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ANALYSIS OF BENZO(A)PYRENE IN AIRBORNE
PARTICULATES BY GAS CHROMATOGRAPHY

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ANALYSIS OF BENZO(A)PYRENE IN AIRBORNE PARTICULATES

BY GAS CHROMATOGRAPHY

by Eva Luedecke

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SUMMARY

A routine method was developed to measure benzo(a)pyrene in airborne particulates. Although other techniques are involved, the method is designated as a gas chromatographic procedure. Samples were collected on a filter and the organic portion was extracted with cyclohexane. The polynuclear hydrocarbon (PNHC) fraction was separated from the aliphatics by column chromatography. An internal standard was added to the extract and a portion of it was injected into a gas chromatograph. Although the gas chromatographic method has often been reported in the literature, satisfactory separation of benzo(a)pyrene and benzo(e)pyrene has not been achieved. With the introduction of a nematic liquid crystal as the stationary phase good separation is now possible.

INTRODUCTION

The objective was to demonstrate the ability to routinely measure benzo(a)pyrene (BaP) in the presence of benzo(e)pyrene (BeP). Many techniques have been described for analyzing BaP by gas chromatography but up to now no column separated BaP-BeP satisfactorily. In the search for a gas chromatographic method for analyzing BaP in the presence of BeP the following stationary phases were studied: SE-30, Dexsil 300, OV1, OV7, BMBT [N, N'-bis(p-methoxybenzylidene- $\alpha\alpha'$ -bi-p-toluidine)] (ref. 1). Of these the only stationary phase was BMBT as shown in figure 1.

EXPERIMENTAL

The method consists of three separate steps:

1. Extraction of sample with solvent.
2. Column chromatography to separate aromatic hydrocarbons from aliphatics.
3. Separate aromatic hydrocarbons into components using gas chromatography.

PNHC's decompose if exposed to light and it is therefore important to perform the analysis while protecting the sample from light. This can be accomplished by using aluminum foil screens especially during extraction, evaporation, and column chromatography.

CHEMICALS

All chemicals were used as supplied by the manufacturer unless otherwise stated.

Benzo(a)pyrene, Eastman Organic Chemicals

Benzo(e)pyrene, Pfaltz and Bauer

1, 3, 5 Triphenylbenzene, Aldrich Chemical Co.

Cyclohexane, 99 Mol% pure Fisher Scientific Co. was purified by percolating it over activated charcoal, dried overnight at 200^o C (473 K). The purification was judged satisfactory when 150 ml of purified cyclohexane concentrated to 50 μ l showed no impurity peaks by gas chromatography (Dexsil 300) at 2×10^{-11} AFS (ampere full scale).

Benzene, GC Spectroquality, J. T. Baker Chem. Co., purified and analyzed like cyclohexane.

2, 2, 4-Trimethylpentane, GC Spectroquality, J. T. Baker Chem. Co.

Carbon Disulfide, Spectroquality, MCB

Silica Gel, 60/200 mesh, Baker A. R for chromatography was activated according to oral communication from Dr. William Prater (ref. 2) as follows:

1. Wash with diethyl ether.
2. Wash with cyclohexane (as received).
3. Spread on aluminum foil which has been washed with cyclohexane (as received). Air dry until the diethyl ether smell is gone.
4. Dry in an oven for 48 hours at 140^o C (413 K).
5. Store in stoppered bottle in a desiccator over Drierite.

Columns, supplied by Analab (ref. 5)

1/8 inch \times 4 feet stainless steel, packed with 1.5 percent BMBT on
100/200 mesh HP chromosorb W

Injector T: 265^o C (538 K)

Detector T: 265^o C (538 K)

Temperature program: Initial T: 185^o C (458 K) hold 2 minutes
Program rate 4^o C/min (4 K/min)
Final T: 265^o C (538 K)

Sample size: 2 μ l

N₂ flow: 50 ml/min

The columns should be conditioned overnight at 265^o C (538 K) with a slow flow of nitrogen. The life of the column can be lengthened by not allowing it to be held unnecessarily at 265^o C (538 K) except when conditioning. While using the column, do not cool it below 185^o C (458 K) maintaining always a slow flow of nitrogen. Column bleeding restricted the minimum concentration analyzable to about 0.3 μ g of BaP because at sensitivities higher than 2×10^{-10} AFS bleeding was a problem even using dual columns.

