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Multiple Purge Technique for Determining Organic Pollutants in Groundwater

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Contamination of groundwater with organic chemicals from industrial wastes, agricultural residues, and household cleaners and solvents is becoming a major concern. Analyses of groundwater samples by gas chromatography (GC) from a number of landfill sites in Connecticut revealed the presence of mixtures of many organic compounds over wide concentration ranges. This makes identification and quantitation of these compounds difficult because of overlapping of peaks when packed gas chromatographic columns are used (GROB AND GROB 1979). The use of specific detectors recommended in many of the EPA priority pollutants protocols for routine monitoring of given classes of compounds (EPA 1979) are not readily applicable for the general identification of pollutants in landfill leachates. The use of GC/MS is beyond the reach of many laboratories because of high initial and maintenance costs as well as lack of necessary expertise (LICHTENBERG 1979). In addition, the GC column materials compatible with the commonly used purge and trap technique have considerably more bleed than column packings normally used in GC/MS. This, along with the large differences in concentrations of various components in groundwater samples, makes adequate background correction of mass spectra difficult for minor constituents.

We describe here a novel procedure for analyzing volatile organic pollutants by GC using the purge and trap method. The procedure involves a series of successive purges on a sample. The ratio of the area of a peak to its area on the previous purge, purge ratio (PR), can be used to confirm the identity of a peak by comparison to the PR of a standard. Furthermore, a constant PR of a series of purges can be used to demonstrate the absence of underlying peaks. Successive peaks can also reveal the correct retention time of a less volatile component whose peak was merged with a more volatile component. Using this multiple purge method we have analyzed a number of groundwater samples from landfill sites.

METHODS

Groundwater samples were collected from test wells by lowering a 2-ft section of stainless steel tubing (1-in ID) closed at the bottom and withdrawing it when filled. The samples were stored

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in a refrigerator (EPA, 1979) until analyzed. The analyses were performed with a HP-5840A gas chromatograph equipped with a HP-7675A purge and trap unit and a FID detector. The primary GC column was 8-ft x 1/8-in. OD stainless steel packed with 1% SP-1000 on 60/80 mesh carbopack B. The temperature program was begun at 45°C with a 3-min delay followed by a 8°C/min heating rate up to 220°C. The second column used for confirmation was 10-ft x 1/8-in stainless steel packed with 3% SP-1500 on 80/100 mesh carbopack B. The purge and trap sample tube was kept at 30°C and the flow rate through the tube was controlled by a mass flow controller. Successive 5-min purges were made using He at a flow rate of 20mL/min. The major peaks were confirmed with a 5992 HP GC/MS system equipped with a HP purge and trap unit. Standards were prepared by injecting 5 μL of a methanol solution of the standard into 10mL water. They were then purged as well as the unknowns to obtain the purge ratios. The purge ratios of the smaller peaks were obtained from peak heights and of the larger peaks from peak areas.

RESULTS AND DISCUSSION

Figure 1 shows a gas chromatogram of a groundwater sample obtained from a test well at a landfill site in Southington, CT and is used here to demonstrate the application of the proposed multiple purge technique. Retention times (RTs) and successive PRs of 10 major peaks were obtained using two different columns. The compounds were identified by comparing their RTs with those of the standards. The PRs tend to have a constant relative error, with a mean coefficient of variation of about 4% for the data in Table 1, excluding benzene and ethyl benzene.

The purge ratios of peaks from the leachate sample are in good agreement their respective standards except for benzene, toluene, and ethyl benzene. The increase in PRs for benzene and ethyl benzene with successive purges is indicative of an underlying peak of lower volatility. Figure 2 shows the unmasking of the peak underlying benzene with successive purges. The benzene peak at RT = 19.59 in the first purge produces a shoulder at higher RT in the second purge and a distinct peak at RT = 19.74 corresponding to 2-pentanone in the third purge.

