THE RAPID MEASUREMENT OF POLYCYCLIC HYDROCARBONS IN AIR BY MICROSUBLIMATION

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ABSTRACT

Interest in the carcinogenic factors associated with combustion processes goes back to about 1800, when skin cancer was observed as an occupational disease of chimney sweeps. Benzo(a)pyrene (BaP), a carcinogenic polycyclic hydrocarbon, was only isolated from coal tar *ca.* 1950 by Kennaway by means of its fluorescence properties and BaP has been observed by various workers as a frequent constituent of air samples and biological materials. Up until quite recently, the methods used by most workers were based on ultraviolet absorption; fluorescence had been forgotten. These methods have been laborious in execution and unreliable. When, in the ultraviolet, diagnosis and measurement of BaP was based on the peak at *ca.* 402 mn, results had to be particularly unreliable because of the strong interference of benzo(k)fluoranthene (BkF) which was always present in the same extracts or eluants. The interfering effect of BkF was pointed out in 1960 but ultraviolet measurements of BaP continue to be made without correction for BkF. In our laboratory, over a period of 15 years, continuing improvements and new techniques have led to the use of activated alumina for chromatographic separation using toluene, a polar solvent, for elution, followed by fluorescence measurement of BaP and BkF. Using this more rapid method, it has been found possible to make daily measurements of these 2 polycyclic hydrocarbons in Ottawa air over a period of several years. This fairly rapid method does retain the lengthy soxhlet extraction of each sample, followed by a shortened chromatographic separation.

In the method to be described, both the extraction and chromatography are dispensed with by direct sublimation of the polycyclics from the air sample. The sublimation is carried out at an optimum temperature under an inert atmosphere, the sublimate is collected in spectrograde solvent and the BaP and BkF are measured by fluorescence in the usual way. The results obtained by sublimation agree very well with those carried out by our present standard method. Being simpler and more rapid, it should be quite feasible to make this the basis of a rapid method for the routine measurement of BaP and BkF levels as indicators of air pollution, analysing 20 or more air samples per day.

INTRODUCTION

The measurement of polycyclic aromatic hydrocarbons in air samples involves the use of lengthy and tedious methods where the separations are usually made by column, paper or thin layer chromatography, and quantitative measurement by fluorescence spectroscopy or spectrophotometry in the ultraviolet[1-6]. Recently faster methods to measure BaP in air samples have been developed[7, 8]. In these shorter methods, column chromatography or

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thin layer chromatography are used for separation, and fluorescence for identification and measurement.

Some polycyclic hydrocarbons such as naphthalene and anthracene are rarely identified in air samples on account of their volatility[5].

The volatility of pyrene, fluoranthene, chrysene, BaP, BkF has been studied in our laboratory and from these results it seems possible to sublime most of the polycyclics[9]. *Table 1* lists the vapour pressures of four polycyclics at

Table 1. Variation of vapour pressure with temperature.

	$T.$	P. mm Hg	$T.$	P. mm	$T.$	P. mm
Naphthalene	20°	48·5 $\times 10^{-3}$	80°	7590 $\times 10^{-3}$	200°	3973
Anthracene	20°	0·0030 $\times 10^{-3}$	80°	3·69 $\times 10^{-3}$	200°	24·58
Phenanthrene	20·0°	0·092 $\times 10^{-3}$	80°	38·59 $\times 10^{-3}$	200°	68·25
Pyrene	20·0°	0·0034 $\times 10^{-3}$	80°	2·38 $\times 10^{-3}$	200°	1·005

three different temperatures, 20°, 80° and 200°. These vapour pressures were calculated from the equation given by Sears and Hopke. We assume that the curve was linear over this temperature range[10]. A few experiments were performed in order to see if a method, based on the sublimation properties, could not be developed. Since no extraction with a solvent will be needed, such a method will be faster.

