MULTICOMPONENT POLYCYCLIC AROMATIC HYDROCARBON ANALYSIS OF INLAND WATER AND SEDIMENT

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DISCLAIMER

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Many polycyclic aromatic hydrocarbons (PAHs) exhibit considerable carcinogenic, mutagenic, or toxic activity. Methods for reliable identification and quantification of PAHs in the aqueous environment are important for assessment of the potential environmental impact of processes releasing such compounds in aqueous discharges. This paper reports the development of multicomponent PAH analytical methods for inland water and sediment.

The method consists of separate steps for PAH extraction, isolation and concentration, and identification and quantification. Each step is considered separately below.

PAH EXTRACTION

A gross organic extract containing PAHs must first be obtained from the sample matrix. Ideally, the method should provide quantitative recoveries with a minimum of time and manpower. Traditionally, water samples are shaken (eg., Strosher and Hodgson, 1975) with an immiscible organic solvent and sediments are soxhlet extracted (eg., Giger and Schaffner, 1978) with an organic solvent. Radio-labeled PAH tracers were utilized to determine optimum conditions for extraction of PAHs from sediment and water. One liter samples of water were spiked in separate experiments with known activities of carbon-14 labeled naphthalene (^{14}C-Nap) and carbon-14 labeled benzo(a)pyrene, (^{14}C-BaP) and were extracted with 100 ml portions of water-equilibrated cyclohexane in 2 l separatory funnels equipped with Teflon stopcocks. Liquid scintillation counting of an aliquot of the pooled cyclohexane extract indicated

quantitative recovery of both tracers in three extractions. Four extractions of water samples with 0.1 volumes of cyclohexane are carried out routinely to strive for complete recovery of all aqueous PAHs.

Sediments pose a greater extraction problem, but extended soxhlet-extraction with acetone is effective in recovering PAHs. One hundred gram aliquots of wet sediment were thoroughly mixed in separate experiments with ^{14}C-BaP or ^{14}C-Nap, packed into 43 X 123 cm cellulose thimbles, and were soxhlet-extracted with 250 ml of acetone. Periodically, aliquots of the acetone extract were withdrawn for tracer recovery measurements. Whereas aliquots of the water extracts could be directly analyzed by liquid scintillation spectrometry, the scintillation quenching from gross amounts of organic compounds in the raw sediment extracts necessitated a simple purification of an aliquot on a short layered Florisil/alumina column (3.5 cm x 1.1 cm OD each) with benzene prior to liquid scintillation tracer recovery measurements. Soxhlet extraction for 68 hours was sufficient to quantitatively recover both tracers. For convenience, such extractions are routinely extended to 72 hours.

Separate aliquots of sediment are dryed at 110°C to constant weight to allow calculation of a dry/wet weight ratio for expression of PAH analytical results in terms of the dry weight of the sediment sample. Aliquots of sediment for PAH measurements are not dried; thus losses of volatile PAHs are reduced by this separate dry weight measurement.

PAH ISOLATION AND CONCENTRATION

The PAHs in the raw water and sediment extracts are next isolated by a two step adsorption column chromatography procedure. More complex isolation procedures (Kubota, Griest, and Guerin, 1975) incorporating liquid-liquid partitioning prior to adsorption column chromatography are not necessary to prepare a PAH isolate suitable for analysis by gas chromatography (GC). Cyclohexane extracts of water are concentrated to 10 ml and are applied to 10 g of Florisil in a 25 ml burette and are eluted with 150 ml of 6/1 hexane/benzene (volume/volume convention will be used throughout). Acetone extracts of sediment are reduced to 10 ml, diluted to 60 ml with water, and extracted four times with 20 ml of cyclohexane. These cyclohexane extracts are then treated identically to the water extracts described above.

The entire eluate from the Florisil column is then re-concentrated to 10 ml and passed through 20 g of neutral, deactivated (4 percent moisture) alumina, using a hexane/benzene step gradient of 6/1 (100 ml) and 2/1 (300 ml). The PAH isolate is obtained in two

fractions defined by the tracers: a diaromatic fraction containing mainly alkyl naphthalenes, acenaphthenes, and acenaphthalenes, and a polyaromatic fraction consisting of three to seven ring PAHs and their alkyl derivatives. Each fraction is separately reduced to a known volume by evaporative concentration with dry flowing nitrogen under reduced pressure and temperature.

