EXTRACTION AND IDENTIFICATION OF ORGANIC MATERIALS PRESENT IN SOOT FROM A NATURAL GAS FLAME

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FOREWORD

Man and his environment must be protected from the adverse effects of pesticides, radiation, noise, and other forms of pollution, and the unwise management of solid waste. Efforts to protect the environment require a focus that recognizes the interplay between the components of our physical environment--air, water, and land. The Ames Laboratory of U.S.D.O.E. contributes to this multidisciplinary focus through programs engaged in

- studies on the effects of environmental contaminants on the biosphere, and
- a search for ways to prevent contamination and to recycle valuable resources.

The identification of polynuclear and other hydrocarbons which are sorbed on soot and fly ash from power plants burning fossil and other fuels has important implications. This report emphasizes the analytical technologies that apply easily to soot may not necessarily be applicable to fly ash emissions from a power plant burning coal and combustible trash.

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ABSTRACT

Aliphatic and polynuclear aromatic hydrocarbons are readily extracted from soot formed from a natural gas flame using methylene chloride and ultrasonic agitation. Identification of 24 organic compounds via capillary column GC retention times and GC-MS data is reported along with details of experimental procedures.

LIST OF ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

PAH -- polycyclic aromatic hydrocarbons

GC -- gas chromatograph

FID -- flame ionization detector

I.D. -- internal diameter

GC-MS -- gas chromatograph-mass spectrometer

TIM -- total ion monitor

DBP -- dibenzpyrene

SYMBOLS

$\bar{\Delta}$ -- average deviation

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INTRODUCTION

The analysis of environmental polycyclic aromatic hydrocarbons (PAH) is a problem of growing concern for many researchers[1-28]. We are currently studying the organic emissions from a combination coal-refuse fired utility plant, with emphasis on their PAH content. Several reports[1-8] state that PAH are ubiquitous pollutants resulting from inefficient burning. After more than one year of sample collection and analyses we have found very little if any PAH in either the vapor or on the particulate emissions from the power plant.

These consistently negative results have led us to test our analytical methodology extensively, including both standard methods described in the literature and our own original procedures. This report describes one of these tests using soot generated from the combustion of natural gas. In a similar study, Hase et.al.[9] have reported the presence of PAH in the soot from methane diffusion flames.

EQUIPMENT AND METHODS

Instrumentation

A 100 watt Bransonic B220 ultrasonic bath was used for the solvent extraction.

A Perkin-Elmer 3920 gas chromatograph (GC) equipped with a flame ionization detector (FID) and modified for splitless injection on capillary columns was used for the analysis of the components extracted from the soot. The following conditions were used:

Column: SE-30 glass capillary, 30m x 0.25mm I.D. (J & W Scientific)

Detector Temp.: 300°C

Injector Temp.: 300°C

Column Temp.: 2 min hold at 50°C followed by an 8°C/min increase to 250°C with a 16 min hold

Column Pressure: 2.8Kg cm^{-2} at 50°C

Injection Type: Splitless for 15 s.

A DuPont 21-490-1 gas chromatograph-mass spectrometer (GC-MS) was used to obtain GC separations and mass spectral data for identification purposes. The gas chromatograph part of this instrument, a Varian 1400, was equipped with a septum purge and a vacuum operated solvent vent valve. The following conditions were used:

Column: 3% OV-17 on 80-100 mesh Gas Chrom W-AW-DMCS packed glass, 2m x 17mm I.D.

Injector Temp.: 310°C

Interface Temp.: 310°C

Column Temp.: 15°C/min increase from 100°C to 325°C.

A Honeywell 2106 Visicorder was used to record the mass spectral data and conventional one millivolt strip chart recorder was used to record the output of the total ion monitor (TIM).

Sample Generation

A petri dish supported over an oxygen deficient natural gas flame was used to collect 120mg of soot.

The soot was extracted with methylene chloride for 15 min using ultrasonic agitation of the solvent-soot mixture. The solution was filtered through a medium porosity sintered glass frit. The filtered extract was concentrated by distillation to 200μl for capillary column gas chromatography and further concentrated by free evaporation to 10μl for packed column GC-MS work. Four-μl aliquots of the concentrate were used for both analyses.

