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LARGE BORE COATED COLUMNS IN ANALYSIS FOR TRACE ORGANIC POLLUTANTS IN WATER

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SUMMARY

Large bore coated (LBC) columns were used in model systems for concentration and recovery of trace organic chemicals in water. The chemicals used represent various types of possible pollutants, with emphasis on aromatic hydrocarbons. The LBC column is used to concentrate the trace organics from water simply by passing a sample of water through this device. The trapped organics are then themally desorbed onto a short porous polymer or charcoal pre-column. After the residual moisture is driven off, the trapped material is eluted onto the analytical gas chromatographic column and analyzed under programmed temperature conditions. The chemicals used in the model analyses were benzene, dodecane, naphthalene, *o*-cresol, dibenzyl and fluorene; three concentrations between 50 ppb (ng/ml) and 5 ppm (μg/ml) were examined. Only 20 ml of sample was needed for analysis. Manipulation of sample volume and number of passes through the LBC column resulted in good quantitative recovery for most of these chemicals. Recovery for benzene, however, was poor. The LBC column, coated with SE-30, showed different retention efficiencies for each compound at different concentrations. The lowest concentration gave best recoveries. The polynuclear compounds gave particularly good results and quantitative recoveries of these components were possible at the 50-ppb level.

The results obtained with the LBC column compared favorably with those obtained by headspace nitrogen sparging or solvent extraction. Reference is also made to the analysis of petroleum fractions dissolved in water (10 ppm) and to the influence of dissolved substances in affecting recovery efficiency. Some discussion of the effect of column dimensions upon performance is also given.

INTRODUCTION

Since the first use of large bore coated (LBC) columns in the trapping of airborne volatiles and those from breath was described[1], several applications for these devices have been reported for the trapping of trace amounts of flavorants in water and beverages[2,3]. Analyses in both cases can be performed at the ppb level or below, though recoveries of flavors can be poor from some aqueous systems in the presence of fixation phenomena probably due to colloidal components.

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Water pollution is an important problem, and analyses for water pollutants have commanded considerable attention. The diversity of pollutants has required the use of varied techniques for trapping these chemicals, which are usually at trace levels. The techniques reported are numerous for specific pollutants, but less so for generalized methods which seek comparable concentration of all foreign compounds whether known or not. Direct trapping on activated charcoal[4] was for many years the only general technique, but more recently these techniques have expanded to include resins[5,6], porous polymers[5,7,8] and stripping of volatiles followed by trapping[9]. LBC columns are very simple devices, consisting of long lengths of open metal tubing which are wall-coated with standard chromatographic substrates. The substrate of choice has been silicone (SE-30) rubber, but this choice is based primarily on its thermal stability in the desorption phase of the analysis rather than solvent efficiency in the trapping phase. Of all the substrates examined, only SE-30 has shown great reliability and consistency in providing the minimum number and amount of artifacts upon thermal stripping of the LBC column. This stripping, performed with a backwards flush of nitrogen at 250°C for 12 min, effects the transfer of the absorbed organics from the LBC column to the gas chromatograph itself, usually via the medium of an intermediate short pre-column of porous polymer sized to fit into the injector heater of the gas chromatographic unit, although other transfer media may at times be used.

This paper deals with the specific application of LBC columns in water pollution analysis, whereby they are used as traps for the trace organics. Model pollutants, representing various classes of chemicals, were used in the analyses. The chemicals used were benzene, dodecane, naphthalene, *o*-cresol, dibenzyl and fluorene. The trapping efficiency of the LBC column was demonstrated by recovery of traces of the model pollutants in water when an aliquot of the spiked water was sampled directly on the column. The recovered amounts were compared to those obtained from direct injection of the same amounts as in the water sample.

In addition to analysis for model pollutants, trace gasoline was analyzed for in water. Comparison of performance of LBC columns to other techniques was carried out by analyses for the model pollutants at similar concentration by solvent extraction and by headspace purge and trap technique.

Reproducibility of the LBC column technique was checked by repetitive analyses of identical samples over a period of 3 weeks.

EXPERIMENTAL

Gas chromatographic conditions are shown in Table I.

