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Atmospheric Concentration of Polycyclic Aromatic Hydrocarbons (PAH) in Greater Vancouver

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Summary

Concentrations of atmospheric PAH were measured at two sites in the Greater Vancouver region. One site was in the downtown core of the city, the other at a rural site on Westham Island. Hi-vol samplers fitted with polyurethane foam (PUF) plug back-up traps were used.

Although PAH were detected in the samples, the concentrations appeared to be in the low range as compared to values measured in other cities. Recommendations for further monitoring are made.

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Atmospheric Concentration of Polycyclic Aromatic Hydrocarbons (PAH) in Greater Vancouver

D.A. Faulkner

Atmospheric Environment Service

1. Introduction

Polycyclic Aromatic Hydrocarbons (PAH) are a class of complex organic compounds formed through the incomplete combustion of organic materials. Through pyrolysis, "organic components are cracked to smaller and unstable molecules"; subsequently through pyrosynthesis "fragments, mostly radicals recombine to larger, thermodynamically favored and relatively stable aromatic ring hydrocarbons (PAH), and heterocyclic hydrocarbons" (Hoffman and Wynder, 1968). PAH may result from natural or anthropogenic processes. They are commonly released as by-products of the burning of fossil fuels or wood.

Emitted directly to the atmosphere, PAH are absorbed on aerosols and since approximately 80 percent of these are in the respirable size range (Pierce and Katz, 1975), they are easily ingested into the lungs. Although found in small concentrations in the atmosphere (0.1 to 10 nanograms/cubic metre), the National Academy of Sciences (1972) has stated that "... an increase in urban pollution corresponding to an average benzo(a)pyrene (concentration) of 1 ng m^{-3} may result in an increase of five percent of the lung cancer death rate. The coefficients for non-white males are larger - about 15 percent."

PAH may be transported large distances in the atmosphere or be transformed by sunlight. To quote a draft DOE Fact Sheet:

> "Photochemical degradation (destruction by light) is probably the chief source of destruction of PAH in the atmosphere. However, PAH compounds in air are known to photodegrade in some cases to products which are more mutagenic than the parent chemical. In addition to their reaction with sunlight, many PAH are reactive with ozone, nitric and sulphuric acids (constituents of acid rain) and nitrogen oxides. For example, when pyrene (a non-toxic, non-carcinogenic PAH) reacts with nitric acid or nitrogen dioxide in the atmosphere, a major reaction product is 1-Nitropyrene, one of the most potent mutagens evaluated.
>
> The atmosphere is now considered to be the chief source of PAH to the Great Lakes, with an annual deposition of almost 500 metric tonnes."

Concentrations of PAH, in particular benzo(a)pyrene (BaP) have been measured in many urban and rural environments. In urban areas, concentrations of BaP are generally in the range 1-15 ng m^{-3} but may reach as high as 2.0×10^4 ng m^{-3}, the highest value documented in London (Hoffman and Wynder, 1968). Concentrations vary with the season; highest concentrations usually occur in winter when more fossil fuels are burned for space heating.

The Environmental Protection Service (EPS) measured PAH concentration in Vancouver in 1981 on five days at up to four stations using a standard Hi-vol sampler to collect particulates on a fibreglass filter. Ranges of concentrations measured are listed in Table I below under the column headed "1981"..

Table I

PAH Concentrations (ng m^{-3}) in Greater Vancouver in 1981 and 1985

	1981		1985	
	Low	High	Low	High
Fluoranthene (Flt)	0.0	0.0	1.0	15.4
Pyrene (Pyr)	0.8	5.9	0.2	8.9
Benzo(a)Pyrene (BaP)	0.2	6.5	0.0	0.7

Most of the samples were taken during winter, i.e. in the months January to March. One observation at a downtown site was made in July and, in general, PAH concentrations in the summer sample were lower than the winter ones.

2. Sampling Equipment and Methods

For some time it has been recognized that PAH loss through re-volatization from aerosol filters in Hi-vol samplers is significant (see for example, Galasyn et al, 1984). The magnitude of the loss, which depends on the volatility of the compound and the ambient air temperatures, may amount to as much as 85 percent of the more volatile species. It has been found possible to overcome this problem to a degree by installing a polyurethane foam (PUF) plug in the flow stream of the air sampler (Galasyn et al, 1984; Keller and Bidleman, 1984).

Two Hi-vol samplers (General Metal Works GMW-2310) each fitted with a stainless steel PUF plug back-up trap (GMW 10282) were employed in this study. Aerosols were collected on 20.3 x 25.4 cm glass fiber filters (GMW-1HV); gaseous PAH were collected on either one or two 8.3 cm diameter by 7.6 cm PUF plugs (GMW 10294). Sample periods were approximately 24 hours except in one case in which the timer mechanism failed and the sampler ran for almost 48 hrs. Flow rates were measured at the beginning and end of the sample periods to determine mean flow rates.

One sampler was located in the downtown core of Vancouver, the other in a rural setting on Westham Island. (See Figure 1 for locations). Brief descriptions of the sites follow:

(i) Downtown B.C. Hydro Site

The sampler was located at the B.C. Hydro main office in the downtown core of Vancouver. It was placed on the roof of a building at a height of about 4 m above ground level and about 5 m from the edge of a busy thoroughfare (Hornby Street). Thus it was exposed to vehicular emissions from passing traffic as well as the background urban pollution.

(ii) Westham Island Site

Westham Island is a small island at the mouth of the Fraser River (Figure 1); it is almost entirely used for agriculture. Automotive traffic on the island is light. The sampler was placed on the ground at the south end of a barn used for storage. No paved roads lead to the site and automobiles, tractors, etc. do not have ready access to within 50 m of the site. Refuse is burned occasionally at a site about 200 m northwest of the site and ships dock at Roberts Bank about 9 km due south.

Samplers were set for a flow rate of 0.6 - 0.8m^3 min^{-1}. Because of the increased resistance to air flow offered by two plugs, flow rates dropped to about 0.4 m^3 min^{-1} when two were used.

Care was taken to prevent contamination of the filters and plugs during handling. PUF plugs were cleaned at the laboratory by Soxhlet extraction (see Appendix A) and kept in glass bottles with tight metal lids. The filters, after exposure, were likewise transported in glass bottles. Technicians - both non-smokers - wore sanitized plastic gloves when handling samples and used an aluminum foil-covered stick to insert the plugs into the back-up traps. The stainless steel back-up traps were washed with toluene, acetone and methylene chloride before their first use. Samples were taken at 3-day intervals; plugs and filters were left in the samplers for the three days although the sampling period was only 24 hr. In general, the samples were collected for delivery to the laboratory immediately after the end of each sampling period, however, on some occasions (such as weekend sampling periods) the samples were not collected until about 24 hr after the end of the sampling period. Delivery was made to the laboratory within a few hours of collection time.

As part of the quality control procedure, technicians carried clean PUF plug travel blanks with each change of samplers. These blanks were treated in an identical fashion to the sampler plugs but were removed immediately after insertion in the back-up trap. These were submitted for analysis together with sampler plugs. The results of analyses comparing the travel blanks with sampler plugs are listed in Table II. In that table, 'Blank' refers to travel blanks, 'Tplug' to top plug (i.e. the primary collecting plug) and 'Bplug' to the bottom plug (or secondary collector, if one were used). It is evident from the table that no significant amounts were found on the blanks - in most cases

TABLE II

PAH Quantities on Travel Blanks and Sampling Plugs

Sampling Period (day/month/year/hour)			Quantities Measured (ng)											
Begin	End	Type	Flt	Pyr	BaA	Chry	Bep	Per	BbF	BkF	BaP	dBahA	BghiPer	I123cdP
21/02/85:0800	22/02/85:0800	Blank	0	0	0	0	0	0	0	0	0	0	0	0
		Tplug	4930	7590	0	0	0	0	0	0	0	0	0	0
		Bplug	0	0	28	TR	43	0	56	TR	31	0	133	0
24/02/85:0800	25/02/85:0800	Blank	0	0	0	0	0	0	0	0	0	0	0	0
		Tplug	612	165	0	0	0	0	0	0	0	0	0	0
		Bplug	0	0	0	0	0	0	0	0	0	0	0	0
24/02/85/0800	25/02/85:0800	Blank	0	0	0	0	0	0	0	0	0	0	0	0
		Tplug	0	0	20	0	0	0	0	0	0	0	0	0
		Bplug	4000	2230	0	0	0	0	0	0	0	0	0	0
27/02/85:0800	28/02/85:0800	Blank	0	0	0	0	0	0	0	0	0	0	0	0
		Tplug	1870	440	0	0	0	0	0	0	0	0	0	0
		Bplug	0	0	60	133	147	TR	399	38	34	0	0	0
02/03/85:0800	83/03/85:0800	Blank	0	0	TR	0	TR	0	TR	0	0	0	0	0
		Tplug	595	115	29	0	TR	0	0	64	77	0	0	0
		Bplug	0	0	31	54	119	0	93	TR	TR	0	0	0
05/03/85:0800	06/03/85:0800	Blank	0	0	0	0	TR	0	TR	0	0	0	0	0
		Tplug	8890	5210	0	0	0	0	0	0	0	0	0	0
		Bplug	0	0	26	0	0	0	0	0	0	0	0	0
05/03/85:0800	06/03/85:0800	Blank	0	0	0	0	0	0	0	0	0	0	0	0
		Tplug	1176	612	0	0	0	0	0	0	0	0	0	0
08/03/85:0800	09/03/85:0800	Blank	0	0	0	0	0	0	0	0	0	0	0	0
		Tplug	5670	4320	0	0	0	0	0	0	0	0	0	0

TABLE II (Cont'd)

PAH Quantities on Travel Blanks and Sampling Plugs

Sampling Period (day/month/year/hour)			Quantities Measured (ng)											
Begin	End	Type	Flt	Pyr	BaA	Chry	Bep	Per	BbF	BkF	BaP	dBahA	BghiPer	I123cdP
11/03/85:1300	12/03/85:1300	Blank	0	0	0	0	0	0	0	0	0	0	0	0
		Tplug	8500	6560	145	0	0	0	0	0	0	0	0	0
11/03/85:1300	12/03/85:1300	Blank	TR	TR	0	0	0	0	0	0	0	0	0	0
		Tplug	2630	1010	0	0	0	0	0	0	0	0	0	0
17/03/85:0800	18/03/85:0800	Blank	TR	0	0	0	0	0	0	0	0	0	0	0
		Tplug	7570	5240	0	0	0	0	0	0	0	0	0	0
20/03/85:0000	20/03/85:2400	Blank	TR	0	0	0	0	0	0	0	0	0	0	0
		Tplug	1030	656	0	0	0	0	0	0	0	0	0	0
20/03/85:0000	20/03/85:2400	Blank	TR	0	0	0	0	0	0	0	0	0	0	0
		Tplug	7630	5720	103	0	0	0	0	0	0	0	0	0
23/03/85:0000	23/03/85:2400	Blank	TR	TR	TR	0	0	0	0	0	0	0	0	0
		Tplug	912	494	47	0	0	0	0	0	0	0	0	0
23/03/85:0000	23/03/85:2400	Blank	TR	0	0	0	0	0	0	0	0	0	0	0
		Tplug	3070	2610	56	0	0	0	0	0	0	0	0	0

amounts were below detectable limits and the highest amount detected was a trace. Thus one can be very confident that insignificant contamination occurred during transport and handling.

Several difficulties were encountered in modifying the equipment to include the back-up traps. The traps themselves were too long for the space inside the sampler and cross-bars of the Hi-vol samplers had to be moved to make room for them. The PUF plugs were found to have varying densities and some were so dense that they restricted air flow to the point the flow-rate fell below the measurable rate; such plugs were not used. It was intended to use up to four plugs for some sampling periods in order to estimate the amount of PAH passing through the primary collector plug. It was found, however, that insertion of more than two plugs restricted flow to the point that the electrical drive motor over-heated. In a few cases, two plugs were used and, as will be seen below, it appears that losses were not detectable.

3. Chemical Analysis

The PAH compounds were extracted from the fiber filters and PUF plugs by Soxhlet extraction and analysed by high pressure liquid chromotography (HPLC). Extraction and analysis were carried out by CanTest Ltd. in their Vancouver Laboratory. A report by CanTest giving details of extraction and analysis method, quality control procedures and analysis results is included as Appendix A.

4. Results and Discussions

Analysis for the PAH listed in Table III was carried out.

Table III

Compound	Abbreviation	Carcinogenicity*	Typical Urban Concentrations** (ng m^{-3})
Fluoranthene	Flt	-	0.1-13
Pyrene	Pyr	-	0.2-10
Benzo(a)anthracene	BaA	+	0.06-5
Chrysene	Chry	+	0.04-5
Benzo(e)pyrene	Bep	+	0.05-5
Perylene	Per	-	0.01-14
Benzo(b)fluoranthene	BbF	++	
Benzo(k)fluoranthene	BkF	-	0.06-5
Benzo(a)pyrene	BaP	+++	0.03-10
Dibenz(a,h)anthracene	dBahA		
Benzo(ghi)perylene	BghiPer	-	0.02-20
Indeno(1,2,3-cd)pyrene	I123cdP	+	0.03-3

* Reference - Hoffman and Wynder, 1968. '-' = non-carcinogenic, '+' = carcinogenic

* Reference - Eisenreich et al, 1981

The measured PAH concentrations of samples are listed in Tables IVa and IVb. In all, samples were obtained for fourteen periods, however cases of known or doubtful data were rejected for reasons given in Table V. Excessively high concentrations (particularly of Flt and Pyr) at Westham Island in comparison to other readings were observed for samples 11 and 12 leading to the suspicion of local contamination from refuse or slash burning. On those occasions, the filters were visibly 'dirtier' from black carbon particles suggesting the filters for a period were directly in the plume from a local fire.