PAH IDENTIFICATION AND QUANTIFICATION

Qualitative identification of PAHs in the purified PAH fractions is achieved by comparison of GC retention times and mass spectra with those of authentic PAH standards. Routine GC analyses are performed on a 6.6 m x 3 OD glass column packed with 3 percent Dexsil 400 on 100/120 mesh Supelcoport. Temperature programming from 100°C to 320°C at 1°C/min allows elution of PAHs ranging from two rings (eg., naphthalene) through seven rings (eg., coronene) in approximately four hours. Difficult-to-resolve PAH isomers which are separated with fairly good success include phenanthrene/anthracene, benz(a)anthracene/chrysene, and benzo(e)-pyrene/benzo(a)pyrene.

PAH concentrations are calculated by comparing GC peak areas with those of an external standard. Recovery corrections for losses of PAHs in isolation and handling are estimated by liquid scintillation counting 0.1 volume aliquots of the fractions in 10 ml of scintillator solution prepared by dissolving 15 g of 2,5-diphenyl-oxazole and 190 mg of 1,4-bis-[5-phenyl-oxazole]-benzene in one gallon of reagent grade toluene.

EVALUATION

Initial evaluation of the method has focused upon PAHs in sediment because of the ability of stream and river sediments to concentrate PAHs from water by three to four orders of magnitude (Andelman and Suess, 1970). An experiment was conducted to determine the stability of sediment PAHs during storage of samples, and to define the accuracy and precision of the analytical method. For this experiment, eight 100 g replicate samples of stream sediment previously demonstrated to be free of detectable PAHs (limit of detection approximately 0.05 µg/g for this sample size) were spiked with multiple unlabeled PAHs at concentrations of about 3 µg/g each to simulate contaminated sediment. Each sample was spiked with ^{14}C-Nap and ^{14}C-BaP, and after addition of 10 ml acetone was stored at 4°C in the dark. Four samples were analyzed immediately; two others were analyzed after two weeks of storage and the final two after four weeks of storage. The results of the analyses expressed in terms of the percentage corrected recoveries of the polyaromatics are shown in Table 1. Data for picene and o-phenylene pyrene are

not included because they were not recovered. The constant absolute recovery of the ^{14}C-BaP tracer and the corrected recoveries of the spiked PAHs indicate that there is no significant loss of PAHs (other than the two noted) from these sediment samples over a four week period of storage under these storage conditions. Thus, we conclude that the combination of acetone, reduced temperature, and darkness suppress PAH degradation mechanisms for this particular sediment, and that chemical analysis may be delayed at least one month with no appreciable effects on results. However, this conclusion may not necessarily hold true for sediments collected from other sites.

Analytical accuracy and precision are defined by the last two columns of data in Table 1. Recoveries of most polyaromatics are close to quantitative, for species ranging from alkylated three-ring PAHs through six-ring PAHs. These data indicate the ability of the multicomponent method to quantitate a large number of PAHs with reasonable accuracy. PAHs on both extremes of the polyaromatic fraction are recovered with a low bias, suggestive of evaporative losses for the more volatile PAHs (eg., fluorenes), and incomplete sediment extraction for the very large PAHs (eg., anthanthrene). Precision, as indicated by the relatively low standard deviations, is very good for such a wide range multicomponent method.

Table 2 shows the absolute recoveries of seven representative diaromatics. Absolute recoveries are reported because of the low and widely differing recoveries, which prevent any one species (such as ^{14}C-Nap) from accurately defining the recoveries of the others. The recoveries are inversely proportional to vapor pressures of the diaromatics, suggesting evaporative losses during solvent concentration steps. Differential recovery factors relating the recovery of each diaromatic to a single species could be employed to correct the recoveries of the diaromatics, but the precision of these factors is poor. Further work on improving the analysis of diaromatics is in progress.

