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FEASIBILITY OF USING CANINE OLFACTION AS A MEANS
OF DETECTING HAZARDOUS SUBSTANCES

by
Stuart D. Messur

Thesis submitted to the Faculty of the Graduate
School of the New Jersey Institute of Technology
in partial fulfillment of the requirements for the
degree of Master of Science in
Environmental Engineering/(Toxicology option)
1987

APPROVAL SHEET

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as a Means of Detecting Hazardous
Substances

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ABSTRACT

Title of Thesis: Feasibility of Using Canine Olfaction as a Means of Detecting Hazardous Substances

Stuart D. Messur, Master of Science, 1987

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Two specific applications for using canine olfaction as a means of detecting hazardous substances have been recognized: detection of residual contamination on hazardous waste cleanup equipment (DECON), and detection of leaking underground gasoline tanks (LUST).

With the DECON project, the dog's ability to detect low emissions of some common hazardous compounds was tested. As a safe and effective training tool for presenting hazardous compounds to the dog, permeation tubes filled with m-xylene or 1,1,1-trichloroethane were constructed and calibrated. Hidden tubes emitting as low as 0.5 $\mu\text{g}/\text{min}$ were consistently detected by the dogs. During olfactory field tests, "hot spots" of m-xylene contaminated mud with emission rates as low as 0.19 ng/min were detected on pieces of waste site cleanup equipment.

In order for a dog to accurately identify vapors emitting from leaking underground gasoline tanks, it must be

trained to discriminate between tank leak vapors and spilled gasoline vapors. Chromatographic analysis of aged and water-washed gasoline identified a general decrease in the more volatile compounds, and an increase in the heavier compound vapor concentrations with time. However, the more volatile compounds predominate in gasoline vapors rising through a water saturated soil column. The use of canine olfaction in detecting leaking gasoline tank vapors appears to depend upon dog's ability to discriminate between mixtures. Other ways of using canine olfaction as a means of detecting underground tanks are suggested.

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I.

INTRODUCTION

During the past decade, the public has become deeply concerned with the environmental and human health risks created by hazardous wastes. In response to this, the nation has begun to develop comprehensive plans that help minimize future waste development, and clean up sites that are presently contaminated. The success of these programs is directly dependent upon the development of new and innovative technologies that are quick, efficient, and cost effective at dealing with environmental problems.

In 1983, a new technique for monitoring hazardous wastes sites was proposed to the New Jersey Releases Control Branch of EPA's Hazardous Waste Research Laboratory. It involved the use of dogs and their highly developed olfactory system to track and/or identify hazardous chemicals. Could dogs be trusted with such a highly responsible task?

Canine scent capabilities had long ago gained honor in the enforcement field, with scent discrimination used to track people, explosives, and concealed weapons. In 1976, detector dogs were responsible for 27 % of the narcotic seizures made by Customs (a 50 to 1 return in terms of seizure value vs. program expenditures), checking more than 232,000 transport vehicles, 14 million mail packages, and 6 million

cargo shipments (1). Applications of the dog's highly acute scent capabilities in the environmental field appears to be a sensible extension of their use.

A few cases have been documented of canine olfactory use in areas closely related to the environmental field, further reinforcing their use in the area of hazardous wastes. Nine days before the opening of a new 94 mile track of natural gas pipeline, Glen R. Johnson was commissioned to train dogs to search for and locate any leaks (2). Portions of the track (known to contain leaks) had been searched several times with electronic, chemical, and sonic detectors without any success. With 2.5 days of training on butyl mercaptan identification, 3 dogs began the leak search. After completely covering the 94 mile track 3 times, the dogs had successfully detected over 150 leaks and 4 leaky valves, one 12 feet in the air. The dogs covered up to 60 miles of ground each day, detecting microscopic leaks in pipeline buried 18 feet deep in wet, heavy clay. Some of the dog's finds were analytically examined, and found to be emitting gas concentrations below 1 ppt.

Another case was staged in the streets of New York City (3). Dogs from the Guardian Training Center Academy (Ontario, Canada) were hired by Con Edison to detect insulating fluids leaking from underground electric power transmission cables. Training proved hopeful, with the 3 dogs searching areas saturated with spilled fluids and only

indicating the vapors emanating from leaks that were below the ground. On three documented occasions (as of article publication) the dogs were successful in identifying leaks that were known to exist, but impossible to detect by conventional means, giving the dogs a 100% detection average. Leaks were identified by the dogs from odors seeping through 10 inches of concrete, covered by 8 inches of asphalt. The dogs were praised for their ability to work undisturbed in fast moving traffic, crowds of people and dogs, and the unforgiving weather.

A similar project was undertaken by Glen Johnson in 1976, contracted by Bell Telephone to train dogs to detect specific odorless gases (freon, nitrogen, helium) emanating from buried electrical cables up to 4 feet deep (4). Experimental testing showed all 3 gases could be detected by the dog, with freon the most easily identifiable. Working exclusively with freon, and approximating the flow rate of a typical leak in the field, the dogs were asked to locate leaks being emitted 4 ft. below the ground. In every trial performed, the dogs were able to detect the presence of a leak.

With such reports as a basis, preliminary studies on the use of canine olfaction for monitoring hazardous wastes were performed and completed in 1984 (5). The study was designed to see if trained dogs could identify specific chemical contaminants in the environment, and if so, be used

to help delineate the perimeter of known contaminated areas. Small quantities of toluene, 2,4,5-trichlorophenol, 2,4,6-trichlorophenol, and 1,2,3-trichloropropane were presented to the dogs. The dogs successfully tracked and identified these contaminants, often at concentrations undetectable by sophisticated instrumentation (such as the Photovac G.C. and the Foxoboro 128 Organic Vapor Analyzer). Although a field test at a remediated Superfund site (Tyson's Wastesite near Prussia, Pa.) provided no supporting evidence, it was concluded from the overall feasibility study that olfactory detection could assist environmental workers in site characterization, as well as "hot spot" identification (to aid in more efficient sampling).

In light of the data collected from the preliminary feasibility study (5), additional studies of canine detection seemed necessary. Acceptance into the environmental field meant increased confidence in the technology's capabilities, as well as identification of specific applications that were both time and cost effective. In answer to the previous statements, two areas of application were investigated in this study:

- (1) Canine detection of Leaking Underground Storage Tanks (LUST); specifically leaking gasoline tanks.
- (2) Canine detection of residual contamination on cleaned hazardous waste site equipment (DECON).

Leaking underground storage tanks can be dangerous and costly. Leaking tanks have been recognized as a major source of groundwater contamination. In 1984, Congress amended the Resource Conservation and Recovery Act (RCRA), giving the U.S. Environmental Protection Agency (EPA) broad new areas to regulate. In September of 1984, EPA issued a Chemical Advisory on leaking underground storage tanks containing motor fuel (6).

With more stringent rules and great personal liability, companies are spending more time and money monitoring their tanks for leaks. Along with this increased awareness of tank leaks comes a vast array of new technology for identifying leaks (7). It was speculated that canine olfaction might be a reliable, cost effective means of detecting leaking vapors from an underground tank.

The methods presently used to detect leaking underground storage tanks can be broken into two general categories; external tests and in-tank tests. In-tank tests use equipment that is placed directly inside the tank or piping. The majority of these tests detect changes in the tank's liquid volume by measuring: gasoline level changes, buoyancy float changes, manometric movement, or tank pressure tests. All the volumetric tests are subject to error through factors like evaporation, condensation, temperature change of the liquid, tank shape changes, vibrations from traffic, or

level changes caused by air pockets. With methods that claim a sensitivity of 0.02-0.05 gal/hr, these factors can lead to erroneous conclusions. A system called the "Tankology" uses the acoustic triangulation of sound to detect incoming air bubbles in a vacuum sealed tank. Soils outside the tank can be drawn to the leak, blocking it and interfering with test results. A psuedo in-tank test is the tracer gas test. Its use involves filling a tank with a diffusive gas (such as helium or freon) and using a gas analyzer to detect it at the surface. The major drawback of the gas tracer test is the expense of a mass detection system.

External tank tests look for leaked fuel outside the tank. Among these tests, the most commonly used are groundwater monitoring wells, soil core analysis, and surface geophysical methods (like ground penetrating radar, electromagnetic induction and x-ray fluorescence). Wells and core analyses can be very effective methods of leak identification, but are only functional if properly placed. The analytical tests can be both time consuming and costly. The precision of surface geophysical tests may be dependent upon the amount of leaked material present in the ground.

Since vapors move faster through the ground than waterborne contaminants, vapor detection systems would appear to be yet another sensible means of detecting leaks. According to Russell and Hart (7), no vapor detection systems are at present commercially available. With the need for more de-

pendable and cost effective methods of detecting leaking tanks (and with the area of vapor detection wide open) we decided to examine the dog's ability to distinguish leaking vapors. Gasoline tanks became the target of this study. The question was not whether the dog's detection limit was keen enough (in several instances, the dog has detected gasoline/other components in the ppt range (2,5) and even the ppq (8) range, which is well below the detection range of "state-of-the-art" vapor detectors), but whether its discriminatory capabilities were sharp enough to detect leaking gasoline vapors in a background of "spilled" gasoline vapors. Similar circumstances were not a problem in the N.Y.C. experiment (3) .

Use of equipment (heavy machinery and vehicles, tools, reusable protective clothing, etc.) in the cleanup of a hazardous waste site leads to contamination of the devices. Subsequent use elsewhere may spread the contamination to the surrounding community, unless sound decontamination procedures are enforced. "State-of-the-art" methods presently used to remove surface contamination from on-site equipment include dusting, vacuuming, gritblasting, hydroblasting, steam cleaning, rinsing, and solvent washing (9,10). A formal, systematic approach for determining acceptable levels of contamination remaining on equipment surfaces (following decontamination techniques) does not currently exist. Sam-

pling methods for determining the degree of surface contamination present after cleanup are thus poorly documented, developed, and verified (9).

One technique for determining the degree of surface contamination on equipment (following use in a waste site cleanup) is the wipe (also called swipe or swab) test (9,11). It can take the form of a dry test (in the examination of radiological contamination), or with the application of a solvent (for contaminant extraction), a wet test. Though frequently used, an investigation of the present OSHA wipe sampling procedure by Chavalitnitkul and Levin (12) shows serious limitations in both accuracy and reproducibility (in defining surface contamination levels). Poor choice of solvents, insufficient application of pressure, use on a rough surface (for porous surfaces like wood or cement, a leach test (10) or chip test (11) is generally recommended), or improper storage of a sample before analysis can cause erroneous results.