In Tables IVa and IVb, nil values (0) should be interpreted as "below concentration detection limits" which differ from the "sample detection limits" of Table V of Appendix A. Since the volume of air sampled varied from sample to sample, but the sample detection limits remained constant, the concentration detection limits varied with the volume. The concentration detection limits may be calculated by dividing by the sample volumes. For example, since the fluoranthene sample detection limit is 12.8 ng, for B.C. Hydro sampling period No. 1, the concentration detection limit is 12.8/1084 = .012 ng m^{-3}. Similarly, trace amounts may be related to the "quantitation detection limits" given in Table V, Appendix A.

TABLE IVa

Filter, Top/Bottom Plugs Concentrations (ng m^{-3}) for B.C. Hydro

Sample	Start	Finish	Volume (m^3)	Type	Flt	Pyr	BaA	Chry	Bep	Per	BbF	BkF	BaP	dBahA	BghiPer	I123cdP
					[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	.2	.8	.3	[illegible]		[illegible]	[illegible]
001	12/02/85:1800	13/02/85:1800	1084.0	Filtr	1.6	1.4	0.9	0.2	0.6	0.1	0.7	0.2	0.3	TR	1.1	0.6
				Tplug	7.1	4.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
				Total	8.7	5.7	0.9	0.2	0.6	0.1	0.7	0.2	0.3	0.0	1.1	0.6
					[illegible]	9.5	1.5	.33	1.0	.17	1.2	.3	.5		1.8	[illegible]
002	15/02/85:1000	16/02/85:1000	2113.8	Filtr	1.2	1.3	1.1	1.1	1.2	0.1	1.7	0.4	0.5	0.5	2.3	1.1
				Tplug	2.6	2.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
				Total	3.8	3.4	1.1	1.1	1.2	0.1	1.7	0.4	0.5	0.5	2.3	1.1
					[illegible]	2.8	.9	.9	1.0	.1	1.4	.3	.4	.4	1.9	.9
003	18/02/85:1200	19/02/85:1200	1080.9	Filtr	1.9	1.7	1.4	1.4	1.5	0.1	1.3	0.5	0.7	0.2	2.6	2.7
				Tplug	7.0	5.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
				Total	9.0	7.1	1.4	1.4	1.5	0.1	1.3	0.15	0.7	0.2	2.6	2.7
					[illegible]	[illegible]	.9	.9	[illegible]	.1	.9	.1	.5	.1	1.7	1.8
005	24/02/85:0800	25/02/85:0800	831.8	Filtr	0.3	0.3	0.3	0.3	0.3	0.0	0.5	0.1	0.1	TR	0.7	0.8
				Tplug	4.8	2.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
				Total	5.1	3.0	0.4	0.3	0.3	0.0	0.5	0.1	0.1	0.0	0.7	0.8
					17.0	1.0	1.3	1.0	1.0	0	1.7	.3	.3		2.3	2.7
008	05/03/85:0800	06/03/85:0800	1111.5	Filtr	0.5	0.6	0.7	0.9	0.8	0.1	1.0	0.3	0.4	0.2	2.1	1.5
				Tplug	8.0	4.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
				Bplug	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
				Total	8.5	5.3	0.7	0.,9	0.8	0.1	1.0	0.3	0.4	0.2	2.1	1.5
					10.6	6.6	.9	1.1	1.0	.1	1.3	.4	.5	.3	2.6	1.9
009	08/03/85:0800	09/03/85:0800	1005.1	Filtr	0.8	0.8	0.4	0.8	0.7	0.1	1.3	0.3	0.2	0.0	2.9	0.8
				Tplug	8.0	4.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
				Total	6.4	5.1	0.4	0.8	0.7	0.1	1.3	0.3	0.2	0.0	2.9	0.8
					8.1	7.3	.6	1.1	1.0	.1	1.9	.4	.3		4.1	1.1

10.1

TABLE IVa (Cont'd)

Filter, Top/Bottom Plugs Concentrations (ng m^{-3}) for B.C. Hydro

Sample	Start	Finish	Volume (m^3)	Type	Flt	Pyr	BaA	Chry	Bep	Per	BbF	BkF	BaP	dBahA	BghiPer	I123cdP
010	11/03/85:1300	12/03/85:1300	1168.9	Filtr	1.4	1.2	1.2	1.2	1.0	0.2	1.2	0.4	0.5	0.2	3.2	0.6
				Tplug	7.3	5.6	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
				Total	8.7	6.9	1.3	1.2	1.0	0.2	1.2	0.4	0.5	0.2	3.2	0.6
011	14/03/85:0800	15/03/85:0800	1064.0	Filtr	0.9	1.0	0.3	0.6	0.6	0.1	0.9	0.2	0.3	0.2	0.9	4.0
				Tplug	7.7	4.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
				Total	8.6	5.3	0.3	0.6	0.6	0.1	0.9	0.2	0.3	0.2	0.9	4.0
012	17/03/85:0800	18/03/85:0800	1195.6	Filtr	0.6	0.6	0.3	0.7	0.6	0.1	1.0	0.2	0.2	0.2	1.9	2.4
				Tplug	2.0	1.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
				Total	2.6	1.8	0.3	0.7	0.6	0.1	1.0	0.2	0.2	0.2	1.9	2.4
013	20/03/85:0000	20/03/85:2400	957.5	Filtr	1.5	1.5	1.8	1.7	1.2	0.2	1.7	0.4	0.5	0.4	6.4	6.3
				Tplug	8.0	6.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
				Total	9.5	7.4	1.9	1.7	1.2	0.2	1.7	0.4	0.5	0.4	6.4	6.3
014	23/03/85:0000	23/03/85:2400	984.7	Filtr	0.4	0.5	0.1	0.4	0.4	0.0	0.6	0.1	0.1	0.1	2.5	0.0
				Tplug	3.1	2.7	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
				Total	3.5	3.1	0.2	0.4	0.4	0.0	0.6	0.1	0.1	0.1	2.5	0.0

Filtr = Fiberglass filter; Tplug = Top Plug; Bplug = Bottom plug

TABLE IVb

Filter, Top/Bottom Plugs Concentrations (ng m^{-3}) for Westham Island

Sample	Start	Finish	Volume (m^3)	Type	Flt	Pyr	BaA	Chry	Bep	Per	BbF	BkF	BaP	dBahA	BghiPer	I123cdP
002	15/02/85:1000	16/02/85:1000	1000.8	Filtr	0.1	0.2	0.5	0.6	0.4	0.0	0.5	0.2	0.2	TR	0.8	0.9
				Tplug	1.9	0.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
				Total	2.0	0.9	0.5	0.6	0.4	0.0	0.5	0.2	0.2	0.0	0.8	0.9
003	18/02/85:1200	19/02/85:1200	895.7	Filtr	0.4	1.2	0.5	0.8	1.0	0.0	0.7	0.2	0.1	0.4	1.0	0.9
				Tplug	2.5	0.8	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
				Total	2.9	2.0	0.5	0.8	1.0	0.0	0.7	0.2	0.1	0.4	1.0	0.9
005	24/02/85:0800	25/02/85:0800	769.4	Filtr	0.1	TR	0.0	0.1	TR	TR	0.2	TR	TR	0.0	0.0	0.0
				Tplug	0.8	0.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
				Bplug	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
				Total	0.9	0.2	0.0	0.1	0.0	0.0	0.2	0.0	0.0	0.0	0.0	0.0
007	02/03/85:0800	03/03/85:0800	701.1	Filtr	0.3	0.3	0.3	0.5	0.4	0.1	1.0	0.2	0.1	0.0	0.8	1.2
				Tplug	0.8	0.2	0.00.0		TR	0.0	0.0	0.1	0.1	0.0	0.0	0.0
				Bplug	0.0	0.0	0.0	0.1	0.2	0.0	0.1	TR	TR	0.1	0.0	0.0
				Total	1.1	0.4	0.4	0.6	0.6	0.1	1.2	0.3	0.2	0.0	0.8	1.2
008	05/03/85:0800	06/03/85:0800	1161.2	Filtr	0.3	0.1	0.2	0.3	0.3	0.0	0.6	0.1	0.1	0.0	0.5	0.4
				Tplug	1.0	0.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
				Total	1.3	0.7	0.2	0.3	0.3	0.0	0.6	0.1	0.1	0.0	0.5	0.4
009	08/03/85:0800	09/03/85:0800	1029.6	Filtr	0.9	0.4	0.4	0.7	0.6	0.1	1.4	0.2	0.2	0.3	1.6	1.4
				Tplug	2.2	0.8	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
				Total	3.1	1.2	0.4	0.7	0.6	0.1	1.4	0.2	0.2	0.3	1.6	1.4

TABLE IVb (Cont'd)

Filter, Top/Bottom Plugs Concentrations (ng m^{-3}) for Westham Island

Sample	Start	Finish	Volume (m^3)	Type	Flt	Pyr	BaA	Chry	Bep	Per	BbF	BkF	BaP	dBahA	BghiPer	I123cdP
010	11/03/85:1300	12/03/85:1300	1102.5	Filtr	0.4	0.3	0.2	0.4	0.4	0.2	0.6	0.2	0.1	0.2	0.5	0.8
				Tplug	2.4	0.9	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
				Total	2.8	1.2	0.2	0.4	0.4	0.2	0.6	0.2	0.1	0.2	0.5	0.8
013	20/03/85:0000	20/03/85:2400	1054.9	Filtr	0.4	0.3	0.3	0.2	0.4	0.0	0.5	0.2	0.1	0.2	0.5	1.5
				Tplug	1.0	0.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
				Total	1.3	1.0	0.3	0.2	0.4	0.0	0.5	0.2	0.1	0.2	0.5	1.5
014	23/03/85:0000	23/03/85:2400	939.5	Filtr	0.1	0.0	0.0	0.1	0.1	TR	0.3	0.1	TR	TR	0.2	0.0
				Tplug	1.0	0.5	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
				Total	1.0	0.5	0.1	0.1	0.1	0.0	0.3	0.1	0.0	0.0	0.2	0.0

Table V

Rejected Samples

Period No.	Location	Reason
1	Westham Island	Power Failure Westham Island
4	Both	Vandalism, probable contamination
6	Both	Probable contamination
7	B.C. Hydro	Timer failure
11	Westham	Contamination - local burning
12	Westham	Contamination - local burning

From Table IV it is seen that PAH were observed at both locations, however, the concentrations tended to be small as compared to values measured in other cities. For comparison, values quoted by Eisenreich et al (1981) are reproduced in Table III. These latter values are for particulate plus vapour concentrations hence may be compared directly with the Vancouver data. Also, for comparison, Table I lists ranges of concentrations of three PAH measured in 1981 and 1985. A direct comparison in this case is invalid, however, since the 1981 data include only particulate concentrations.

One of the objectives of the study was to find any significant differences in concentrations of PAH at a rural and an urban site in Greater Vancouver. Means and standard deviations of total concentrations (particulate plus gaseous phase) for all species were calculated for each site. These are listed in Table VII. Mean concentration for each species is seen to be higher at the urban site than at the rural Westham Island site. However, application of Student's t-test to the data showed that for most species, differences were not significant. In the case of Fluoranthene and Pyrene, the differences were found to be different at the 99 percent confidence level, and the differences for BaP and BghiPer were significant at the 95 percent level. (Application of the Chi-squared test to the data indicated they could be fitted to a normal distribution, hence it was felt the t-test could be applied with confidence).

As noted above, PAH loss from glass fiber filters through re-volatization can be high. Barton et al (1981) as quoted by Galasyn et al (1984), say the loss can be as high as 85 percent for the more volatile species such as Fluoranthene. In this study, it was found that PUF plugs collected large portions (see Table VI) of volatile Flt and Pyr but only minor or undetectable amounts of the other species. The large proportions of Flt and Pyr collected on the plugs are in accord with the findings of Galasyn et al (1984). The PUF plug at the downtown site collected a larger portion of Pyr than did the plug at the rural site. This may be because of higher ambient air temperatures in the heat island of the city.

Table VI

Percent of Sample Collected on PUF Plugs

Compound	B.C. Hydro Site	Westham Island
Flt	85	82
Pyr	80	65
BaA	3	4
Chry	0	0
BeP	0	0
Per	0	0
BkF	0	7
BaP	0	10
dBAhA	0	0
BghiPer	0	0
I123cdP	0	0

5. Summary and Recommendations

PAH have been measured at a rural and an urban site in Greater Vancouver using Hi-vol samplers fitted with PUF Plug back-up traps. PAH were detected in both environments, however, the concentrations appear to be low in comparison with levels measured in other cities. While the mean concentrations of all PAH were found to be higher at the urban site than at the rural site, differences were found to be statistically significant (at the 95 percent confidence level, or higher) only for Flt, Pyr, BaP and BghiPer.

In this study, high concentrations of PAH were not detected in the Vancouver atmosphere, however, it must be remembered that the period of study was relatively short and concentrations might be significantly higher at other times. In particular, one might anticipate higher levels in the late summer and early fall as a result of the burning of garden refuse and when slash is burned, or when ambient oxidant concentrations are high. Furthermore, PAH levels might be expected to increase during periods of cold weather when more fuel is burned. Therefore, it is recommended that further sampling be done during a period of dry, fall weather and during a period of cold, winter weather (with afternoon temperatures near or below 0°, say).

