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DETERMINATION OF AIR-BORNE POLYCYCLIC HYDROCARBONS BY PAPER CHROMATOGRAPHY

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SUMMARY

A paper chromatographic solvent system and an extraction and concentration microtechnique were used to determine air-borne 1,2:3,4-dibenzopyrene, 3,4-benzofluoranthene, 3,4-benzopyrene, 1,12-benzoperylene and anthanthrene in an automobile tunnel, in frequented cross roads, and in sites with little or no automobile traffic. Fluoranthene, pyrene, chrysene, 1,2-benzanthracene, 1,2:5,6-dibenzanthracene, 11,12-benzofluoranthene and coronene were identified on the same chromatogram, 1,2-benzopyrene was presumed. Using at least three filters in series, quantitative air-sampling of penta- and higher cyclic hydrocarbons is claimed. The results are tabulated.

INTRODUCTION

The development of a paper chromatographic (PC) solvent system to separate the neutral portion of high-temperature tar mixtures, and of a suitable microtechnique, has made it possible to undertake the determination of the polycyclic hydrocarbons found in streets and other locations.

EXPERIMENTAL

Air sampling

The air samples were collected in such a manner that volumes from 2.0 to 100 m^3 were drawn through discs 30 or 50 mm in effective diameter and at least three in series. Thick Whatman No. 3 or 31 ET papers were chosen, as the slow-flow-rate papers such as Schleicher & Schuell 589[3] (blue ribbon) proved to be unsuitable. The time needed for drawing the required air volumes through this paper was very protracted. Thus the polycyclic hydrocarbons retained moved from the first filter to the last. This was possibly due to sublimation. The filter discs were mounted in disposable aluminium frames, which were fitted four in series in a holder (Fig. 1). Part B served for light protection only and was removed during the air sampling. A flow-rate over

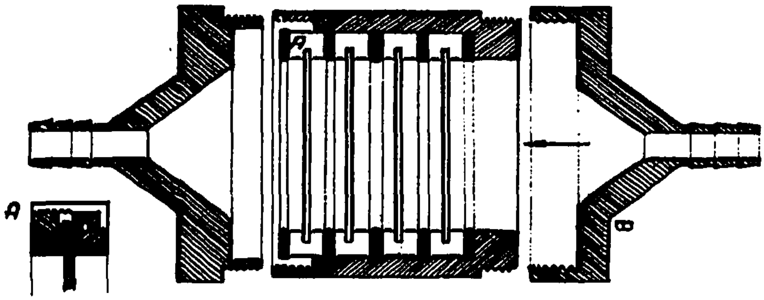

Fig. 1. Holder with disposable aluminium frames for the filter paper discs.

2000 l/h was achieved with 50-mm-diameter discs, and below 2000 l/h when 30-mm-diameter Whatman 31 ET discs were employed. The volumes drawn through were a little less when Whatman No. 3 paper was used.

At least three filters in series had to be employed, as our experiments had shown that a single filter was not sufficient for quantitative retention of polycyclic hydrocarbons. It has been reported that a few Schleicher & Schuell filters placed tightly in a tube in series are permeable to fluorescing high-temperature tars[1]. We analysed each filter separately to determine the amounts of 1,2:3,4-dibenzopyrene, 3,4-benzopyrene, 3,4-benzofluoranthene, 1,12-benzoperylene, and anthanthrene. Experiments carried out repeatedly confirmed that three Whatman 31 ET filters are sufficient to retain amounts not surpassing 0.5 μg of 3,4-benzopyrene and lesser amounts of 1,2:3,4-dibenzopyrene and 3,4-benzofluoranthene (Fig. 2). The distribution of air-borne poly-

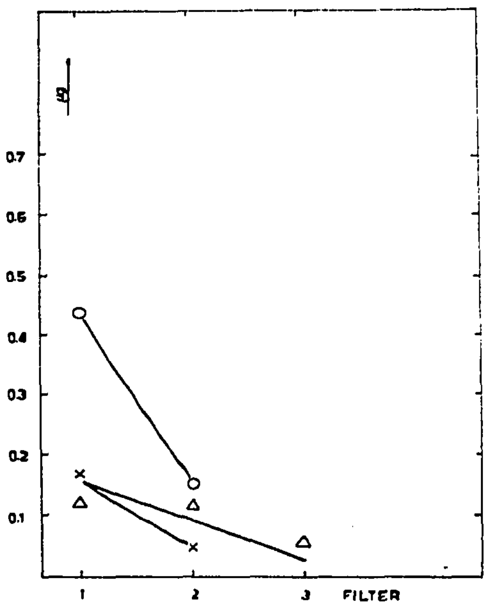

Fig. 2. Decreasing amounts of 1,2:3,4-dibenzopyrene (×), 3,4-benzopyrene (○), and 3,4-benzofluoranthene (△) found from filter to filter in the series.

cyclic hydrocarbons on four Whatman No. 3 filters, 50 mm in diameter, sampled at a flow-rate of 100 l/min, is shown in Fig. 3.