Identifications

Tentative identifications were made by comparing absolute retention times of standard PAH to those of the extracted components separated on the capillary GC column. Confirmation was based on the coincidence of relative retention times and mass spectral matches of sample and standard compounds from the GC-MS analysis.

An example of the raw data used to make mass spectral matches is shown in Fig. 1. The difference spectrum between the unknown and dibenzpyrene (DBP) was used to calculate an absolute

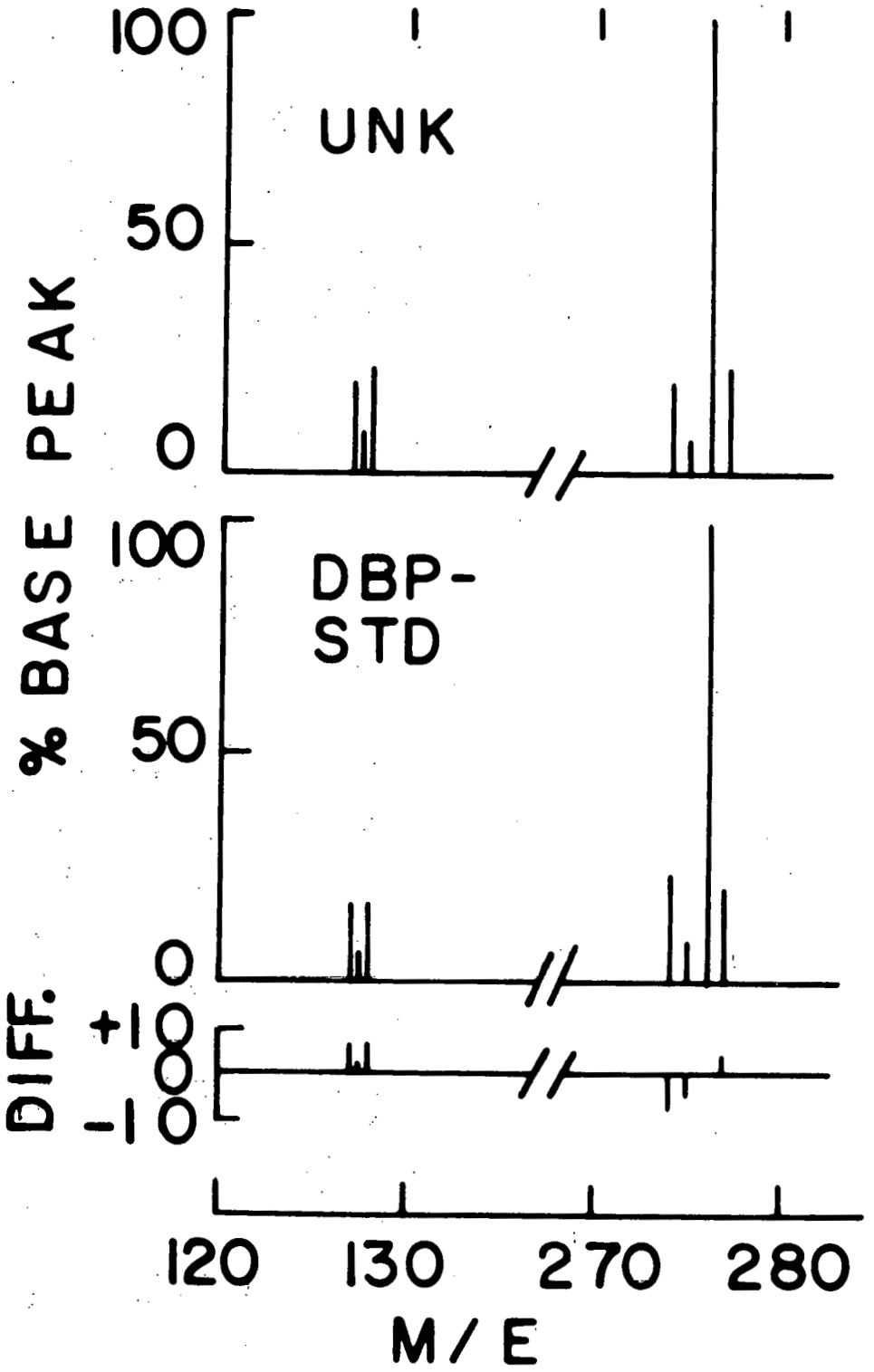

Figure 1. Mass spectral matching data for DBP.