The biggest problem with sampling for residual contamination is properly characterizing the equipment in question. Random sampling may completely miss small "hot spots" of contaminant, threatening the health of those later in contact with it. It can also lead to the collection of far more samples than necessary, with laboratory analysis both time consuming and very costly. A good example is the dioxin sampling plan implemented in Missouri (13). Of the

more than 10,000 samples collected, approximately 8,000 were found to be negative. Sampling strategies have been designed that statistically verify, to a desired confidence level, the cleanliness of a contaminated area (14,15). Although decreasing somewhat the randomness of sampling, the method can still lead to the collection of far too many insignificant samples.

With the need for new and improved sampling techniques for determining the effectiveness of equipment decontamination, the use of canine olfaction was examined. Training and experimentation was carried out using m-xylene and 1,1,1-trichloroethane. By having the dog screen decontaminated equipment for residual contamination (having first trained the dog on the contaminant(s)), a "select" number of samples can be obtained and analyzed in the lab. If the results of our field work are successful, the dog will provide an increased probability of locating residual contamination on hazardous waste cleanup equipment at a decreased cost.

II.

MATERIALS AND METHODS

The feasibility of using canine olfaction as a means of detecting hazardous substances was examined through two major studies:

(1) Testing the dog's ability to detect residual contamination on hazardous waste site cleanup equipment (DECON).

(2) Examining the usefulness of canine olfaction as a means of detecting "Leaking Underground Storage Tanks" (LUST).

Several tests were performed to aid in the examination of these environmental applications.

A. DECON

1. Permeation Tube Experiments

Permeation tubes were found to be a valuable training tool, and a good way of examining the acuity of a given dog's olfactory senses. Experiments were done to examine construction of permeation tubes, and to better identify the limits of their calibration and subsequent use.

Pieces of 1/4" and 1/8" O.D. teflon TFE tubing were cut with variations in tube length and wall thickness. Solid pieces of glass rod 1 cm in length were wrapped with teflon tape and inserted into one end of the tubes. To ensure a

good seal, 20 gauge copper wire was wrapped and twisted several times around the tubing overlying the glass rod. Next, the liquid compound of interest was pipetted into the tubes. Before inserting the second glass plug into the tubes, a piece of the 20 gauge wire was partially inserted into the same end of the tube (this was done to prevent a build-up of pressure above atmospheric as the plug was being pushed in). After the glass plug was in place, the wire was removed, and the end was wrapped and twisted with wire as done to the other end. Once constructed, the permeation tubes were placed in an open 600 ml beaker, and the beaker was placed in a constant temperature water bath. The tubes were periodically weighed on a Mettler balance to measure weight loss per unit time (permeation rate). Gloves were worn whenever handling the tubes (oils from the skin can affect the weight), and care was taken to keep them dry.

After constructing and running several permeation tubes, some improvements were made in the protocol. Self locking nuts with leak-proof gaskets replaced the teflon wrapped glass plugs. This provided ease in construction as well as refilling of the tubes. The air temperature inside the beaker was easily disturbed by changes in the air temperature of the room (the temperature was not being held constant). To alleviate this problem, 7/8" by 6" test tubes, having a greater surface to volume ratio (thus, more

dependent upon the bath temperature than the room air) were placed in the bath, with 1 permeation tube in each.

If a permeation tube can last for several weeks without being refilled, will its permeation rate at a given temperature be the same throughout the duration? Permeation tubes were calibrated, and allowed to stand for eight weeks. They were then re-examined at the same temperature to see just how reliable initial calibration values were.

When a permeation tube becomes empty, can it simply be refilled by the trainer without recalibration? After calibrating 4 permeation tubes, they were emptied, refilled, and recalibrated at the same temperature.

A calibration curve of permeation rate vs. temperature for a given permeation tube would provide the trainer with a more accurate idea of the dog's capabilities, given the air temperature. Could a general curve be attained, and if so, would it be the same for any compound? To examine these questions, four 1/8" O.D. teflon TFE permeation tubes, all 7 cm. in length were constructed. M-xylene, toluene, benzene, and ethylbenzene (four common solvents) were each pipetted into a separate tube. Permeation rate was calculated using the "weight loss method" at 25, 36, 41, and 50°C. Permeation rates were low enough so that refilling of the tubes throughout the experiment was not needed.

Finally, a test was done to see if the permeation tubes could be calibrated using a gas chromatograph. A Varian

3700 Gas Chromatograph with a 0.30 mm I.D. methyl silicone capillary column and a Flame Ionization Detector (FID) was used. A piece of glassware with an inlet, outlet, and a gastight lid was used to contain the permeating tube. Nitrogen carrier gas was allowed to flow through the glass permeation tube container and exit (carrying with it vapors emitted by the permeation tube) into a 6 port gas sampling valve mounted on the GC. Once in the valve, the gas mixture flows through a 2 ml volumetric loop, and exits into the atmosphere. The system was initially allowed 10-15 minutes to reach equilibrium. The valve was then switched, to redirect the 2 ml sample to a cryogenic focusing trap (cryospot) located just outside the G.C. oven. Five minutes elapsed before the complete sample reached the cryospot. The sample was then passed on to the FID for area detection by a computer integrated software program. The system is depicted in Figure 1 (see APPENDIX 1. for all Figures).

In order to correlate integrated peak area to gas concentration (and ultimately permeation rate), 2 gas standards were run a series of times through the volumetric loop (they were sent directly into the 6 port valve, bypassing the glass permeation tube container apparatus). The FID is a linear detector. Considering response factors, and using the 9.12 ppm benzene standard as the basis of 1 (or 6/6 carbon atoms), sample concentrations sent through the loop can be calculated. Once permeation tube concentrations are cal-

culated, their permeation rates can be determined using the equation:

$$P = \frac{F C}{K_m}$$

where: P=permeation rate in ng/min
F=N₂ flow rate in cc/min
C=concentration in ppm
K_m=the molar constant

(K_m=24.46/mol.wt., where 24.46 is the molar volume in liters at 25°C and 760 mmHg)

This experimental procedure was performed on several of the permeation tubes previously calibrated using the weight loss method.

2. Field Study Experiments

To further examine the feasibility of using canine olfaction as a means of identifying/differentiating low levels of various toxic chemicals, a decontamination field study was performed. A dog had been previously trained to detect low level emissions of m-xylene. After the placement of a m-xylene/mud mixture on various portions of some waste site cleanup equipment, the dog's ability to identify the contaminated mudspots was observed and quantified.

Design of a method to consistently reproduce a low emitting level of m-xylene mud in the lab was not possible. M-xylene is only slightly soluble in H₂O . If another sol-

vent was used, its emitting vapors might interfere with the experiment. Subsequently, 1-3 drops of m-xylene were added to 50 ml of distilled water and thoroughly shaken. Various concentrations of contaminated mud could be produced by pouring or pipetting 1.8 ml of the m-xylene solution onto 5 grams of alumina powder (an inert substrate chosen to represent mud) and mixing to a paste.

Permission was obtained to use a front end loader at a construction site in Morris Plains, New Jersey. Prior to the dog's arrival, a xylene-contaminated mud spot and 2 blanks (5 gm alumina powder plus 1.8 ml distilled H₂O) were made. Glass stirring rods were used to mix the materials on weighing paper until a homogeneous paste was attained. The contaminated and control muds were placed in chosen areas of the backhoe by pressing on the weighing paper (mudspots down) and drawing it slowly across the location. Latex gloves were worn at all times, to avoid transmission of human scent to the samples. To aid in emissions analysis, the spots were no more than 7 cm in diameter. The air temperature, wind direction, velocity, and relative humidity were recorded. The experiment was repeated 3 times, with 3 different m-xylene contaminated mudspots (see Figure 2).

After the dog identified each spot (or after it attempted to), air samples were collected to determine the mudspot m-xylene emission rates. This was done using air sampling pumps. Teflon funnels (7 cm in diameter) were

placed directly over the mudspots, and air was drawn up through polyphenylene oxide (Tenax G.C.) traps at a known flow rate for 10 minutes. The adsorbant traps were then capped and placed in sealed glass canisters. Background samples of air were also collected in close proximity to the backhoe.

In a second set of experiments at another location, two xylene-contaminated alumina muds and a blank water/alumina mud were made following the procedure described earlier. Five shovels were scattered on a 150 ft² snow covered lawn, and the 3 mud spots were placed on 3 of the shovels (see Fig. 3). The air temperature, wind direction, velocity and relative humidity were recorded. The dog was then asked to search the area for contamination. After identifying each spot (or attempting to) air samples were collected using the procedure discussed in the backhoe experiment.

The Tenax traps were then returned to the laboratory for quantitation. A VARIAN 3700 G.C. with a methyl silicone capillary column and an FID detector were connected to a Tekmar 5000 auto-desorber. The traps were uncapped and placed in the Tekmar tube furnace. The Tekmar desorbed the trap sample, and sent it to the G.C. for FID area detection. This procedure was performed on each trap. The instrument was again calibrated using the 9.12 ppm Benzene standard, and emission rates of the mud samples were calculated (see Results section for details).

B. LEAKING UNDERGROUND STORAGE TANKS

Tests were done to see if vapors rising from a leak might be different from fresh or old surface-spilled gasoline. If significant differences did exist, the dog could possibly be trained to differentiate, and thus identify leaks at a gasoline station. For all gasoline experiments, a sample of Exxon regular unleaded gasoline was used.

1. Changes in Gasoline

The first experiment was performed to see if water-extracted gasoline emitted a different vapor fingerprint than the original gasoline. 10 ml of gasoline were added to 80 ml of distilled water in a 125 ml separatory funnel. The funnel was agitated by hand for 2 minutes, and the water discarded after reseparation. The gasoline sample was washed 4 more times with fresh distilled water, and 0.5 ml of the gasoline layer was then put in a 1.5 ml septum capped vial. After allowing 15-20 minutes for the vial headspace to equilibrate, an 8 μ l aliquot of the headspace was removed with a 10 μ l gastight syringe, and injected into the gas chromatograph. Five minutes were allowed for the He carrier gas to carry the sample to the cryospot, at which time it was passed to the column for subsequent FID detection. The column temperature program was:

Initial temperature: 10° C
Hold time: 5 min.
Ramp: 15° C/min.
Final temperature: 190° C

A 0.5 ml portion of the water used to extract the gasoline was placed in a 1.5 ml vial, and treated and analyzed in a similar manner. The same was done with a 0.5 ml sample of unwashed gasoline.

To see if significant changes occurred when gasoline was exposed to the open atmosphere for an extended amount of time, a 0.5 ml portion of gasoline was placed in an open vial and allowed to stand for 24 hrs. A septum cap was then placed on the vial, and the above procedure for evaluating the headspace was carried out. Chromatograms and integration areas obtained from all four vials were compared to identify any changes which may have occurred. Certain peaks were identified using a gas chromatograph/mass spectrometer.