Preliminary results suggested that no separation by column chromato-graphy will be needed to measure BaP and/or BkF by fluorescence as can be seen from *Figure 1*. A fluorescence spectrum of an air sample at the two maximum excitation wavelengths for BaP and BkF shows the typical emis-sion pattern while a cyclohexane soxhlet extract of an air sample does not show in general this structure (unless it contains large amounts of BaP and BkF) and a separation is needed. By sublimation only some compounds of the organic fraction of an air sample are extracted; there is a specific separa-tion. *Figure 2* shows the effect of the sublimation temperature upon the recovery of BaP and BkF. At 230° all the BaP and/or BkF are sublimed and no increase is observed with further increases of temperature. 250° was then chosen as the working temperature. The recovery of BaP and BkF is also a function of the time allowed for the sublimation to proceed. In *Figure 3* we can see that recovery is complete after 40 minutes at 230°, but a sublimation time of 60 minutes was used in the method.

Table 2 lists some of the results obtained by the sublimation method which will be described. These values are compared to results obtained by fluores-cence after chromatography on an alumina column[7].

EXPERIMENTAL CONDITIONS

Figure 4 shows a scheme of the apparatus used for the sublimation of polycyclics in an urban air sample taken on glass fibre sheet. Two discs 35 mm in diameter were cut from an 8′ × 10′ glass fibre sheet and placed in the sublimation tube (*Figure 4*) which was then connected to the nitrogen line. The tube was put in the oven which had been preheated at 250° and sublimation allowed to proceed over a period of 60 minutes. While sublima-
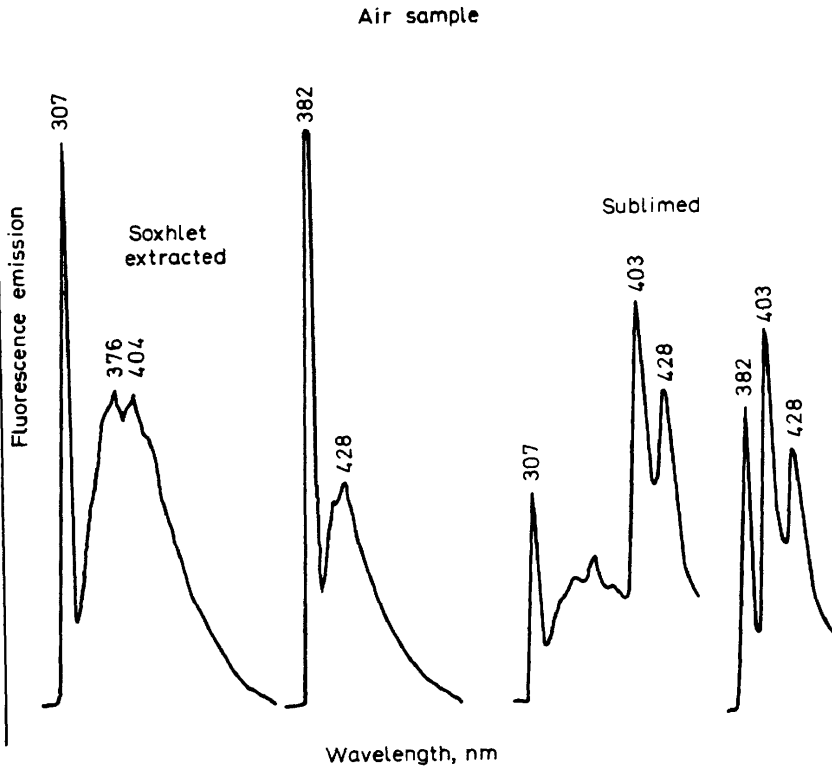
Air sample

