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A Procedure for Determining Benzene in Soil by the Purge-and-Trap Technique

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Presently there is heightened concern about the potential hazards posed by landfills and chemical waste dumps. As is well recognized now, the potential for contamination of the environment often exists. Hence, the ability to detect chemicals that may have leached into the ambience is of the utmost importance. Methodology for detecting pollutants in various waters is in a relatively high state of development. In soils a great deal of work has been done on the determination of persistent compounds - i.e., nonvolatiles such as pesticide residues. However, to date, much less attention has been paid to the determination of volatile components in soils and sediment. One such compound of current environmental concern is benzene.

Most procedures for the determination of benzene at low or trace levels rely on gas chromatography as the determinative step. At parts-per-million levels in water, direct-aqueous injection GC with FID detection may be used to determine benzene. At lower concentrations extraction from water with a suitable solvent (CHALAYA et al. 1975) or vaporization into a headspace in a closed vessel (DROZD and NOVAK 1978) can be used to isolate benzene from its matrix. In the last few years purging and trapping of benzene by the purge-and-trap (PAT) technique has found considerable use (KOPFLER et al. 1976, VOZNAKOVA et al. 1978) with aqueous samples. Several approaches are possible for the determination of benzene in soil: a soil slurry may be extracted with an immiscible organic solvent or the soil may be Soxhlet extracted prior to GC determination. A drawback of the latter is that it would tend to be unwieldy and time-consuming with many samples and both extraction techniques may suffer losses of the relatively volatile benzene. Direct-aqueous injection (after making a slurry of the soil) at higher levels can yield low results, because in a soil/water system much of the benzene could remain bound to the soil.

Because of the significant volatility of benzene, a headspace technique was selected for the determination of benzene in soil. Headspace techniques offer several advantages: 1) high sensitivity, 2) avoidance of a solvent peak, and 3) isolation of volatiles from nonvolatiles that might otherwise interfere. While static headspace analysis (HACHENBERG and SCHMIDT 1977) proved workable for the determination of benzene in soil, a dynamic headspace procedure utilizing the purge-and-trap (PAT) technique yielded a lower limit of detection (1 ppb). The application of the PAT technique to the determination of benzene in contaminated soil is the subject of this report.

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EXPERIMENTAL

The PAT technique consists of purging volatiles from an aqueous sample onto a retentive packing held in a trap, followed by thermal desorption onto a GC packing which is usually held at ambient or subambient temperature. Quantitation is then effected in a temperature-programmed GC run. PAT is typically used for aqueous systems with a minimum amount of suspended or particulate matter. However, by purging benzene from a soil slurry in water, a concentration gradient is maintained between the soil and water, and hence, a driving force exists for the diffusion of benzene from soil into the water.

A specialized purge vessel, shown in Fig. 1, was constructed to accommodate a soil slurry. A 9 mm opening at the top facilitates introduction of the sample. A fine frit coupled with a pear-shaped purge vessel promotes vigorous agitation of slurried soil. Up to 2 g of soil (plus 20 ml of water) could be conveniently placed in the device. The purge device was connected via a ball-joint to a purge/trap assembly constructed in the laboratory. This apparatus consisted of two 4-port Valco valves, associated fine-bore metal tubing, heaters, and a 6" x 1/8" stainless steel trap. To encompass a dynamic range of 10^5, two detectors, a FID and a HNU photoionization detector (PID), were used in parallel in conjunction with a splitter. With this arrangement area measurements were linear to 100 ppm when a 2 g sample was used. A schematic of the PAT system is shown in Fig. 2.

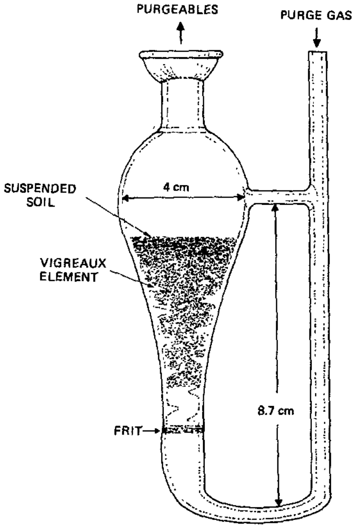

Fig. 1. Purge vessel for the determination of benzene in soil.

