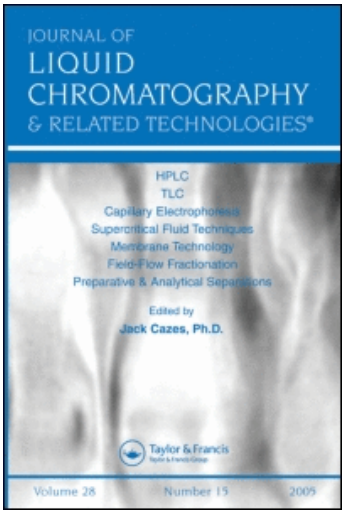

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USE OF SEP-PAK^{R} C_{18} CARTRIDGES FOR THE COLLECTION & CONCENTRATION OF ENVIRONMENTAL SAMPLES *

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ABSTRACT

High Pressure Liquid Chromatography (HPLC) is being increasingly employed in environmental analysis. However, HPLC is somewhat limited by the sensitivity of the detection systems commercially available. Many are not sensitive enough to cope with the lower levels being demanded by various governmental agencies. The purpose of this study is to show the efficiency of a simple sampling device, a SEP-PAK which not only allows efficient on-site sampling but offers the ability to concentrate samples down to a level where UV or fluorescent detection can determine trace quantities in the ppb range.

INTRODUCTION

It has been previously possible to concentrate large volumes of aqueous samples for analysis by HPLC by use of a technique called trace-enrichment (1). In this technique, the water sample is passed through a column containing non-polar packing such as octadecylsilane bonded onto silica. Because the organics have a much greater affinity

*Based on lectures given at the Pittsburgh Conference (Cleveland, 1979) & Eastern Pesticide Conference (Guelph 1979).

for the packing material than for the aqueous mobile phase they will be adsorbed at the head of the column. If the organic content of the mobile phase is then increased (as in a solvent gradient) the organics will be selectively eluted. In this way, "injections" of large volumes of sample can be made onto the chromatographic column without any of the deleterious effects associated with such large injection volumes. An examples of this is shown in Figure 1 where 175 µl of a mixture of anthracene and pyrene are directly injected (concentrations 0.6 + 0.2 ppm respectively) with a mobile phase of 100% water. If the mobile phase is then stepped to 60% acetonitrile-

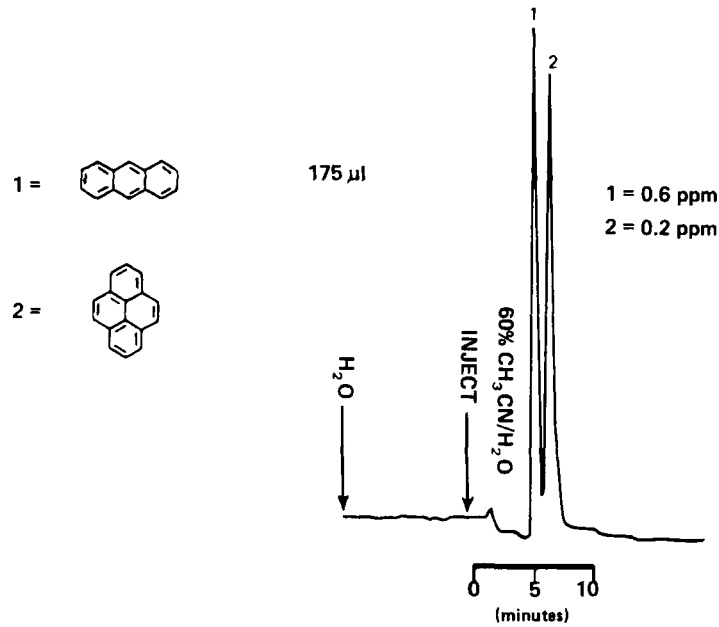

FIGURE 1 Trace enrichment of anthracene and pyrene on C-18.
Sample: 175 µl injection of 0.6 ppm anthracene & 0.2 ppm pyrene.
Conditions: column-µBondapak C-18 column; solvent-water stepped up to 60% CH_3CN/water after injection' flow rate of 4 ml/min.