Materials

The pre-column packing was Tenax GC (60–80 mesh; Applied Science Labs., State College, PA, U.S.A.). The LBC coating material was SE-30 methyl silicon rubber (Analabs, North Haven, CT, U.S.A.).

The pre-columns were short lengths of Pyrex glass tubing, 15 × 0.6 cm (0.38 cm I.D.). The packing (200 mg Tenax) was contained between glass wool plugs to ensure it was always within the hot zone of the pre-column heating oven used for sample desorption. The pre-column was conditioned at 275°C for a minimum of 3 h, with a nitrogen flow of 50 ml/min prior to use.

TABLE I

GAS CHROMATOGRAPHIC CONDITIONS

Gas chromatograph	Perkin-Elmer Model 3920 with FID
Column	8 ft. aluminum, 0.25 in. O.D. (0.186 in. I.D.) packed with 10% Carbowax 20M on Chromosrob W 80–100 mesh (acid washed and DMCS-treated)
Carrier	Nitrogen at 50 ml/min
Column oven temperature	4 min at 70°C, then programmed at 8°/min from 70 to 230°C and held at the final temperature
Injector and interface temperatures	250°C
Integrator	Perkin-Elmer M-1
Recorder	0–5 mV with a chart speed of 0.5 in./min

LBC columns

An aluminum tube [25 ft. × 0.25 in. O.D. (0.186 in. I.D.)] with a coating of 2.1 g SE-30 was used. The calculated film thickness was 19 μm. The technique for coating and conditioning the column, which may be sectioned or joined in series to obtain other lengths, was as described previously[2]. The effect of varying column diameter or length with a given weight of substrate, or of varying coating thickness for a given column diameter or column length, has also been reported[2], but with a major emphasis on sampling air rather than aqueous systems.

Sampling

An aliquot of 20 ml or more of the aqueous solution was poured into the LBC column and allowed to pass through with gravity. A gentle nitrogen flow can also be used to assist in the flow of the sample. The emerging sample was collected in a beaker and then poured through the column up to four times more; if needed, it can be centrifuged or filtered prior to sampling.

The column was washed with 3 × 50-ml portions of distilled water. This step is not necessary if the sample has no dissolved materials which will cause interference if they decompose with heat during the elution step. The bulk of residual moisture is then removed from the LBC column using nitrogen at 500 ml/min for 10 min. The LBC column temperature is ambient, or the column can be slightly warmed at this point to speed water removal.

Sample desorption

The LBC column is transferred to a heating oven for reverse flushing with nitrogen. The trapped volatiles are eluted by heating the oven to 250°C and passing a nitrogen flow of 50 ml/min for 12 min through the LBC column onto a Tenax-GC pre-column, which is at ambient temperature just outside the oven. The pre-column may also be cooled, if desired. The pre-column is then dried with nitrogen at 100 ml/min at ambient temperature until the condensed moisture is no longer obvious.

The sample is eluted for analysis directly onto the analytical column by heating the pre-column at 250°C for 6 min in a special tube oven (Chromalytics 1022) which

fits on the injection port of the gas chromatograph. The temperature of the tube oven is controlled with Chromalytics' power supply and temperature controller (Model 1047). The carrier gas is rerouted with a toggle valve to pass through the pre-column while eluting the sample. The chromatographic analysis is initiated concurrently with the initiation of sample desorption. The sample may also be eluted directly from the LBC trap into a small volume of organic solvent, by bubbling into a cooled aliquot, and after subsequent concentration analyzed by direct injection into the gas chromatograph. In fact, 3–5 ml of cooled methylene chloride in a small test tube can replace the porous polymer pre-column, allowing direct transfer from the LBC column into methylene chloride. In this case, the test tube will also contain condensed water which can be easily separated.

RESULTS AND DISCUSSION

The factors which were shown previously[2,3] to affect the efficiency of trapping by LBC columns are length and diameter of the column, size of sample and number of sampling passes through the column. The number of sampling passes is very important to achieve equilibrium of the trace solute between the aqueous solution and the wall coating. Five passes were adopted for convenience and as a compromise between time and maximum recoveries. The time required to promote equilibrium differs for each component. The original concentration of the trace organics in water

TABLE II

RECOVERIES OF TRACE MODEL POLLUTANTS FROM WATER

Pollutant concentrations: 50 ppb, 200 ppb and 5 ppm; trapping column: LBC, 25 ft. × 0.186 in. I.D., with 0.019 mm SE-30 wall coating; the effluent of the trapping column was subsequently eluted onto a Tenax-GC pre-column. Samples of 20 ml were analyzed. The recoveries are relative to direct injection of equivalent amounts.