Fluorescence emission

307

Soxhlet
extracted

376
404

382

428

Sublimed

403

428

307

382

403

428

Wavelength, nm

Figure 1. Air sample fluorescence spectra

BaP or BkF concentration γ/ml

0·06

0·05

0·04

0·03

0·02

0·01

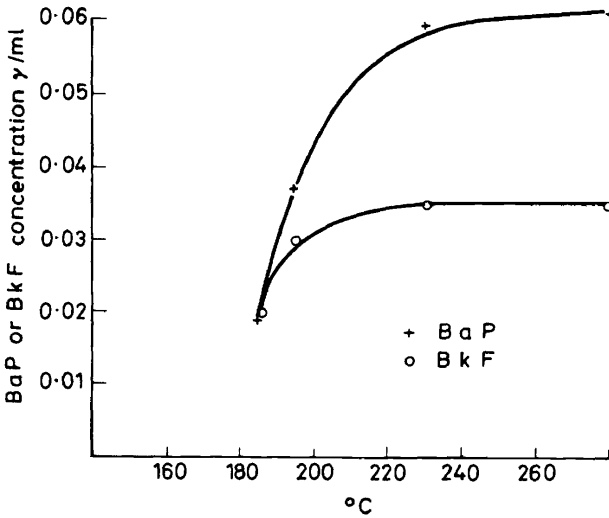160   180   200   220   240   260

°C

+   B a P
o   B k F

Figure 2. Effect of temperature on sublimation.

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Table 2. Comparison of results obtained by sublimation and column chromatography.

	Micrograms of Hydrocarbon per 8″ × 10″ sheet			
Sample No.	Sublimation		Column Chromatography	
	BkF	BaP	BkF	BaP
1	2·1	2·0	3·3	3·9
2	1·1	1·5	2·1	1·3
3	1·1	1·4	2·2	2·5
4	1·6	1·8	2·3	3·4
5	1·0	1·1	1·3	2·1
6	0·5	0·4	0·6	0·5
7	1·3	1·4	3·4	2·4
8	0·6	0·4	1·1	1·0
9	1·4	2·0	2·7	2·4
10	1·8	3·1	2·5	3·7
11	7·2	13·6	17·3	27·8
12	1·4	1·9	1.7	2·2
13	0·7	0·7	1·3	1·2
14	0·6	0·6	1·1	1·1
15	1·8	2·9	3·0	2·6
16	0·7	0·7	1·3	1·2
17	2·6	2·7	4·2	3·5
18	1·1	1·6	1·5	1·6
19	0·4	0·3	0·6	0·5
20	2·7	2·4	4·0	1·4
21	1·1	1·9	1·2	0·9
22	0·2	0·2	0·2	0·2
23	2·1	2·4	3·9	4·4
24	1·4	1·7	1·5	1·6
25	2·1	2·2	3·4	2·1
26	1·0	0·8	3·5	2·6
27	0·6	0·7	0·4	0·3
28	1·2	1·8	1·3	1·9
29	0·2	0·3	0·5	0·4
30	0·8	0·8	1·3	0·9
31	0·4	0·3	1·3	1·0
32	nil	nil	0·1	0·1
33	0·1	0·1	0·6	0·7
34	0·3	0·3	1·1	0·8
35	0·9	0·6	2·1	0·7
36	1·0	0·5	2·9	2·1
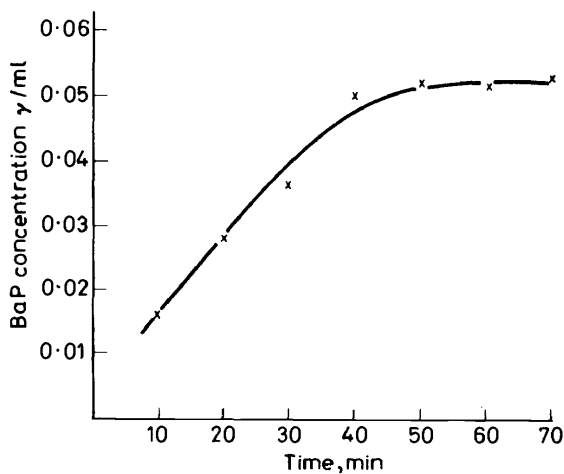
Figure 3. Effect of time on sublimation.