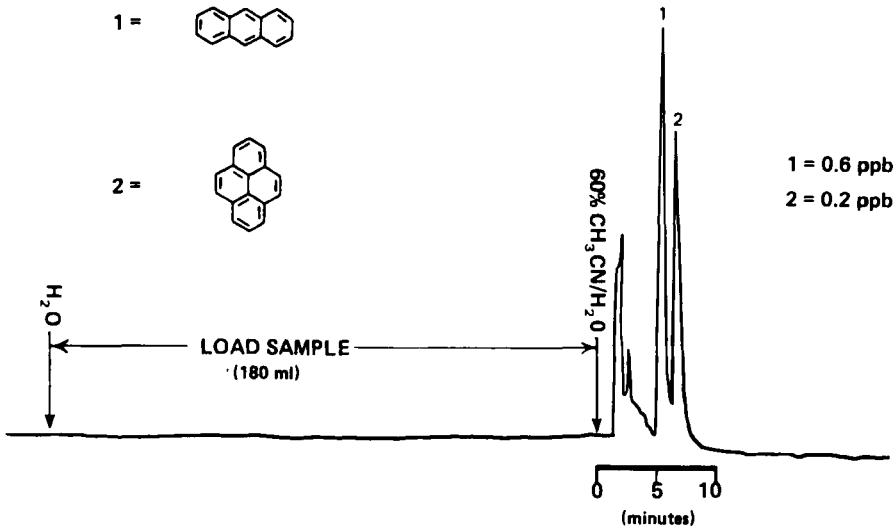

FIGURE 2 Trace enrichment of anthracene and pyrene on C-18. Sample: 180 ml injection of 0.6 ppb anthracene & 0.2 ppb pyrene. Conditions: same as Figure 1

water the organics are eluted. For more dilute solutions, the sample can be pumped onto the column. Figure 2 shows the result of a 180ml sample of 0.6 and 0.2 ppb of anthracene and pyrene respectively, being pumped onto the column and subsequently eluted in the same fashion as above. A comparison of the two chromatograms shows nearly identical resolution for 1000-fold concentration procedure done directly on the column.

An obvious extension of this technique is to prepare a disposable column packed with a non-polar packing material. Since the organics are concentrated at the head of the column, a short column should suffice. This is in fact a SEP-PAK* (Sample Enrichment Purification)

*SEP-PAK, Porasil and Milli-Q are registered trade marks.

which is a small prepacked column containing about 0.4 g of C-18 on Porasil A.

The packing material is contained in a virgin polyethylene sheath which has undergone Radial Compression to form a highly reproducible homogeneous chromatographic bed. The SEP-PAK is also available with a silica packing but for this aqueous work C-18 is the obvious packing of choice.

The use of SEP-PAK offers certain advantages over collection of samples in the usual manner. In most cases, larger volumes of water samples are collected in glass bottles, a preservative being added if necessary. This can lead to problems where compounds of interest are adsorbed onto the glass resulting in erroneous analysis (2). In addition, the transportation of large volumes of samples can be quite costly. Subsequent extraction of these samples can cause difficulties in loss of very volatile components, multi-solvent requirements for multi-residues, cross-contamination of samples and costly solvent requirements. A SEP-PAK can be taken directly to the sampling site and a known quantity of water passed through the SEP-PAK thereby trapping any trace organics. These organics can be eluted in a small volume of organic solvent (usually about 1-2 ml) affording a 500 to 1000 fold increase in concentration (depending on the initial volume samples).

In this work, the efficiency with respect to collection and concentration of environmental samples of the SEP-PAK was studied. The actual study involved passing a quantity of material through the SEP-PAK and checking the SEP-PAK "Effluent" for compounds which were not retained, i.e. checking for "breakthrough." Two studies were done, (a) carbamate pesticides and (b) polynuclear aromatic hydro-

carbons (PNA's). Samples were run at fairly high concentrations so as to look at loading capabilities and to make small percentages of breakthrough easily detectable.