2. Leaking Tank Simulation Test

When gasoline leaks from an underground tank, it must permeate through a soil medium before escaping to the atmosphere. To simulate this condition in the lab, soil columns were constructed.

Glass tubing, 76.2 cm in length with a 5 cm I.D. bore, was mounted vertically in a column stand. With screening

held beneath, 1200 cm³ of potting soil was poured into each column. Next, 1.0 liter of distilled water was poured into the tubes to saturate the soil. Teflon caps with latex liners were then placed on the column bottoms. Protruding from the cap was a piece of 1.3 cm threaded tubing with a septum nut screwed on the end. Similar caps were placed on the column tops, without the septa nuts. A 300 cm³ headspace above the soil allowed air samples to be collected for G.C. analysis.

30 ml of gasoline were injected into the bottom of the soil column. A light vacuum was applied to the column tops for 5 sec. to stimulate vapor movement. 32 μ l of headspace air was collected periodically and examined by G.C. (using the program and protocol mentioned in part 1.). The vapor profile was compared with those attained through the previously mentioned experiments.

3. Training Tools

In an attempt to train the dogs to differentiate and identify washed and unwashed gasoline, samples were presented to the dog through 35 mm film canisters. Perforations in the canister caps allowed the emission of gasoline vapors from the 1-2 drops placed on cotton inside the canisters. To date, the dogs have not been able to differentiate washed and unwashed gasoline when presented in this manner. The question was raised as to how representative the film

canister emissions were (over extended periods of time) of the washed and unwashed gasoline samples.

To test this, emissions from the film canisters were periodically examined by G.C.. A film canister was half filled with cotton, and 2 drops of gasoline were placed on it. The lid was perforated several times with a knife and placed on the canister. After allowing 10 minutes for the canister to equilibrate, an 8 μ l. gas sample was removed from within the canister with a syringe and injected into the G.C. The G.C. procedure used was similar to that stated in the previous gasoline experiment. Sampling was done 3 times over a period of one hour, and the resulting chromatograms were compared. For statistical justification, the complete experiment was performed 3 times.

A training tool that may emit a more representative fingerprint of washed/unwashed gasoline samples is the diffusion tube. The diffusion tube consists of a 1.5 ml septum capped vial with a 26 gauge hypodermic needle inserted in the top to allow emission. To test this, 0.5 ml of fresh gasoline were placed in the diffusion tube. The vial cap was replaced, the needle was inserted, and the assembly was allowed to equilibrate for 10 minutes. Next, 8 μ l of head-space was removed with a hypodermic needle and injected into the G.C. The G.C. procedure used was similar to that stated in the previous gasoline experiment. Samples were taken 3 times over a period of one hour, and the resulting

chromatograms were compared. The same experimental procedure was performed on a diffusion tube containing a small piece of cotton and 2 drops of gasoline.

C. CANINE SAFETY

Care must be taken to assure canine safety while it is working with hazardous compounds. The dog's exposure to m-xylene and 1,1,1-trichloroethane was measured with a dosimeter, which was attached to the dog's collar during training and field work. The badge was dismantled at the end of the canine olfaction project, and the adsorbent (Anasorb CA) was placed in a clean, empty trap. Auto-desorption of the trap sample, followed by G.C. detection provided quantitative analysis of the dog's exposure to m-xylene and 1,1,1-trichloroethane.

III.

RESULTS AND DISCUSSION

A. DECON

1. Permeation Tube Experiments

Emission rates from the permeation tubes were very consistent. In each instance, emission rate was calculated using linear regression of weight vs. time. Generally, the first few points deviated from the straight line. This occurred because the tubes had not yet reached a steady state condition (16). These points were discarded. Data acceptance was based on the weight loss vs. time correlation and % uncertainty. Results were rejected if the correlation was < 0.99 . Two examples are given in Figure 4.

The results calculated on permeation tube length vs. emission rate (Table 1) were unexpectedly erratic. Virtually no relationship was seen between tube length and emission rate, with correlation coefficients of:

	<u>TUBES</u>	<u>CORR. COEFF.</u>
(1)	m-xylene tube #1 (above):	- 0.649
(2)	m-xylene tube #2:	- 0.394
(3)	1,1,1-trichloroethane tube:	- 0.228

Previous work done on teflon permeation devices identified a direct relationship between tube length and permeation rate (16,17). In explanation of our results, we feel our permea-

tion tube design allows permeation through the end caps due to variations in cap tightness. Micro-variations in wall thickness of the teflon tubing used were also noted. Since the tubes were reliable sources of vapor after calibration, the lack of correlation of emission with length was not seen to be a problem.

Table 1.
Emission rate of m-xylene and 1,1,1-trichloroethane from permeation tubes of varying lengths and calibers.

COMPOUND	TUBE SPECIFICATIONS (cm)	TUBE LENGTH (cm)	PERMEATION RATE ($\mu\text{g}/\text{min}$) at 25°C
m-xylene	(a) 0.635	5.6	106.0
		6.7	5.5
		7.9	53.0
		8.7	10.9
m-xylene	(b) 0.089	4.6	10.1
		5.2	191.0
		9.1	4.3
		10.2	43.4
1,1,1-tri-chloroethane	(a) 0.318	4.0	2.8
		6.0	2.2
		8.0	5.6
		10.0	0.4

(a) - outside diameter (O.D.)

(b) - wall thickness

The emission rate of four 1/8" O.D. permeation tubes over an eight week period appears in Table 2. The permeation rate remained consistent for both compounds at 25°C and 35°C. At least for m-xylene and 1,1,1-trichloroethane, the

trainer should be able to use low emitting teflon TFE filled permeation tubes for several weeks and be confident that the permeation rate will not change.

Table 2.
Permeation tube calibration and recalibration over an 8 week time interval.

COMPOUND	TEMP (° C)	PERMEATION RATE INITIAL (µg/min)	PERMEATION RATE FINAL (µg/min)
m-xylene	25	0.47	0.32
m-xylene	35	0.27	0.21
1,1,1-tri- chloroethane	25	0.06	0.08
1,1,1-tri- chloroethane	35	0.30	0.31

Permeation rates also remained somewhat consistent for 1/4" tubes that were uncapped and refilled with the same compound (Table 3). If the trainer is only concerned with the gross permeation rate of a given tube (the order of magnitude which is being emitted), then reuse of an empty tube will simply involve refilling the tube with the chemical that it was calibrated for. Care must be taken to tightly replace the end caps (possibly even using pliers for a few turns). This is both a time and cost saver when training the dogs, using tubes of this design. If a quantitative

study is underway to measure the dog's capabilities, then recalibration is recommended.

Table 3.
Emission rates of permeation tubes before and after cap removal and refill.

COMPOUND	TEMPERATURE (° C)	PERM. RATE INITIAL (µg/min)	PERM. RATE REFILL (µg/min)
m-xylene	25	23.6	5.3
m-xylene	35	45.9	104.8
1,1,1-tri chloroethane	25	33.8	35.4
1,1,1-tri- chloroethane	35	73.6	109.8

To provide information on the effects of temperature on the permeation rate of our tubes, data were collected on emission rates at four temperatures (Table 4). Past work done on permeation devices cited a direct relationship between temperature and permeation rate (sensitive to changes as small as 0.1 °C). As can be seen with all four compounds, a temperature increase resulted in a permeation rate increase. In general, the lower the boiling point of the compound examined, the greater the permeation range over the temperature span examined. To examine the relationship between permeation rate and temperature, the data from Table 4 were plotted (see Figure 5). With such a graph at the

trainer's disposal, quantitation of the dog's detection can be quickly and accurately attained, given the temperature.

Table 4.
Permeation rate of 4 compounds at 4 different temperatures calculated by Weight/Time.

COMPOUND	BOILING PT. (° C)	EMISSION RATE (µg/min)			
		25° C	36° C	41° C	50° C
m-xylene	138.8	0.13	0.22	0.23	0.50
ethylbenzene	136.2	0.14	0.17	0.23	0.56
toluene	110.7	* 0.89	0.51	0.59	1.31
benzene	80.1	0.31	0.55	0.74	1.55

* tube spent a period of time submerged in ethylene glycol

Finally, tests were run to see if permeation tubes could be quickly calibrated using the G.C. The G.C. was calibrated against the benzene standard six times to attain an average peak area. The concentrations of compounds were calculated from the peak area and response factor. Response factors were based strictly on the number of carbon atoms in the compound of interest. The results of the G.C. tube calibration method are shown in Table 5, along with the values by weight loss/time.

Table 5.

Comparison of permeation rate for 4 tubes using the G.C. apparatus and the Weight loss method at 25°C.

COMPOUND	PERMEATION RATE ($\mu\text{g}/\text{min}$)	
	G.C. METHOD	WEIGHT LOSS METHOD
m-xylene	0.12	0.13
ethylbenzene	0.13	0.14
toluene	0.43	0.89
benzene	0.28	0.31

Values were formulated in the following manner:

(For m-xylene permeation tube)

$$\text{Average peak area} = 4126.4$$

$$\text{Response factor} = 6/8 = 0.75$$

$$\text{Mol. wt.} = 106.17$$

$$K_m = 24.46/106.17 = 0.2304$$

(1) Calculating concentration (ppm)

$$4126.4(.75) = 3094.8$$

$$23816.3/9.12 = 3094.8/X$$

$$X = 1.19\text{ppm}$$

(2) Calculating permeation rate

$$P = FC/K_m = 28(1.19)/.2304$$

$$P = 144.6 \text{ ng/min} = 0.145 \mu\text{g/min}$$

The emission rates attained by the two methods were almost identical. It was noted in Table 4. that complications occurred with the weight loss experiment for toluene. The value produced with the G.C. method fits the toluene plot (Figure 5d) more precisely. When permeation tubes are being calibrated in the laboratory, the G.C. provides quick and accurate quantitation.

2. Field Study Experiments

a. Backhoe site

The ability and persistence of the dog to locate the alumina-contaminated mud spots was very impressive. Initial data was collected at the site:

Air temperature (dry)	:	1° C
Air temperature (wet)	:	-3° C
Wind velocity	:	0-400 ft/min (gusty)
Wind direction	:	from northwest

Trial 1 involved the dog's attempt to identify contamination mudspot #1 (#2 and #3 blanks were already on the backhoe; see Figure 2), located on the underside of the beam supporting the shovel. The dog was able to localize the odor, but never actually identified the spot. Upwind of this spot on the backhoe was a diesel leak. High concentrations of diesel vapor (rich in xylene) were thought to have greatly complicated the dog's task at this spot. It is possible that the mudspot was emitting at a rate that was lower than background. Also, because of the spot location, the dog could not physically pass downwind of the sample, nor could he pass his nose over it easily. An air sample was collected from the mudspot to determine its emission level.