TABLE VII

Means and Standard Deviations of Conc. (ng m^{-3})

		Flt	Pyr	BaA	Chry	Bep	Per	BbF	BkF	BaP	dBahA	BghiPer	I123cdP
B.C. Hydro	Mean:	6.20	4.50	0.37	0.76	0.74	0.09	1.00	0.25	0.31	0.16	2.22	1.72
	S.D.:	3.14	2.28	0.58	0.51	0.42	0.05	0.51	0.15	0.22	0.15	1.64	1.86
		4.4	[illegible]	.5	1.0	1.0	.1	1.4	.3	.4	.2	3.0	2.3
Westham Island:	Mean:	1.82	0.90	0.30	0.43	0.42	0.05	0.67	0.15	0.11	0.12	0.65	0.81
	S.D.:	0.89	0.54	0.19	0.26	0.29	0.05	0.37	0.09	0.08	0.16	0.48	0.56
		4.3	2.1	.7	1.0	1.0	.1	1.6	.4	.3	.3	1.5	1.9

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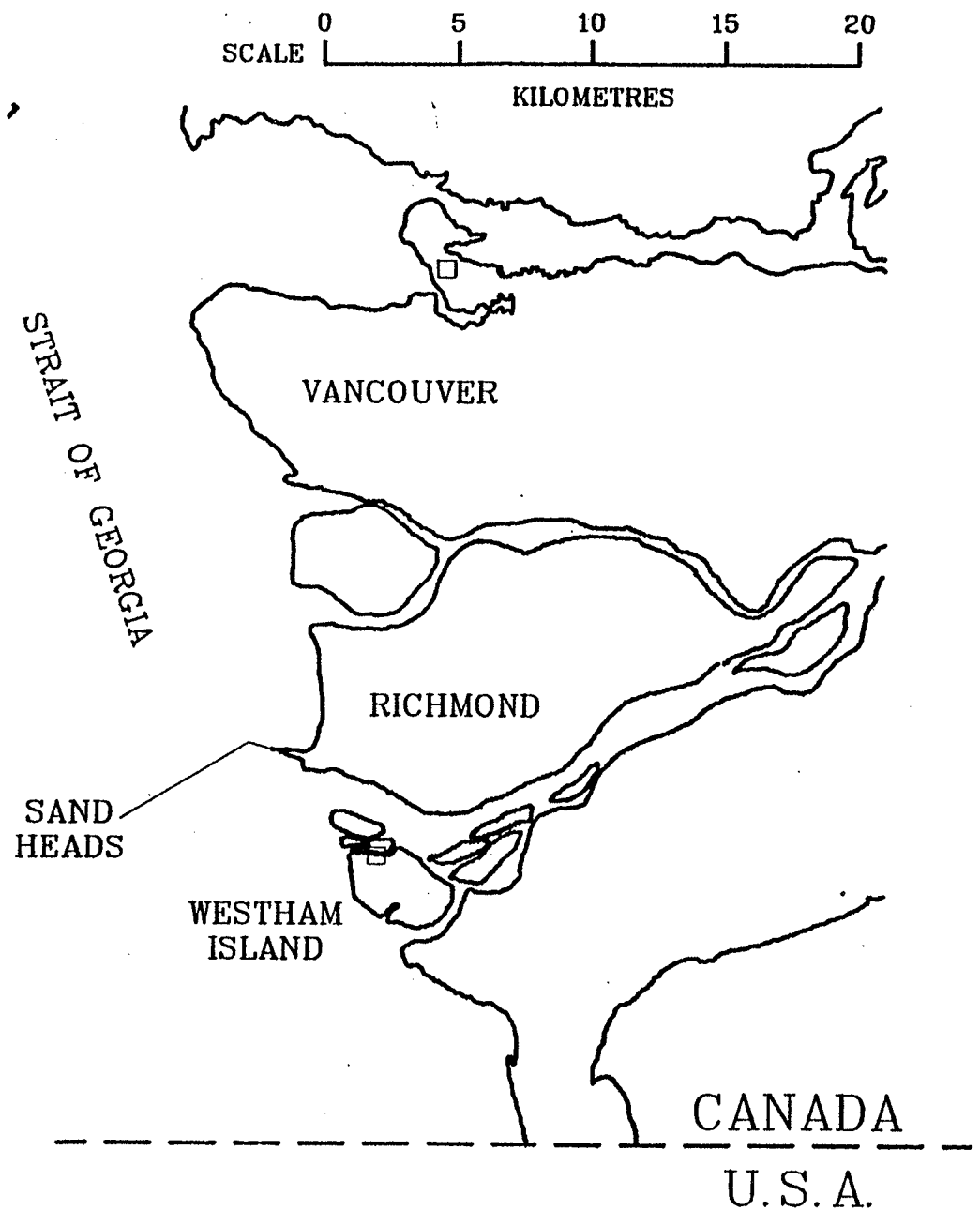
List of Figures

Figure 1 Location Chart


SCALE
0
5
10
15
20
KILOMETRES
STRAIT OF GEORGIA
VANCOUVER
RICHMOND
SAND HEADS
WESTHAM ISLAND
CANADA
U.S.A.

APPENDIX A

Appendix H

CHEMICAL ANALYSES OF PARTICULATE AND GAS PHASE POLYCYLIC AROMATIC HYDROCARBONS COLLECTED IN GREATER VANCOUVER REGIONAL DISTRICT AREA

Contract No: VAN84-5711 WB

Submitted To: ENVIRONMENT CANADA
ATMOSPHERIC ENVIRONMENT SERVICE
(Suite 700 - 1200 West 73rd Avenue)
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TABLE OF CONTENTS

	PAGE NO.
1.0 SUMMARY	1
2.0 INTRODUCTION	2
3.0 EXPERIMENTAL	3
3.1 Materials	3
3.2 Clean-up on Pre-sample PUF Plugs	4
3.3 Sample Submission	4
3.4 Extraction of PAH's in PUF Plugs	5
3.5 Extraction of PAH's in Glass in Air Filters	6
3.6 Instrumentation	6
3.7 Quantitation and Quality Control	7
4.0 RESULTS AND DISCUSSION	9
5.0 REFERENCES	10
TABLES	13-17
FIGURES	18-28

1.0 SUMMARY

Eighty-six samples of polyurethane plugs and glass fiber filters were analyzed for twelve polycylic aromatic hydrocarbons requested by Environment Canada, Atmospheric Environment Section. The samples were soxhlet extracted and quantified by high performance liquid chromatography. The analytical results are presented in tabular form in Table 2. The samples are identified by their submission numbers. Quality control and detection limits are also included in this report.

2.0 INTRODUCTION

Polycylic aromatic hydrocarbons (PAH's) in air represent an important class of toxic pollutants which have deleterious effects on human health. PAH's originate both from anthropogenic and natural sources, the former being the major source. Since many PAH's are carcinogenic the determination of their levels in urban areas is deemed necessary.

Can Test Ltd. undertook the analytical work of PAH determinations for Environment Canada, Atmospheric Environment Service. A total of 86 samples consisting of three different porosities (high, medium and low) of polyurethane foam (PUF) plugs and glass fiber filters were submitted for analysis.

The twelve PAH compounds requested for analysis are as follows:

Fluoranthene	(Flt)
Pyrene	(Pyr)
Benz(a)anthracene	(BaA)
Chrysene	(Chry)
Benzo(e)pyrene	(BeP)
Perylene	(Per)
Benzo(b)fluoranthene	(BbF)
Benzo(k)fluoranthene	(BkF)
Benzo(a)pyrene	(BaP)
Dibenz(a,h)anthracene	(dBahA)
Benzo(ghi)perylene	(BghiPer)
Indo(1,2,3-cd)pyrene	(I123cdP)

The original analytical procedure proposed consisted of soxhlet extraction followed by high performance liquid chromatography (HPLC). However, during the initial stages of this project, the LC chromatograms frequently displayed interfering peaks in the region of PAH absorption. Consequently, additional steps to purify the PAH's was necessary, resulting in increased detection and better quantitation of the compounds. This report details the methodology and results of the analysis together with a discussion of the overall analysis.

3.0 EXPERIMENTAL

3.1 Materials

All of the PAH analytical standards, except Per and BeP, were obtained from Supelco, Inc., Bellefonte, PA, USA. The Per and BeP standards were supplied by Aldrich Chemical Co., Milwaukee, WI, USA.

Two hundred - ug/mL stock solutions of composite PAH standards were prepared by dissolving the appropriate amounts of the PAH standards in acetone. Since this analysis was performed at the same time as another PAH project, which required some lower molecular weight PAH's, the composite standard solutions contained the following extra compounds:

Naphthalene	(Nap)
Acenaphthylene	(Anapty)
Acenaphthene	(Anap)
Fluorene	(Flr)
Phenanthrene	(Phe)
Anthracene	(Anth)

Twenty - ug/mL (for spiking purposes) solutions were prepared by diluting the stock solution in acetone. Two-ug/mL and 0.2 ug/mL working solutions were prepared by diluting the stock solution in the HPLC mobile phase [acetonitrile:water (1:1)]. All solutions were freshly prepared at the beginning of the project and stored in the dark and at -20°C.

All reagents were analytical grade or better. All solvents used in the extraction procedures were distilled in glass and all solvents used in the final reconstitution of the extract and in preparing the HPLC mobile phase were non-UV absorption HPLC grade. They were used without further purification.

Soxlets with large capacity extractors (90 mm I.D. x 410 mm long) were used for the PUF plug extraction. The large size of extraction apparatus was necessary to accommodate the PUF plugs which measured 80 mm diameter x 75 mm long. During the cleaning of the pre-sample plugs, 4 plugs were stacked together for soxhlet extraction. For the sample extraction, the original syphon tube which had a capacity of 2.2 L syphoning action was reduced in length so that the syphoning capacity was reduced to approximately 1.6 L for the extraction of a single plug.

3.2 Clean-up on Pre-sample PUF Plugs

Blank PUF Plugs (80 mm diameter and 75 mm long; supplied by Atmospheric Enviroment Service) were cleaned by soxhlet extraction prior to sample collection. Four plugs were placed in the extractor and cycled in hexane:acetone (9:1) for 16 hours (overnight). The plugs were air-dried and stored in a washed and solvent rinsed glass container for sample collection. The lids of the containers were lined with solvent rinsed aluminum foil.

3.3 Sample Submission

The PUF plug and glass fiber filter samples were brought to the laboratory by Atomospheric Environment Service staff. The staff was advised of possible common contaminations, such as tobacco smoke.

All samples were submitted in cardboard boxes to exclude them from light. Each sample was contained in an individual clean glass container previously cleaned in our laboratory (lids lined with solvent rinsed aluminum foil). The samples were logged in and immediately refrigerated at 4°C. Extraction of the samples was normally done within a 2 day period. Toward the end of the sampling schedule, a backlog of samples temporarily developed but all samples were extracted within 7 days.

3.4 Extraction of PAH's in PUF Plugs

Individual whole PUF plug samples were soxhlet extracted with 2 L of hexane:acetone (9:1) for five hours. During the extraction, the soxhlet apparatus was covered with aluminum foil to protect the sample from the laboratory's fluorescence lighting. For the subsequent work-up procedure and storage of sample extracts, precautions were taken to minimize exposure of the samples to light.

At the end of the soxhlet extraction, the extract was cooled to room temperature and the volume of the extract was reduced to 2 mL in a rotary evaporator. The extract was then solvent-exchanged for hexane by adding 5 mL hexane to the concentrated extract and rotary-evaporating to 2 mL volume. Five mL hexane was again added to the extract and the volume further reduced to 2 mL by rotary evaporation.

The sample extract (in 2 mL hexane) was diluted to 4 mL of hexane and washed with 10 mL of alkaline solution (7% NaCl in 0.025N NaOH). The aqueous solution was extracted twice with 2 mL hexane and all combined hexane extracts were then concentrated to a volume of 5 mL by rotary evaporation prior to clean-up by alumina column chromatography.

The alumina column was prepared in a 15 cm (5 3/4") pasteur pipette by loosely plugging the tip with silanized glass wool, filling with 5 - 6 cm of activated alumina, and topping with a layer of anhydrous sodium sulfate (0.5 cm in depth). The column was then washed with 5 mL of hexane. The sample extract (in hexane) together with 2 rinses of the sample (1 mL hexane each) were transferred to the top of the column. The hexane eluate was discarded. Ten milliliters of dichloromethane (DCM) was added to the column to elute the PAH fraction. The DCM eluate was concentrated to a volume of 1 mL inside a 15 mL graduated conical test tube under a stream of nitrogen at room temperature. The concentrated eluate was then solvent - exchanged for acetonitrile (ACN) by adding 2 mL ACN to the eluate and evaporating down to a volume of 0.75 mL under nitrogen at room temperature. One milliliter of ACN was added to the concentrated eluate followed by a similar evaporative technique to reduce the volume to 0.5 mL. The eluate was adjusted to a final volume of 2 mL with the mobile phase mixture (ACN:water, 1:1) pending HPLC analysis.

3.5 Extraction of PAH's in Glass Fiber Air Filters

Glass fiber filters (approximately 25 x 25 cm) were placed inside a soxhlet extractor (40 mm ID x 205 mm body length) with the collection surface folded inside and extracted with 200 mL of DCM for 5 hours. The extract was then treated identically to that from the PUF plug extraction procedure.

3.6 Instrumentation

The HPLC analytical parameters were as follows:

Instrument	-Waters high performance liquid chromatograph with autosampler W1SP 710B, system controller 720, two model M45 pumps and two data module integrators.
Ultra-Violet (UV) Detector	-Waters variable UV detector model 480 LC set at 280 nm; AUFS set at 0.01.
Fluoresence Detector	-Waters model 420 consisted of 3 sets of filters:(1) 254 nm (excitation)/395 nm (emission), (2) 280 nm (excitation)/395 nm (emission), and (3) 395 nm (excitation/ 440 nm (emission).
Column	-10 micron Radial-Pak PAH; 8 mm ID x 10 cm
Initial Mobile Phase	-50% acetonitrile in water for 5 min.
Gradient	-50% to 100% acetonitrile in 30 min.
Final Condition	-100% acetonitrile for 20 min.
Flow Rate	-1 mL/min.

The above HPLC conditions provided baseline separation for all the PAH's using the appropriate detection parameters (i.e. UV and/or fluorescence detection with different wavelength filters). Quantitations of peak areas were achieved by valley to valley integration as set up in the data modules.

The determination of PAH's for each sample was done by 3 separate analytical HPLC runs, each with different fluorescence detection while UV detection was always set at 280 nm.

3.7 Quantitation and Quality Control

PAH's were quantified by the external standard calibration factor procedure as described in the EPA method 610 (1). Before the analysis, PAH standards were injected into the HPLC system to determine the elution patterns. Reagent blanks were also processed through the extraction procedure to insure absence of interferences due to laboratory contaminations.