average deviation ($\bar{\Delta}$) using the following equation:

$$\bar{\Delta} = 1/n \sum_{i=1}^{n} \left| I_i(\text{unk}) - I_i(\text{std}) \right|$$

where n ≡ number of ion intensity comparisons,

I(std) ≡ intensity of the ion normalized to the base peak of the standard spectrum

and I(unk) ≡ intensity of the ion normalized to the peak of the unknown spectrum corresponding to the base peak of the standard spectrum.

The $\bar{\Delta}$ for the above example was 3.5. Tests with standard materials have shown that to confirm an identification, the $\bar{\Delta}$ must be less than 5. Ions used in the equation were selected by a method based on the reverse search principle described by several authors[29-33].

RESULTS

The extract from the soot is a very complex mixture of organic materials as shown by the capillary column chromatogram in Fig. 2. However, most of the material present is concentrated into only a few peaks. This relative simplicity allowed for direct packed column separations in the GC-MS analysis of the extract from soot without resorting to prior class separations.

The components of the extract that have been identified are listed in Table 1. An "X" was placed in the appropriate space if the following conditions were met:

GC-MS, Rt_R; retention times of unknown and standard, relative

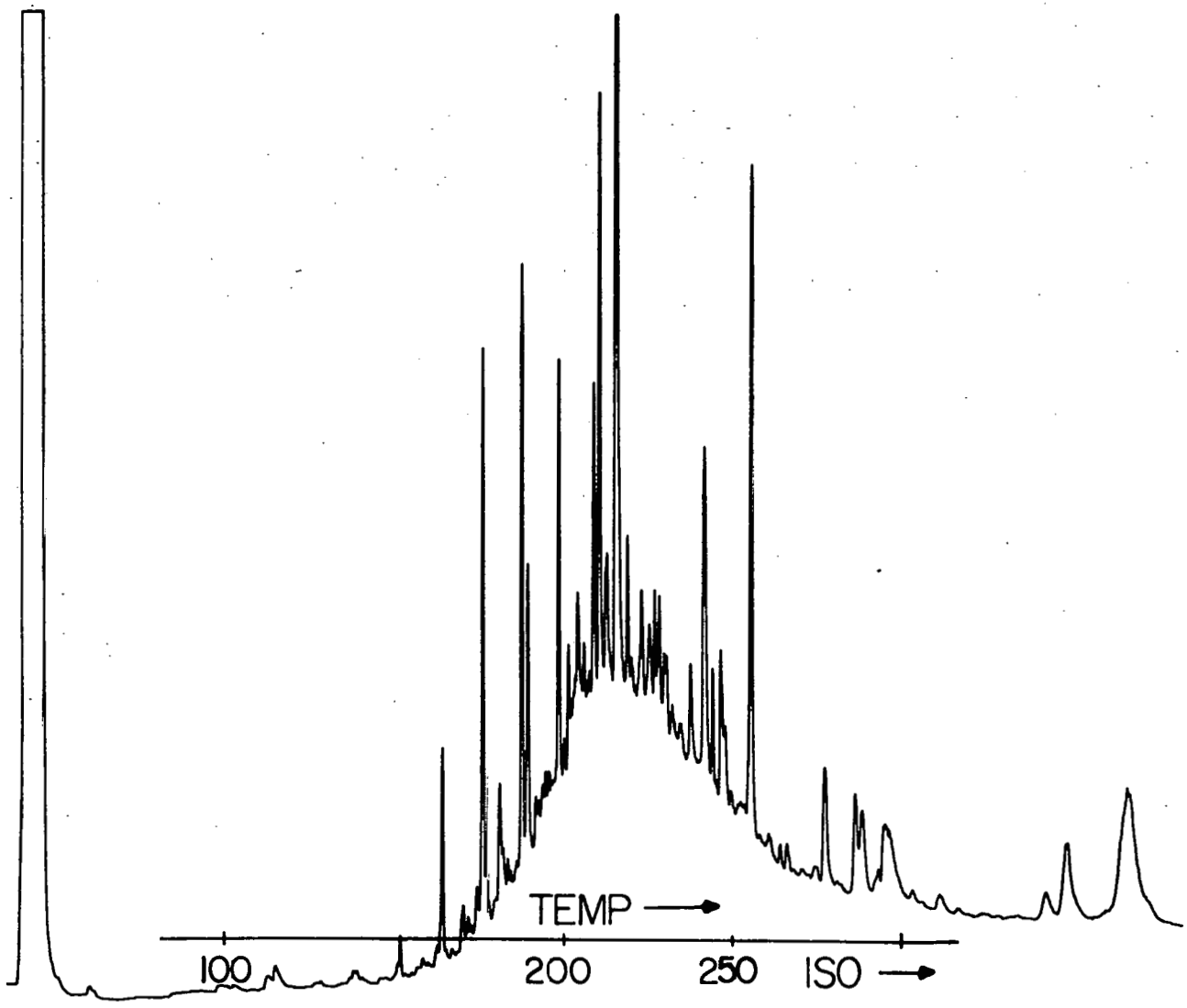

Figure 2. Capillary column chromatogram of natural gas flame soot extract.

TABLE 1. IDENTIFICATION DATA - METHANE FLAME SOOT

Compound	GC-MS Rt_R	GC-MS MS	GC-MS % Total Peak Area	Capillary Column GC t_R	Capillary Column GC % Total Peak Height	Positively Identified +
n-hexadecane	X	X	6.12	X	2.86	+
n-heptadecane	X	X	12.90	X	6.11	+
n-octadecane	X	X	12.90		5.81	+