In the second trial, contaminated mudspot #4 was placed in a lower frame member of the backhoe. Within 3 minutes of intense searching, the dog identified and pawed the sample out of the crevice. Collection of an emission air sample was not possible, because the dog had removed the spot.

Mudspot #5 was placed on the rear of the left backhoe track. When the dog was 1.5-2.0 ft downwind of the contaminant, he immediately picked up on the scent, and followed it to its source (see Figure 6). An air sample was collected immediately afterward. A background sample was collected approximately 1 ft downwind from the left tread of the backhoe.

In between placement of samples, as the dog was awaiting the command to search the backhoe, he showed (without a command to do so) an interest in the vicinity of the research assistant's car. Soon afterwards, Ramos was showing signs of a "find" on the front bumper; a spot where a contaminated mudspot had been placed the night before as a trial run for the air sampling equipment. An air sample was collected from the bumper (none of the mudspot was remaining on the car, only a stain where it had been before being wiped off 19.7 hrs. before!).

The results of the air samples are found in Table 6. Emission rates in Table 6 were arrived at in the following manner:

-- using the background sample as an example--

- (1) Benzene Standard (data)
 - 9.12 ppm
 - 2.0 ml. sample
 - Average peak area = 2381.6
 - Sample loop temperature = 150°C

--- No. of moles of gas (n_g) :

$$n_g = \frac{PV}{RT} = \frac{(1 \text{ atm})(0.002 \text{ L})}{(0.08206 \text{ atm/mol}^\circ\text{K})(423^\circ\text{K})}$$

$$n_g = 5.76 \times 10^{-5} \text{ moles gas injected}$$

--- No. of moles of Benzene in 2.0 ml loop (n_B) :

$$n_B = 5.76 \times 10^{-5} \frac{(9.12 \text{ moles Benzene})}{(1 \times 10^6 \text{ moles gas})}$$

$$n_B = 5.25 \times 10^{-10} \text{ moles Benzene}$$

(2) Background sample (data)

-Collected air volume : 720 ml
-Peak area : 206

--- Calculation of moles m-xylene (n_x) :

$$n_x = \frac{(5.25 \times 10^{-10})}{(2381.6)} (206) \frac{(0.75 \text{ moles m-xylene})}{(1 \text{ mole Benzene})}$$

$$n_x = 3.41 \times 10^{-12} \text{ moles m-xylene}$$

--- Emission rate (R) :

$$R = \frac{(106 \text{ g m-xylene})}{(1 \text{ mole})} \frac{(3.4 \times 10^{-12} \text{ moles})}{(10 \text{ min})} \frac{(10^9 \text{ ng})}{(1 \text{ g})}$$

$$\boxed{R = 0.36 \text{ ng/min}}$$

Again, it should be noted that the backhoe had a significant diesel fuel leak. Subsequent G.C. analysis of the fuel identified xylene in it. The ability of the dog to identify localized (but very low) levels of m-xylene in a background of m-xylene and other odorous compounds greatly reinforces its qualifications and value.

Table 6.
Backhoe experiment air samples.

SAMPLE	EMISSION RATE (ng/min)
background	0.36
* #1	1.12
#2 (blank)	0.0
#3 (blank)	0.0
#4	Lost (dog pawed)
#5	0.77
car bumper	16.32

* sampling funnel contaminated with mud, causing high results

b. Shovel site

Five shovels were randomly positioned on a 150 ft² snow covered lawn. Using the mudspot placement technique mentioned earlier in the backhoe study, two m-xylene contaminated mudspots (#6 and #7) and a blank mudspot (#8) were placed on the shovels (see Figure 3). Background data were collected at the site.

Air temperature (dry) : 5°C
 Air temperature (wet) : 2°C
 Wind velocity : 0-50 ft/min
 Wind direction : variable

After scouting the perimeter of the yard for a minute, Ramos was directed in towards the shovels. Without hesitation, a scent was picked up about 1 ft from mudspot #6, and

Ramos quickly homed in on and identified the contamination (see Figure 7). The shovel was immediately removed from the site, and an air sample was collected from the mudspot.

After examining each remaining shovel without a find, Ramos was commanded to look at each shovel more thoroughly. Upon close investigation of the other contaminated shovel, mudspot # 7 was identified. As in the backhoe study, the blank mudspot was completely ignored by the dog. Results of the emission rates of each mudspot are seen in TABLE 7.

Table 7.
Shovel experiment air samples.

SAMPLE	EMISSION RATE (ng/min)
#6	3.83
#7	0.19
blank	0.0
background	0.0

Sample #7, which was the most difficult contaminated mudspot for Ramos to identify, was also the lowest emitting mudspot made for either experiment. The m-xylene level was even lower than the background sample collected at the backhoe site! Everyone witnessing these experiments was con-

vinced that canine olfaction bears remarkable capacities for location of hazardous substances.

B. LEAKING UNDERGROUND STORAGE TANKS

1. Changes in Gasoline

a. Washed vs. unwashed

The headspace chromatograms attained from 0.5 ml of washed and unwashed gasoline, as well as a 0.5 ml aliquot of used water are displayed in Figure 8. As seen in Figure 8c, many of the gasoline compounds were solubilized into the water phase upon gentle agitation. Comparing 8a to 8b, many of the lighter compounds solubilized, creating a significant difference in the earlier eluting peaks in both chromatograms. The areas of various chosen peaks were directly compared to better quantify the changes that occurred (see Table 8). Certain general trends are observed. A decrease in the vapor concentration of the more volatile compounds occurs while an increase in the vapor concentration of the heavier compounds exists. When the gasoline was washed, similar results were attained by W. Emile Coleman and her associates (18).

Table 8.
Chosen peaks from the washed/unwashed/aged
gasoline samples.

PEAK	RETENTION TIME (sec.)	INTEGRATED GASOLINE PEAK AREA		
		(unwashed) area/%mass	(washed) area/%mass	(aged) area/%mass
(a)	189	34164/3.18	1132/0.19	* N.D.
(b)	228	28158/2.62	5525/0.91	N.D.
(c)	304	8477/0.79	3639/0.60	N.D.
(d)	348	17254/1.60	18081/2.97	1456/2.42
(e)	448 (benzene)	6068/0.56	6130/1.01	2348/3.90
(f)	482	4856/0.45	6612/1.09	4916/8.17
(g)	495	2611/0.24	3687/0.61	3256/5.41
(h)	608 (toluene)	4181/0.39	5993/0.98	7579/12.60
(i)	743 (m-xylene)	1129/0.10	1998/0.33	3291/5.47
(j)	855	209/0.02	332/0.05	651/1.08

* N.D. (Not Detected)

In explanation, it is noted that a definite composition of vapor corresponds to each composition of solution. Raoult's law states that the vapor pressure (of which vapor concentration is a function) of a solution at a particular temperature is equal to the mole fraction of the solvent in the liquid phase multiplied by the vapor pressure of the pure solvent at the same temperature. Looking again at Figure 8c, we note from the water extract headspace that water

solubilizes and thus removes a large portion of many gasoline compounds upon mixing (note that this was the headspace of a 0.5 ml aliquot from 400 ml of H₂O). Since the compound headspace concentration depends upon the mole fraction of each compound in the aqueous gasoline solution, changes in compound concentration of the gasoline yield changes in the vapor profile. Further examining the trend seen in Figure 8, the loss of many of the more volatile compounds to water (and to the air during the washing process) caused an increase in the mole fraction of many of the heavier compounds. This, in turn caused an increase in their headspace concentrations.

Another cause of the apparent increase in the vapor concentrations of the heavier compounds when exposed to water could be related to their respective activity coefficients. Smith, Bomberger and Haynes (19) noted that some low solubility, high molecular weight compounds volatilize at an appreciable rate due to high activity coefficients in aqueous solutions.

There is indeed a difference in the vapor emissions from washed and unwashed gasoline. The question that remains to be answered is, 'Can the dog distinguish between the two?'

b. Fresh vs. aged

A rather unavoidable complication with the dog's pursuit of a gasoline leak is the background emission of spilled gasoline. To attack this problem, a gasoline sample was allowed to age for 24 hours at 25°C, and the headspace was then examined (Figure 9). Comparing 9a to 9b, many of the more volatile compounds have completely (or nearly) disappeared from the gasoline sample. Evaporation has been noted to greatly modify the fraction of lower molecular weight compounds in petroleum mixtures (20). Highly volatile components have high air-oil partition coefficients. This results in very low air and liquid resistance, and thus relatively quick evaporation. As explained in the previous section, this effect produced higher concentrations of the heavier compounds in the headspace sample (compare the peak areas in Table 8).

Comparing the previous two experiments, the washing and weathering process seem to have the same general effect on gasoline. Depending upon the degree of washing, or time of exposure to the air, the vapors emitted from gasoline could have an infinite number of vapor profiles.

2. Leaking Tank Simulation Test

The column experiment was expected to produce results similar to those of washed gasoline. The results obtained can be summed up by examining the chromatogram in Figure 10

(experimental design does not allow quantitative comparisons between chromatograms, only qualitative). Unlike washed and aged gasoline, the lighter (more volatile) compounds seem to predominate the vapor profile of soil permeated gasoline emissions. Unlike fresh gasoline, there is a marked decrease in relative amounts of the heavier compounds. Examination of the column headspace at 24 and 48 hr. intervals following initial sample collection gave similar results.

If the laboratory apparatus is a good representation of an actual tank leak, then lab results point to a new training procedure. Rather than asking the dog to distinguish between washed and unwashed gasoline, training should be done to enhance the dog's response to lighter end gasoline distillates and to teach him to ignore aged gasoline.

3. Training Tools

Film canisters were sampled periodically for one hour. Using unwashed gasoline as an example, chromatograms taken over a one hour duration are represented in Figure 11. Significant changes occurred in the gasoline fingerprint. Similar results were seen in all three trials of both washed and unwashed gasoline. With only 2 drops of gasoline, and a relatively fast rate of effusion from the container (many large holes in the cap), the more volatile compounds became depleted very quickly in the sample.

During training, an assumption was made that a consistent fingerprint (representative of the original gasoline sample) was being emitted from the film canister. Any differences existing in the samples (washed and unwashed) were thought to be strictly from washing the gasoline. The experiment shows this not to be the case. With a constantly changing vapor being emitted from each film canister, there is no way of knowing what the dog was being asked to distinguish! Taking into account the previous discussion on similarities between aged and washed gasoline, there may have been no significant differences between the washed/unwashed samples by the time the dog reached them.