C   N₂ Cylinder
M   Manifold
V   Needle valve
R   Flow meter
O   Sargent furnace No S-21586
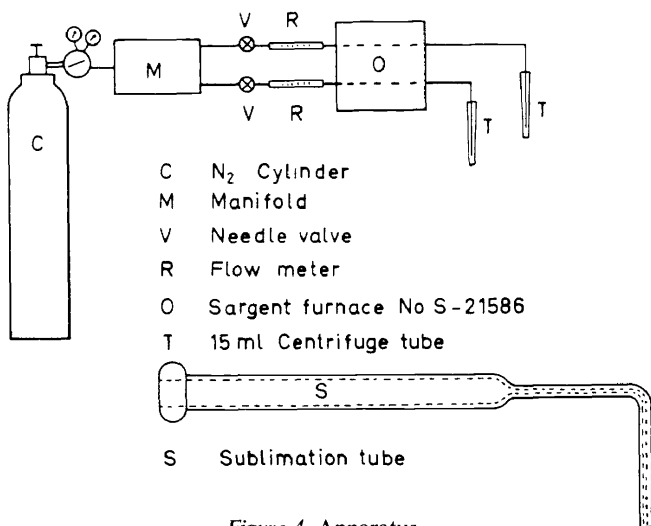T   15 ml Centrifuge tube

S   Sublimation tube

Figure 4. Apparatus

tion takes place clean water pumped nitrogen is flowing through the tube at a flow rate of 10 ml per minute. The exit of the tube is placed in a 15 ml centrifuge tube containing 10 ml of pure cyclohexane, so that any polycyclics which could escape can be trapped. After the sublimation is complete, the tube is allowed to cool, and the inside is washed with the cyclohexane contained in the test tube. The solvent is moved back and forth many times.
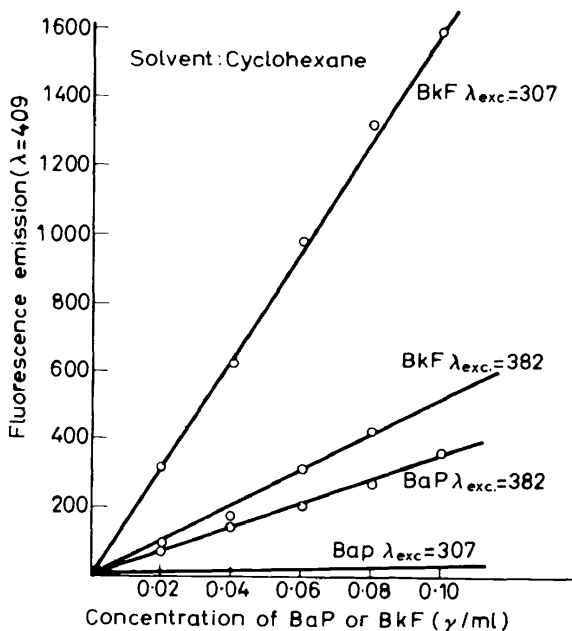

Figure 5. Standard curves.

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After the polycyclics are dissolved, the sample is transferred to a 10 ml volumetric flask and made up to volume. It is then ready for the measurement by fluorescence.

FLUORESCENCE MEASUREMENT

BaP and BkF have similar fluorescence emission spectra. In a mixture of the two, their main emission peaks at approximatively 403 (in cyclohexane) cannot be resolved[11]. Since the relative fluorescence emission intensity of BkF is much greater than that of BaP (approximately twenty times) when a mixture of the two is excited at 307 nm, the reading at this wavelength is essentially due to BkF only. Knowing the concentration of BkF, one can calculate the effect of this hydrocarbon when a mixture is excited at 382, after which the concentration of BaP may be calculated.

Fluorescence emission measurements are then made at 403 on these prepared samples when exciting at 307 nm and 382 nm which are respectively the maximum excitation wavelengths for BkF and BaP. The instrument used is an Aminco Bowman Spectrophosphorimeter with slit arrangement 2. At the same time the emission fluorescence intensity at 403 is also measured at the two previously mentioned exciting wavelengths on standards of BaP containing 0·02, 0·04, 0·06, 0·08, 0·10 μg per ml and standards of BkF also containing 0·02, 0·04, 0·06, 0·08 and 0·1 μg per ml. Four curves are obtained shown in *Figure 5*. This emission intensity is measured by the base line technique as shown in *Figure 6*. The height above the X sloping base line is taken as the emission intensity.