APPLICATIONS

The bulk of the multicomponent PAH analytical applications have been made with an older version of the present isolation procedure, which incorporated a serial solvent partitioning prepurification step prior to the adsorption column chromatography steps (Kubota, Griest, and Guerin, 1975). This prepurification step subsequently has been found to be unnecessary for sediment analysis, but results of the older procedure are equivalent to those obtained by the present procedure. Some of the former are described below.

Table 1

Corrected Recoveries of Polyaromatics and Tracer in Spiked Sediment as a Function of Storage Time

PAH	Corrected Percent Recovery at Storage Time			Cumulative Data	
	Initial	2 Weeks	4 Weeks	Avg. ± Std. Dev.	
Fluorene	56.8	41.1	67.8	55.6 ±	12.5
1-Methyl Fluorene	80.4	78.5	85.8	81.3	7.6
Phenanthrene	87.4	84.7	92.3	87.9	6.6
Anthracene	90.3	94.3	95.7	92.7	5.7
2-Methyl Anthracene	96.9	102.9	102.9	99.9	5.8
1-Methyl Phenanthrene	99.3	100.6	102.1	100.0	5.2
9-Methyl Anthracene	66.7	78.6	75.2	71.8	12.0
Fluoranthene	102.8	104.5	106.6	104.7	4.6
Pyrene	102.3	101.4	106.6	103.1	4.6
Benzo(a)fluorene	109.4	110.6	110.5	110.0	4.6
Benzo(b)fluorene	110.3	110.7	110.1	110.3	5.1
1-Methyl Pyrene	107.3	106.5	108.7	107.5	4.6
Benz(a)anthracene	111.7	111.1	110.0	111.2	4.9
Chrysene	111.8	108.0	107.7	109.8	5.9
Benzo(a)pyrene	111.2	112.8	109.8	111.2	4.9
Perylene	116.9	116.3	111.6	115.6	5.7
3-Methyl Cholanthrene	106.8	108.8	104.8	106.8	6.2
Benzo(ghi)perylene	101.4	102.2	102.5	101.9	4.4
Anthanthrene	86.4	105.4	85.5	90.9	12.8
^{14}C-BaP Absolute Recovery	96.2	98.6	97.6	97.1	3.0