MATERIALS AND METHODS

HPLC

The chromatographic system consisted of a Waters Model 244 Luquid Chromatography equipped with two M6000A pumps and an M660 gradient programmer. Ultraviolet detection was done with a Waters Model 440 UV detector at 254 nm and Fluorescence detection using a Waters Model 420 Fluorometer with excitation and emission filters of 360 nm and 440 nm respectively. Integration was performed using a Shimadzu ElA integrator. For quantitation purposes, standards were injected with a Waters Model 710 WISP.

Columns used were either a μBondapak C-18 (3.0 mm ID x 30 cm) or a Radial-PAK A used with an RCM-100 (Waters Radial Compression Separation System).

The mobile phase used was acetonitrile (Burdick & Jackson-Spectro-grade) and water abtained from a Milli-Q system. This water required further polishing for the gradient work at low sensitivities. This was achieved by putting a Bondapak C-18 on Porasil B column, (7.8 mm ID x 122 cm) on line after the water pump and before the mixing chamber located on the acetonitrile pump. This allows us to obtain an essentially flat baseline for the gradient (Figure 3) while operating at high sensitivity on the UV detector.

Chemicals

Standards were obtained from commercial sources and used without purification. Standard solutions were made up in acetonitrile

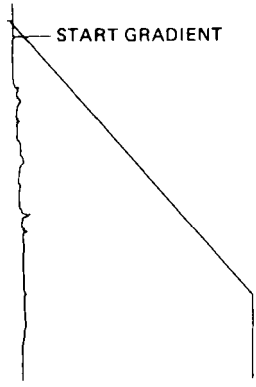

FIGURE 3 Blank Gradient Sample: 50 ml of treated water (see text)
Conditions: column-μ-Bondapak C-18, 3.9mm I.D. x 30 cm; solvent-A-water, B-acetonitrile; gradient: 0.100% B, 30 minutes, linear; flow rate 2.0 ml/min; UV detection at 254 nm at 0.05 AUFS.

and then diluted with the appropriate volume of water for trace enrichment studies.

Methods

For trace enrichment studies on SEP-PAK C-18 the following procedure was employed. The SEP-PAK was activated with 5 ml acetonitrile or methanol, then flushed with 5 ml water. The appropriate volume of the test solution was passed through the SEP-PAK at approximately 10 ml/min The effluent from this step was then trace enriched on the chromatographic column and the sample was eluted off the SEP-PAK with 2 ml of THF.

The response factors of each of the compounds was determined by making multiple automatic injections. Calibration data are given in TABLES 1 & 2. Note the excellent reproducibility of the two pump gradient system on the gradient running from o - 100% acetonitrile.

TABLE 1

Calibration data for carbamates *

PEAK IDENTIFICATION	RETENTION TIME (MIN)	SLOPE ($\times 10^{-2}$)	INTERCEPT	CORRELATION COEFFICIENT
Carbofuran	13.28±0.03	380	115	0.9997
Carbaryl	13.99±0.03	2513	-193	0.9996
IPC	15.06±0.03	947	- 96	0.9995
CIPC	17.13±0.03	2021	-185	0.9997

*for conditions see Figure 4

TABLE 2

Calibration data for PNA's **

PEAK IDENTIFICATION	RETENTION TIME (MIN)	SLOPE ($\times 10^{-2}$)	INTERCEPT	CORRELATION COEFFICIENT
Impurity in Benzanthrone (area vs. µl)	21.65±0.01	21311	33730	0.9999
Benzanthrone	23.59±0.01	20.09	1.31653	1.0000
Fluroanthene	25.61±0.01	21.21	.92885	1.0000
Benzo(a)Pyrene	28.35±0.02	50.02	-2.92475	0.9993
Benzo(ghi) Perylene	29.46±0.02	15.75	- .50435	0.9998