During the initial stage of sample analysis, it was determined that different PAH's would have different detection parameters for quantitation and they are listed as follows:

	Detector	**Wavelength (nm)**
Flr	UV	280
Pyr	fluorescence	280/395
BaA	fluorescence	280/395
Chry	fluorescence	280/395
BeP	fluorescence	280/395
Per	fluorescence	395/440
BbF	fluorescence	280/395
BkF	fluorescence	280/395
BaP	fluorescence	280/395
dBahA	UV	280
BghiPer	UV	280
I123cdP	UV	280

A calibration factor for each PAH standard was established based on the ratio of the peak area response to the amount injected. The ratio, or calibration factor, varied less than 10% relative standard deviation throughout the working range of 0.5 ng to 50 ng for all PAH's except dBahA, BghiPer and I123cdP where the range was 2 ng to 50 ng. Triplicate injections were performed at each level of standard with a minimum of 5 levels throughout the working range. The average ratio yielded was then used to calculate the amount of PAH found in the sample extract injected. Daily variation of the ratio was less then 15% of the overall value. Table 1 depicts the average ratios, their overall standard deviations (SD) and the relative SD of the PAH standards. A quality control (QC) sample was also analyzed concurrently with every 10 authentic samples to monitor the PAH recoveries. The spiking of the QC samples was performed on a clean, low pore size PUF plug at a level of 2 ug of each PAH (0.1 mL of 20 ug/mL working solution). The QC sample was allowed to air dry for 20 minutes prior to soxhlet extraction.

4.0 RESULTS AND DISCUSSION

Eighty-six samples of PUF plugs and glass fiber filters were analyzed. In addition, eight QC samples were analyzed concurrently with the samples. All sample results are given as nanograms (ng) per sample unit (ng/sample=total amount in nanograms of the specific PAH found in a PUF plug or glass fiber filter) in Table 2. The results are not corrected for recoveries.

Further interpretation of the results are not possible since other sampling data such as air mass collected and collection times are not available. Information such as sample location and sampling dates was not provided during the analysis period but was kindly supplied at a later date. Complete and more meaningful results can be achieved if the data mentioned above is available.

The extraction of PAH's from the glass fiber filters using soxhlet extraction overnight with DCM followed by alumina column clean-up was a modification of the procedure used by Keller and Bidleman (2). For the extraction of PAH's in PUF plugs, instead of using petroleum ether as recommended by the same workers, we found that a mixture of hexane:acetone (9:1) gave overall satisfactory recoveries.

The individual recovery data for each PAH on the eight QC samples are provided in Table 3. The average recoveries and their SD for each PAH are also given in the table. The precision of the method used in the analysis, based on the eight QC samples over the 20 day period of the analysis, can be expressed by the relative SD. With the exception of I123cdP, the values of the average recoveries and their relative SD's ranged from 76 to 96% and 8.8 to 18.4%, respectively. The reason for the lower recovery values of I123cdP in 3 of 8 QC results might be explained below. A wide range of recovery from just detectable to 116% was documented in the EPA method 610 on I123cdP. The recovery and SD data show better results than the QC acceptance criteria set out by the EPA method 610.

The precision of the method is undoubtably affected by the additional manipulative steps required to evaporate 2 L of solvent after the soxhlet extraction. Three consecutive evaporations were necessary whereas using less solvent would require one evaporative step, thus increasing the precision. The poor recoveries of I123cdP might also be due to this fact.

The detection limits (DL's) based on the pure standards injected onto the HPLC column are listed in the first column in Table 4. The average recoveries of the eight QC samples indicate that approximately 20% of the PAH's was lost in the extraction procedure (i.e. approximately 80% recovered). Thus, the corrected DL's based on the extraction loss are calculated accordingly and expressed in the 3rd column of the same table. During the analysis, the volume of the final extract was 2.0 mL and a maximum of 0.1 mL was injected in the HPLC. The minimum DL of each PAH for each sample unit is then calculated and listed in the next column of the table. Since spiking to a sampled plug (and glass fiber filter) or a matrix with similar background was not possible, the quantitative DL's in this analysis are assumed to be three times the minimum DL's to accommodate the background noise encountered in the real sample situation. The quantitative DL's are provided in Table 4.

In general, we found both the plug and the filter samples contained some interfering compounds which eluted close to the PAH peaks in the HPLC analysis, even after the extra effort required for the alkaline wash and the alumina column clean-up. Typical chromatograms of a QC extract and a glass fiber filter sample extract are shown in figures 1 and 2. Further investigation on the interfering compounds using GC/MS (a Finnigan OWA equipped with 15 meter DB-5 column) revealed the presence of alkylated PAH's and other hetrocylic compounds. Examples of the mass spectra and library search of such interfering compounds are found in figure 3.

To improve the chromatography so that complete separation of the PAH's and the interfering compounds can be achieved, a 5 micron HPLC column, which increases the theoretical plates for chromatographic separation, may be necessary.

The similarity in polarity and molecular size of the PAH's and the interfering compounds would make these compounds co-elute in most clean-up procedures. GC/MS analysis using internal standards such as deuterated PAH's and the characteristic ions for quantitation would be a better alternative. The problems of interfering compounds in the HPLC analysis can be solved by identification of the mass spectrum and the retention time of the characteristic ion of PAH's in the selected ion chromatograms. As described earlier, three separate HPLC runs were used to complete the quantitation of each PAH in the analysis, analysis time can be cut down by a single GC/MS run for each sample. The overall method precision can also be improved using the appropriate deuterated standards.

5.0 REFERENCES

1. Method 610. Federal Register Part VIII, Environmental Protection Agency 40 CFR Part 136, 49(209) October 1984.

2. Keller, C.D. and Bidleman, T.F. Collection of Airborne Polycylic Aromatic Hydrocarbons and other Organics with a Glass Fiber Filter - Polyurethane Foam System. Atmospheric Environment 18(4), 837-845 (1984).

TABLE 1 -CALIBRATION FACTOR DATA

	MEAN CALIBRATION FACTOR	SD	% SD
Fluoranthene	0.00431	0.000308	7.15
Pyrene	0.00128	0.0001524	11.90
Benz(a)anthracene	0.000164	0.000018	10.98
Chrysene	0.000906	0.0001196	13.2
Benzo(e)pyrene	0.000682	0.0000829	12.2
Perylene	0.00361	0.000265	7.34
Benzo(k)fluoranthene	0.001511	0.0001716	11.35
Benzo(b)fluoranthene	0.0002763	0.0000265	9.58
Benzo(a)pyrene	0.0001841	0.0000205	11.15
DiBenz(a,h)anthracene	0.004838	0.000624	12.9
Benzo(ghi)perylene	0.004976	0.000597	11.98
Indeno(123-cd)pyrene	0.004514	0.0006398	14.17

TABLE 2-PAH RESULTS (IN NG/SAMPLE) FOR ATMOSPHERIC ENVIRONMENT SERVICE SAMPLES

LAB #	SAMPLE ID	Flt AMT	Pyr AMT	BaA AMT	Chry AMT	BeP AMT	Per AMT	BbF AMT	BkF AMT	BaP AMT	dBahA AMT	BghiPer AMT	I123cdP AMT
	001-HIGH PORE SIZE PLUG	7738	4625	ND	ND	ND	ND	ND	ND	ND	ND	ND	[illegible]
2	002-AIR FILTER 3998747	1687	1527	923	193	653	65	780	177	280	TR	1153	630
3	003-AIR FILTER 3998746	TR	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
4	004-HIGH PORE SIZE PLUG	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
5	005-HIGH PORE SIZE PLUG	1912	645	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
6	006-AIR FILTER 3998744	108	207	516	575	425	38	535	209	181	TR	827	936
7	007-HIGH PORE SIZE PLUG	5467	4375	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
8	008-AIR FILTER 3998745	2460	2790	2220	2375	2539	267	3661	833	1101	1000	4861	2308
9	009-HIGH PORE SIZE PLUG	2222	750	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
10	010-AIR FILTER 3998701	350	1043	487	700	880	35	633	157	90	367	897	780
11	011-HIGH PORE SIZE PLUG	7619	5833	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
12	012-AIR FILTER 3998702	2107	1833	1533	1500	1610	161	1430	567	810	228	2857	2939
13	013-LOW PORE SIZE PLUG	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
14	014-LOW PORE SIZE PLUG	57	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
15	015-AIR FILTER 3998743	60	67	200	367	310	36	260	87	77	390	560	1030
16	016-HIGH PORE SIZE PLUG	4930	7590	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
17	017-HIGH PORE SIZE PLUG	ND	ND	28	TR	43	ND	56	TR	31	ND	133	ND
18	018-LOW PORE SIZE PLUG	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
19	019-AIR FILTER 3998742	345	218	78	173	125	ND	115	40	30	150	238	198
20	020-HIGH PORE SIZE PLUG	5743	4340	350	325	140	TR	275	55	130	120	620	405
21	021-HIGH PORE SIZE PLUG	ND	ND	220	410	180	46	140	165	290	TR	220	340
22	022-LOW PORE SIZE PLUG	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
[illegible]	023-AIR FILTER 3998740	263	250	285	245	240	37	388	83	93	TR	608	648
	024-MED PORE SIZE PLUG	ND	ND	20	ND	ND	ND	ND	ND	ND	ND	ND	[illegible]
25	025-MED PORE SIZE PLUG	4000	2232	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
26	026-AIR FILTER 3998741	50	TR	28	75	TR	TR	172	TR	TR	ND	ND	ND
27	027-MED PORE SIZE PLUG	612	165	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
28	028-MED PORE SIZE PLUG	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
29	029-LOW PORE SIZE PLUG	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
30	030-AIR FILTER 3998737	115	37	11	109	57	TR	110	ND	ND	ND	ND	ND
31	031-AIR FILTER 3998738	538	357	593	706	711	84	1304	336	285	143	844	1471
32	032-MED PORE SIZE PLUG	ND	ND	60	133	147	TR	399	38	34	ND	ND	ND
33	033-MED PORE SIZE PLUG	1867	440	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
34	034-LOW PORE SIZE PLUG	ND	ND	TR	ND	TR	ND	TR	ND	ND	ND	ND	ND
35	035-AIR FILTER 3998736	178	183	242	357	299	36	733	130	90	ND	556	866
36	036-LOW PORE SIZE PLUG	ND	ND	ND	ND	TR	ND	TR	ND	ND	ND	ND	ND
37	037-AIR FILTER 3998739	1113	1035	612	1346	946	124	1779	348	364	ND	7358	6549
38	038-MED PORE SIZE PLUG	ND	ND	31	TR	TR	TR	TR	TR	TR	TR	TR	ND
39	039-MED PORE SIZE PLUG	9288	6028	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
40	040-MED PORE SIZE PLUG	595	115	29	ND	TR	ND	ND	64	77	ND	ND	ND

NOTE:

Flt= Fluoranthene
Pyr= Pyrene
BaA= Benz(a)anthracene
Chry= Chrysene
BeP= Benzo(e)pyrene
P[illegible]erylene
B[illegible]enzo(b)fluoranthene
BkF= Benzo(k)fluoranthene
BaP= Benzo(a)pyrene
dBahA=Dibenz(ah)anthracene
BghiPer=Benzo(ghi)perylene
I123cdP=Indeno(1,2,3-cd)pyrene

ND = Not detectable
TR = above minimum detection limit; below quantitative detection limit (see table 4 for details)

TABLE 2 (CONTINUED)-PAH RESULTS (IN NG/SAMPLE) FOR ATMOSPHERIC ENVIRONMENT SERVICE SAMPLES

LAB #	SAMPLE ID	Flt AMT	Pyr AMT	BaA AMT	Chry AMT	BeP AMT	Per AMT	BbF AMT	BkF AMT	BaP AMT	dBahA AMT	BghiPer AMT	I123cdP AMT
	041-LOW PORE SIZE PLUG	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	042-MED PORE SIZE PLUG	ND	ND	31	54	119	ND	93	TR	TR	ND	ND	ND
43	043-MED PORE SIZE PLUG	8887	5206	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
44	044-MED PORE SIZE PLUG	ND	ND	26	ND	ND	ND	ND	ND	ND	ND	ND	ND
45	045-MED PORE SIZE PLUG	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
46	046-MED PORE SIZE PLUG	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
47	047-HIGH PORE SIZE PLUG	1176	612	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
48	048-AIR FILTER 3998734	330	146	242	357	299	38	733	130	90	ND	538	505
49	049-AIR FILTER 3998733	779	782	387	786	670	86	1275	257	179	ND	2941	818
50	050-HIGH PORE SIZE PLUG	5667	4318	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
51	051-HIGH PORE SIZE PLUG	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
52	052-AIR FILTER 3998732	953	447	446	752	604	76	1393	250	185	280	1665	1491
53	053-HIGH PORE SIZE PLUG	2267	833	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
54	054-LOW PORE SIZE PLUG	TR	TR	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
55	055-AIR FILTER 3998735	592	721	764	957	901	121	1141	324	398	200	2344	1635
56	056-AIR FILTER 3998730	408	301	179	492	387	194	705	168	117	200	556	904
57	057-HIGH PORE SIZE PLUG	2632	1012	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
58	058-HIGH PORE SIZE PLUG	8504	6556	145	ND	ND	ND	ND	ND	ND	ND	ND	ND
59	059-AIR FILTER 3998731	1669	1459	1348	1361	1198	191	1421	433	561	236	3750	715
60	060-AIR FILTER 3998729	1341	945	5407	2985	2626	715	3381	1029	1534	813	3030	257
61	061 HIGH PORE SIZE PLUG	14000	7483	49	ND	ND	ND	ND	ND	ND	ND	ND	ND
62	062-LOW PORE SIZE PLUG	TR	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
63	063-AIR FILTER 3998728	915	1097	339	613	645	130	953	161	280	165	962	421
	064-HIGH PORE SIZE PLUG	8224	4524	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	065-LOW PORE SIZE PLUG	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
66	066-AIR FILTER 3998727	2136	2143	2450	2900	2187	372	3081	930	1296	671	1786	180
67	067-MED PORE SIZE PLUG	7566	5238	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
68	068-AIR FILTER 3998726	667	703	333	850	758	82	1238	234	280	210	2222	285
69	069-MED SIZE PLUG	2434	1428	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
70	070-AIR FILTER 3998725	372	362	271	188	463	29	476	174	123	229	480	159
71	071-MED PORE SIZE PLUG	1033	656	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
72	072-MED PORE SIZE PLUG	TR	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
73	073-AIR FILTER 3998724	1443	1389	1731	1593	1105	167	1667	378	448	366	6143	601
74	074-MED PORE SIZE PLUG	7633	5724	103	ND	ND	ND	ND	ND	ND	ND	ND	ND
75	075-LOW PORE SIZE PLUG	TR	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
76	076-AIR FILTER 3998723	67	ND	44	131	126	TR	326	57	TR	TR	185	ND
77	077-HIGH/MED PORE SZ PLG	912	494	47	ND	ND	ND	ND	ND	ND	ND	ND	ND
78	078-LOW PORE SIZE PLUG	TR	TR	TR	ND	ND	ND	ND	ND	ND	ND	ND	ND
79	079-AIR FILTER 3998703	374	456	139	381	351	36	595	113	70	142	2476	ND
80	080-HIGH/MED PORE SZ PLG	3067	2611	56	ND	ND	ND	ND	ND	ND	ND	ND	ND
81	081-LOW PORE SIZE PLUG	TR	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
82	BLANK	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
83	BLANK	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
84	BLANK	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
85	BLANK	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
86	BLANK	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