n-nonadecane	X	X	13.60		3.92	+
dibutylphthalate	X	X	4.76	X	1.70	+
di(2-ethylhexyl)phthalate	X	X	6.80	X	0.30	+
biphenyl	X	X	0.68			+
phenanthrene [a]	X	X	1.36	X	1.51	+
anthracene [a]				X	0.31	+
fluoranthene	X	X	3.40	X	6.52	+
pyrene	X	X	8.84	X	8.50	+
benz[e]pyrene	X	X	0.68	X	1.06	+

TABLE 1. (cont'd)

Compound	GC-MS Rt_R	GC-MS MS	GC-MS % Total Peak Area	Capillary Column GC t_R	Capillary Column GC % Total Peak Height	Positively Identified +
benz[a]pyrene [a]	X	X	2.04	X	1.42	+
perylene [a]				X	0.83	+
dibenzpyrene	X	X	2.04			+
benzo[ghi]perylene		X				
benzo[f]fluoranthene		X				
benzperylene		X				
fluorene				X		
1,2-benzfluorene				X		
2,3-benzfluorene				X		
benz[a]anthracene				X		
chrysene				X		
9,10-dimethylanthracene				X		

[a]Packed GC column had insufficient resolution for these compounds.

to internal n-hexadecane, agreed within 2%.

Capillary Column GC, t_R; absolute retention times of unknown and standard agreed within 0.5%.

GC-MS, MS; $\bar{\Delta}$ between unknown and standard mass spectra was less than 5.

A substantial percentage of the identified material was PAH as shown in Table 1. This material plus other components identified constitute 41% and 76% of the total detected by FID and TIM respectively. The TIM values are probably high due to insufficient separation of components on the packed GC-MS column. The FID values may well be low since peak height measurements were used and most of the identified components eluted in the latter part of the chromatogram.

DISCUSSION

The results listed in Table 1 show that the methodology used in this study is adequate for the measurement of PAH from soot. These results are in agreement with those published in similar studies[3,9].