Compound	*Amount in 20-ml sample (μg)*	*Recovery (%)*
Benzene	1.0	0.1
	3.9	4.3
	97.9	2.9
Dodecane	1.1	28.9
	4.3	23.8
	106.3	24.9
Naphthalene	1.0	114.2
	4.0	85.8
	99.3	86.9
o-Cresol	1.0	51.2
	4.1	31.4
	103.2	24.0
Dibenzyl	1.0	91.5
	4.1	80.2
	101.4	62.4
Fluorene	1.0	112.8
	4.0	82.7
	99.8	28.4

also affects the efficiency of their trapping and recovery by the LBC column. Table II shows recoveries of the model pollutants when present in the same volume samples but at different concentrations (0.05, 2 and 5 μg/ml). The recoveries for most of the components, except benzene and dodecane, are better in the lower concentration samples. Very good recovery of naphthalene was achieved at all concentrations examined. Other wall coatings need to be examined for selectivity of certain kinds of compounds or for broad based non-specific absorption characteristics.

Table III shows a comparison of the LBC method with other techniques, based on recoveries of the model compounds when samples of similar concentrations were analyzed by direct trapping on the LBC column, purging with nitrogen and trapping on Tenax-GC, and by extracting with methylene chloride and concentrating the extract to small volume. The results obtained by LBC sampling, except for benzene and dodecane, especially in the most dilute samples, are closer to the results of solvent extraction.

TABLE III

RECOVERIES OF TRACE MODEL POLLUTANTS WITH VARIOUS ENRICHMENT TECHNIQUES

(A) Direct sampling on 25 ft. × 0.186 in. I.D. LBC column with 0.019-mm SE-30 coating. (B) 20-ml sample of 10% sodium sulfate solution containing the indicated amount purged with 12 l of nitrogen at 100 ml/min on Tenax-GC precolumn. (C) Sample extracted with 2 ml methylene chloride and concentrated to a final volume of 0.3 ml.

Compound	*Amount in 20-ml sample (μg)*	*Recovery (%)**		
		A	*B*	*C*
Benzene	104.6	2.9	16.9	70.2
	1.1	7.1	22.4	79.6
Dodecane	102.4	24.9	56.6	107.6
	1.0	17.0	50.9	72.8
Naphthalene	101.4	86.9	98.1	112.8
	1.0	97.1	79.0	99.4
o-Cresol	112.7	24.0	21.2	62.7
	1.1	84.3	50.1	85.0
Dibenzyl	109.4	62.4	92.4	93.7
	1.1	80.4	73.2	109.7
Fluorene	105.2	28.3	66.6	116.2
	1.1	87.1	73.2	116.8

* Relative to direct injection of the same amounts as in the sample.

Direct extractions of the aqueous model pollutant system using Tenax-GC (200 mg) or activated charcoal (10 mg) resulted in poor recoveries and were not pursued. In both, the headspace sparging and LBC sampling methods, the recovery of *o*-cresol especially from the more concentrated sample is quite low. The low recoveries of benzene and dodecane by headspace sparging is due to their low breakthrough volumes from the Tenax trap. This same factor probably accounts for some of the low recovery of these compounds via LBC sampling since the sample transfer is carried out on Tenax.

TABLE IV

REPRODUCIBILITY OF ANALYSES FOR TRACE MODEL POLLUTANTS FROM WATER BY DIRECT TRAPPING ON LBC COLUMN

Column: 25 ft. × 0.186 in. I.D.: 0.019-mm wall coating.