*for conditions see Figure 4
**for conditions see Figure 7

RESULTS AND DISCUSSION

The chromatogram of the carbamate standards used in the study is shown in Figure 4. Figure 5 shows the same standards trace enriched onto a Radial-PAK A column. After passing 45 ml of a standard solution of carbamates, a trace enrichment of the SEP-PAK effluent gave the chromatogram

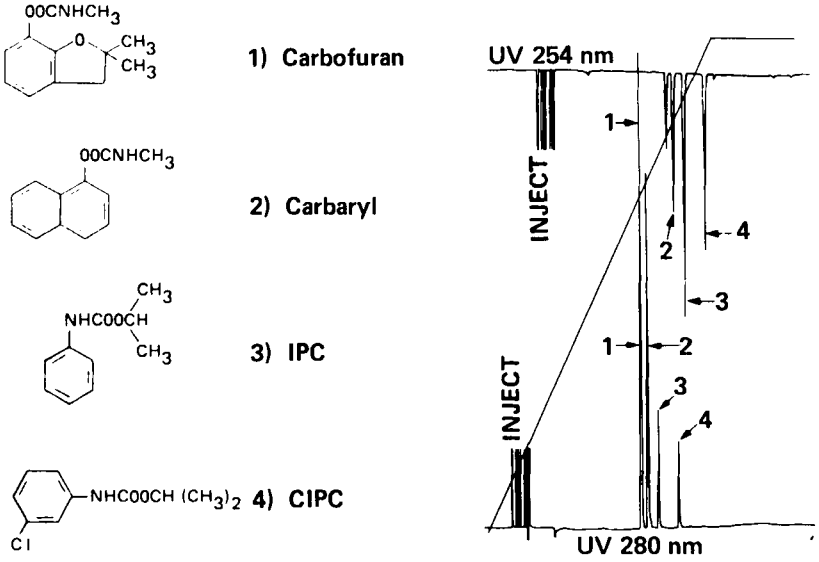

FIGURE 4 Carbamate Standards Conditions: column Radial-PAK A; solvent A-water, B-acetonitrile; gradient 0-100% B, linear, 25 minutes; flow rate 3.0 ml/min. UV detection at 254 & 280 nm, 0.2 AUFS.

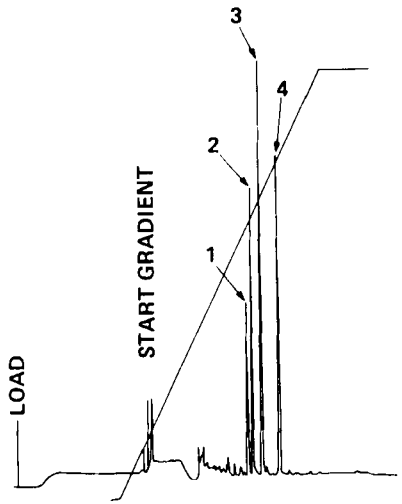

FIGURE 5 Trace Enrichment of Carbamate Standards Sample: 45 ml of diluted standards. Conditions: see Figure 4; UV detection of 0.1 AUFS; 1=carbofuran 157 ppb, 2= carbaryl 39 ppb, 3= IPC 206 ppb, 4= CIPC 70 ppb.

shown in Figure 6. No breakthrough is observable. The quantitation results are summarized in TABLE 3.

Similarly the chromatogram of PNA standards used in the study is given in Figure 7. As above, trace enrichment onto a μBondapak C-18 column gave the chromatogram shown in Figure 8. Trace enrichment on the SEP-PAK effluent (Figure 9) showed breakthrough of two components - fluoranthene and benzo(a)pyrene. Quantitive results are summarized in TABLE 4. These show that breakthrough of benzo(a)pyrene is the highest, somewhere in the

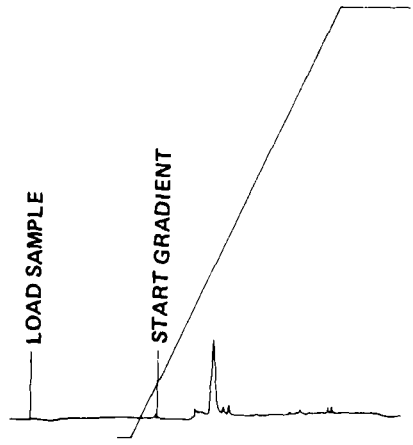

FIGURE 6 SEP-PAK Effluent (45 ml) of carbamate standards. Conditions: same as in Figure 5.

