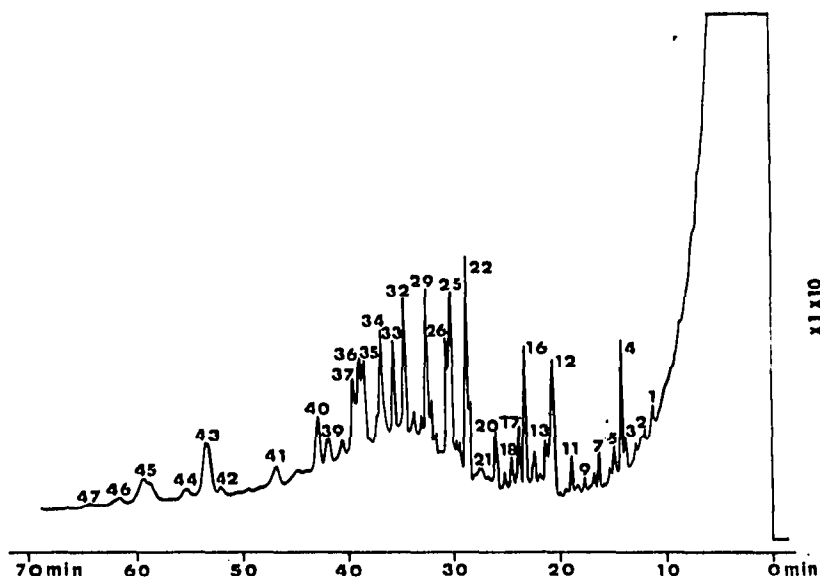


Fig. 14. Gas chromatogram of glass fibre filter No. 2 from coke oven source on Dexsil 400 packed column.

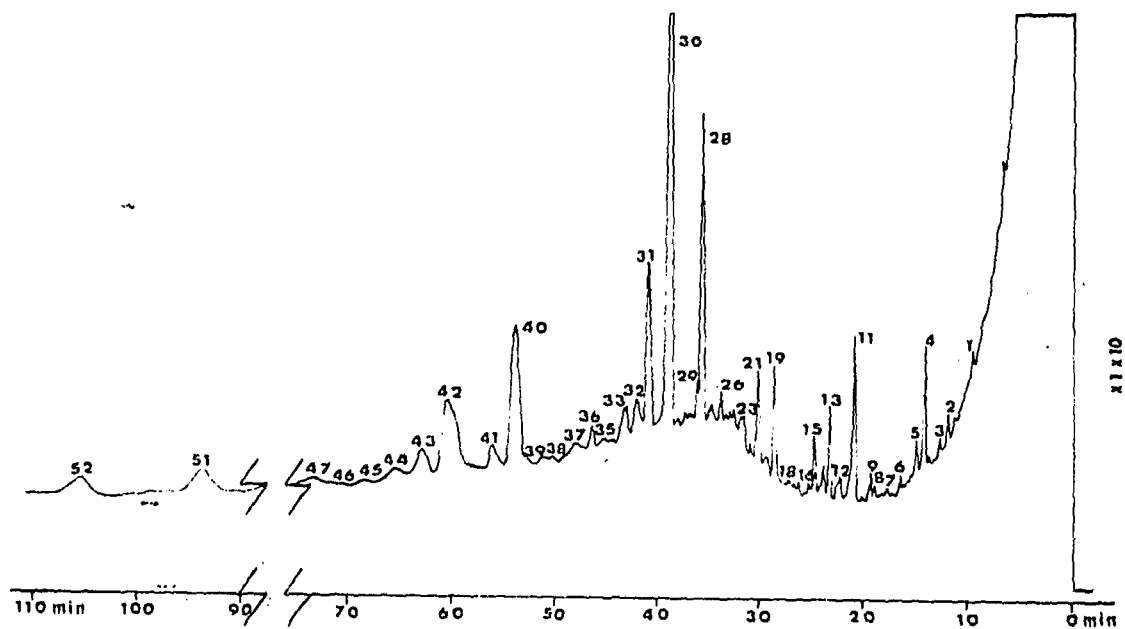


Fig. 15. Gas chromatogram of silver membrane filter No. 1 from coke oven source on Dexsil 400 packed column.