The difference in PRs between the toluene peak in the sample and the toluene standard is significant and apparently results from increased solubility of toluene in the leachate sample. Spiking the Southington sample (depleted of toluene by purging) to its original concentration resulted in the same PR for toluene as in the original leachate sample. The major water soluble components in the leachate were not found to increase the solubility of toluene when a standard was spiked with these major water soluble components. Indeed, PRs for the extreme cases of toluene in pure water and in water with 250 ppm of methanol differed by only 0.01. The slight foaming observed when the Southington water is shaken suggest that a detergent may be responsible for the enhanced solubility of toluene in this sample.

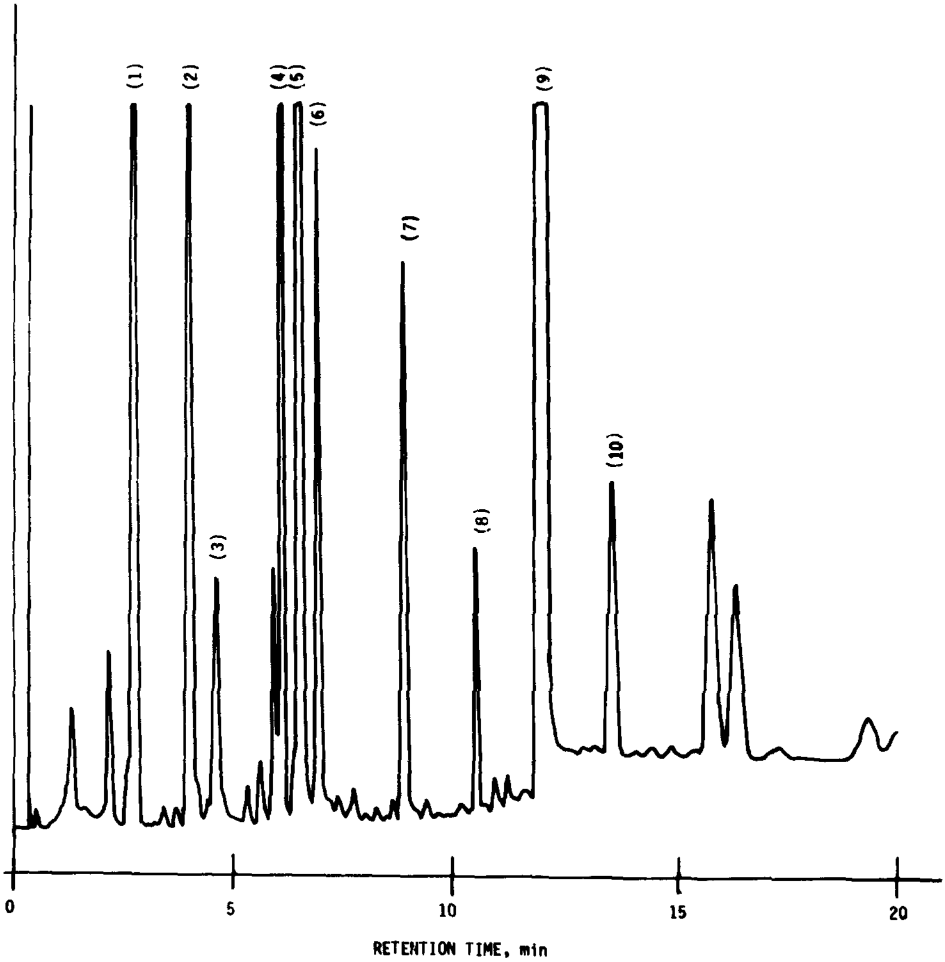

Fig. 1. Gas chromatogram of a leachate sample from the Southington landfill site, using a SP-1000 GC column: (1) ethyl chloride; (2) acetone; (3) isopropanol; (4) diethyl ether; (5) methyl ethyl ketone; (6) 2-butanol; (7) benzene; (8) methyl isobutyl ketone; (9) toluene; (10) ethyl benzene.