TABLE 3

SEP-PAK TRACE ENRICHMENT

STANDARD	AMOUNT TRACE ENRICHED (ng)	" % BREAKTHROUGH"
Carbofuran	7065	not detectable (minimum amount detectable is approx. 0.05 - 0.3 ng)
Carbaryl	1755	
IPC	9270	
CIPC	3150	

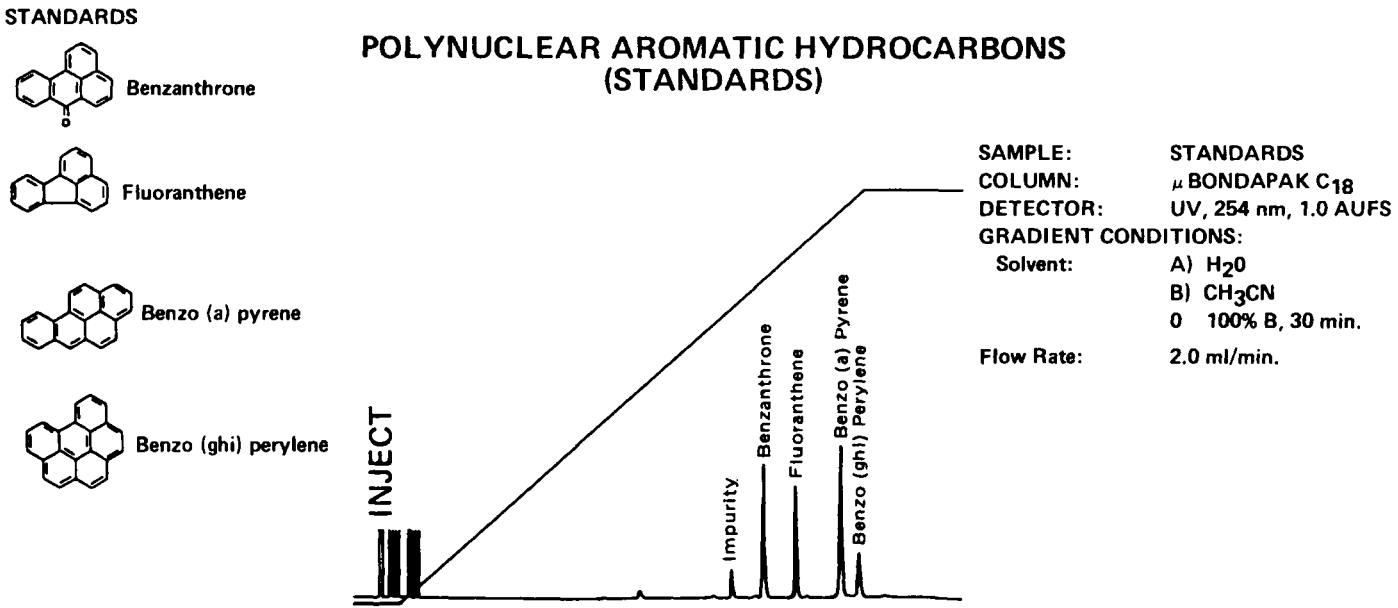

FIGURE 7 Chromatogram of PNA standards used in this study. Conditions same as in Figure 3. UV detection at 254 nm, 1.0 AUFS.