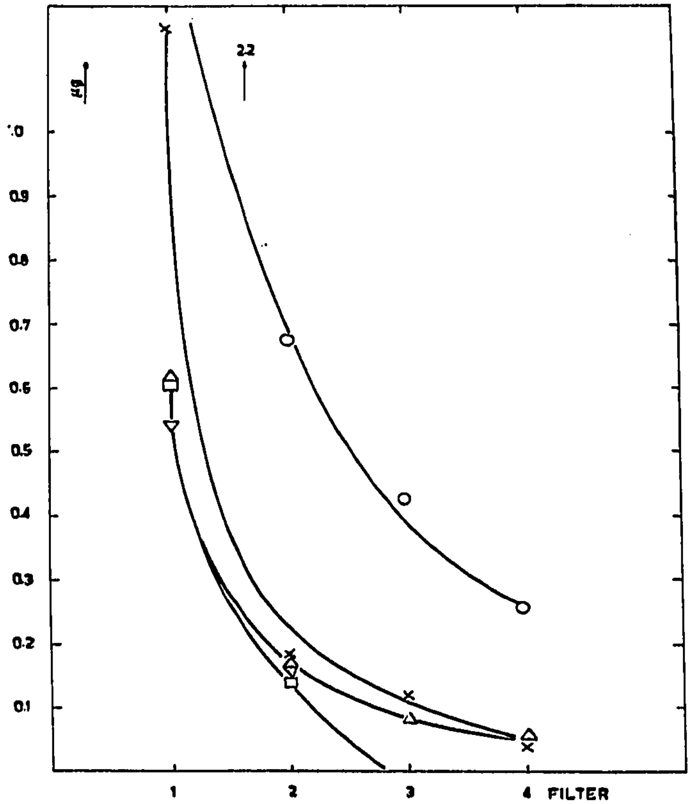

Fig. 3. Decreasing amounts of 1,2:3,4-dibenzopyrene (×), 3,4-benzopyrene (○), 3,4-benzofluoranthene (△), 1,12-benzoperylene (□), and anthanthrene (▽) found from filter to filter in the series (amounts larger than in Fig. 2). The curves for 1,12-benzoperylene and anthanthrene are overlapping.

A highly sensitive analytical method is required for such small amounts. A larger set of experiments has shown that the decreasing amounts found from filter to filter in the series satisfy the following formula

$$S_n = a_1 + a_1 q + a_1 q^2 + a_1 q^3 + \ldots\ldots$$

or

$$S_n = \frac{a_1 - a_n q}{1 - q}$$

where $q = {}^1/_3$ and a_1 is the amount found on the first filter. Whether this equation remains true when a_1 found for other analytical procedures[2–6] is from 10^4–10^6 times larger than in our case is unknown. Quantitative air sampling on a single filter had been considered as usual, without any proof of it being achieved. Thus we claim a quantitative air sampling.

Extraction of the filters

The first three filters containing the air-borne polycyclic hydrocarbons were extracted six times with cold benzene in a Philips beaker for 15 min. The cut filters were submerged below the solvent surface. Thus 10 ml of benzene were used for the first three 35-mm cut filters (and 25 ml for the 55-mm filters) and 8-ml (and 20-ml) volumes were sufficient for the following extractions. The fourth filter was extracted

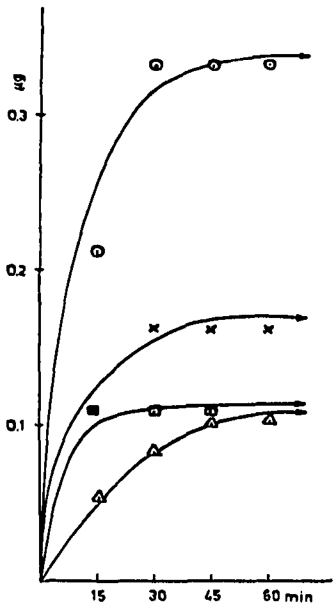

Fig. 4. Extraction curves of 1,2:3,4-dibenzopyrene (×), 3,4-benzopyrene (○), 3,4-benzofluoranthene (△), 1,12-benzoperylene and anthanthrene (□).

separately, being a control of quantitative air sampling on three filters. The six-fold extraction of the first three filters was repeated once or twice when larger amounts of air-borne polycyclic hydrocarbons were expected. An extraction curve, when the total did not surpass 0.4 µg, is shown in Fig. 4.