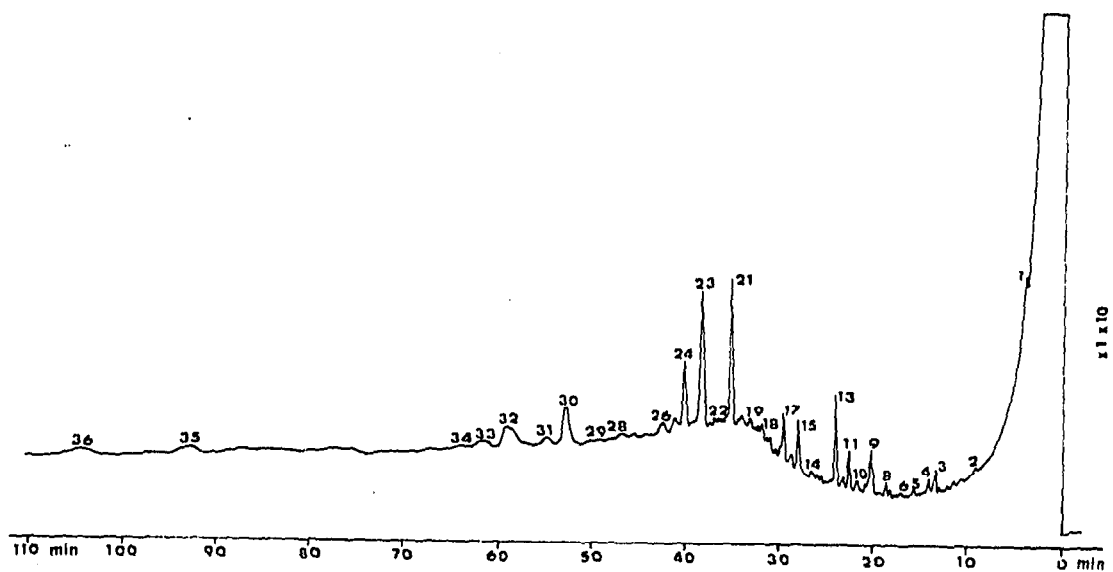


Fig. 16. Gas chromatogram of silver membrane filter No. 2 from coke oven sources on Dexsil 400 packed column.

TABLE VI
PAH CONCENTRATION IN COKE OVEN EMISSIONS
GC columns: Dexsil 400, packed.

| Compound | Sample No. 1* | | Sample No. 2** | | Sample No. 3*** | | Sample No. 4§ | |
|--|---------------|--------------------------------|----------------|--------------------------------|-----------------|--------------------------------|---------------|--------------------------------|
| | Peak No. | Concentration (µg/g of sample) | Peak No. | Concentration (µg/g of sample) | Peak No. | Concentration (µg/g of sample) | Peak No. | Concentration (µg/g of sample) |
| Octahydrophenanthrene | 1 | 31.85 | - | - | - | - | - | - |
| Octahydroanthracene | 1a | 29.89 | 1 | 8.77 | 1 | 29.98 | 2 | 70.31 |
| Dihydrofluorene | 2 | 30.31 | 2 | 13.62 | 1a | 15.68 | 2a | 18.26 |
| Dihydrofluorene | 2a | 18.76 | - | - | - | - | 2b | 23.20 |
| Benzindene | 3 | 106.73 | 2a | 6.72 | 2 | 58.15 | 2c | 20.81 |
| Fluorene | 4, 4a | 271.52 | 3 | 20.86 | 3 | 19.29 | 2d | 15.37 |
| Dihydrophenanthrene | 4b, 5 | 586.98 | 4 | 79.55 | 4 | 316.49 | 3 | 325.83 |
| Dihydroanthracene | 6 | 168.88 | 5 | 21.92 | 5 | 101.68 | 4 | 232.54 |
| 2-Methylfluorene | 7 | 98.71 | 6 | 9.06 | 5a | 8.87 | 5 | 40.28 |
| 1-Methylfluorene | 8 | 73.46 | 7 | 24.35 | 6 | 44.01 | 6 | 102.83 |
| 9-Methylfluorene | 9 | 44.32 | 8 | 11.81 | 7 | 6.71 | 6a | 10.38 |
| Methylfluorene | 10 | 87.84 | 9 | 10.77 | - | - | 7 | 79.77 |
| Benzoquinoline | 11 | 77.74 | 10 | 8.34 | 8 | 31.41 | 8 | 172.79 |
| Acridine | 12, 12a | 85.98 | 11 | 32.44 | 9 | 74.98 | 9 | 636.98 |
| Phenanthrene | 13 | 2,828.54 | 12 | 163.53 | 11 | 458.80 | 9a | 500.36 |
| Anthracene | 14 | 942.85 | 13 | 46.44 | 11a | 305.89 | 9b | 11.47 |
| Fluorene carbonitrile | 15 | 180.29 | 14 | 16.76 | 11b | 32.55 | 10 | 283.92 |
| Methylphenanthrene | 16 | 1,023.41 | 15 | 44.67 | 12 | 130.22 | 11 | 573.25 |
| Methylanthracene | 17 | 1,692.26 | 16 | 85.30 | 13 | 258.93 | 12 | 197.39 |
| Ethylphenanthrene | 18 | 1,578.60 | 17 | 58.04 | 14 | 202.97 | 13 | 1,473.68 |
| Ethylanthracene | 19 | 1,096.71 | 18 | 49.19 | 15 | 249.86 | 13a | 44.53 |
| Octahydrofluoranthene and octahydro-pyrene | 20 | 280.42 | 19 | 11.06 | 16 | 64.36 | 13b | 31.86 |
| Dihydrofluoranthene | 21 | 115.07 | 20 | 73.57 | 17 | 64.87 | 14 | 404.25 |
| Dihdropyrene | 22 | 575.06 | 21 | 36.65 | 18 | 52.29 | 15 | 1,097.82 |
| Fluoranthene | 23 | 5,979.74 | 22 | 269.74 | 19 | 451.95 | - | - |

