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Use of Reverse Phase C-18 Minicolumns for Concentrating Water-soluble Hydrocarbons

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In most cases water-soluble hydrocarbons are present in such low concentrations they cannot be detected without first being concentrated. A variety of methods have been developed to do this, but most are limited in that they require a fairly expensive set-up, are technically difficult and time-consuming to run, or are inefficient. As an example, solvent extraction (ASTM: D2778-70 1979) has often been used to determine trace amounts of hydrocarbons, but in this procedure many of the volatile components are lost during extraction. Consequently, purge and trap methods are frequently used for volatile organics (GROB & ZURCHER 1976). Macroreticular resins such as XAD-2 or XAD-4 and pellicular reverse phase liquid chromatography supports have also been used in the analysis of water-soluble hydrocarbons (JUNK et al. 1979, CHANG & FRITZ 1978, TATEDA & FRITZ 1978, OGAN et al. 1978, SANER et al. 1979), but these methods are either technically difficult or limited as to their general use for different hydrocarbons. Some of these methods for trace enrichment were recently reviewed by DRESSLER (1979).

This study was initiated to find a rapid, simple, yet efficient method of concentrating petroleum-derived water-soluble hydrocarbons. The aliphatics and alkylbenzenes selected for study are those which are the major water-soluble components of the jet fuel, JP-4.

MATERIALS AND METHODS

The hydrocarbon standards used were analytical grade (Alltech Assoc.). Solvents were spectral grade (Burdick and Jackson). The JP-4 jet fuel was obtained from the North Dakota Air National Guard, Fargo, N.D. Each mini-column (Sep-Pak C18, Waters & Assoc.) was a polyethylene cartridge filled with a silica pellicular support having octadecylsilane chemically bonded to the surface. These cartridges were designed to fit onto the end of a syringe.

Every Sep-Pak used for concentration of standards or JP-4 from water was attached to a syringe and condi-

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tioned with 2 ml ethyl acetate followed by 7 ml glass-distilled water. The sample was applied to the column with a syringe at a rate of about 20 ml/min. Two ml of ethyl acetate was used to elute the sample from the Sep-Pak. These particular volumes were empirically chosen as optimal for quantifiable recovery. Elution of the Sep-Pak with methanol or acetonitrile resulted in a large GC solvent peak which masked many of the compounds of interest. Recovery of the ethyl acetate was enhanced by passing .5 ml of water and 2 ml air through the Sep-Pak. The eluate was then frozen to separate the solvent and aqueous phases. The unfrozen solvent layer containing the ethyl acetate and the water-soluble hydrocarbons was then decanted and the volume measured.

Hydrocarbon-free water was prepared by passing tap water through a conditioned Sep-Pak. The efficiencies of the Sep-Pak in concentrating the selected hydrocarbons were determined by injecting a controlled amount of mixed standards (Table 1) into 20 ml of hydrocarbon-free water in a glass syringe. This sample mixture was forced through a conditioned Sep-Pak. Two successive rinses of 20 ml hydrocarbon-free water were each forced through the Sep-Pak. Efficiencies were estimated from a graph of volume of hydrocarbon recovered as a function of volume of each hydrocarbon forced through the Sep-Pak. The slope of the line is reported as the percent efficiency. The same procedure was used to determine Sep-Pak efficiency for the recovery of hydrocarbons in JP-4 (Table 1).

To test the ability of this method to concentrate dilute samples of petroleum-derived water-soluble hydrocarbons from water, 10 ul of JP-4 was mixed slowly in 500 ml of tap water for 2 hours at room temperature. The mixture was then allowed to stand for 2 hours in a separatory funnel. 450 ml of the aqueous phase was then drawn off and put through a conditioned Sep-Pak with a glass syringe. The hydrocarbons retained on the Sep-Pak were eluted as described above.

Hydrocarbons were detected using a Beckman GC 45 gas chromatograph with a flame ionization detector. A stainless steel chromatographic column (2 mm i.d. by 2.4 m) was packed with 10% 1,2,3-Tris (2 cyanoethoxy) propane (TCEP) on 100/200 mesh Chromosorb PAW (Supelco, Inc.).