Membrane filters cannot be used because they dissolve in benzene.

The decanted extracts were united in a special evaporation vessel (Fig. 5). After evaporation of the benzene to dryness, the inside of the vessel was rinsed at least six times with small amounts of petroleum ether and then with benzene again. The polycyclic hydrocarbons were now found in the tip of the vessel. To the remaining solids 50 or 100 µl of benzene were added (or more if the solution was too dark: yellow

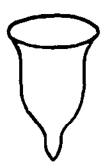

Fig. 5. Special evaporation and concentration vessel.

or orange being optimal) and 0.75-μl aliquots, or appropriate multiples (seven mostly), were applied to the origin of the chromatographic paper with a Kirby automatic micropipette, the whole volume being applied at once. The paper had been impregnated by liquid paraffin (10% in petroleum ether solution).

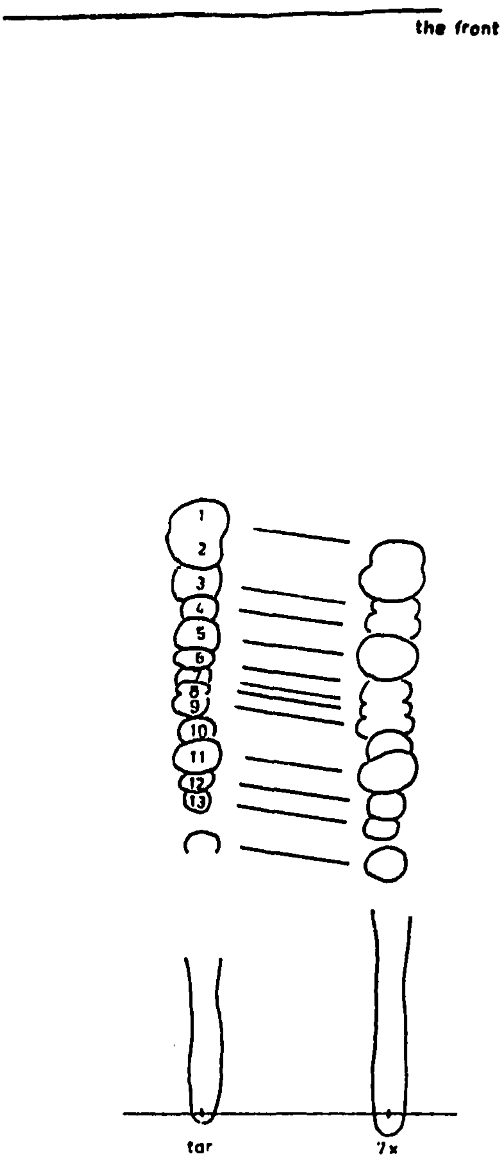

Fig. 6. PC pattern of high-temperature tar (numbered spots) compared to the pattern of an air sample extract chromatogram from a cross road. 1 = Fluoranthene, 2 = pyrene, 3 = chrysene, 4 = 1,2-benzoanthracene, 5 = 3,4-benzofluoranthene, 6 = perylene, 7 = possibly 10,11-benzofluoranthene, 8 = 11,12-benzofluoranthene overlapping 1,2-benzopyrene, 9 = 3,4-benzopyrene, 10 = dibenzoanthracenes zone, 11 = 1,2:3,4-dibenzopyrene, 12 = 1,12-benzoperylene, 13 = anthanthrene.