(Continued on p. 696)

| | | | | | | | | |
|---|---------|----------|-----|--------|--------|----------|-----|----------|
| Dihydromethylbenzo[<i>k</i>] and <i>b</i> fluoranthene and <i>a</i> pyrene | 43 | 434.38 | 40a | 8.63 | 34, 35 | 185.08 | 26a | 137.26 |
| methylbenzo[<i>a</i>]anthracene and <i>e</i> pyrenes | | | | | 36 | 174.71 | | |
| Dimethylbenzo[<i>a</i>]anthracene, dimethyltriphenylene and dimethylchrysene | 44, 44a | 246.35 | 41 | 46.73 | 37 | 62.25 | 27 | 160.89 |
| Benzo[<i>j</i>]fluoranthene | 45 | 176.92 | 42 | 18.66 | 38 | 30.16 | 28 | 451.70 |
| Benzo[<i>k</i>]fluoranthene and benzo[<i>b</i>]fluoranthene | 46 | 3,930.34 | 43 | 155.03 | 39 | 80.04 | 29 | 285.34 |
| Methylbenzo[<i>k</i>]fluoranthene and methylbenzo[<i>b</i>]fluoranthene | 47 | 735.95 | 44 | 33.05 | 40 | 2,170.92 | 30 | 2,556.98 |
| Benzo[<i>e</i>]pyrene | 48 | 103.86 | | | 41 | 430.05 | 31 | 492.13 |
| Benzo[<i>a</i>]pyrene | 48a | 2,630.92 | 45 | 122.15 | 42 | 2,007.75 | 32 | 2,297.83 |
| Perylene | 49 | 702.12 | 46 | 22.07 | 43 | 616.85 | 33 | 698.44 |
| Methylbenzo[<i>a</i>]pyrene | 50 | 330.85 | 47 | 5.88 | 44 | 344.12 | 34 | 247.96 |
| Dimethylbenzo[<i>k</i>]fluoranthene and dimethylbenzo[<i>b</i>]fluoranthene | 51 | 116.74 | | | 45 | 73.13 | | |
| anthene | 52 | 82.68 | | | 46 | 70.18 | | |
| Dimethylbenzo[<i>a</i>]pyrene | 53 | 123.66 | | | 47 | 84.52 | | |
| Dibenzanthracene | 54 | 101.54 | | | | | | |
| <i>o</i> -Phenyleneperylene | 55 | 72.35 | | | | | | |
| Benzo[<i>ghi</i>]perylene and anthanthrene | 56 | 89.04 | | | | | | |
| Methylidibenzanthracene | 57 | 36.79 | | | | | | |
| Methylbenzo[<i>ghi</i>]perylene | 58 | 864.55 | | | 51 | 833.30 | 35 | 766.58 |
| Coronene | 59 | 693.21 | | | 52 | 587.05 | 36 | 493.27 |
| Dibenzopyrene | | | | | | | | |

* Glass fibre filter No. 1: total weight of material collected, 12.59 mg; total volume of solvent extract, 1 ml; injected sample size, 10 μ l.

** Glass fibre filter No. 2: total weight of material collected, 39.67 mg; total volume of solvent extract, 1.0 ml; injected sample size, 10 μ l.