Table 2

Absolute Recovery of Representative Diaromatics in Spiked Sediment

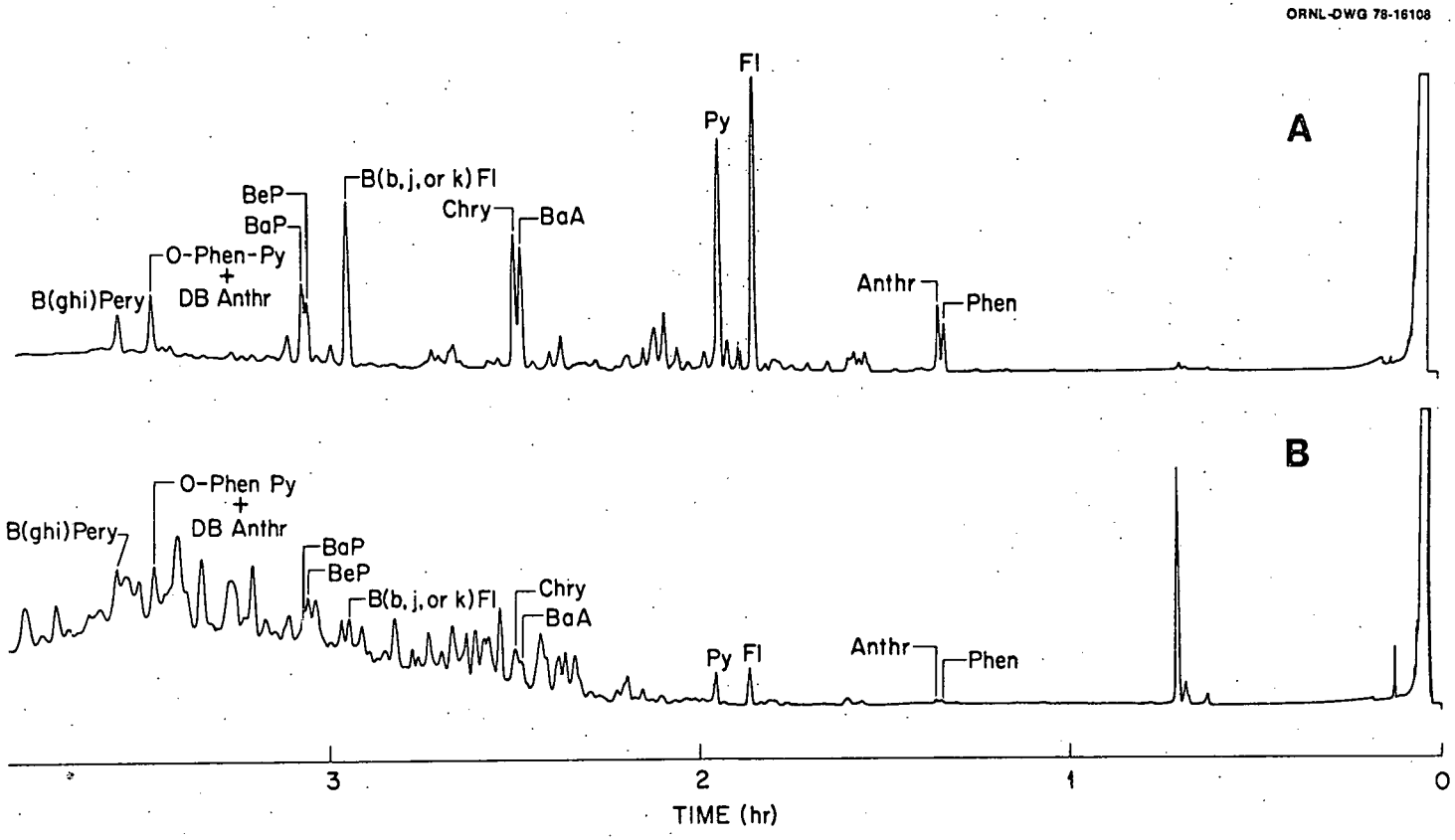
Diaromatic	Average ± Standard Deviation	
	Absolute Recovery (%)	Differential Recovery Factor
Naphthalene	26.0 ± 11.1	1.0
2-Methyl Naphthalene	36.7 ± 11.7	1.30 ± 0.11
1-Methyl Naphthalene	44.0 ± 9.7	1.63 ± 0.35
Biphenyl	47.2 ± 12.6	1.71 ± 0.26
2,6-Dimethyl Naphthalene	50.0 ± 12.6	1.74 ± 0.27
1,5- + 2,3-Dimethyl Naphthalenes	56.8 ± 8.8	1.93 ± 0.34
Acenaphthene	61.5 ± 10.8	2.09 ± 0.48

Figures 1 and 2 show the polyaromatics in stream sediments collected in the vicinity of a coking plant, a steel rolling mill (and a nearby city), and a petroleum tank farm. A characteristic "PAH fingerprint" is obtained for each source. The coking plant releases mainly the parent, unsubstituted PAHs ranging up to at least six rings in size, characteristic of high temperature PAH formation processes (Blumer, 1976). Concentrations of PAHs in the sediment (Table 3) range from 0.1 to 31 μg/g (dry weight basis), and are very similar to those reported in an EPA study (Bass et al., 1974). Concentrations of PAHs in the effluent channel water are included in Table 3. Although they are three to four orders of magnitude lower than in sediment, (in agreement with data reviewed in Andelman and Suess, 1970) they do not parallel those of the sediment. This result may arise from the fact that the samples were taken from a dynamic, flowing system in which sediment and water PAHs probably are not in equilibrium.