The water-soluble hydrocarbons from JP-4 were identified by comparison with retention times of standard mixtures and by peak enhancement methods. Concentrations were calculated from peak areas using the external standard method with a Spectra Physics SP-4000 data system. A mixture of standards (Table 1) was used for

calibration and to determine the response factors for each hydrocarbon used. Individual response factors were used to convert respective peak areas to concentrations in PPM by volume (ul/l). For each hydrocarbon tested a range of concentrations was used to obtain a line so that the slope could be calculated over a range of 1-500 PPM, which gave linear recovery. This slope multiplied by 100 yielded percent recovery.

RESULTS

The reproducibility between individual Sep-Paks of the same lot number averaged ±5%. All values tabulated are the average results of duplicate runs. Reproducibility of injections and quantitation was ±2.6%. The efficiency of recovery depended upon the total amount of hydrocarbon forced onto the Sep-Pak and not upon concentration. The two different lots of Sep-Paks used in this study gave average recovery efficiencies of hydrocarbon standards of 78% and 63%.

Tests were performed to determine the fate of the hydrocarbons not recovered from the Sep-Pak. This was done by placing six Sep-Paks in a series with a one inch glass tubing connector between each pair of Sep-Paks. A mixture of JP-4 in water was then forced through the series and each one was eluted as described previously, with ethyl acetate. All of the alkylbenzenes recovered were in the first two Sep-Paks. Aliphatics, however, were recovered in small amounts even in the last Sep-Pak in the series. When the same Sep-Paks were then eluted with hexane, the only component which came off any of them was toluene.

Data obtained regarding the capability of a Sep-Pak to concentrate hydrocarbons from water is presented in Table I. When hydrocarbons were analyzed singly, Sep-Pak recovery efficiency was greater than when more complex standard hydrocarbon or JP-4 mixtures were analyzed. The use of ethyl acetate as a solvent for the addition of the single standards, standard hydrocarbon mixture or JP-4 improved the ability of the Sep-Pak to concentrate hydrocarbons from water.

Concentrations of JP-4 in ethyl acetate were chosen so that no more than 300 ul of ethyl acetate was put into the water to be forced onto the Sep-Pak. With larger volumes of ethyl acetate lower recovery efficiencies were noted. This may be because the greater amount of ethyl acetate forms a layer on top of the water. When this ethyl acetate is forced through the Sep-Pak after the water, it may elute the hydrocarbons retained on the Sep-Pak. The concentration range for JP-4 in water was chosen so that the concentrations of

Table 1. Percent recovery of single and mixed hydrocarbon standards and JP-4 from water using Sep-Pak C_{18} cartridges.

	Single Hydrocarbon Standard a)	Single* Hydrocarbon Standard a)	Standard* Hydrocarbon Mixture a)	JP-4* b)	JP-4 c)
Aliphatics				90	94
hexane			75		
heptane			74		
octane			69		
decane			61		
Alkylbenzenes					
toluene	80	88	73	71	60
n-propylbenzene			87	77	61
ethylbenzene	50	75	82	66	35
m- & p-xylene	42	74	87	69	40
isopropylbenzene			85		10
o-xylene			68	73	35
3- & 4-ethyltoluene			86	70	33
2-ethyltoluene			84	73	32
1,2,4-trimethylbenzene			86	66	33
1,2,3-trimethylbenzene			71	65	37
Average recovery of hydrocarbons			78	72	43

* in ethyl acetate

Concentration of hydrocarbon placed in a glass syringe containing 20 ml of water and concentrated with a Sep-Pak ranged from: a) 1-150 PPM, b) 10-500 PPM, and c) 50-1500 PPM. These concentration ranges were selected so that they nearly equalled that found in JP-4 in b) or in c) so that quantitative amounts of JP-4 could be delivered.

the individual major components of JP-4 were comparable to the concentration range for the single hydrocarbons (1-1500 ppm). These concentrations were all based on amount of hydrocarbon of interest per 20 ml of water.