The area ratios (BaP/Int. Std.) were plotted against the weight ratios (BaP/Int. Std.) to obtain a calibration curve as shown in figure 2. Table I shows the reproducibility of the data. After extraction and column chromatography of the sample, the benzene fraction was evaporated to dryness at room temperature. It was then taken up with (<5 ml) cyclohexane and transferred to a 5 ml micro reaction vessel (MRV) with Teflon lined cap. An accurately known amount of the internal standard TPB was added to the unknown sample in the MRV. The solution was evaporated to dryness at room temperature under the hood and the residue taken up with CS₂ so that the TPB concentration was equal to the one in the calibration. It was then chromatographed under the same condition as the calibration. Area ratios were measured using an integrator and from the calibration curve the weight ratio of the unknown to the standard was read. Since the amount of the internal standard added was known, it was a simple calculation to determine the amount of BaP present.

RESULTS AND DISCUSSION

A synthetic mixture of internal standard and BaP was analyzed using column and gas chromatography. Two μ l of injected sample contained 3.5 μ g BaP theoretically - 3.4 μ g BaP were found.

The following two samples were analyzed for BaP according to the proposed method:

1. Composite sample of W41 filters taken upwind from coke ovens in July 1975. The volume of air sampled was 237 m³. Figure 3 shows a gas chromatogram of BaP, BeP, TPB, and other not identified aromatics.
2. Composite sample of W41 filters taken downwind from coke ovens in July 1975. The volume of air sampled was 290 m³. Figure 4 shows a gas chromatogram of BaP, BeP, TPB, and other not identified aromatics.

Because of the small amounts of BaP collected only an estimate of the BaP could be made. It was estimated that sample 1 contained about 0.3 μg BaP or 1 ng/m³ of air in the suspended particulate matter. Sample 2 contained about 0.6 μg BaP or 2 ng/m³ of air in the suspended particulate matter.

In the above samples the composition may have changed due to exposure to light (ref. 6). Samples were received in July 1975 and analyzed in December 1975. They were also handled previous to this analysis since part of the filters were sent out for trace element analysis. Difficulty was encountered by working with carbon disulfide which is the recommended final solvent for dissolving the sample (ref. 5). Even though all samples were kept in a freezer at about -10⁰ C (263 K) between analyses, CS₂ evaporated rapidly due to its high vapor pressure.

Since only two samples were available for use with this nematic liquid crystal (BMBT) column, more investigation is advisable. From the number of peaks as shown in the gas chromatograms of figures 3 and 4 it is obvious that this column will also separate other aromatics.

Based on retention data from Analabs (ref. 5) the peaks in figures 3 and 4 could indicate the presence of fluorene, fluoranthene, benzo(a)anthracene and other unknowns.

CONCLUSIONS

The described method for the gas chromatographic separation of BaP from BeP is good on the nematic liquid crystal (BMBT) column. The disadvantage lies in column bleed at high sensitivities. It is estimated that the lowest limit of detection is 0.3 μg since at sensitivity setting above 2×10⁻¹⁰ AFS the column bleeding gives too much distortion to quantitatively determine the BaP. Column and gas chromatography of a synthetic mixture of BaP and TPB show good recovery of components.

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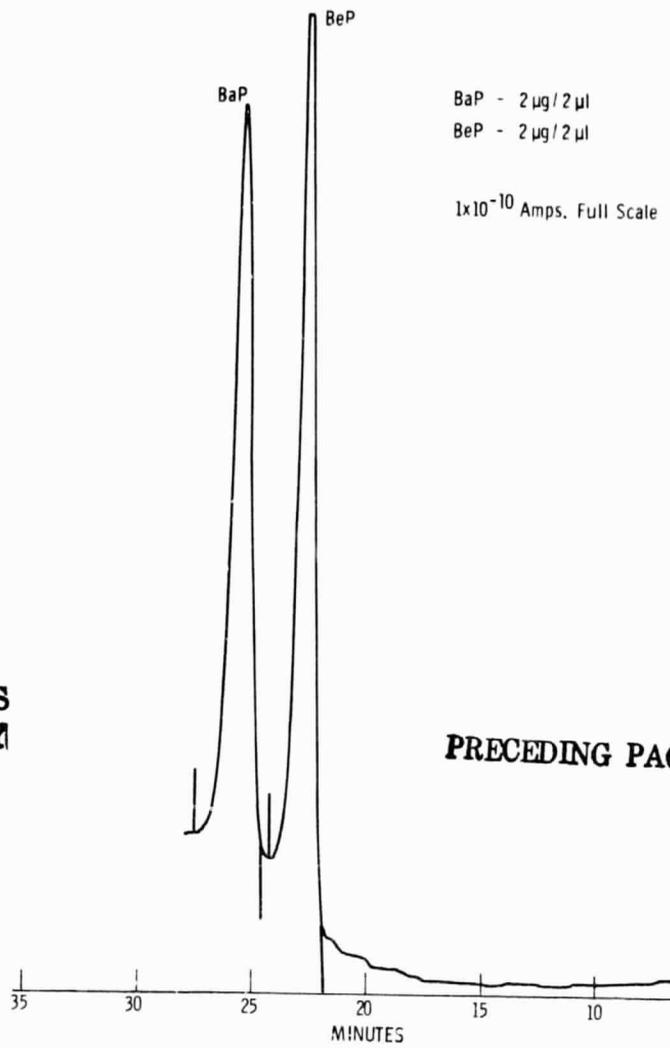
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TABLE I. - CALIBRATION FOR BaP ON BMBT COLUMN