In search of a better tool for presenting specific gasoline to the dog, diffusion tubes were constructed. The major modification over the film canisters was the greatly decreased effusion rate of vapors from the container. Chromatograms from a 2 hr. span are represented in Figure 12. The diffusion tubes emit consistent vapor profiles. Two hr after constructing the diffusion tube, the vapor profile was still representative of the original gasoline sample. With the use of diffusion tubes as a training and testing tool, washed, unwashed or other gasoline samples may be more readily differentiated by the dog.

C. CANINE SAFETY

M-xylene and 1,1,1-trichloroethane were undetectable in the adsorbant of the dog's dosimeter. Continued emphasis should be placed on the dog's safety when exposure to hazardous chemicals is eminent.

IV.

CONCLUSIONS

Investigation of the techniques available for hazardous waste detection shows much room for improvement. Besides upgrading old technologies, there is always a need for new and innovative approaches to problem solving. Canine olfaction has gained wide acceptance as the "method-of-choice" in the detection work of several disciplines. The method has appeal in the detection of hazardous substances.

Canine olfaction is a very useful technique for residual contamination screening. While a site is being cleaned up, plenty of time exists for training a dog on the compound(s) of interest. After decontaminating the equipment used in the cleanup of hazardous wastes, a trained dog can search for contaminants that were not adequately removed. This would ensure that a much smaller, select number of samples were obtained and analyzed in the laboratory for "cleanliness" confirmation. The primary advantages are cost savings and greater reassurance that the equipment is clean (as mentioned earlier, random sampling with tests like the wipe test has its problems). Their use in this area could also be extended to the evaluation of soil/water samples collected to confirm that waste site remediation was effective. Like screening the luggage and packages on an

airport conveyor belt for bombs or drugs, dogs could also be used to screen samples for residual contamination before they are sent to the lab. This way, expensive laboratory time is not wasted on unnecessary samples.

The ability of the dog to discriminate vapors emitted from underground gasoline needs further study. Tests should be performed with diffusion tubes to see if the canine olfactory system can distinguish between aged gasoline (representative of spilled gas), and a fractionally distilled portion of the lower boiling point components (representative of vapors coming from an underground leak). Even if the results of such tests are positive, variations in gasoline mixtures, the weather, and ground composition may make this an extremely difficult task for the dog and the trainer. Two other possible routes of detecting leaking underground gasoline tanks might be:

- (1) Place a marker compound (such as the butyl mercaptan in natural gas lines) directly into the gasoline, and train the dog for the detection of these vapors.

- (2) Fill the tank with a diffusive gas like freon, and train the dog to detect its presence (recall that the dog's ability to detect freon emitted from a ground source has already been documented). Unlike the "gas tracer test" currently used for detecting leaking underground gasoline tanks, the detection system (dog) is relatively inexpensive.

It also provides greater sensitivity than currently utilized detection systems.

Canine olfaction has the capacity to be a cost and time effective tool in the identification of pollutants in the environment. All that remains now is for someone to put these innate talents to use.

APPENDIX 1.

LIST OF FIGURES

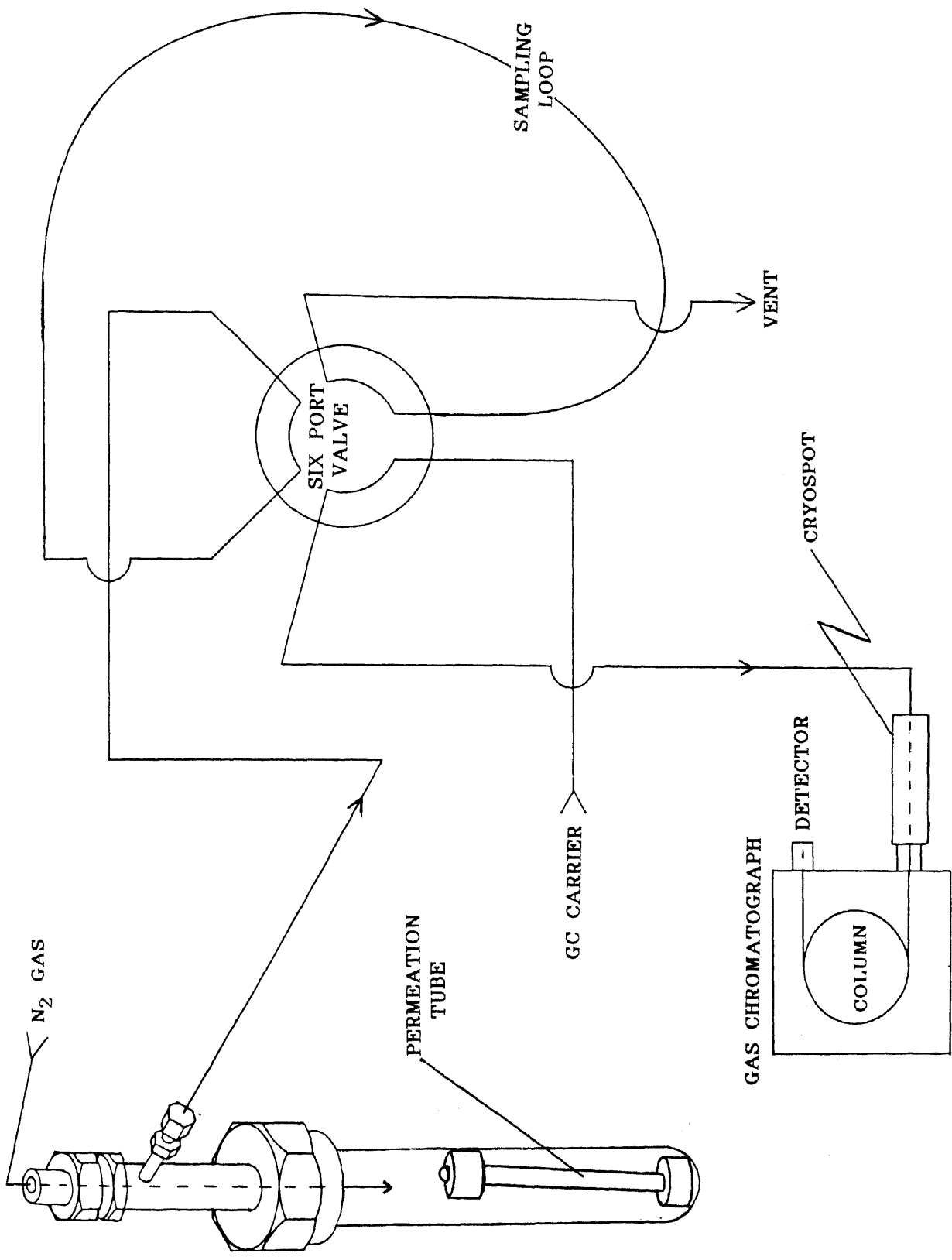


Figure 1. Apparatus for chromatographic determination of permeation tube emission rate.

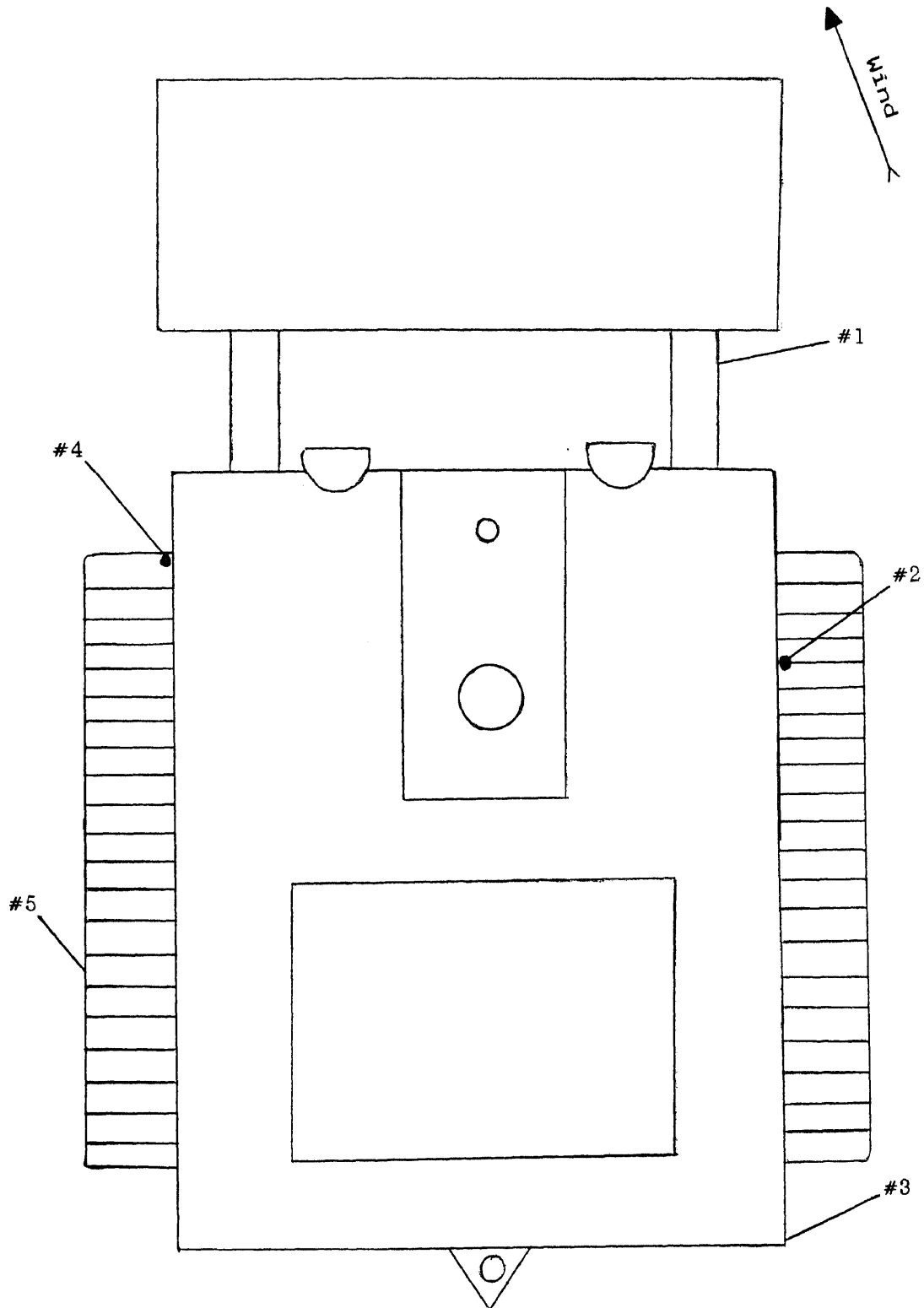


Figure 2. The xylene-contaminated backhoe site.