An example of the capability of the Sep-Pak to concentrate a dilute sample of hydrocarbon from water is demonstrated by the chromatogram in Figure 1. Under the chromatographic conditions used the aliphatics were not well resolved. The alkylbenzenes, however, were well separated and quantitation of each component was possible.

DISCUSSION

Sep-Pak C18 cartridges from a single lot gave consistent recovery efficiencies for the hydrocarbons investigated over a range of 1-1500 PPM in 20 ml of water (Table 1). Different lots of Sep-Paks, however, gave significantly different recovery efficiencies for the same compound. SANER et al. (1979) found the same variation using toluene and benzene in water. For samples containing more than 1500 PPM, we found that volumes less than 20 ml should be processed. On the other hand, larger volumes of more dilute samples would give a measurable recovery. SANER et al. (1979) describe a method for calculating the optimum sampling volume for benzene in water. They observed that when large volumes of a dilute solution were passed through a Sep-Pak the trapping efficiency was reduced, perhaps as a result of the high flow rate they used for loading the Sep-Pak.

Data in Table 1 indicate single hydrocarbons are generally trapped more efficiently than when present in a mixture of hydrocarbons. This has been seen by numerous other investigators using various types of macroreticular (XAD) resins and several column designs (JUNK et al. 1974, STEPHEN & SMITH 1977, CHANG & FRITZ 1978, TATEDA & FRITZ 1978, VAN ROSSUM & WEBB 1978, DRESSLER 1979, SANER et al. 1979, and JANARDAN & SCHAEFFER 1980). Care must be used when applying trapping efficiencies obtained from analysis of single hydrocarbons to experimental samples in which a mixture of hydrocarbons is present. If the trapping efficiency used is unrealistically high, the estimation of the concentration of the hydrocarbon under study will be lower than what is actually present in the sample.

Data in Table 1 also indicate that the efficiency of trapping of the solutes by the Sep-Pak is improved by the addition of a small amount of organic solvent. Several possible explanations can be advanced to explain this result, including: (a) the organic solvent