*** Silver membrane filter No. 1: total weight of material collected, 5.75 mg; total volume of solvent extract, 0.6 ml; injected sample size, 6 μ l.

‡ Silver membrane filter No. 2: total weight of material collected, 1.96 mg; total volume of solvent extract, 1.0 ml; injected sample size, 10 μ l.

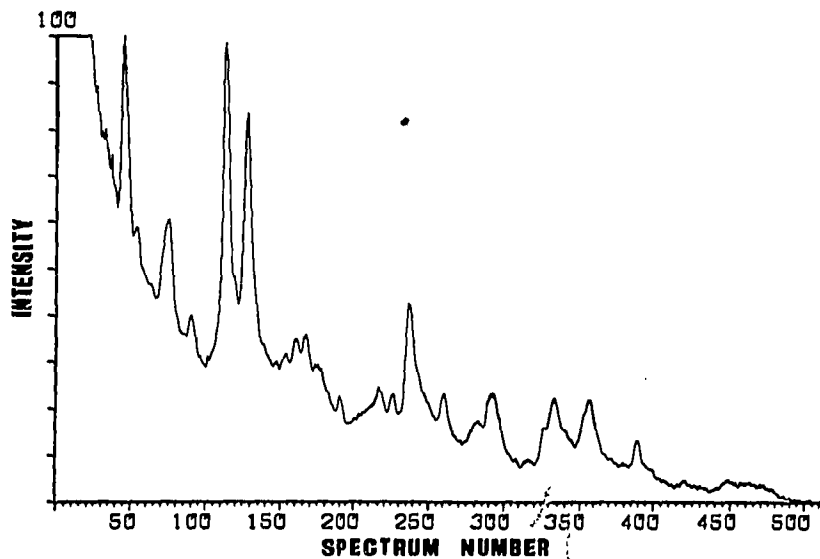


Fig. 17. Computer-reconstructed gas chromatogram of glass fibre filter No. 1 on OV-1 column.

results are given in Table VI. Fig. 17 is the computer-reconstructed gas chromatogram of glass fibre filter No. 1 on an OV-1 column. The mass chromatogram is shown in Fig. 18 and normalized mass spectra are given in Figs. 19 and 20. All "coke oven" samples contained PAH.

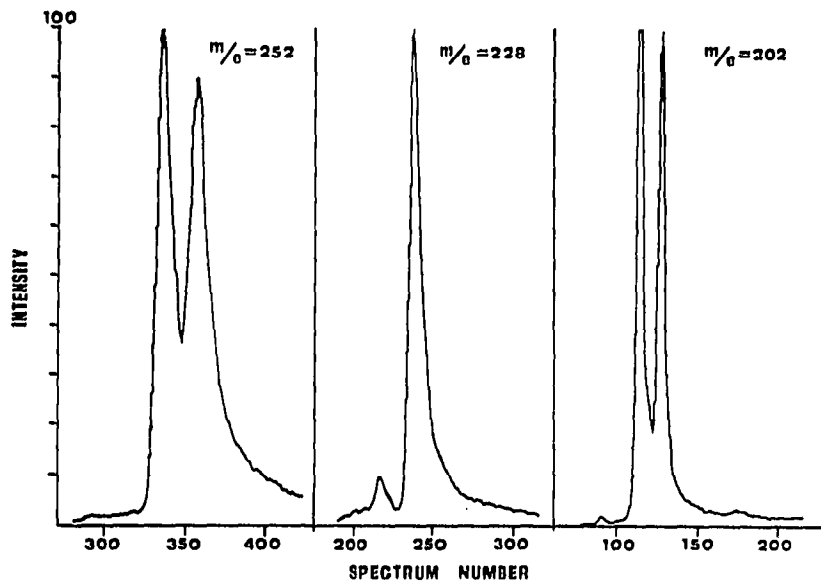


Fig. 18. Mass chromatogram of glass fibre filter No. 1 sample.