In marked contrast to the unsubstituted PAHs from the coking plant, the sediment PAHs near the steel rolling mills and the petroleum tank farm appear to be predominantly multialkylated derivatives, as is commonly observed with PAHs formed at lower temperatures (Blumer, 1976). However, even between the latter two sources, significant differences in concentration as a function of PAH ring size are apparent. The multialkylated sediment PAHs sampled near the steel rolling mill are mainly four through six rings in size while those near the petroleum tank farm are limited to three and four rings. Concentrations of representative PAHs showing these different ring size distributions are presented in Table 4. More detailed analysis of other individual species is made very difficult by the chromatographic peak overlapping of multialkylated PAHs in the latter two samples, but this problem can be overcome by subjecting the polyaromatic isolate to gel filtration on Biobeads (Severson, Snook, Arrendale, and Chortyk, 1976) prior to GC analysis.

IMPROVEMENTS

Applications thus far have centered upon analysis of polyaromatics. Recoveries of diaromatics have been low and difficult to reproduce. One method of alleviating the diaromatic recovery problem is through the use of micro distillation for solvent removal. This method has been successfully employed in the analysis of diaromatics in tobacco smoke condensate (Schmeltz, Tosk, and Hoffmann, 1976), but does not seem suited for the routine analysis of large numbers of samples. An alternate to such procedures is a dual tracer technique in which two tracers (carbon-14 and tritium-labeled) bracketing the volatility range of the diaromatic fraction are added to the sediment and then are simultaneously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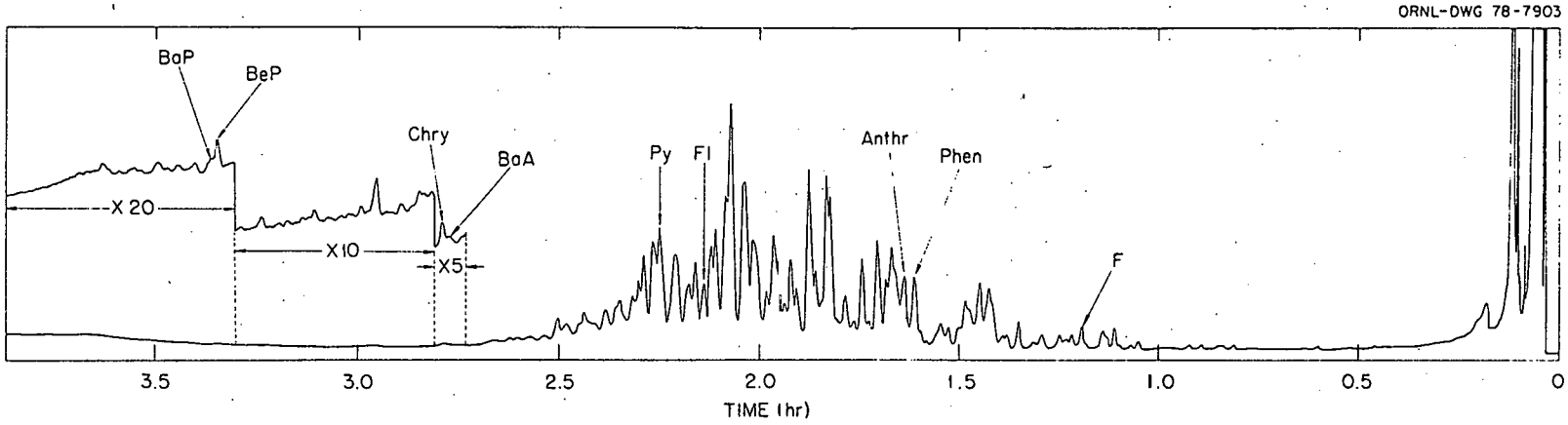
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TIME (hr)