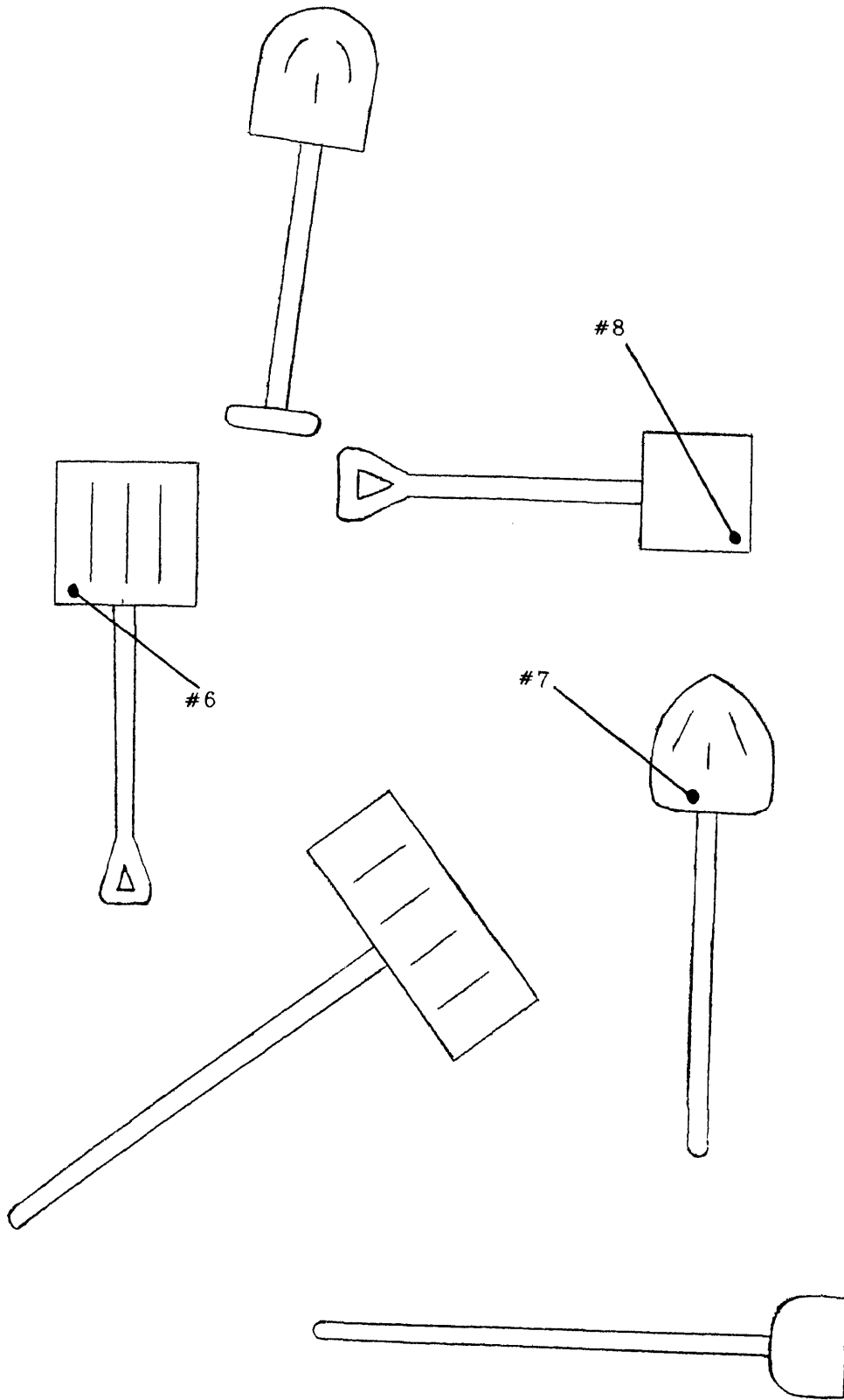
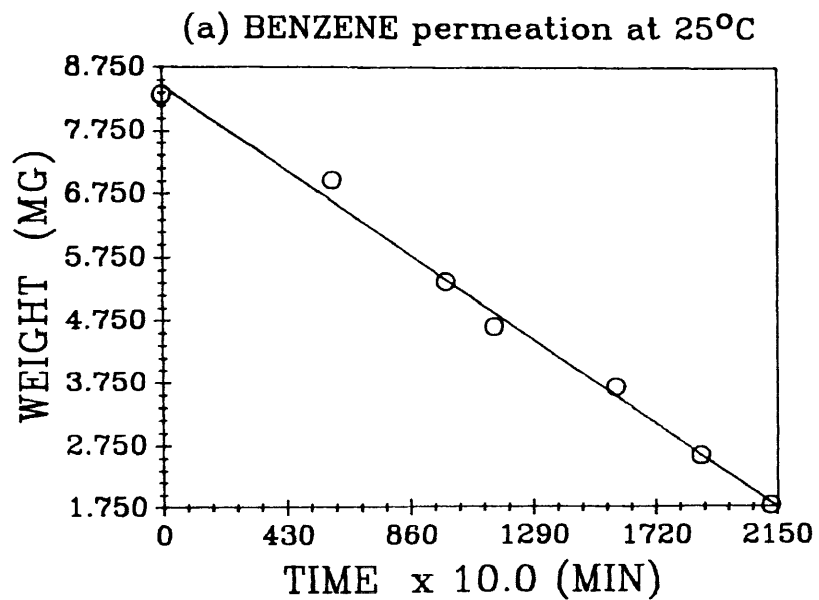
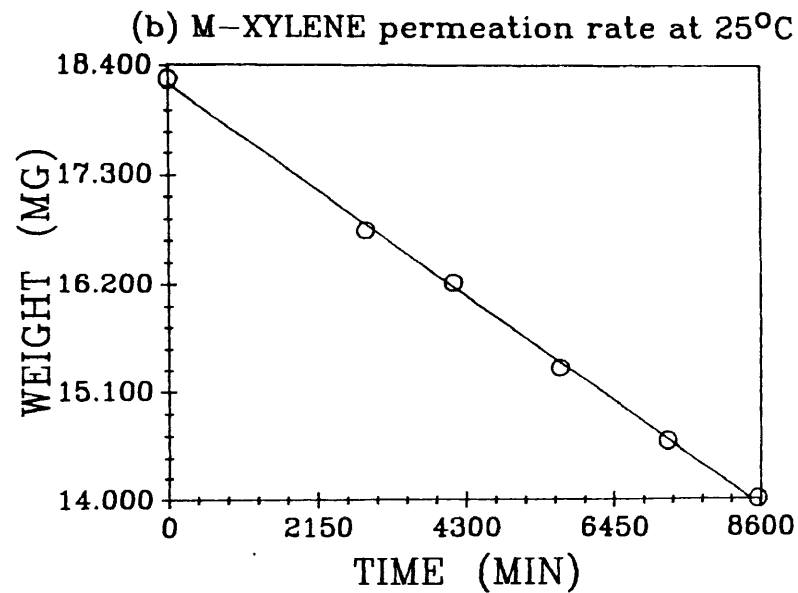


Figure 3. The xylene-contaminated shovel site.



Slope = $-3.125724\text{E-}04$ +/- $1.107144\text{E-}05$
 Intercept = 8.471351 +/- $.2018085$
 Correlation = $.9968778$



Slope = $-4.990334\text{E-}04$ +/- $8.778646\text{E-}06$
 Intercept = 18.225 +/- $6.086402\text{E-}02$
 Correlation = $.9993812$

Figure 4. Two accepted permeation plots, (a) benzene, (b) xylene.

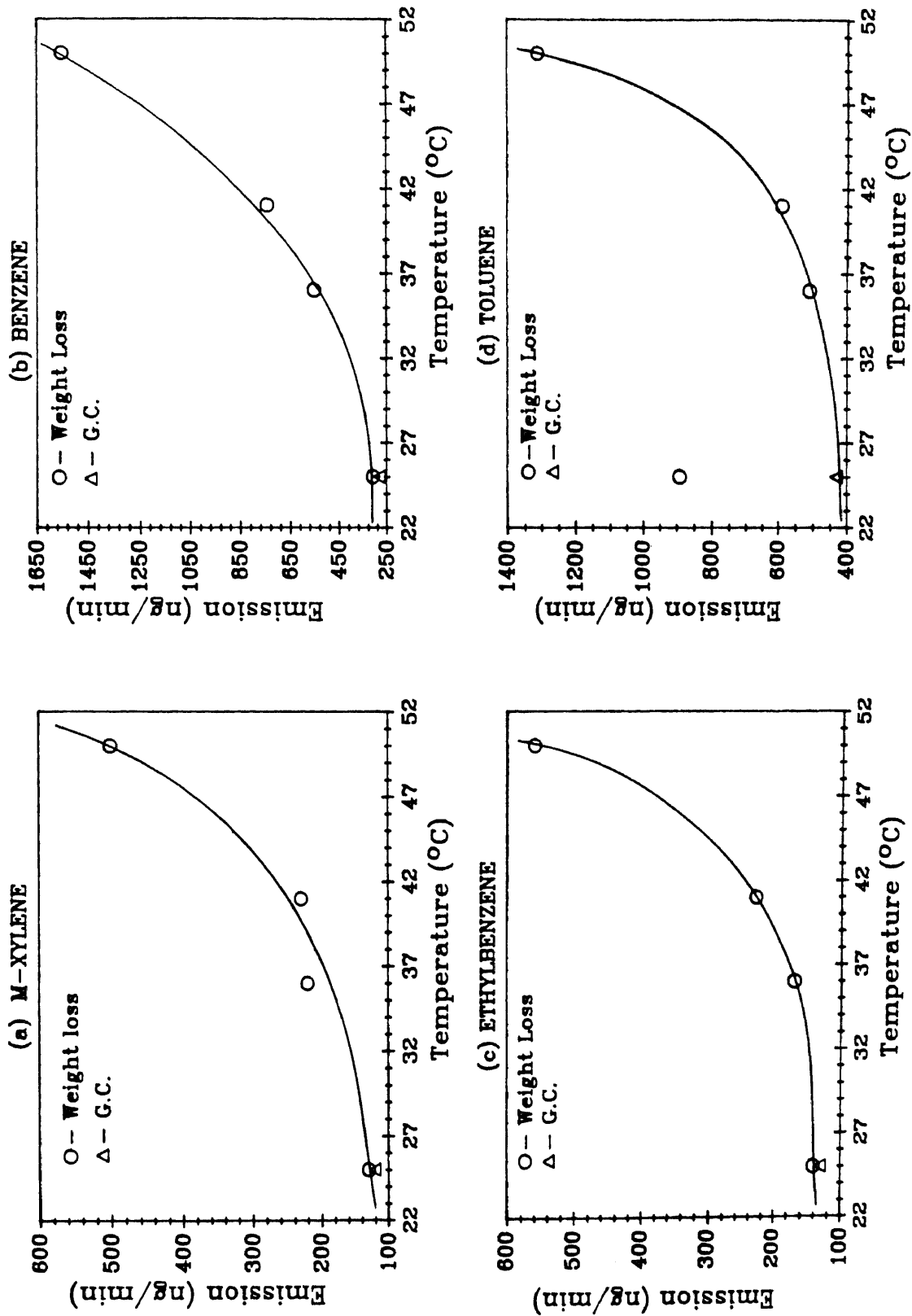


Figure 5. Permeation Rate vs. Temperature curves for 4 compounds.