TABLE 3 - QUALITY CONTROL DATA (in Percentages)

	QC Sample #1	#2	#3	#4	#5	#6	#7	#8	Mean	SD	Relative SD(%)
Fluoranthene	89	77	76	93	76	55	79	82	78	11	14.1
Pyrene	97	78	76	81	78	79	76	74	80	7	8.8
Benz(a)anthracene	100	84	80	79	76	72	72	74	80	9	11.3
Chrysene	110	81	71	73	70	68	69	67	76	14	18.4
Benzo(e)pyrene	100	83	76	76	72	73	71	68	77	10	13.0
Perylene	86	92	86	90	91	86	82	76	86	5	5.8
Benzo(b)fluoranthene	100	85	75	74	71	72	69	66	77	12	15.6
Benzo(k)Fluoranthene	105	82	74	80	71	72	71	66	77	12	15.6
Benzo(a)pyrene	104	91	81	82	71	72	73	74	81	11	13.6
DiBenz(a,h)anthracene	100	93	80	81	73	75	74	71	81	10	12.3
Benzo(ghi)perylene	97	95	76	84	76	78	77	79	83	8	9.6
Indeno(1,2,3-cd)pyrene	99	91	D	108	97	D	84	D	96*	9*	9.4

D = Detected
* = Statistical calculations did not include D value
QC= Quality Control

TABLE 4 - DETECTION LIMITS AND AVERAGE SPIKE RECOVERY DATA

	On Column DL of Pure Std. (ng)	Average Recoveries* (%)	Corrected On Column DL Of Pure Std. (ng)	Minimum DL per Sample (ng)	Quantitative** DL per sample (ng)
Fluoranthene	0.5	78	0.64	12.8	50
Pyrene	0.5	80	0.625	12.5	50
Benz(a)anthracene	0.1	80	0.125	2.5	10
Chrysene	0.5	76	0.66	13.2	50
Benzo(e)pyrene	0.5	77	0.65	13.0	50
Perylene	0.25	86	0.29	6.0	20
Benzo(b)fluoranthene	0.5	77	0.65	13.0	50
Benzo(k)fluoranthene	0.25	77	0.33	6.6	25
Benzo(a)pyrene	0.25	81	0.31	6.2	25
DiBenz(a,h)anthracene	2.0	81	2.5	50	120
Benzo(ghi)perylene	2.0	83	2.4	48	120
Indeno(1,2,3-cd)pyrene	2.0	96	2.1	42	120

* Recoveries based on eight QC samples spiked at 2 ug of each PAH (see Table 3 for details)
** Values in column 4 are approximately three times column 3

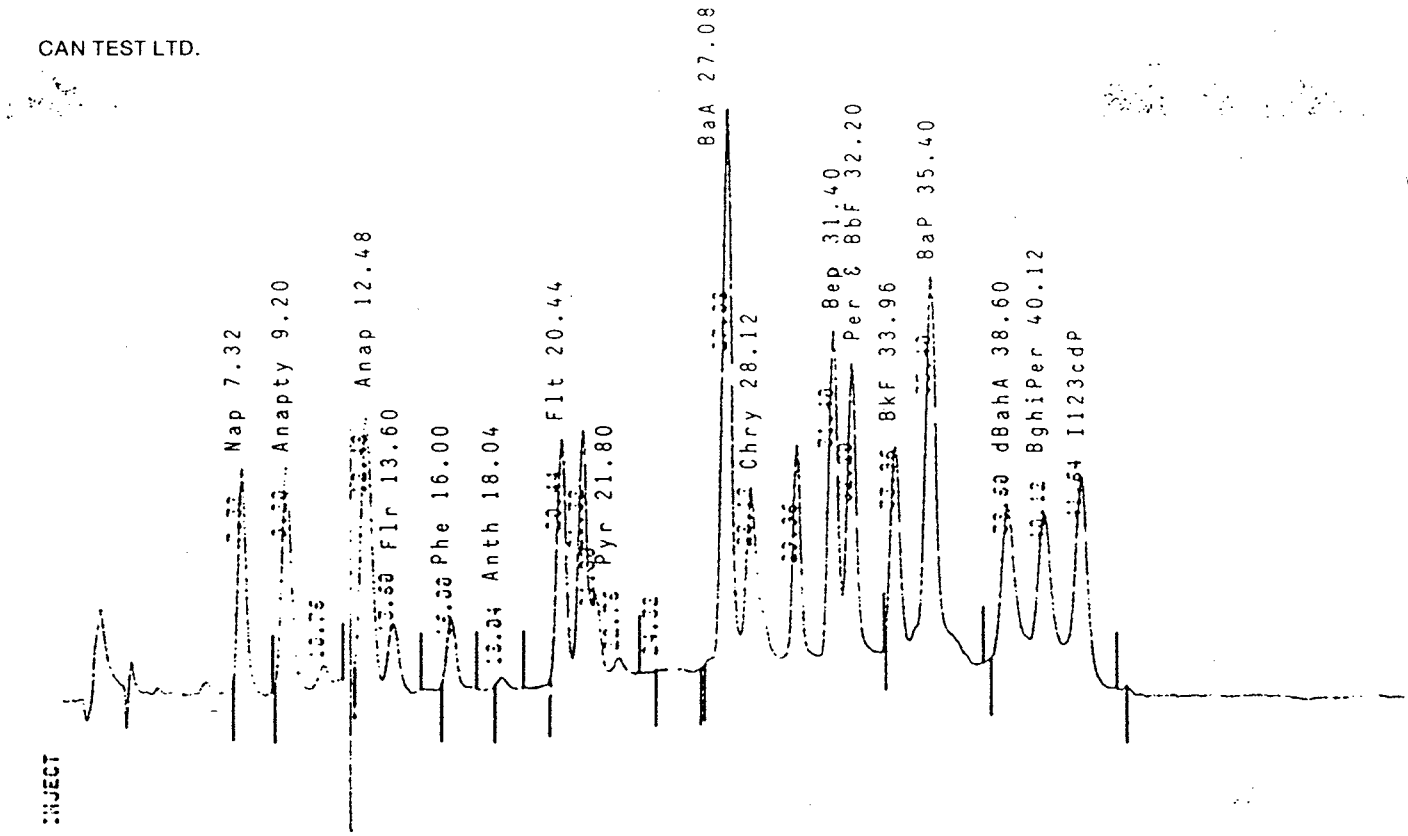

Figure 1a - HPLC/UV chromatogram of a spiked PUF plug extract containing PAH analytical standards.

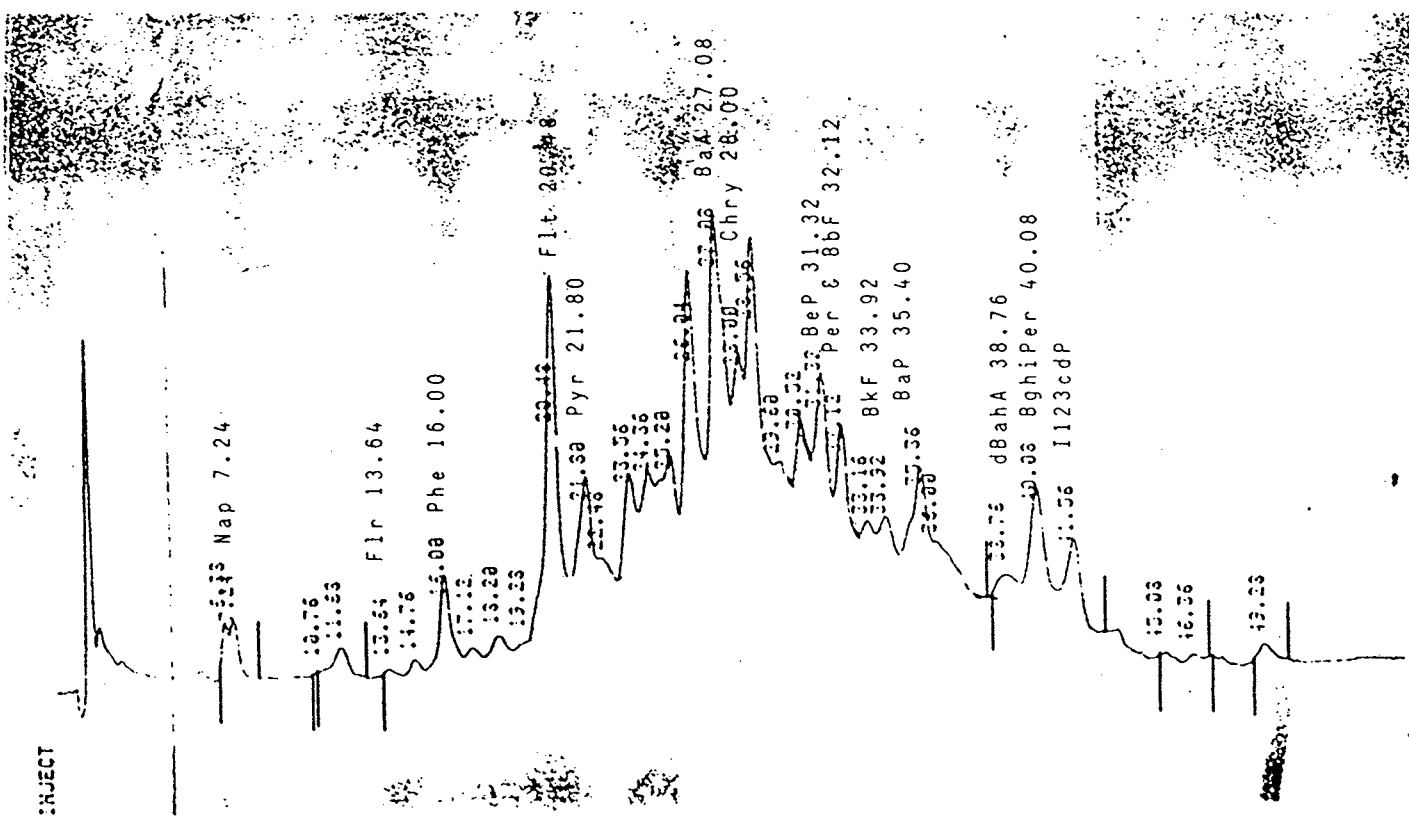

Figure 1b - HPLC/UV chromatogram of a glass fiber filter sample extract (sample #2).

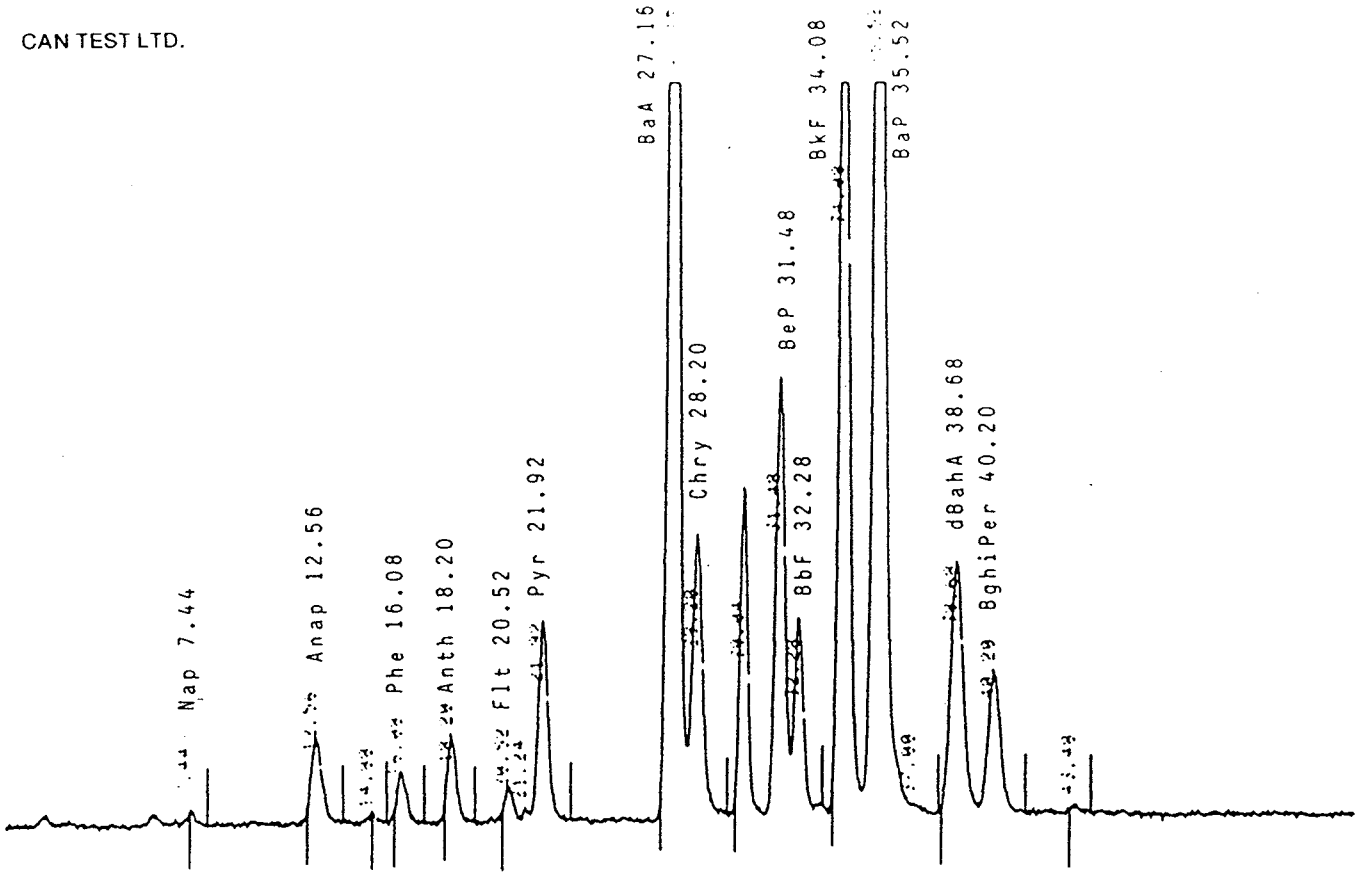

Figure 2a - HPLC/Fluoresence (280 nm Excitation/395 nm Emission) chromatogram of a spiked PUF plug extract containing PAH analytical standards.