Table 3

Concentrations of PAHs in Effluent Channel from a Coking Plant

	Concentration	
	Sediment	Water
	µg/g, dry sediment	µg/L
1-Methyl Fluorene	0.11	ND
Phenanthrene	3.6	0.40
Anthracene	6.7	0.31
2-Methyl Anthracene	1.4	2.4
1-Methyl Phananthrene	0.71	ND
Fluoranthene	31.	2.8
Pyrene	23.	4.0
Benzo(a)fluorene	7.2	0.80
Benzo(b)fluorene	3.2	0.81
Benzo(c)phenanthrene	2.1	ND
Benzo(ghi)fluoranthene	2.3	ND
Benz(a)anthracene	15.	2.0
Chrysene/Triphenylene	15.	1.7
Benzo(b,j, and/or k)fluoranthene	23.	ND
Benzo(a + e)pyrene[a]	19.	1.8
Perylene	3.8	ND
o-Phenylene pyrene + dibenz-(a,c and/or a,h)anthracene	8.6	0.95
Benzo(ghi)perylene	7.3	2.0
Anthranthrene	2.3	ND
TOTAL IDENTIFIED	175 µg/g	20 µg/L

[a]Incomplete resolution. BaP estimated at approximately 10 µg/g.

measured by dual channel liquid scintillation counting after isolation of the fraction. The recovery of each diaromatic eluting between these two extreme tracers presumably could be determined by interpolation.

Studies examining the validity of the dual-tracer approach employed ^{14}C-BaP and tritium-labeled BaP (^{3}H-BaP) which are readily available commercially. These tracers differ only in the radio-label, thus comparison of the recovery of ^{3}H-BaP with that of ^{14}C-BaP would indicate the utility of ^{3}H-labeled PAH tracers

Table 4

Comparison of Representative PAHs from Three Sites

Collection Site	Sediment Concentration, µg/g (dry weight basis)		
	Anthracene	Benz(a)anthracene	Benzo(a)pyrene
Coking Plant	6.7	15.	10.
Steel Rolling Mill	0.065	0.35	0.60
Petroleum Tank Farm	3.4	0.13	<0.049

for such work. Known activities of ^{14}C-BaP and ^{3}H-BaP were applied to a sediment. After extraction and isolation, the recoveries of the tracers were measured. The results expressed as the relative recovery of ^{3}H-BaP to ^{14}C-BaP are shown in Table 5. Included also are the results for column chromatography and gel filtration on commonly available packings. The results indicate that considerable losses of ^{3}H-BaP occur in the analytical procedure, particularly in alumina column chromatography. The data suggest losses of ^{3}H-BaP also during soxhlet extraction. Thus the dual-tracer approach is not compatible with existing purification methods. It is felt that ^{3}H-^{1}H exchange between the ^{3}H-BaP and active surfaces on the adsorbent or sediment is responsible for the loss of ^{3}H activity. This hypothesis is supported by the observation that the more active adsorbents (alumina and silica gel) cause greater losses of ^{3}H activity than less active adsorbents (Florisil) or the "gentle" gels (Biobeads). Thus, a purification procedure featuring the latter two materials would allow a dual-tracer method if a means of suppressing ^{3}H-^{1}H exchange during sediment extraction could be devised. The Biobeads also offer the additional benefit of separating the complex multialkylated PAHs from the parent and simple alkylated PAHs, allowing interference-free analysis of the latter in complex PAH isolates (Severson, Snook, Arrendale, and Chortyk, 1976).

Another improvement to the method is the use of wall coated glass capillary columns. Figure 3 shows the superior resolution of a polyaromatic fraction by a glass capillary column than by a 6.6 m packed column, with both columns operated under the same column oven temperature program (110°C to 320°C at 2°C/min). Normally, the packed column oven is temperature programmed at one-half the rate, and the separation requires twice the time of the capillary column separation. Thus, the capillary column can generate more detailed data in less time than the packed column.

CONCLUSIONS

The multicomponent PAH analytical methodology described in this paper generates a detailed characterization of the PAHs in sediment and water samples. Applications suggest that each source of PAH discharge into the aqueous environment is characterized by its own "PAH fingerprint" which can be differentiated from those of other sources.