Compound	*Amount in 20-ml sample (μg)*	*Recovery (%)*				*S.D.*
		1	*2*	*3*	*4*	
Benzene	1.0	0.1	6.9	7.1	0	4.0
Dodecane	1.1	28.9	13.6	17.0	27.8	7.6
Naphthalene	1.0	114.2	92.2	97.1	97.6	9.6
o-Cresol	1.0	51.2	83.7	84.3	40.2	22.6
Dibenzyl	1.0	91.5	68.4	80.4	97.5	12.9
Fluorene	1.0	112.8	87.1	87.1	110.2	14.1

Table IV shows the extent of reproducibility in LBC sampling. The analyses were performed on identical samples over a three-week period. Except for the wider variation in recoveries of *o*-cresol and low recoveries of benzene and dodecane, the reproducibility is good, as indicated by the standard deviations, considering the extremely low concentrations (0.05 ppm) involved.

Fig. 1 is a gas chromatographic analysis of the model pollutants in water at 0.05 ppm each when extracted directly on the LBC column, which is similar to the direct analysis of 0.1 μl of stock standard solution containing the same amounts of the model compounds except for the much more enhanced peaks of benzene and dodecane in the direct analysis.

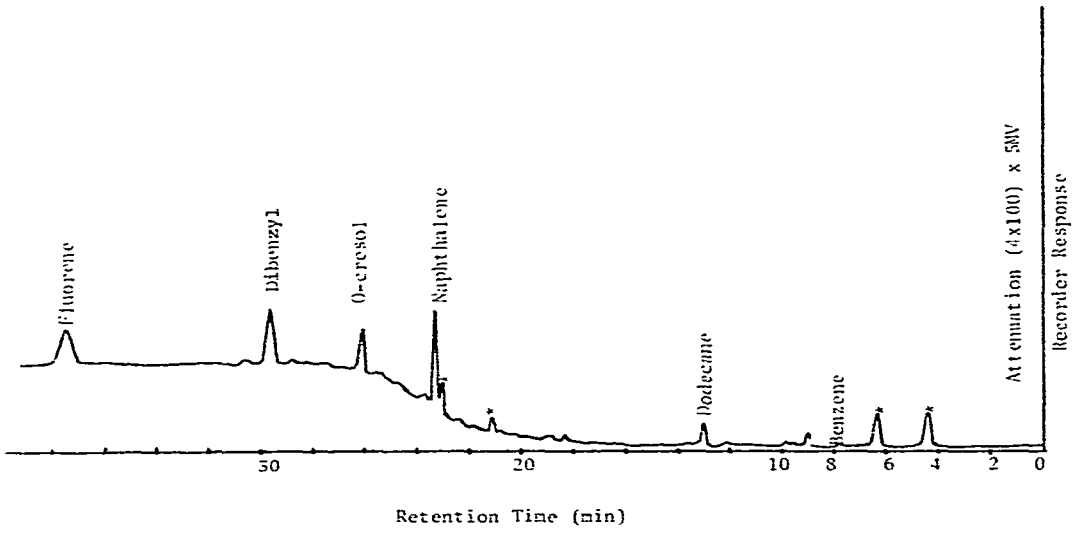

Fig. 1. Analysis for model pollutants spiked in distilled water at 0.05-ppm concentration by direct sampling on LBC column (25 ft. × 0.186 in. I.D.; 0.019-mm SE-30 wall coating). A 20-ml aliquot was recirculated 5 times through the column. Amount of each component in sample is 1 μg. *, Artifact and/or trace impurity.