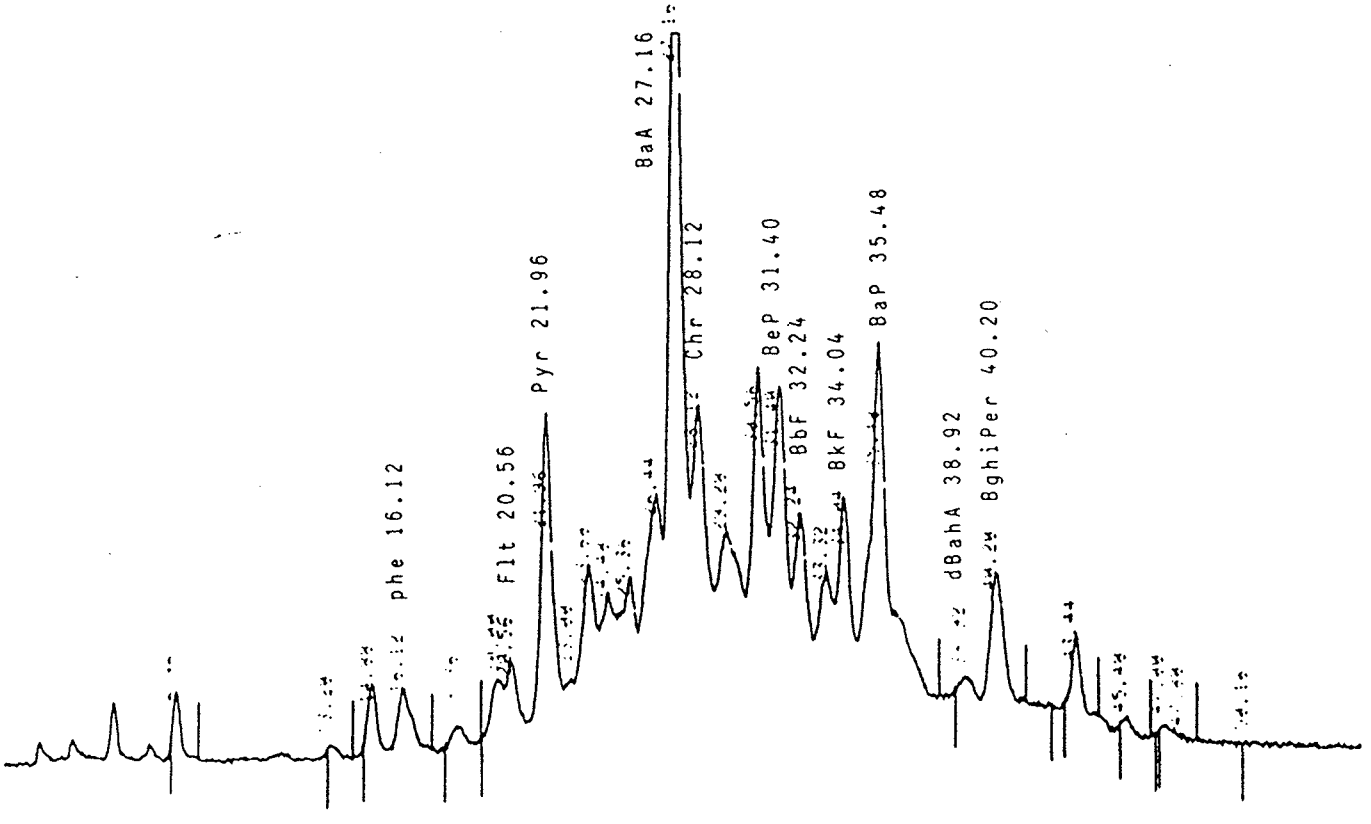

Figure 2b - HPLC/Fluoresence (280 nm Excitation/395 nm Emission) chromatogram of a glass fiber filter sample extract (sample #2).

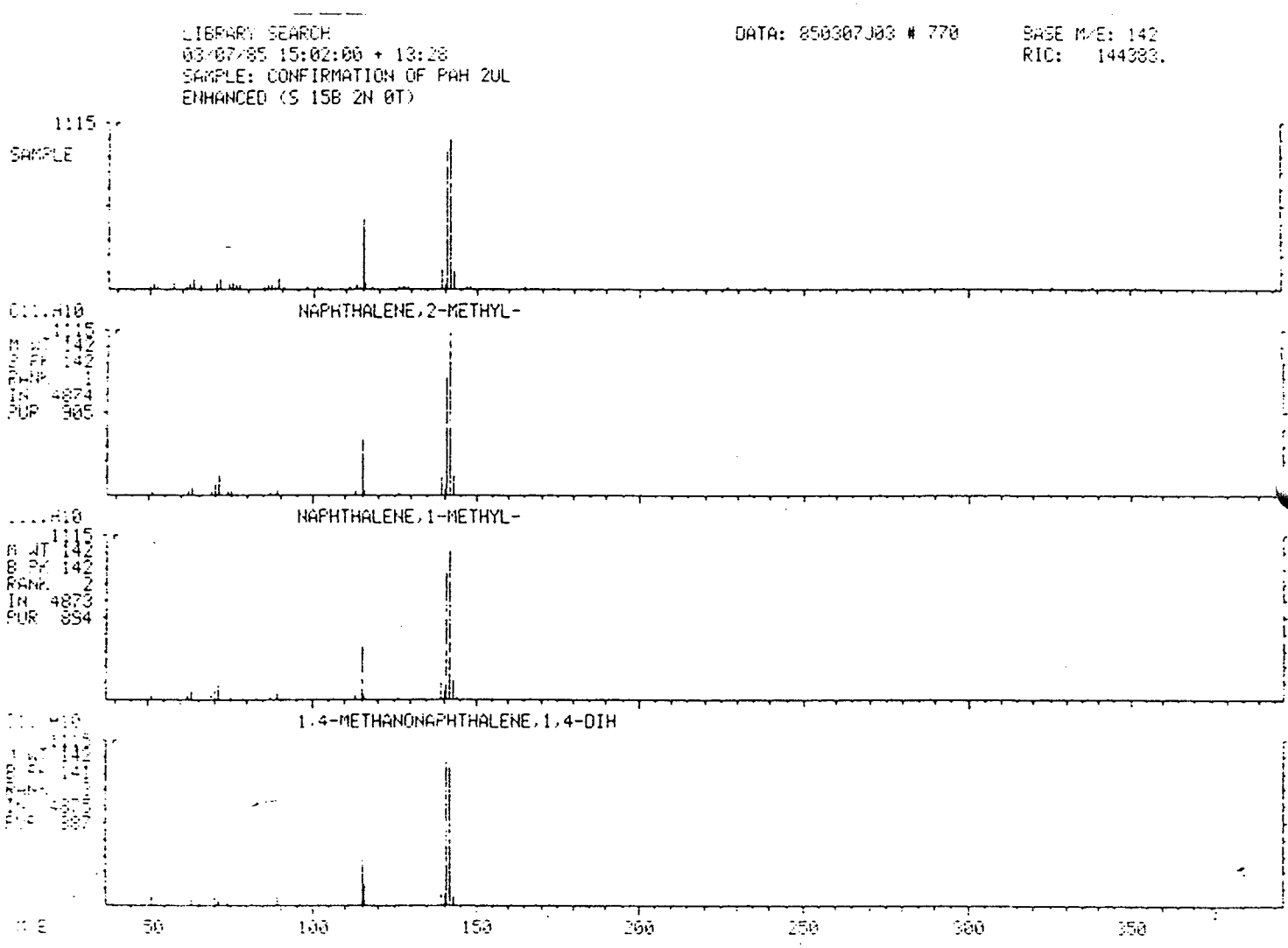

Figure 3(a) - Mass Spectrum (MS) of a Medium Pore Size PUF Plug Extract (top spectrum) Having a Gas Chromatographic Retention Time (GCRT) of 13 min. 28 sec. and the normalized MS of the 3 compounds the library search selected as the three best matches. GC Condition - 15 meter DB-5 column; 30°-270°C at 7°C/min.; hold for 1 min. at initial temperature.

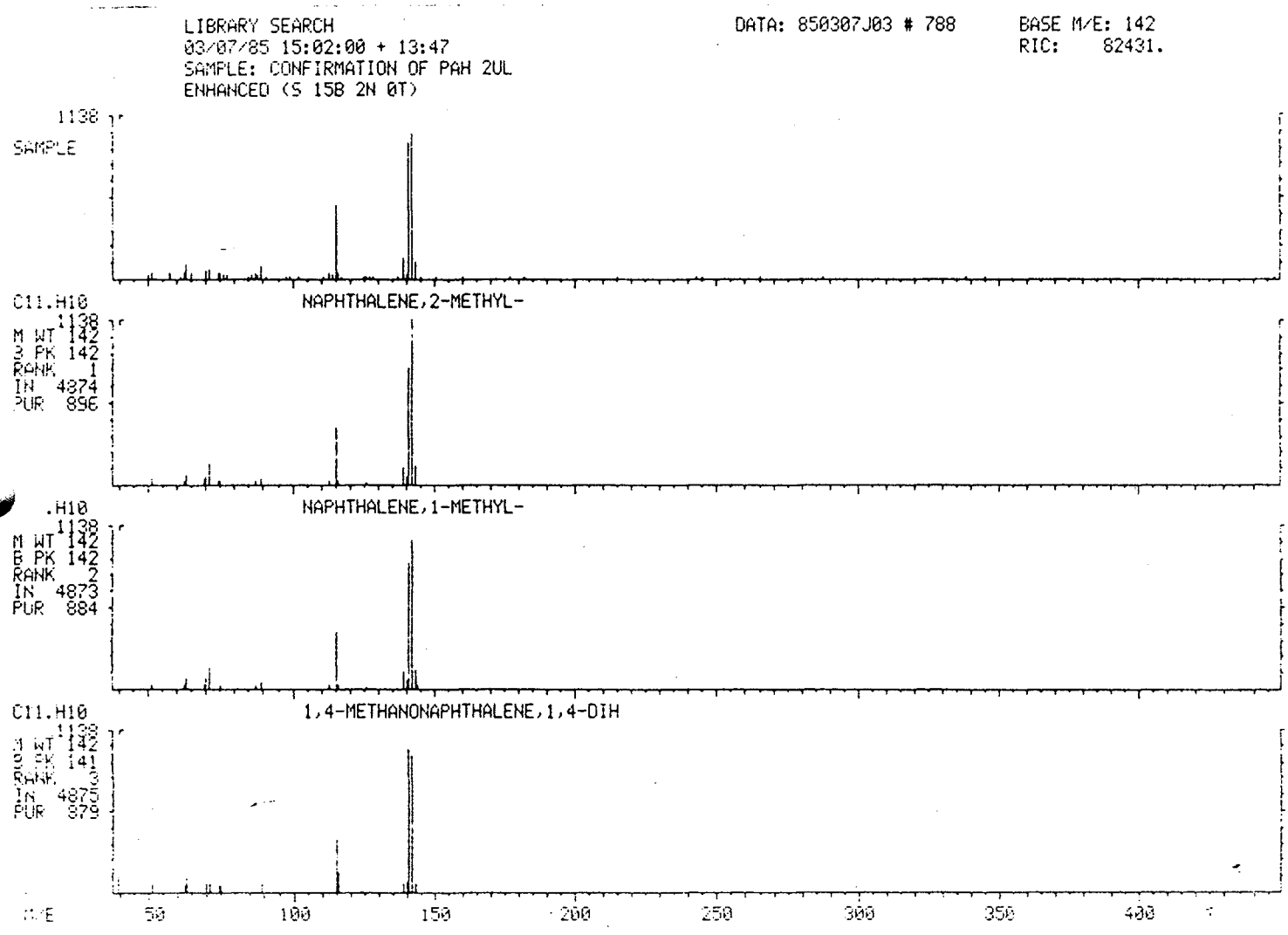

Figure 3(b) - MS of a Medium Pore Size PUF Plug Extract (top spectrum) Having GCRT of 13 min. 47 sec. and the MS of the 3 compounds resulted from library search as the 3 best matches.