Figure 6. Ramos identifying contaminated mudspot #5.



Figure 7. Ramos identifying contaminated mudspot #6.

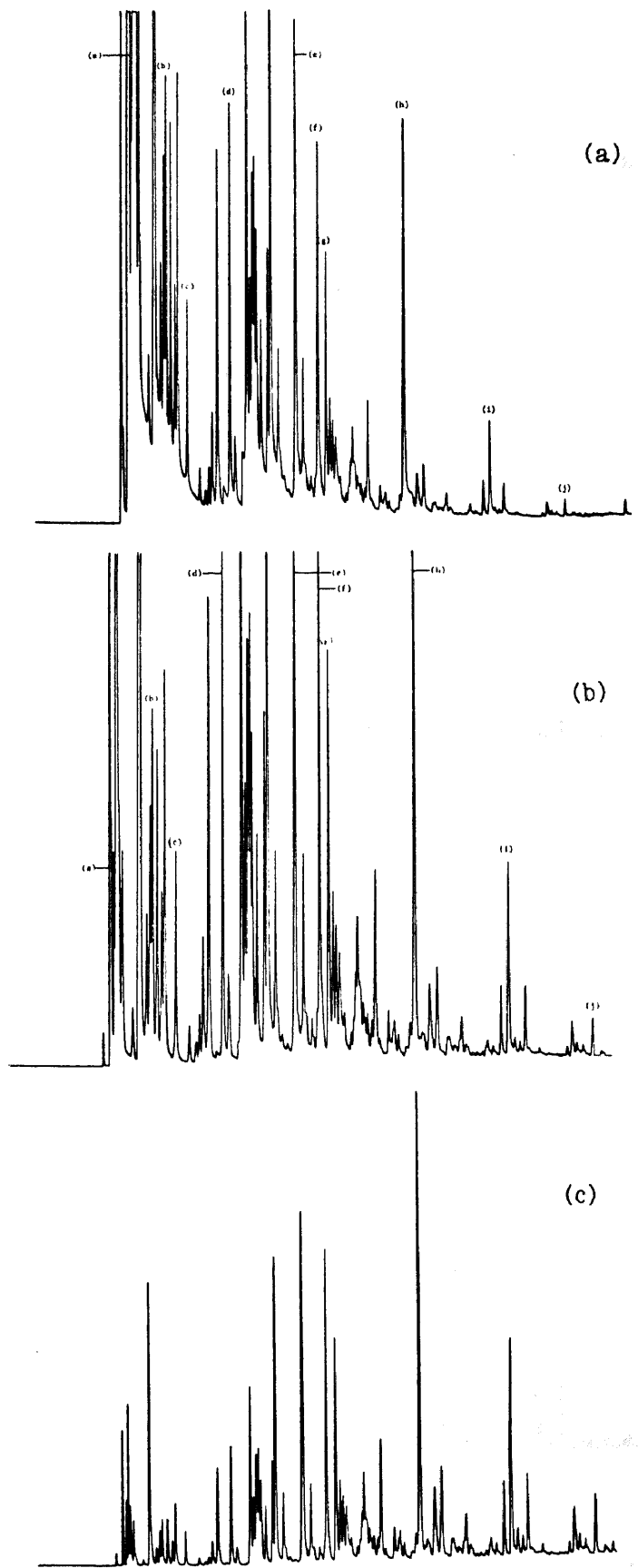


Figure 8. Chromatograms of gasoline vapors emitted from (a) a fresh gasoline sample (b) a water washed sample (c) water used to extract gasoline.

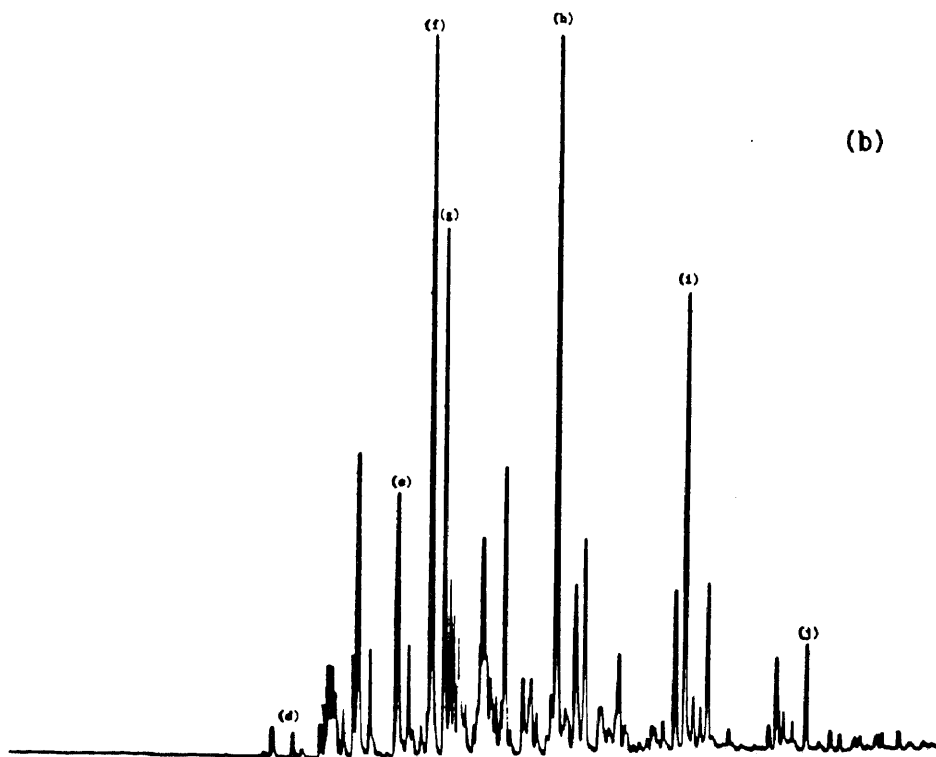
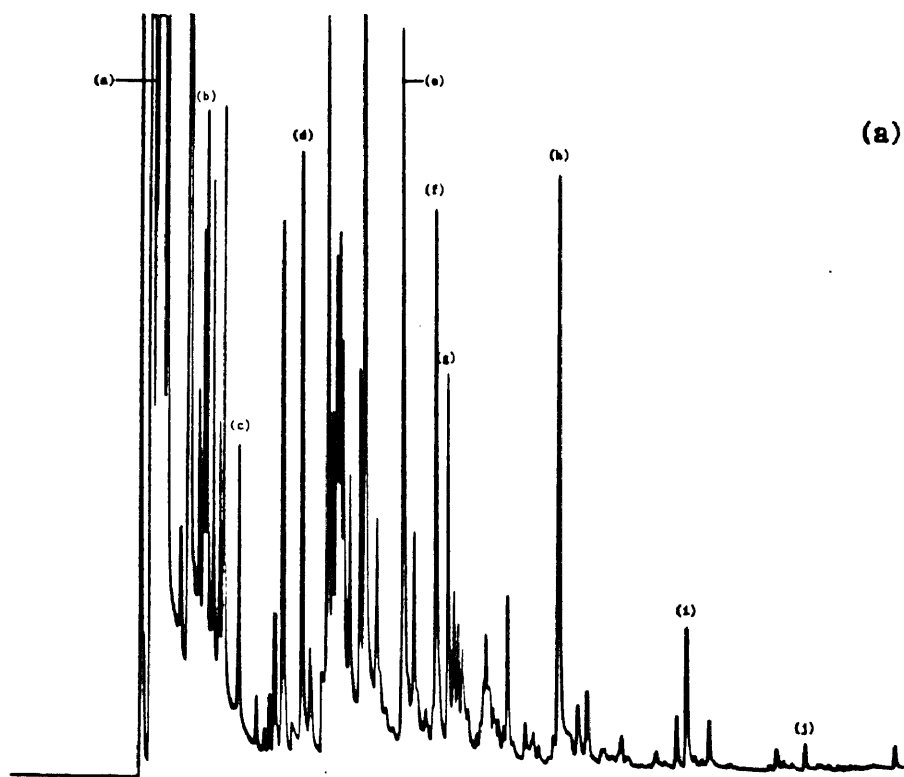


Figure 9. Chromatograms of gasoline vapors emitted from (a) fresh gasoline (b) gasoline left open to the air for 24 hours.