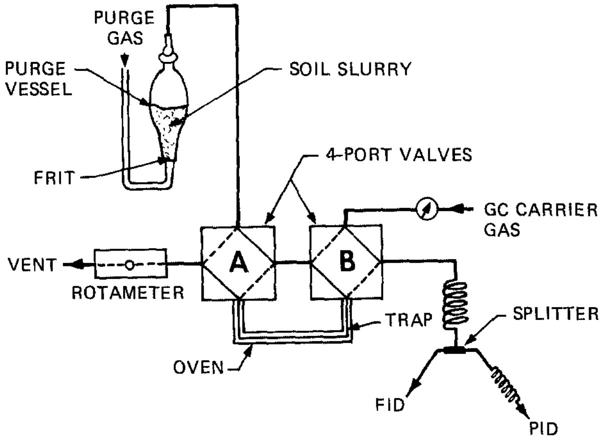

Fig. 2. Schematic of PAT system. The purge gas follows the solid line through the valves. Benzene, which is well retained by the trap (Tenax-GC), collects on the front of the trap. During desorption, the oven is slid over the trap, valve A is first switched to the dashed position, then followed by valve B. With the valves in the dashed positions, components on the trap are backflushed onto the GC column.

Appropriate standards of benzene were prepared in ethylene glycol. Because ethylene glycol is highly polar, miscible with water, and has low volatility it does not purge from an aqueous matrix. These properties make it an excellent solvent for PAT calibration and fortification as no solvent peak appears in the the chromatograms obtained. Quantitation was either by peak height or peak area. Because the adsorption coefficient for benzene may vary from soil to soil, depending on type of soil, soil organic matter, clay content, depth, and water content, it is desirable to include an internal standard. Two internal standards were included in each run - cyclohexane for low concentrations (for use with the FID) and o-difluorobenzene for higher concentrations (for use with the PID).

Sampling. Samples were taken in an area where soil had been exposed to benzene in an environmental incident. Samples were collected from four depths - at the surface and at 2, 4 and 6 feet along a grid in the exposed area. The soil was placed in 8-oz. wide-mouth jars with foil cover liner, filled to the top. The jars were then placed in Ziploc* bags and iced until transferred to the laboratory where they were stored in a refrigerator at 4°C. All soil samples were disturbed samples. Samples were removed from the refrigerator just prior to analysis. Because of possible losses resulting from evaporation from near the surface, the top portion, 1/2 inch or so thick, was scraped or scooped away; then a sample was taken.

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Analysis Conditions. The PAT apparatus was coupled to a Hewlett-Packard 5710A GC. The column was 5' x 1/8" Ni packed with 2.5% SP-1000 on 60/80 Carbopack B. Initially the column was held at 40°C for 4 min., then programmed at 16°/min. to 170°C, then held. Both the FID and PID were maintained at 200°C; the PID source was a 10.2 eV lamp. The column flow was 35 cc/min. N_2 with a ~10:1 split FID:PID. N_2 makeup gas was added to the PID for a combined flow of 25 cc/min. FID gas flows were 35 cc/min. H_2 and 270 cc/min. air.

Purge-and-Trap Analysis Procedure

1. Two grams of a soil sample were weighed into the purge device.
2. Twenty ml of devolatilized Millipore Milli Q water were added. If the amount of benzene exceeded the linear range, a 10-fold dilution of the slurry was made.
3. One µl of internal standard solution was added. Cyclohexane was added at 85 ppb and o-difluorobenzene was added at 4 ppm.
4. The contents were shaken to obtain a suspension of the soil.
5. The sample was then purged vigorously for 12 min. at 40 cc/min. with N_2 onto 60/80 mesh Tenax-GC, contained in the trap; desorption was conducted for 4 min. at 200°C by backflushing the trap with N_2 at 35 cc/min.

RESULTS

Examples of chromatograms obtained by the PAT procedure are shown in Figure 3 (FID response only). Two pens monitored the FID response to benzene, covering a range from 1 ppb to more than 200 ppb. Above approximately 250 ppb quantitation was effected by the PID, which accepted 1/11 of the column effluent (via the splitter).

Table I shows results from soil samples taken in the affected area. The measured concentrations ranged from more than 300 ppm to nondetected (1 ppb detection limit). Use of these data permitted an assessment of the extent of contamination and provided the basis for corrective action to be taken.

TABLE I
BENZENE CONCENTRATIONS (PPM)

Sample No.	Surface	2 Feet	4 Feet	6 Feet
1	2.0	0.11	0.023	0.27
2	0.11	0.13	0.005	ND
3	0.007	2.8	3.3	0.9
4	ND(0.001)	0.037	0.070	0.030
5	0.008	67	335	10
6	0.36	9.6	0.15	0.10
7	0.16	3.6	52	21
8	0.19	ND	0.086	0.006
9	0.10	9.5	118	3.4
10	0.49	0.070	0.035	ND
11	0.79	0.071	50	0.42
12	0.42	0.019	0.18	ND
13	0.82	0.004	0.030	0.20