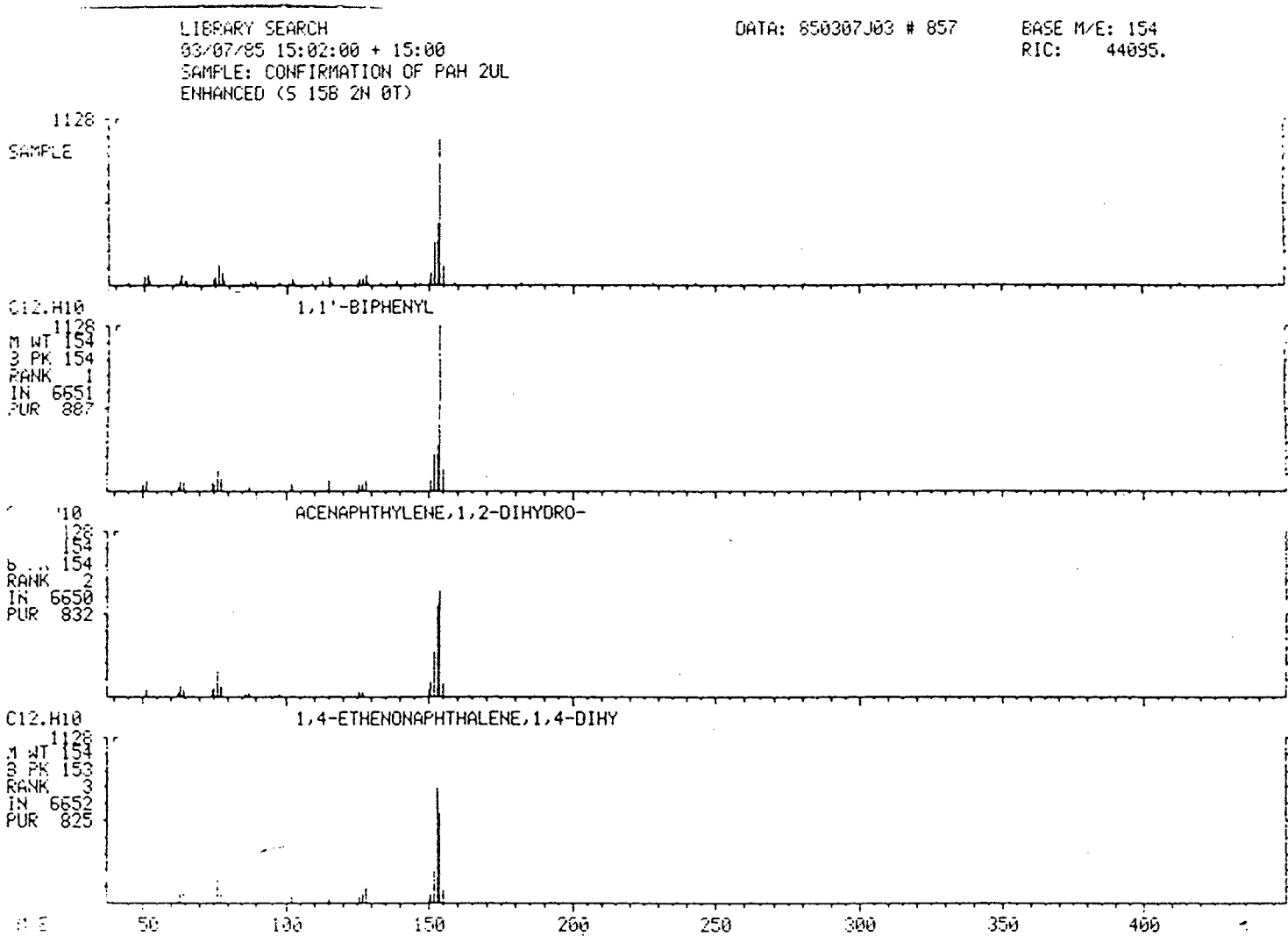

Figure 3(c) - MS of a Medium Pore Size PUF Plug Extract (top spectrum) Having a GCRT of 15 min. and the MS of the 3 compounds resulted from library search as the 3 best matches.

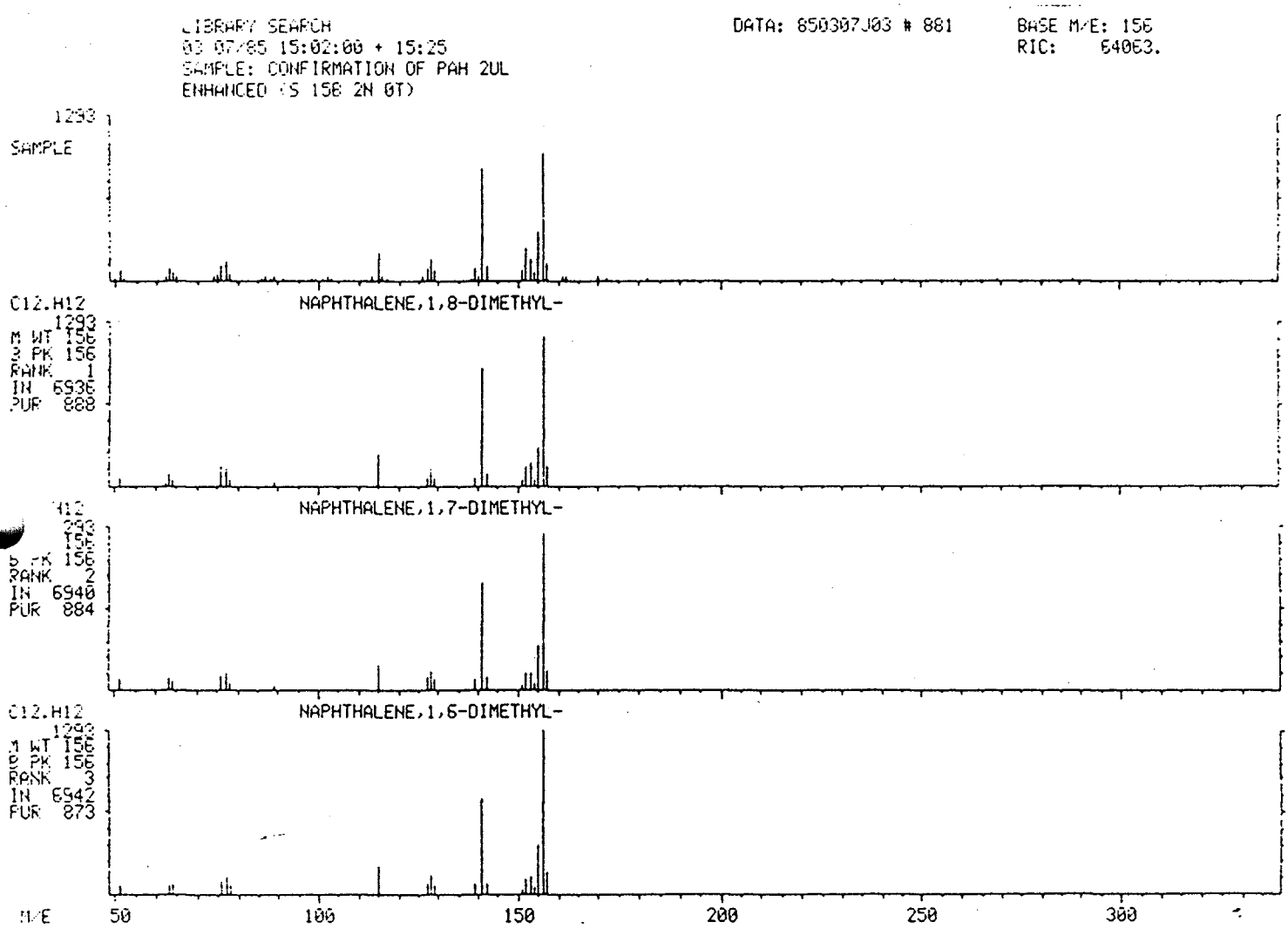

Figure 3(d) - MS of a Medium Pore Size PUF Plug Extract (top spectrum) Having a GCRT of 15 min. 25 sec. and the MS of the 3 compounds resulted from library search as the 3 best matches.

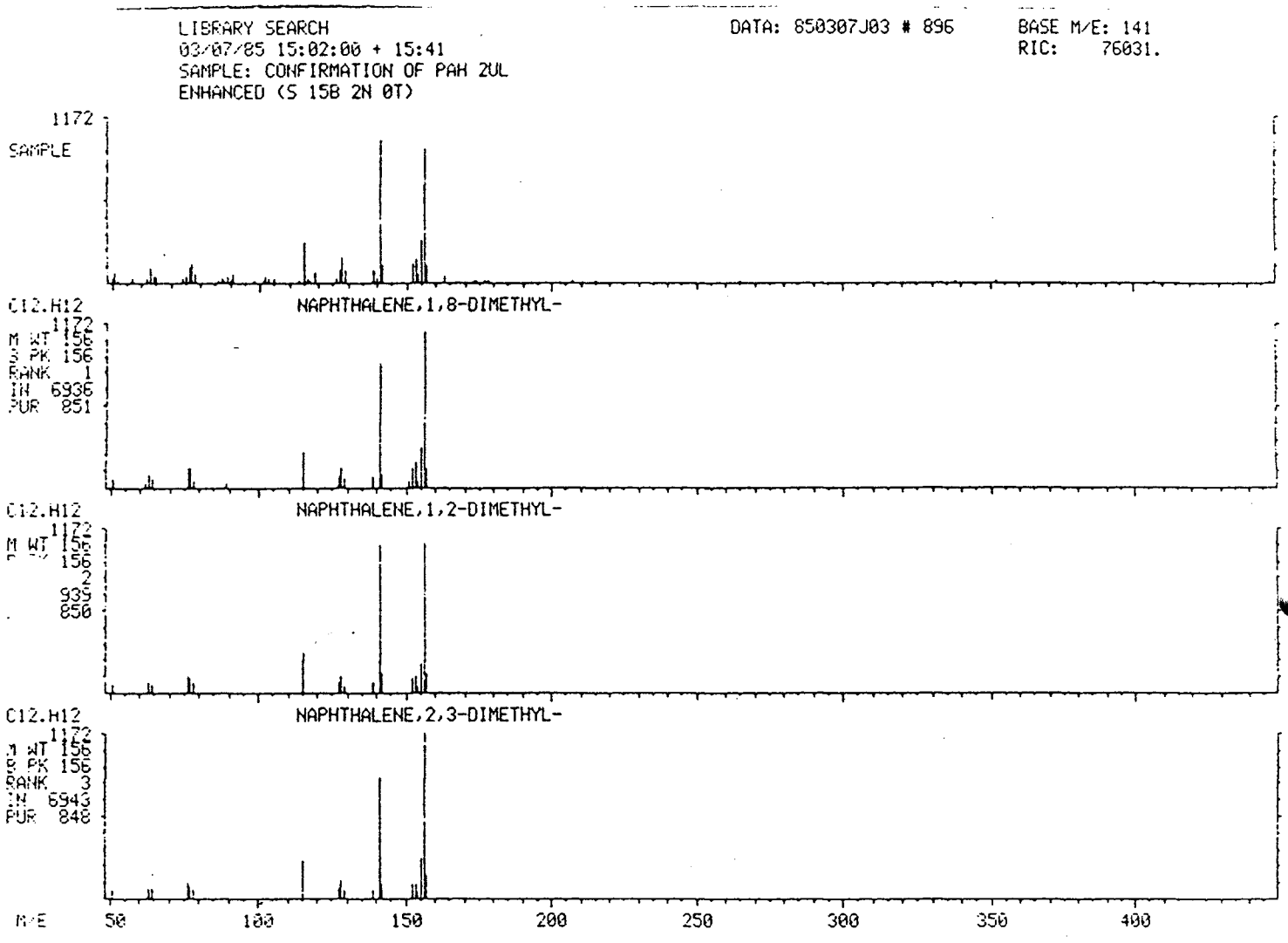

Figure 3(e) - MS of a Medium Pore Size PUF Plug Extract (top spectrum) Having a GCRT of 15 min. 41 sec. and the MS of the 3 compounds resulted from library search as the 3 best matches.

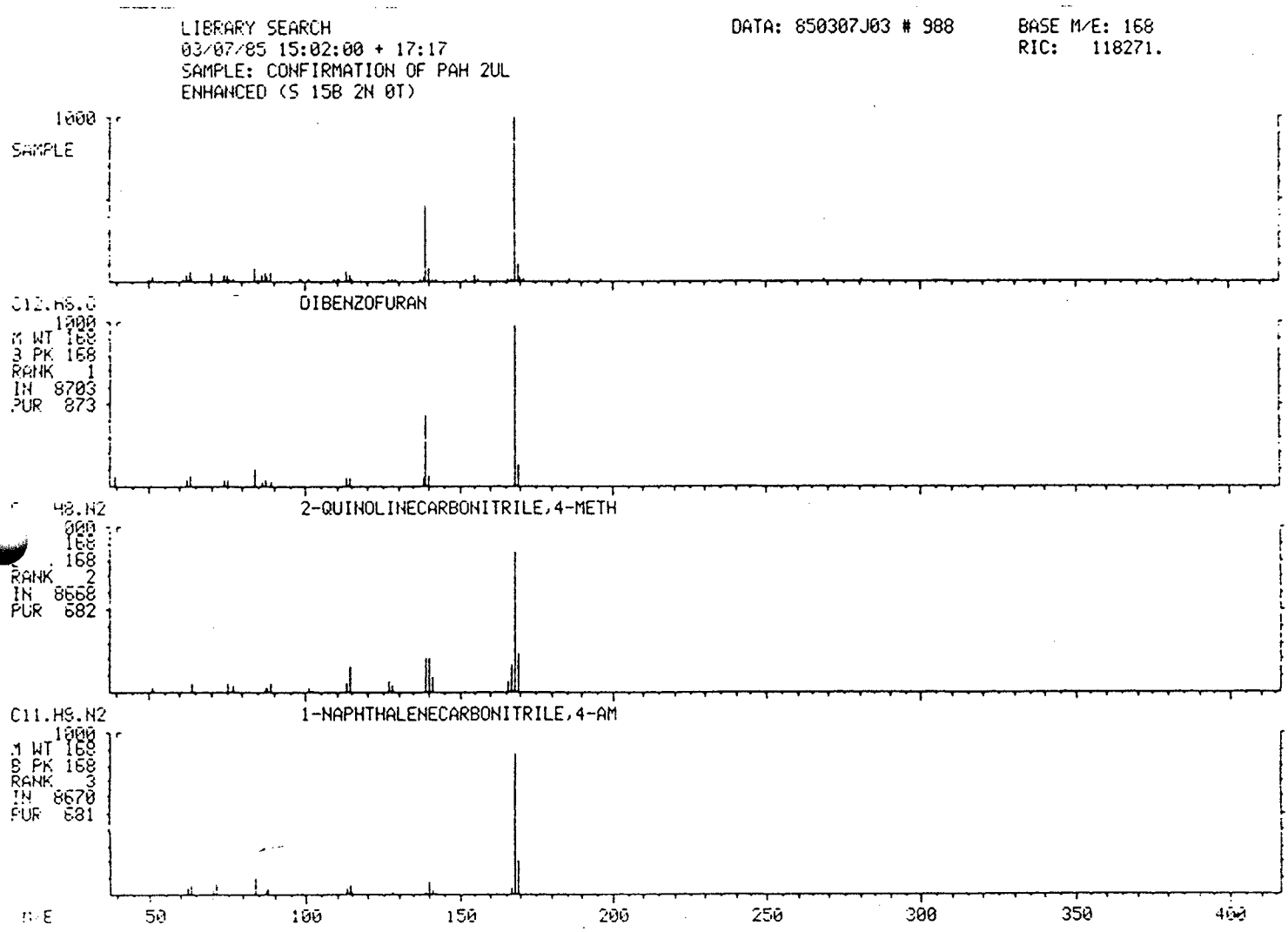

Figure 3(f) - MS of a Medium Pore Size PUF Plug Extract (top spectrum) Having a GCRT of 17 min. 17 sec. and the MS of the 3 compounds resulted from library search as the 3 best matches.