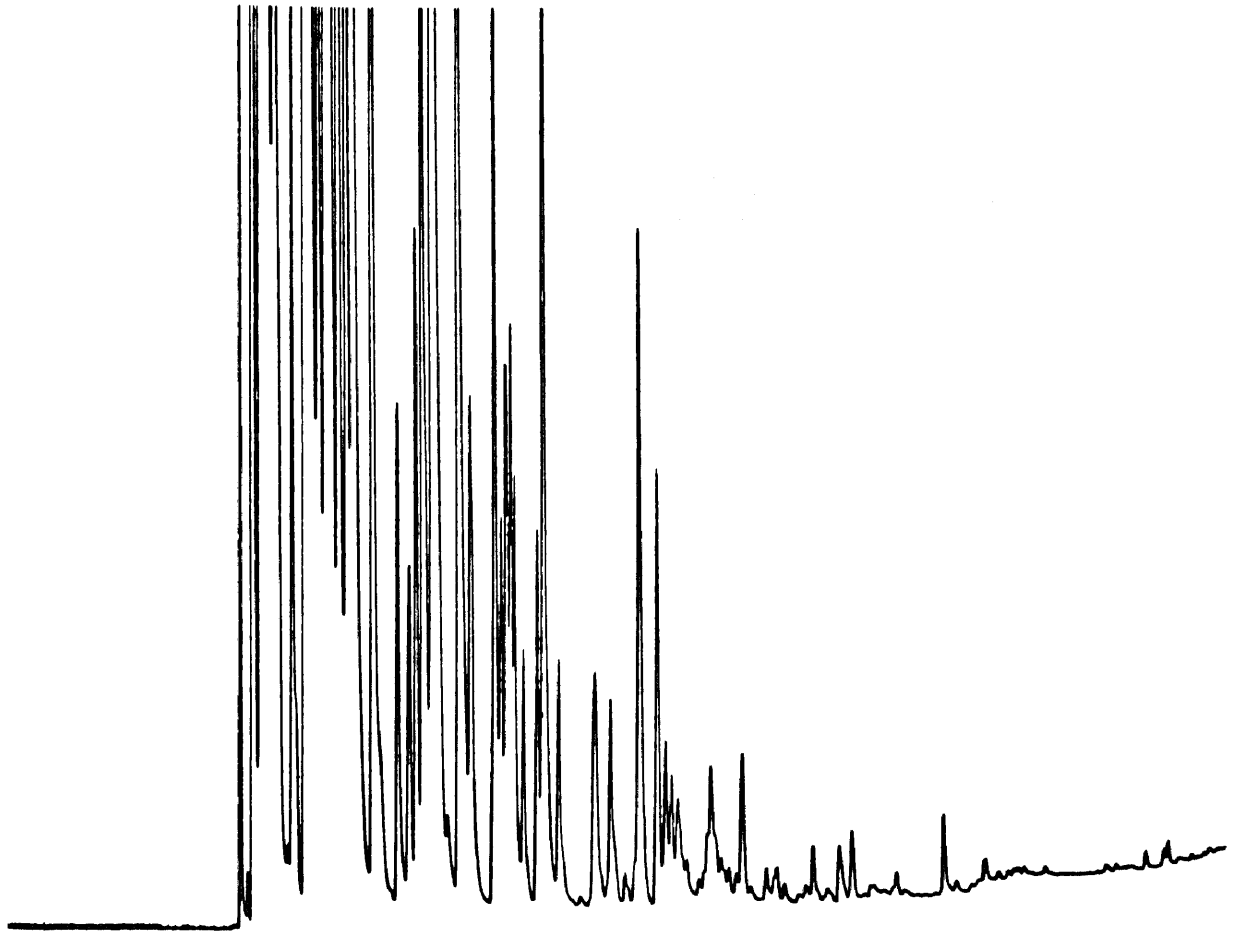


Figure 10. Chromatogram of vapors collected from the top of a gasoline-contaminated soil column.

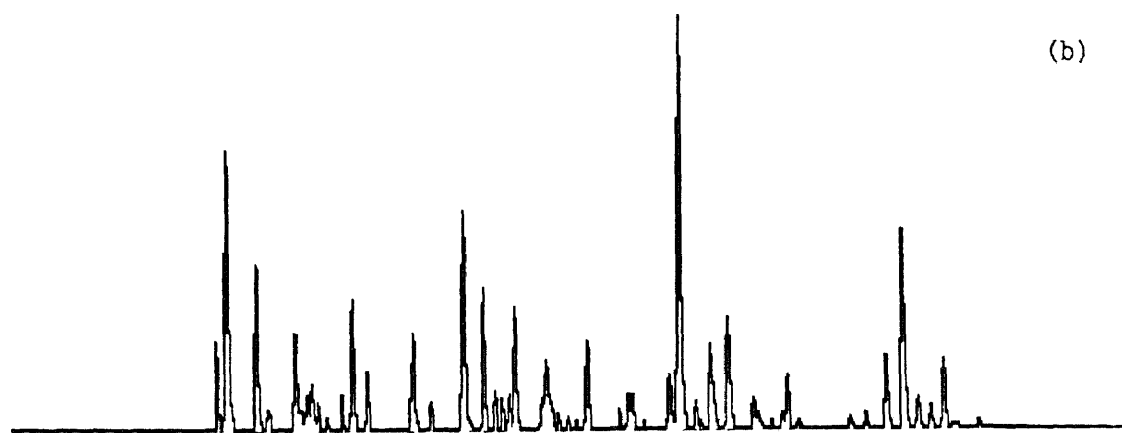
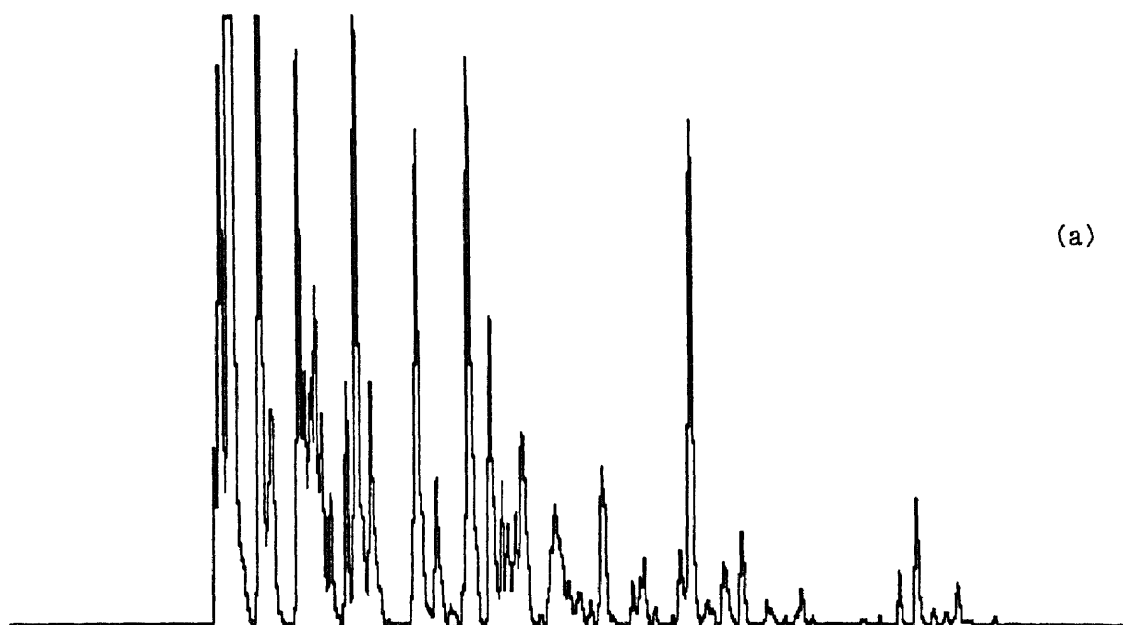


Figure 11. Chromatograms of gasoline vapors emitted from a film canister at (a) time = 0, and (b) time = 1 hour.

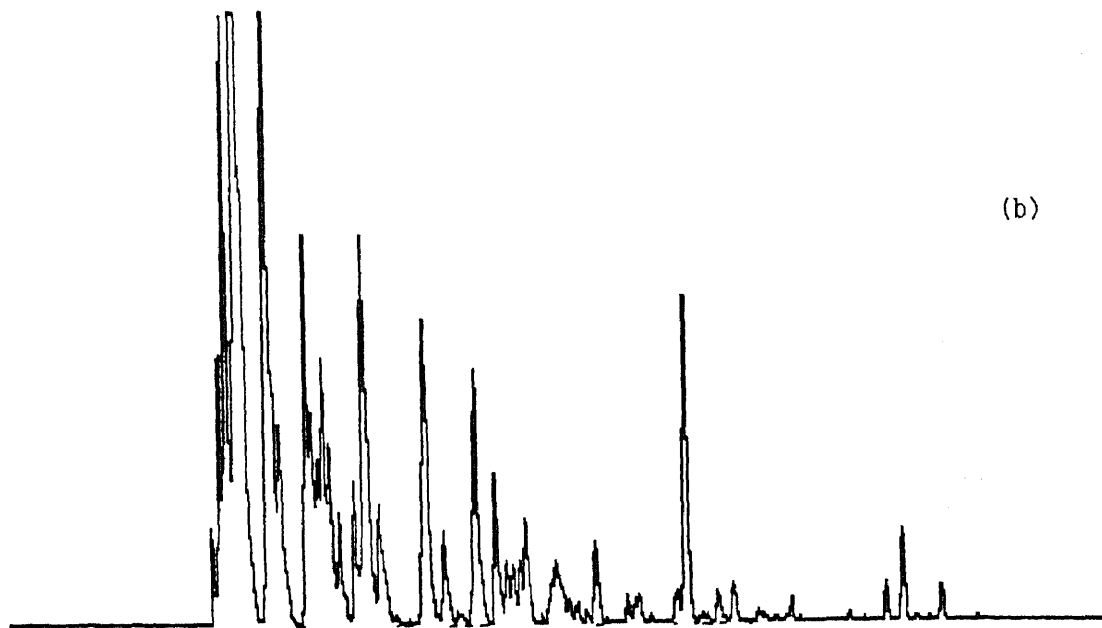
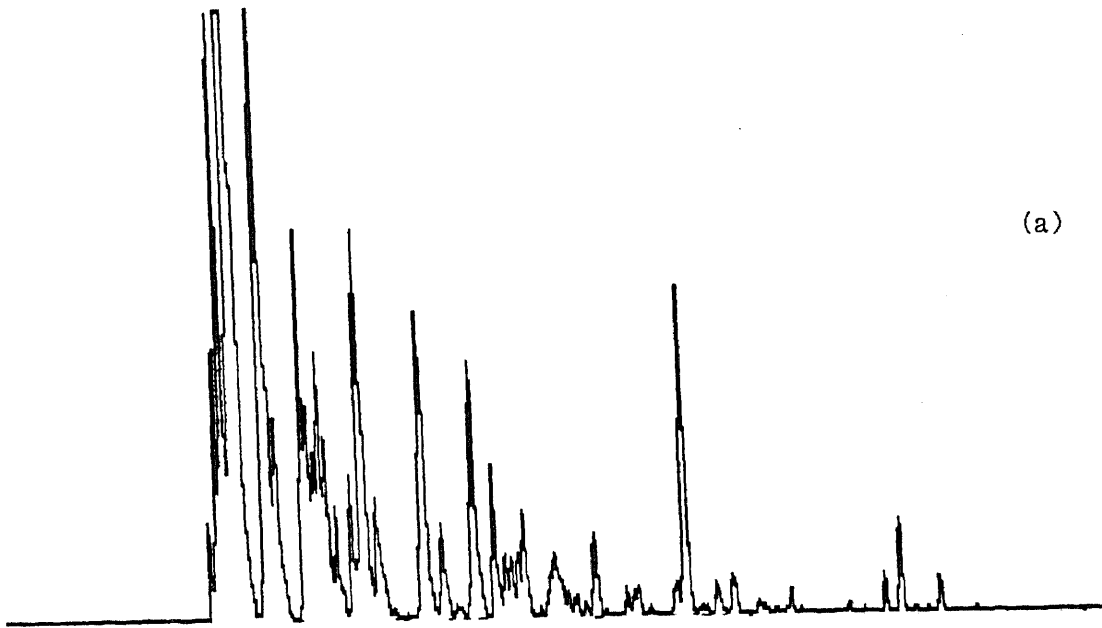


Figure 12. Chromatograms of gasoline vapors emitted from a diffusion tube at (a) time = 0, and (b) time = 2 hours.

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