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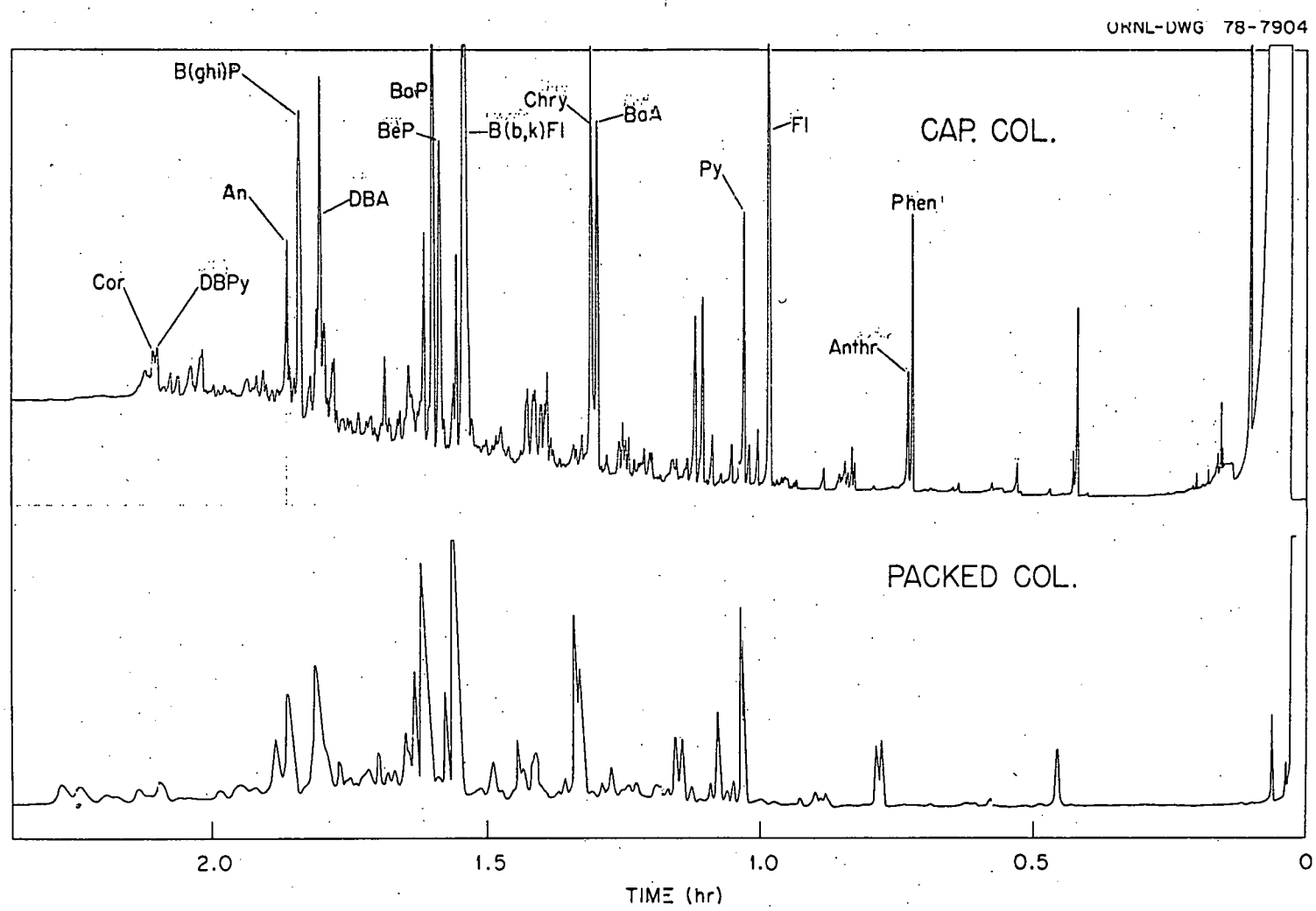
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TIME (hr)

Table 5

Relative Recovery of ^{3}H-BaP to ^{14}C-BaP

Experiment	Relative Recovery[a]
Sediment Extraction, Florisil Alumina Column Chromatography	0.71
Florisil Column Chromatography	∿ 1.0
Alumina Column Chromatography	0.88
Silica Gel Column Chromatography	0.85
Biobeads SX-12 Gel Filtration	0.97

[a] ^{3}H-BaP/^{14}C-BaP

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