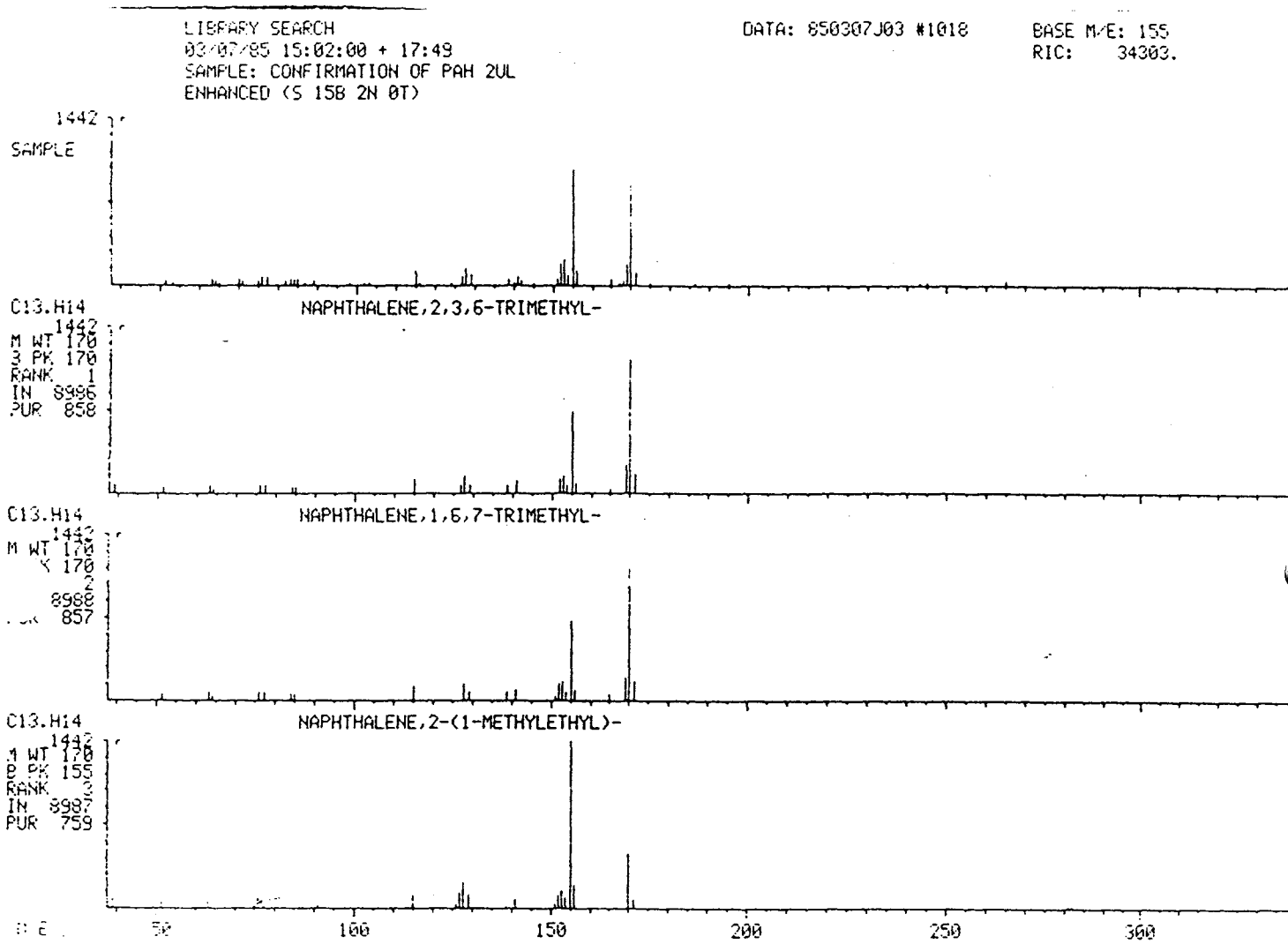

Figure 3(g) - MS of a Medium Pore Size PUF Plug Extract (top spectrum) Having a GCRT of 17 min. 49 sec. and the MS of the 3 compounds resulted from library search as the 3 best matches.

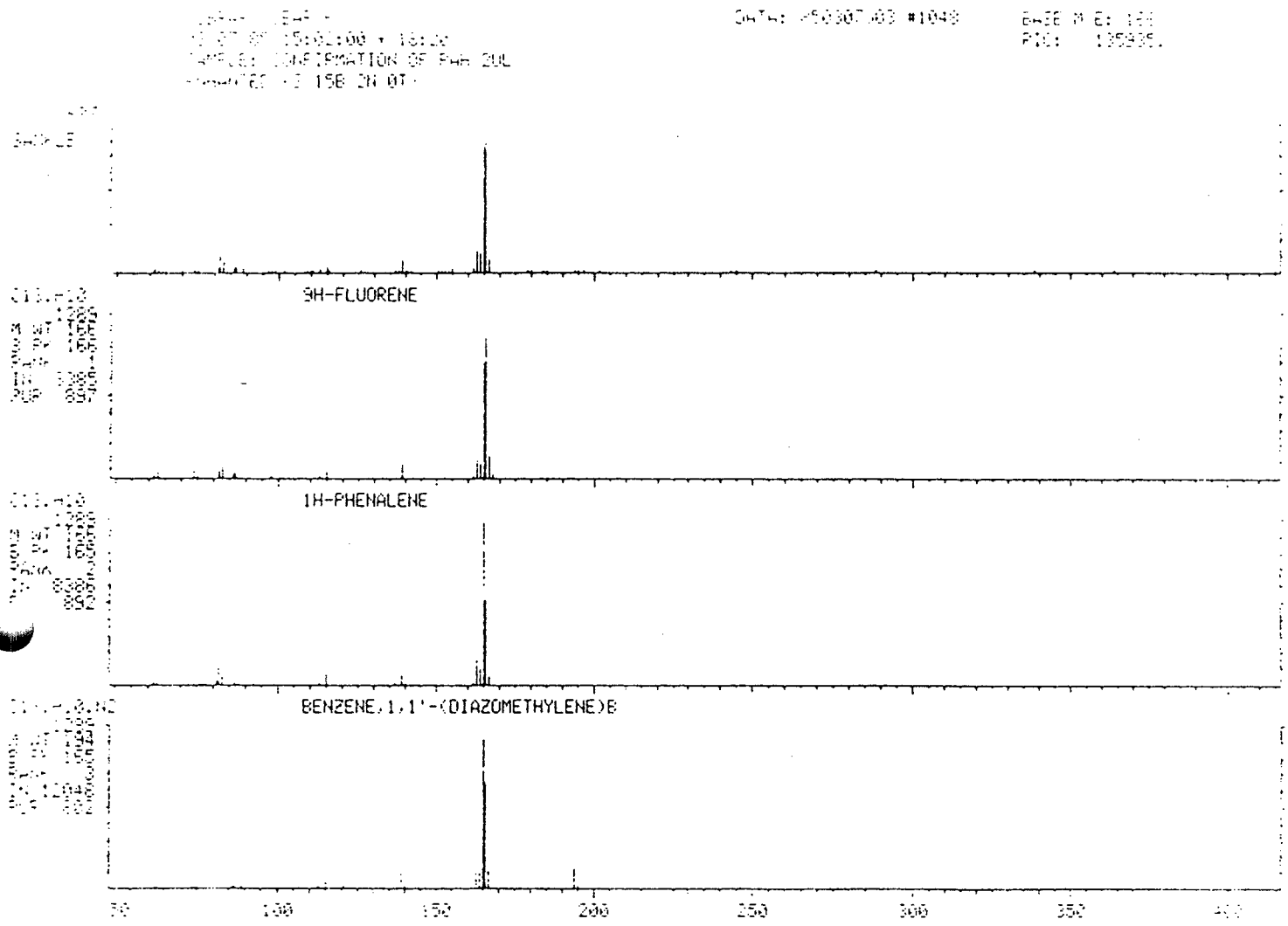

Figure 3(h) - MS of a Medium Pore Size PUF Plug Extract (top spectrum) Having a GCRT of 18 min. 20 sec. and the MS of the 3 compounds resulted from library search as the 3 best matches.

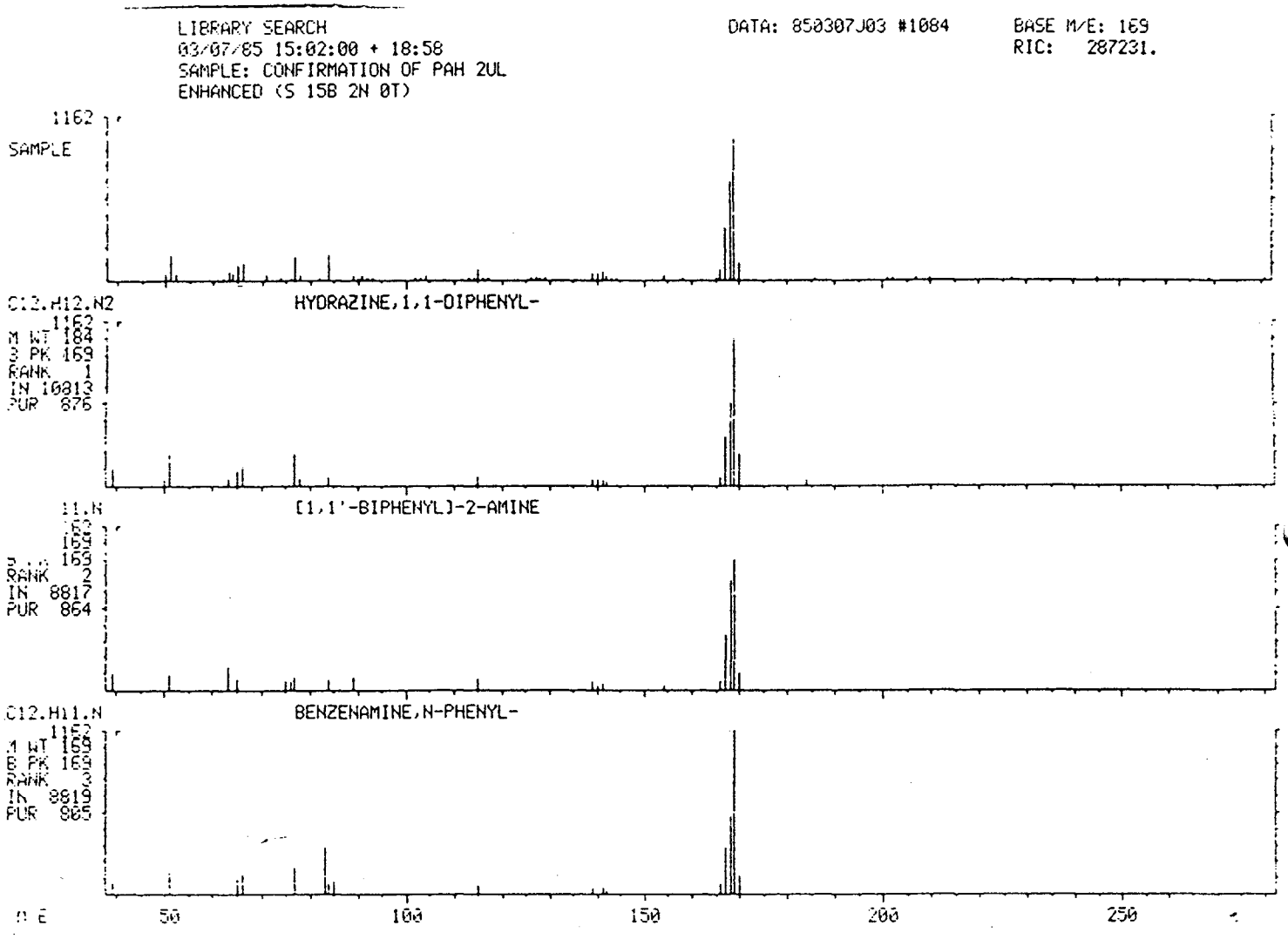

Figure 3(i) - MS of a Medium Pore Size PUF Plug Extract (top spectrum) Having a GCRT of 18 min. 58 sec. and the MS of the 3 compounds resulted from library search as the 3 best matches.