Continued analyses of particulate matter collected from the power plant have resulted in no identifications of PAH. Part of the problem comes from the increased complexity of the power plant emission samples. A chromatogram of such a sample is shown in Fig. 3. The total chromatographable material present in the sample exceeds that of the soot sample, but the material is evenly spread over many hundred peaks making the identification process much more difficult. This complexity necessitates

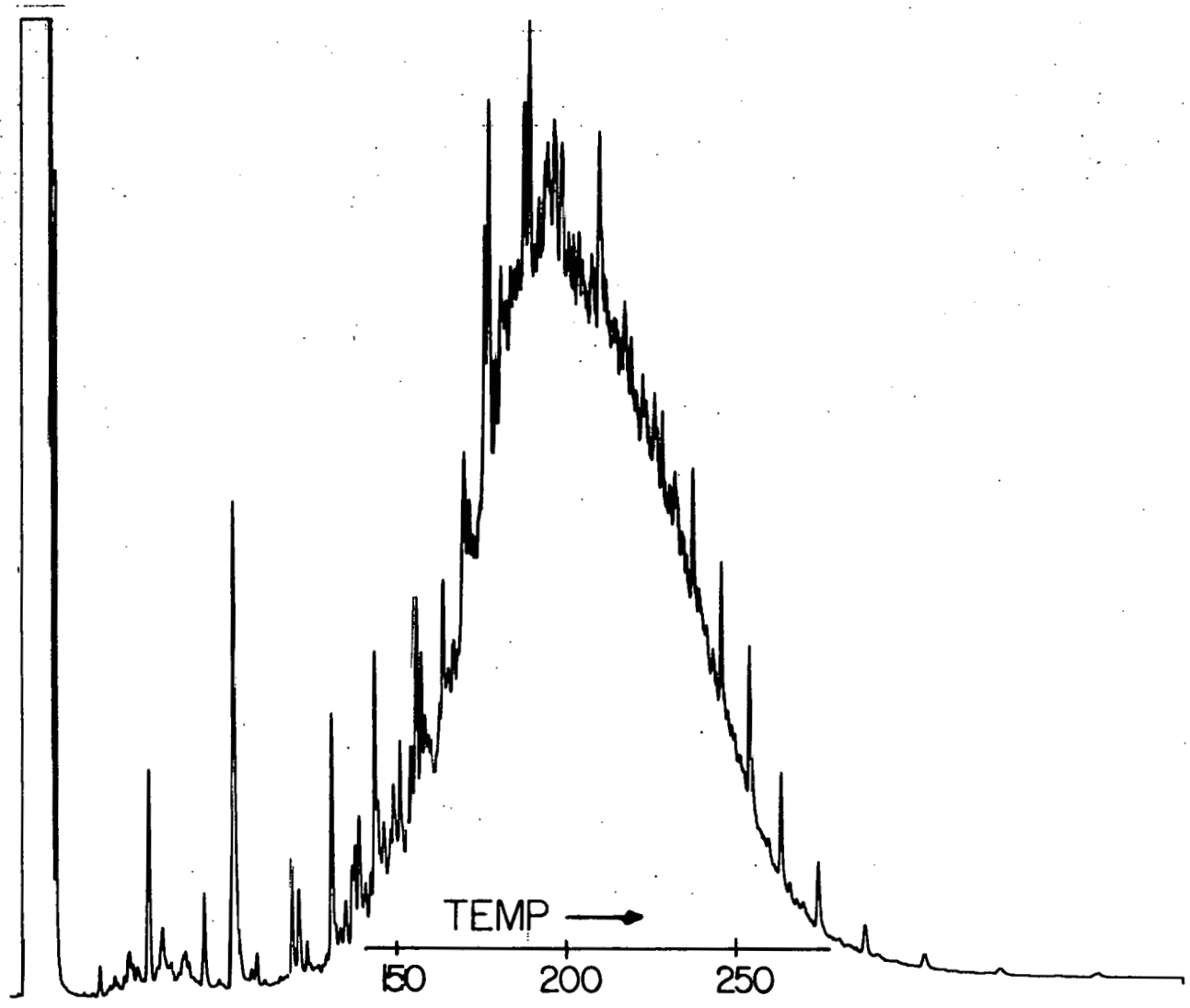

Figure 3. Capillary column chromatogram of power plant fly ash extract.

the use of chemical class separations prior to GC-MS analysis or the use of selected ion monitoring for preselected PAH. However, chemical class separations generally lead to sample loss and increased background. Selected ion monitoring is a highly sensitive and selective tool, but only one compound per GC analysis can be determined. If any are detected by this method, no confirmation can be made using capillary column retention data. It is anticipated that the acquisition of new instrumentation with improved separation capabilities may alleviate some of these problems.

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