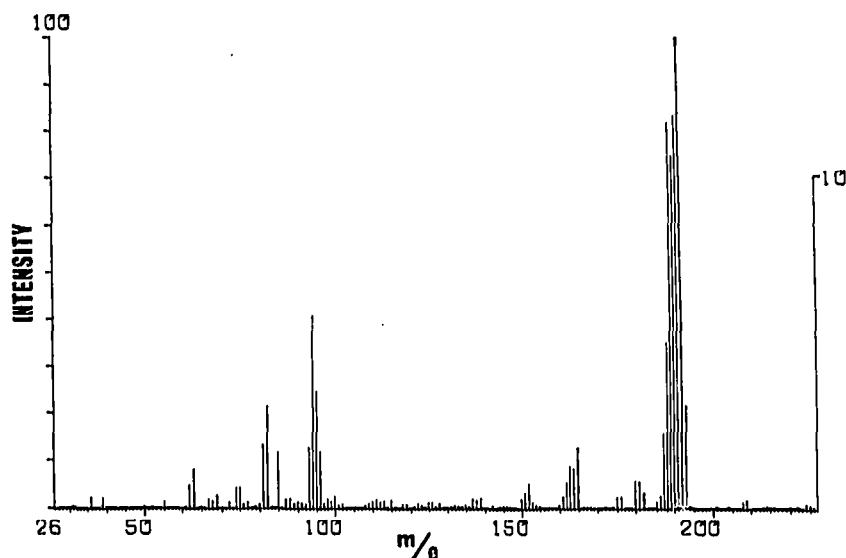


Fig. 19. Mass spectrum of GC effluent peak No. 76 of glass fibre filter No. 1 sample.

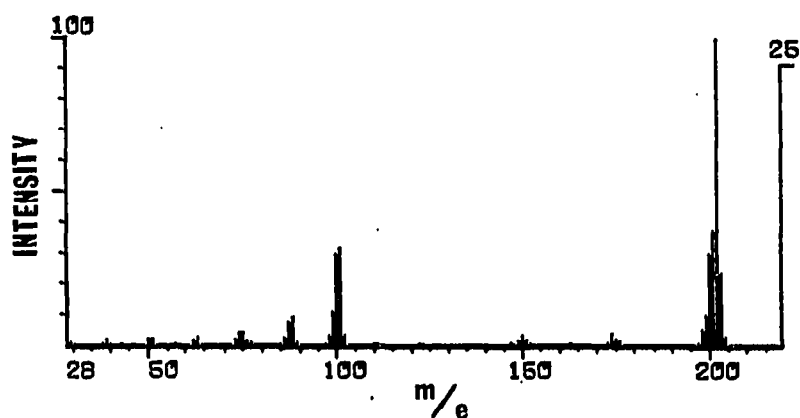


Fig. 20. Mass spectrum of GC effluent peak No. 238 of glass fibre filter No. I sample.

DISCUSSION

The Dexsil 400 packed column yielded equivalent results with shorter retention times when compared with those obtained using Dexsil 410. The elution patterns of hydro and alkyl derivatives of PAH were consistent with the results from Dexsil 300³. Since BaA is a carcinogen and since the carcinogen BaP is often used as an indicator for the presence of PAH in environmental samples, the separation of BaA from chrysene and triphenylene and the separation of BeP from BaP are significant advances. No Rosen separation nor liquid column chromatography was necessary for the samples investigated^{17,18}. Samples of coke oven emissions are known to consist almost entirely of PAH, although we found some low-molecular-weight heterocyclic compounds. The sludge sample, as mentioned previously, contained a large number of aliphatics, oxygenated compounds and aromatics having one benzene ring. No ef-

fort was made to separate these compounds from PAH in the prepared sample, since there was no interference in the GC analyses.

The volume of data which can be provided by the GC-MS during each run makes a data processing capability a prerequisite for acquiring and storing the MS data. By having the MS scanning computer controlled, the burden of manual manipulation of the data is eliminated, which frees the operator to make more efficient use of his time. Final results are produced at high speed and with higher accuracy than by manual data processing.

Computerized data reduction also allows the subtraction of spectral background, thus preventing misinterpretation or confusion of mass spectra with spurious ion interferences contributed by GC column bleeding or other impurities. The resultant mass spectrum, obtained after background subtraction, is simplified and originally intense peaks in the raw spectrum often disappear or show diminished intensity. A new base peak is often found, which had been noticed in the unprocessed data.

CONCLUSIONS

Increasing attention is being given to the contribution of PAH to overall environmental pollution. Investigations of PAH concentrations in the environment have aroused public concern about the impact of these compounds upon the biosphere. The low concentrations of PAH normally found in ambient air require extreme care at all stages of the analytical process, including sampling, to avoid adventitious contamination. Sample preparation, extraction and clean up are fundamental parts of PAH analysis. All determinations must be based upon pure reference materials, corresponding to individual compounds found in the sample and such reference materials are not generally available. The GC-FID-Quadrupole-MS-computer system is, at present, the method of choice for PAH analysis for all types of environmental samples.

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