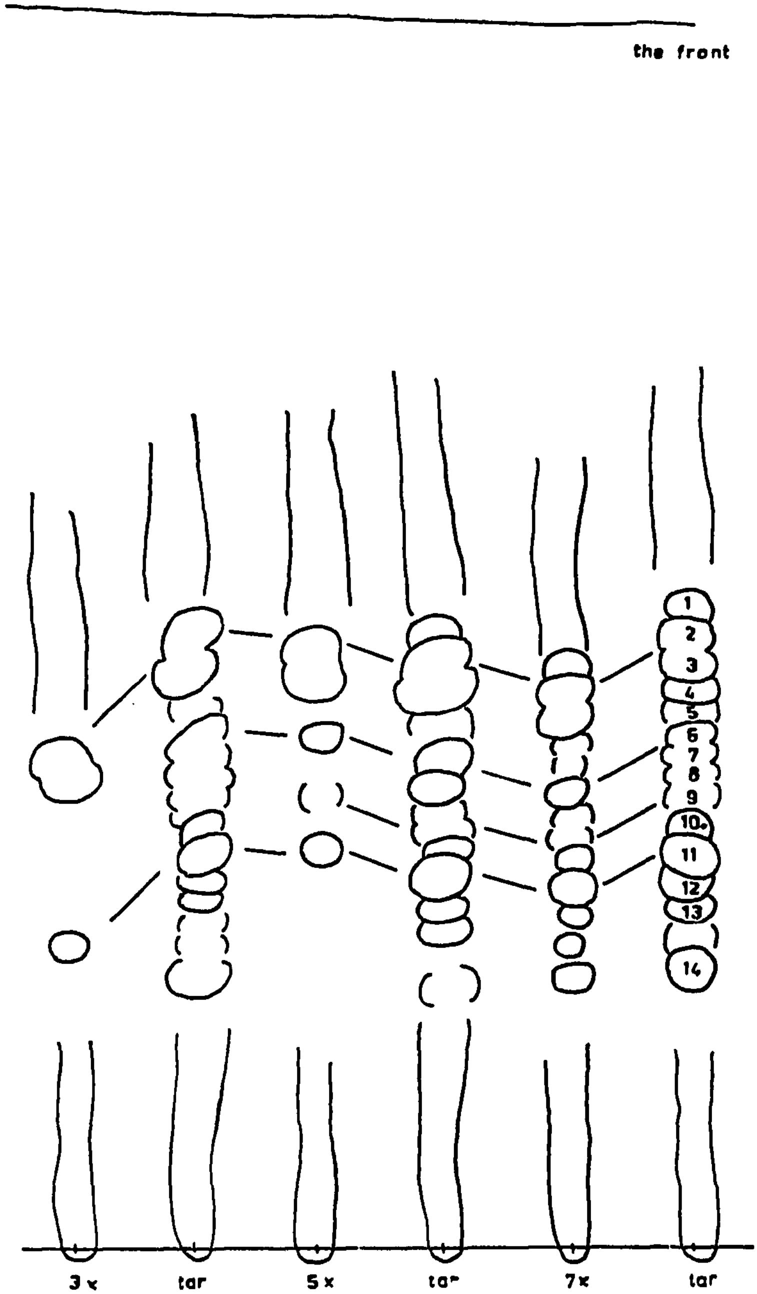

Fig. 7. Another air sample extract chromatogram pattern compared to a high-temperature tar mixture chromatogram. The numbered spots of the tar are as follows: 1 = anthracene, 2 = fluoranthene, 3 = pyrene, 4 = chrysene, 5 = 1,2-benzanthracene, 6 = 3,4-benzofluoranthene, 7 = perylene, 8 = 11,12-benzofluoranthene overlapping 1,2-benzopyrene, 9 = 3,4-benzopyrene, 10 = dibenzoanthracenes zone, 11 = 1,2:3,4-dibenzopyrene, 12 = 1,12-benzoperylene, 13 = anthanthrene, 14 = coronene.

Glass fibre filters for air sampling cannot be used with the microtechnique employed. The tip of the evaporation and concentration vessel contained, in addition to the extract, a glass fibre wool making the application of the extract with an automatic micropipette impossible.