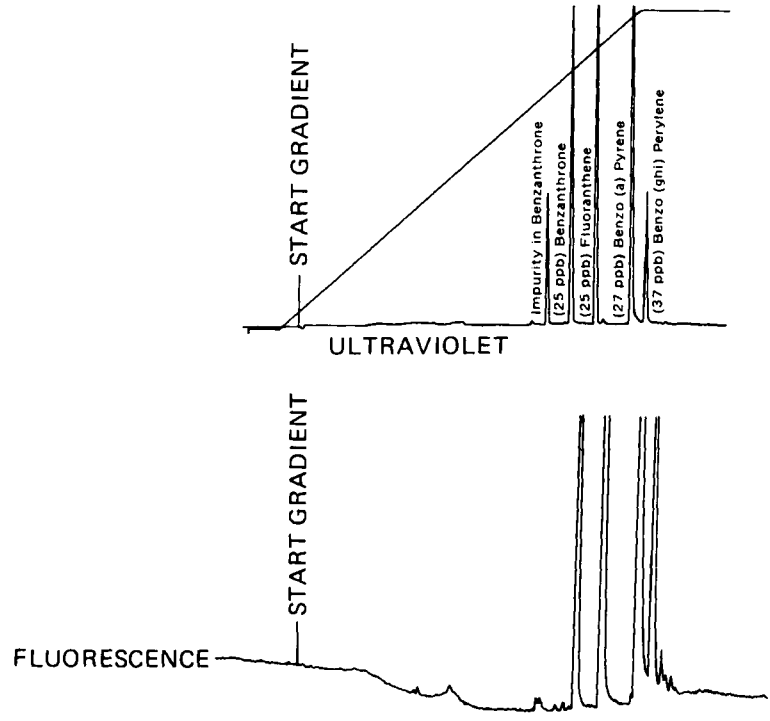

FIGURE 8 Trace enrichment of PNA standards. Sample size - 50ml. Conditions same as Figure 3. UV detection at 254 nm, 0.2 AUFS: Fluorescence detection at 8X.

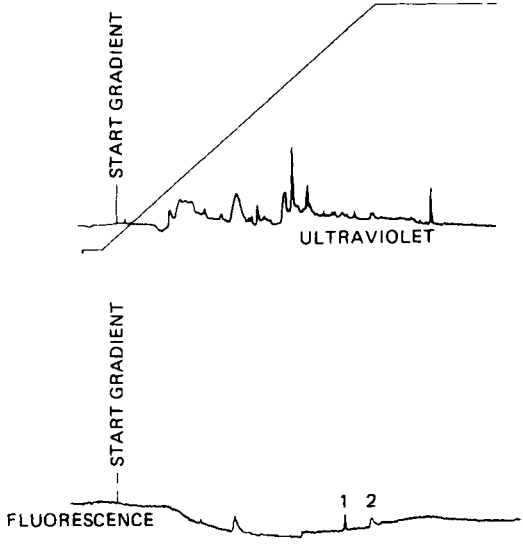

FIGURE 9 SEP-PAK effluent of PNA standards. Sample size 40 ml. Conditions same as in Figure 3. UV detection at 254 nm. 0.02 AUFS, Fluroescence detection at 8X.

CTABLE 4

SEP-PAK TRACE ENRICHMENT

STANDARD	AMOUNT TRACE ENRICHED (ng)	"% BREAKTHROUGH"
Benzanthrone	1000	0.9
	430	1.5
	10	not detectable
Fluoranthene	1468	0.7
	631	1.2
	15	9
Benzo(a)pyrene	1080	3-13
	464	15
	11	9
Benzo(ghi)perylene	1000	1.0
	430	1.1
	10	not detectable

region of 10%. That this compound would breakthrough more easily than the others is unusual since, based on relative retention times, it should have more affinity for the packing than would, say, benzanthrone. The authors have no explanation for this phenomenon as yet, but 90-100% recoveries have been observed in similar systems (3).