INTERNAL STANDARD - 1.3.5-TRIPHENYLBENZENE (TPB) 1.91 $\mu\text{g}/2 \mu\text{l}$

	<u>Area ratio</u>	<u>Weight ratio</u>	<u>BaP</u>	
	<u>BaP</u> <u>TPB</u>	<u>BaP</u> <u>TPB</u>	<u>BaP</u> <u>$\mu\text{g}/2 \mu\text{l}$</u>	
			<u>Theor.</u>	<u>Found</u>
Sol. 1	1.81	1.82	3.48	3.47
	1.82		3.48	3.52
	1.68		3.48	3.25
Sol. 2	1.49	1.52	2.90	2.86
	1.52		2.90	2.94
Sol. 3	1.08	1.21	2.32	2.08
	1.02		2.32	1.97
	1.08		2.32	2.08

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Figure 1. - Separation of BaP and BeP

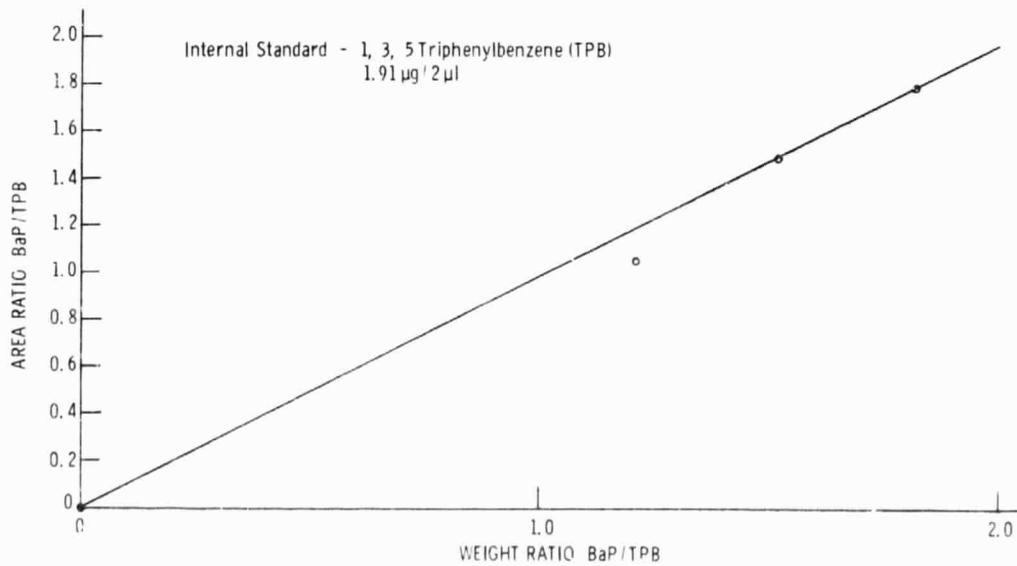


Figure 2. - Calibration for BaP on BMBT Column

TABLE I. - CALIBRATION FOR BaP ON BMBT COLUMN

INTERNAL STANDARD - 1.3.5-TRIPHENYLBENZENE (TPB) 1.91 $\mu\text{g}/2 \mu\text{l}$

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Sol. 3	1.08	1.21	2.32	2.08
	1.02		2.32	1.97
	1.08		2.32	2.08