TABLE I

CONCENTRATION OF POLYCYCLIC HYDROCARBONS IN VARIOUS AIR SAMPLES

Date	*Volume of air samples* (m^3)	*Concentration* (mg/m^3)				
		1,2:3,4-dibenzopyrene	*3,4-Benzopyrene*	*3,4-Benzofluoranthene*	*1,12-Benzoperylene*	*Anthanthrene*
Automobile tunnel						
Nov. 5, 1971	1.455	14×10^{-3}	18×10^{-3}	19×10^{-2}		
Nov. 30, 1971	1.149	20×10^{-3}	23×10^{-3}	10×10^{-3}	16×10^{-3}	10×10^{-4}
Nov. 30, 1971	1.303	16×10^{-3}	19×10^{-3}	11×10^{-3}	12×10^{-3}	72×10^{-4}
March 1, 1972	1.572	41×10^{-4}	54×10^{-4}	49×10^{-4}	51×10^{-4}	36×10^{-4}
March 1, 1972	1.410	16×10^{-3}	15×10^{-3}	85×10^{-4}	51×10^{-4}	16×10^{-4}
March 1, 1972	1.357	25×10^{-3}	30×10^{-3}	13×10^{-3}	27×10^{-3}	14×10^{-3}
March 1, 1972	1.105	11×10^{-3}	94×10^{-4}	79×10^{-4}	60×10^{-4}	21×10^{-4}
June 1, 1972	8.753	28×10^{-4}	73×10^{-4}	31×10^{-4}	56×10^{-4}	33×10^{-4}
Rač. Mýto						
Jan. 5, 1971	10.864	58×10^{-4}	53×10^{-4}	12×10^{-4}	10×10^{-4}	10×10^{-4}
Febr. 3, 1971	9.607	22×10^{-4}	57×10^{-4}	16×10^{-4}	12×10^{-4}	17×10^{-4}
May 17, 18, 1971	28.001	69×10^{-5}	38×10^{-5}	76×10^{-5}	23×10^{-6}	13×10^{-6}
June 7, 11, 1971	117.855	10×10^{-5}	13×10^{-5}	5×10^{-6}	10×10^{-5}	11×10^{-5}
Institute of Hygiene						
Febr. 3, 1971	18.193	30×10^{-4}	69×10^{-4}	14×10^{-4}	26×10^{-4}	17×10^{-4}
March 29, 31, 1971	36.949	20×10^{-4}	60×10^{-4}	11×10^{-4}	13×10^{-4}	90×10^{-5}
Apr. 7, 9, 1971	30.573	19×10^{-5}	56×10^{-5}	21×10^{-5}		
July 26, 1972	4.832	21×10^{-4}	61×10^{-4}	20×10^{-4}		
Nov. 6, 1972	3.368	71×10^{-5}	66×10^{-5}	41×10^{-5}	ground floor	
Nov. 6, 1972	5.754	49×10^{-5}	74×10^{-5}	24×10^{-5}	fourth floor	
March 9, 1973	2.561	42×10^{-4}	55×10^{-4}	14×10^{-4}	39×10^{-4}	26×10^{-4}
Apr. 6, 1973	4.648	10×10^{-4}	11×10^{-4}	73×10^{-4}		
Koliba						
Apr. 11, 1973	5.230	—	—	—	—	—
June 12, 13, 1973	103.413	44×10^{-6}	30×10^{-6}	—	—	—
Zlaté Piesky						
May 29, 1973	7.124	16×10^{-4}	16×10^{-4}	—	—	—
Železná Studienka						
May 4, 1973	3.650	—	—	—	—	—
May 21, 1973	3.489	—	—	—	—	—
SNP Square (near Manderla)						
June 27, 1973	11.430	48×10^{-6}	48×10^{-6}	38×10^{-6}	70×10^{-6}	49×10^{-6}
St. Andrew's churchyard						
July 3, 1973	10.250	27×10^{-6}	46×10^{-6}	16×10^{-6}	—	—
July 4, 1973	14.566	24×10^{-6}	—	95×10^{-7}	—	—
Schiffbeck's garden						
May 11, 1973	4.000	—	—	—	—	—

Paper chromatographic technique

The PC technique has been already described in detail[7]. Strictly speaking, the PC solvent system employed is not ideal, but it was used in order to be able to carry out a trace analysis of amounts of air-borne materials in incomparably smaller amounts than required usually. Furthermore, we wanted to avoid a laborious column chromatographic pretreatment and preparative isolation of the component in question, and we tended to determine as large a number as possible of the hydrocarbons from one chromatogram. The procedure is not instant, however it is of free time one. After the chromatogram has been developed the spots of strongly fluorescing polycyclic hydrocarbons were outlined under UV illumination, and evaluated according to the calibration curves of standard hydrocarbon solutions by horizontal diameter measurement[7]. The but just fluorescing borders of the spots were outlined.

RESULTS

PC patterns of the filter extracts, such as Fig. 6, are comparable to those of high-temperature tar solution chromatograms. This chromatogram is of a sample from a busy cross road, taken in March, when the chimneys are active. Fig. 7 is of another cross road, but the air sample was taken in July, when the chimneys are not active, except for the power station. Thus the sample could be attributed to automobiles only. We determined semi-quantitatively: 1,2:3,4-dibenzopyrene, 3,4-benzopyrene, 1,12-benzoperylene, 3,4-benzofluoranthene, and anthanthrene. Fluoranthene was always found; pyrene, chrysene, 1,2-benzanthracene, 1,2:5,6-dibenzanthracene, 11,12-benzofluoranthene, perylene, and coronene were identified and 1,2-benzopyrene was presumed. We have chosen various sites in Bratislava for air sampling: the automobile tunnel, some frequented cross roads and streets, less frequented streets, and St. Andrews' churchyard, the last location being surrounded by automobile traffic. The findings from the chosen locations are shown in Table I.

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