The concentration of BaP and BkF in micrograms per ml of solution are calculated according to the following equations.

$$\text{conc. BkF} = \frac{\text{Emission at 403 for } \lambda \text{ exc 307}}{\text{Slope of BkF curve at 307 exc}}$$

conc. BaP $=$

$$\frac{\text{Emission at 403 for } \lambda \text{ exc 382} - (\text{conc. BkF} \times \text{slope BkF curve at exc 382})}{\text{Slope of BaP curve at 382 exc}}$$

One can then calculate the concentration of these two compounds in the 10 ml of solution and consequently in the whole sheet or per cubic metre of air by using the appropriate factor.

CONCLUSION

This method permits the measurement of BaP and BkF in air samples faster than by any other methods.

The oven used allowed us to sublime two samples within one hour, but using an appropriate oven one could run as many as required. However, the results obtained by sublimation are in general lower than results obtained on the same samples after chromatography. Of the two compounds measured, BaP and BkF, BkF results by sublimation are the lowest. This discrepancy can be explained by the interference of compounds present in the sublimed samples which are lower or absent in the chromatographed samples. An
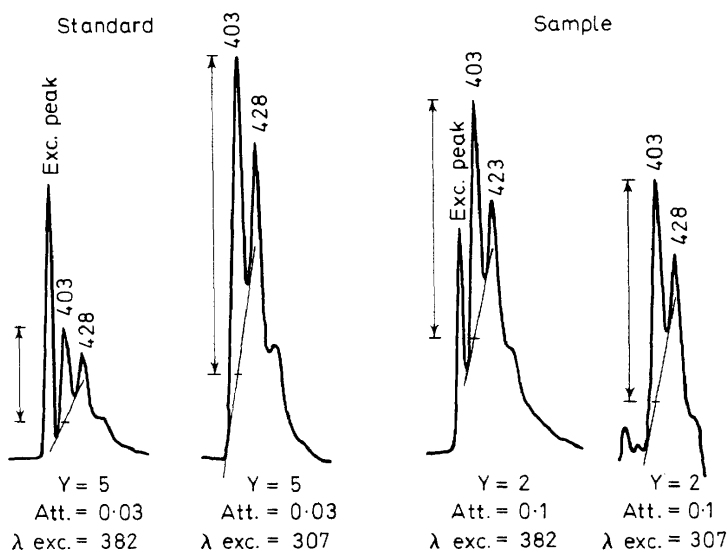
Figure 6. Measurement technique.

evaluation of this interference can be observed from the excitation peaks as shown in *Table 3*. These excitation peaks are given in arbitrary units and are

Table 3. Intensity of Excitation Peaks in Arbitrary Units

	λ 307	λ 382
0·012 γ BkF per ml	360	435
0·025 γ BkF per ml	360	457·5
0·050 γ BkF per ml	375	450
0·075 γ BkF per ml	345	442
0·012 γ BaP per ml	352·5	442·5
0·024 γ BaP per ml	360	465
0·048 γ BaP per ml	345	465
0·072 γ BaP per ml	345	420
Sample a	172·5	410
Sample b	270	465
Sample c	217·5	435
Sample d	157·5	405

measured when the two monochromators are set at the same wavelength. It can be observed that the intensity of the excitation peaks at 307 has decreased for samples a, b, c and d while it remained constant for the peaks at 382 for the standards and the samples. This decrease in intensity at 307 is due to adsorption by impurities. Since these compounds adsorb some of the light at 307 the BkF intensity then diminished by a similar amount. It is then possible knowing this interference, to calculate the true concentration of BkF. More work is being done to study in further detail the experimental conditions.

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