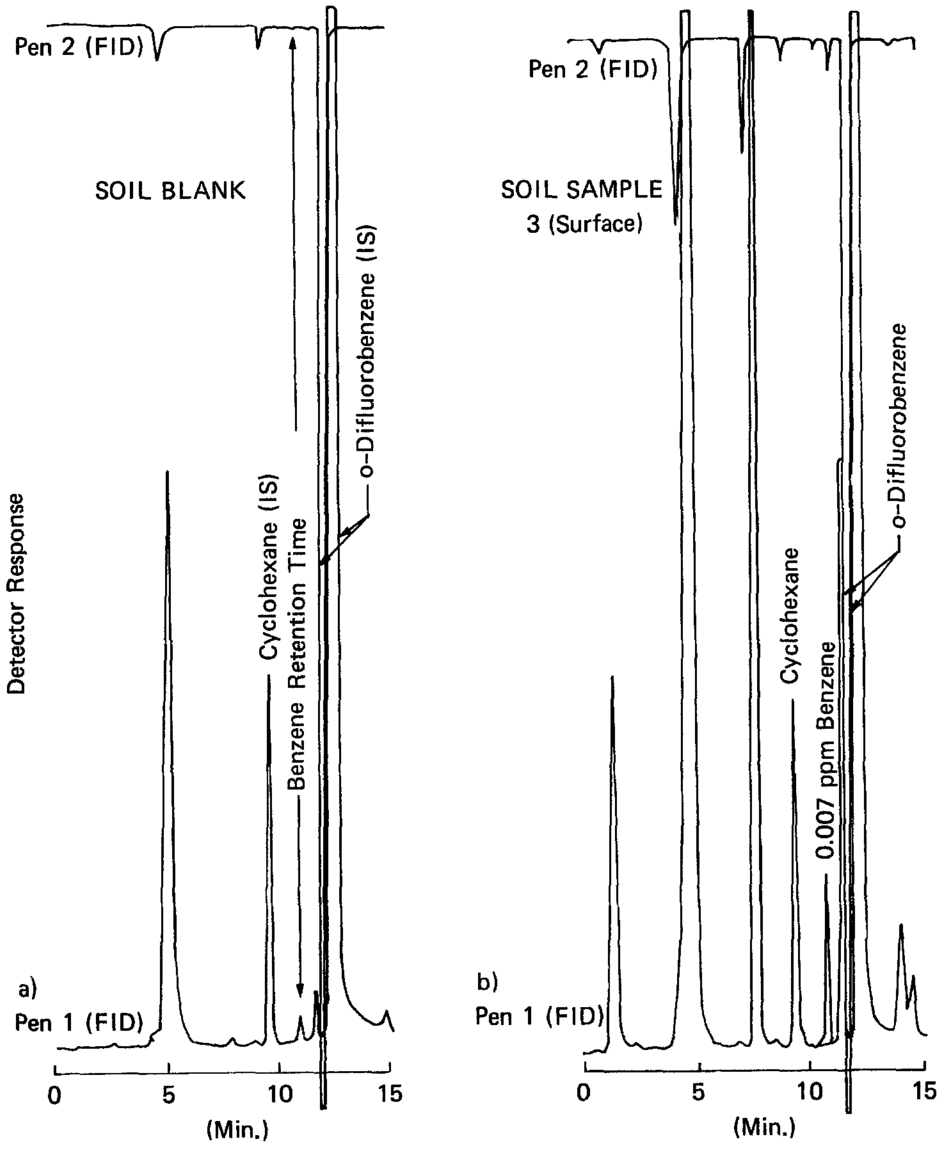

Fig. 3. Chromatograms of a) control soil + internal standards and b) a sample containing 7 ppb of benzene. Pens 1 and 2 monitor FID output: they are displaced slightly in time. Pens 3 and 4 on a separate recorder (not shown) were used to monitor PID output.

The reproducibility of the PAT technique with particulate-free aqueous samples has been documented (6). Similarly, we have repeatedly demonstrated its reproducibility on a control soil (benzene-free) to which a known amount of benzene was added. Contrasted to this is the occasionally-observed poor reproducibility observed for a sample. Once a bottle had been opened, the benzene tended to migrate upward due to losses from the surface via evaporation. Repeated analyses near the surface showed decreasing concentrations of benzene. This is why, as mentioned previously, the top portion of the sample was scraped away before sampling.

The purge-and-trap technique offers a convenient and sensitive approach to the determination of benzene, and presumably, to other purgeables in soil. It may be expected to perform comparably with other particulate samples such as sludge and sediment. With the purge vessel subjected to additional forms of excitation, i.e., forced agitation, ultrasonication and elevated temperature purging, the technique should provide enhanced sensitivity, even in cases where the soil adsorption coefficients are considerable. This is presently under investigation.

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