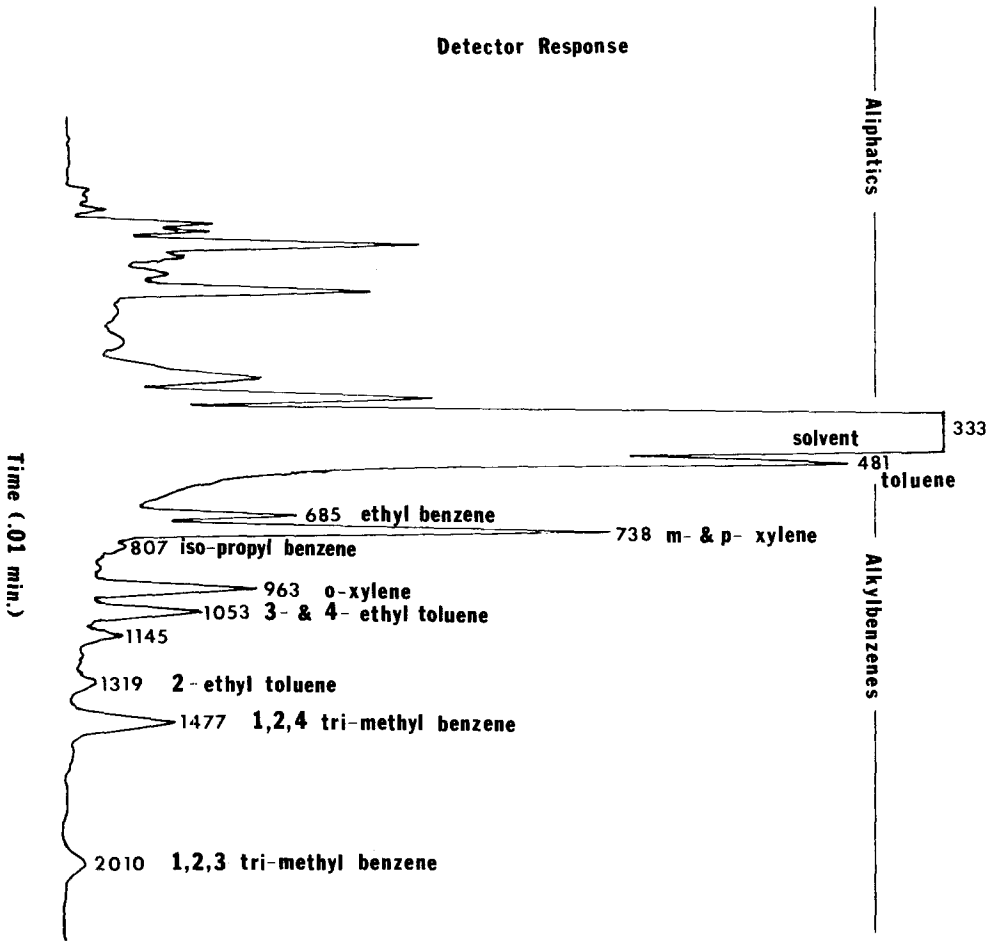

Fig 1. GLC of the water-soluble fraction of JP-4 in water. 10 µl JP-4 in 500 ml of water was mixed for 16 hours and concentrated with a Sep-Pak C18. RT (.01 min), detector: FID, 5 x 10^{-12} A full-scale.

increases the solubility of the solute in water, (b) it alters the hydrophobic interface between the packing material in the Sep-Pak sufficiently so the material can interact with the solute in water, (c) the solvent reduces the loss of solute on the barrel and plunger of the syringe used to push the sample through the Sep-Pak, or any combination of the above options.

SANER et al. (1979) report that the order in which benzene and toluene are concentrated from a water sample with a Sep-Pak influences the trapping efficiency of the Sep-Pak. In a water sample containing a number of components the order in which any component is added cannot be controlled and therefore all components must be concentrated at one time. In the present study, hydrocarbon samples were added to water either individually, in a mixture of 14 compounds, or as JP-4 jet fuel (Table 1). There was variability in the ability of the Sep-Pak to concentrate aliphatics from water. This could have been due to their rather low solubility in water and higher volatility. Recovery of the aliphatics in JP-4 was greater than in the standard mixture.

Efficiency of the Sep-Pak for concentrating alkylbenzenes from water varies. Toluene is more efficiently trapped when it is the only component present. Ethylbenzene and m- & p-xylene are not as efficiently trapped when they are present independently. When the hydrocarbon matrix is complex, as with JP-4, the trapping efficiency is less than in the less complex mixture. The overall average efficiency of recovery of the standard hydrocarbon mixture is somewhat greater than for JP-4. There was a great difference in recovery between the JP-4 added to water in ethyl acetate and JP-4 added directly to water. These observations indicate care should be exercised when drawing conclusions about the efficiency of XAD, Sep-Pak or other trapping matrices and that trapping efficiencies for single organic compounds are not equivalent to those found when multi-component mixtures are involved.

The chromatogram in Figure 1 shows that a Sep-Pak can be used to concentrate a relatively dilute sample of JP-4 mixed with water. When the Sep-Pak is to be used to concentrate hydrocarbons from more dilute solutions of JP-4 in water larger volumes of water must be processed. When larger volumes of water are forced through a Sep-Pak, evaluation and quantitation of data should be done with caution. SANER et al. (1979) report that benzene and toluene are lost from the Sep-Pak when large volumes (more than 150 ml) of seawater are passed through the Sep-Pak.

In this work, a Sep-Pak has proven to be a useful tool for concentrating aliphatics and alkylbenzenes

from water. It was 5 to 10% less efficient than XAD, as reported by DRESSLER (1979), for concentrating some of the same aromatics. This however is not a great reduction in efficiency when the ease and convenience of using these cartridges is considered. The C18 packing material used in the Sep-Pak is rather hydrophobic. A further extension of the usefulness of this technique would be to use a mini-column packed with more polar bonded phase such as C8 or C2. These columns could be used to concentrate the more water soluble organics from water.

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