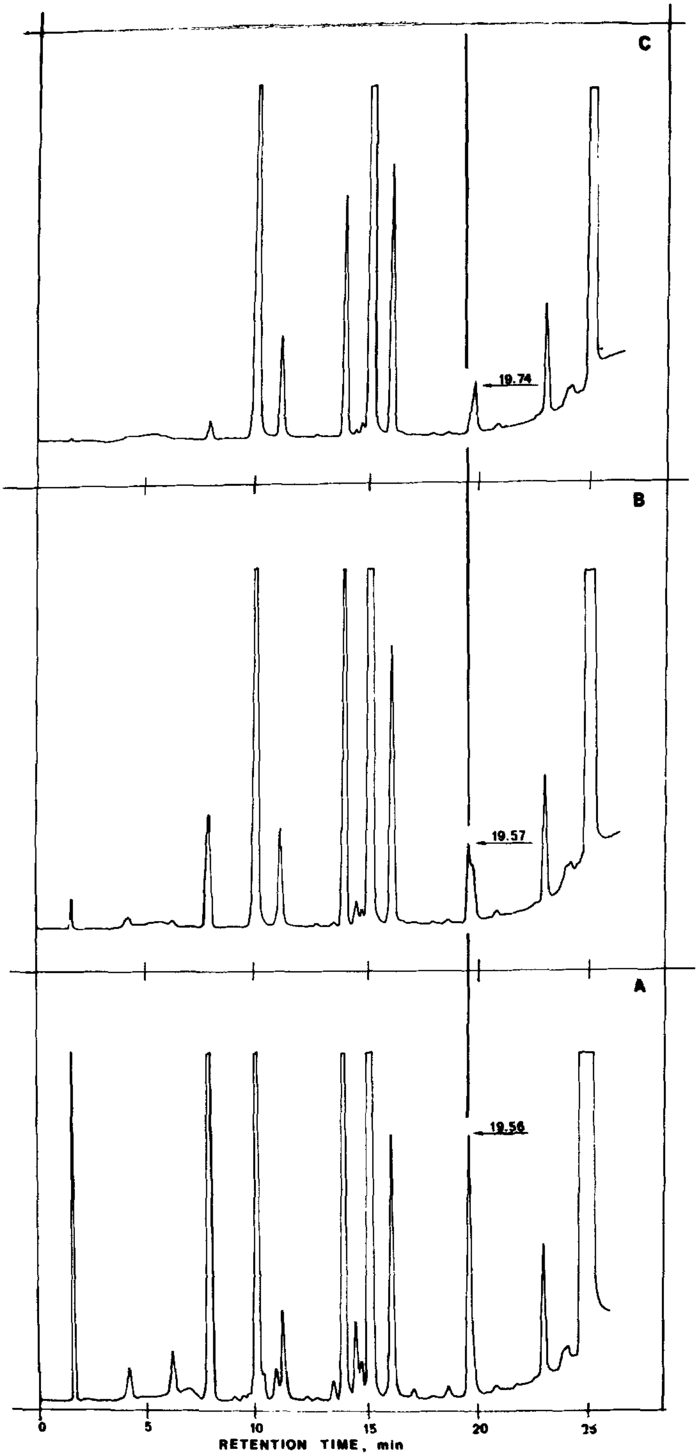

Fig. 2. Gas chromatograms (A,B,C) of leachate from the Southington landfill site, showing unmasking of 2-butanone from the benzene peak with successive purges.

TABLE 1

Ratios of peak areas from successive purges of leachate from Southington landfill site and of standard organic compounds.

Compound	Peak ratio from indicated purges			
	Leachate			Standard
	2nd/1st	3rd/2nd	4th/3rd	2nd/1st
Ethyl chloride[#]	.20	.16	.17	-
Acetone	.97	.97	.97	1.01
Isopropanol	1.00	.95	.98	1.00
Diethyl ether	.64	.60	.61	.60
Methyl ethyl ketone	.99	.96	.97	.97
2-Butanol	1.09	.97	.99	1.05
Benzene	.45	.56	.79	.19
MIBK	.87	.90	.93	.93
Toluene	.26	.25	.25	.19
Ethyl benzene	.34	.42	.78	.16

Identification by GC/MS only.

The multiple purge technique showed constant peak ratios for various other organic compounds including a number of alcohols, ketones, and chlorinated hydrocarbon standards. The technique is not only useful in confirming the identity of the GC peaks but also in determining the purity of the peaks and possible alternations in the solubility of trace organics.

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