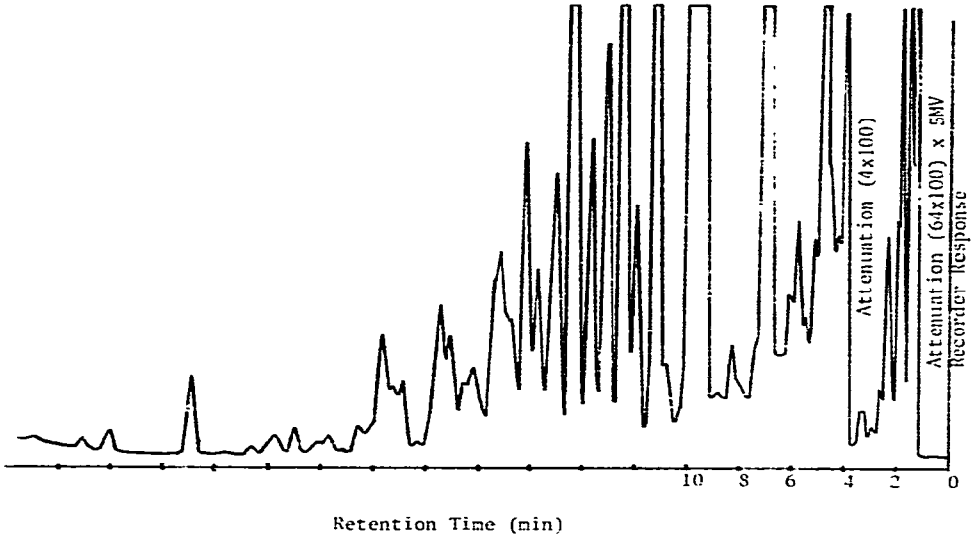

Fig. 2. GC analysis of 1.0 μl gasoline by direct injection.

Fig. 2 shows a chromatogram of gasoline by direct injection while Fig. 3 shows a chromatogram of an LBC analysis of 100 ml of water containing 1 μl of the same gasoline. While the bulk of the highly volatile components is lost from the LBC sample, the pattern of the remaining components is very similar to that obtained by direct injection. The relationship, however, is not quantitative.

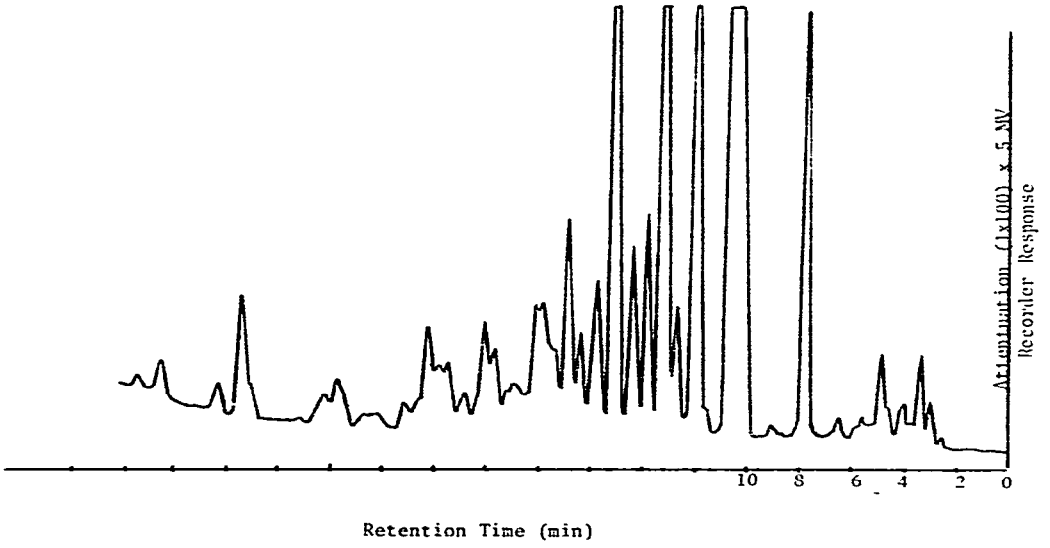

Fig. 3. GC analysis for trace gasoline (0.001 %) in water by sampling directly on LBC column. A 100-ml sample was recirculated 5 times through the column (25 ft. × 0.19 in. I.D.; 0.0019-mm SE-30 wall coating). Sample was then desorbed onto Tenax-GC precolumn and onto the analytical column.

The effect of prolonged residence time of the sample in the column was checked by leaving a 50-ml sample of water, which contained 0.2 ppm each of the model pollutants, in a capped 25-ft. LBC column for 17 h. Appreciable improvement in recovery of dodecane was noted. Up to 75% recovery was obtained for dodecane, but no appreciable improvement in recovery of *o*-cresol was achieved. Good recoveries for naphthalene, dibenzyl and fluorene were still obtained. Improvement in recovery of benzene was only slight.

Recycling the sample through the column with a peristaltic pump for 45 min at 300 ml min also resulted in improved recoveries of dodecane. However, extraneous trace contaminants from the rubber tubing of the peristaltic pump were noted.

CONCLUSION

LBC columns can be effective trapping devices for analysis of trace organic pollutants in water. A potential exists in varying the selectivity of the trap by varying the wall-coating material of the LBC. Improved recoveries may be achieved by manipulating column length, residence time of the sample, sample size and concentration.

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