No work on environmental subjects would be complete without some study, albeit preliminary, of an actual environmental sample. Figure 10 shows the chromatogram obtained from 50 ml of stream water trace enriched across a μBondapak C-18 column. This water sample was collected in a glass bottle and brought back to the laboratory for analysis. Contrast this with the chromatogram obtained when the same stream was sampled on-site using a SEP-PAK, the material then being eluted with THF and chromatograph (Figure 11). It is here that another of the advantages of employing SEP-PAK can be clearly seen. Obviously compounds have been adsorbed on

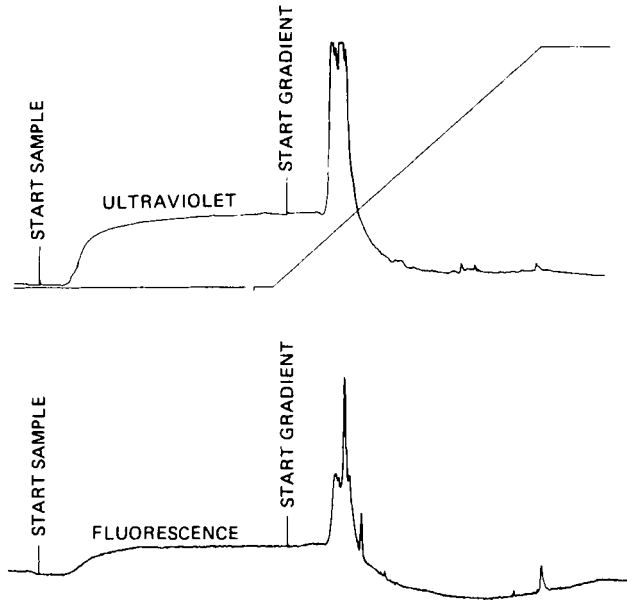

FIGURE 10 Stream water trace enrichment. Sample size 50 ml. Conditions same as in Figure 3. UV detection at 254 nm, 0.05 AUFS. Fluorescence detection at 8X.

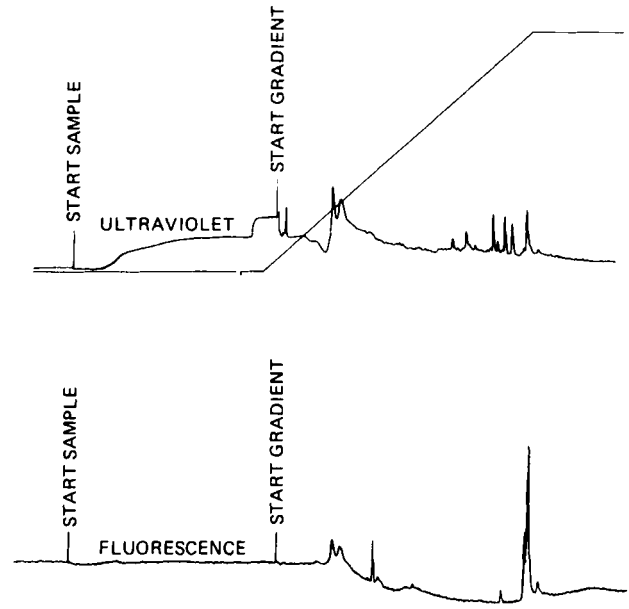

FIGURE 11 Stream water SEP-PAK extract. Conditions same as in Figure 10.

the glass giving an erroneously lower result fro the amount of trace organics in the stream.

Some suggestions to circumvent this problem that have been put forward (1) are pre-silanization of the glass vessels, use of teflon vessels or the addition of 20% methanol to the sample. Obviously none of these are as suitable or easy to use as the methods described above using the SEP-PAK.

The results show that the SEP-PAK is a simple efficient device for the on-site sampling, allowing the dual advantage of simultaneous collection and concentration. It thus reduces the cost of transportation of large water samples, reduces consumption of costly extration solvents, saves man-hours in sample manipulation (cleanups and concentrations) and avoids the serious problems of loss of trace components on the surface of glass collection vessels.

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