

APPENDIX N
SAMPLE COLLECTION PROTOCOLS

SAMPLE COLLECTION PROTOCOLS

1. Soil Samples

- a. *Hydrocarbons*: Soil samples collected from a backhoe, the ground, or a soil coring device, should be collected in a thin-walled stainless steel or brass cylinder at least three inches long by one inch in diameter that has been prepared by the laboratory (cylinders can be made to fit inside the preferred split-barrel core sampler). About one inch of soil should be removed from the immediate surface area where the sample is to be taken and the cylinder then pounded into the soil with a wooden mallet. No headspace should be present in the cylinder once the sample is collected. When the sample is collected, each end of the cylinder should be covered with aluminum foil and then capped with a polyethylene lid, taped, and labeled. The sample should then be immediately placed in an ice chest containing dry ice and kept frozen for delivery to the laboratory. Care should be taken throughout to avoid contamination of both the inside and outside of the cylinder and its contents.

Samples should be kept frozen at the laboratory until they are analyzed. Holding time should not exceed 14 days from the time of collection. Frozen soil cores should be removed from the cylinders by spot heating the cylinder and immediately extruding the sample (or a portion of it). A portion of the frozen sample should be removed and prepared for analysis according to approved NYSDEC methods.

In situations where the above procedure is inappropriate (i.e., semi-solid samples), glass vials (properly prepared by contract laboratory or consultant) with Teflon seal and screw cap should be used, and maintained at 4°C until analysis.

- b. *Organic lead*: Tetraethyl/tetramethyl-lead are volatile; therefore, soil samples should be collected in cylinders and frozen as described for volatile hydrocarbons above.
- c. *Shipping Samples*: Where commercial shippers are involved, dry ice may present Department of Transportation (DOT) shipping problems and "blue ice" may have to be substituted.

Exhibit 1 summarizes the holding times for soil samples.

2. Water Samples

- a. *Free floating product (from a well)*: Sampling of free floating product on the surface of ground water should not be performed until the well has been allowed to stabilize for at least 24 hours after development or other withdrawal procedure. A sample should be collected that is indicative of the thickness of floating product within the monitoring well. This may be accomplished by the use of a clear, acrylic bailer designed to collect a liquid sample where free product and ground water meet. A graduated scale on the bailer is helpful for determining the thickness of free product. Samples should also be field-inspected for the presence of odor and/or sheen.

Exhibit 1

Holding Time for Soil Samples*

Analyte	Holding Time for Soil
Benzene, toluene, xylenes	Analyze as soon as possible (maximum 14 days)
Total Petroleum Hydrocarbons, as gasoline	Analyze as soon as possible (maximum 14 days)
Total Petroleum Hydrocarbons, as diesel	Extract within 14 days, analyze extract within 40 days

* Results from samples not meeting the listed holding times should be considered minimum values; that is, the actual concentration is equal to or greater than the concentration determined after the holding time has expired.

Electronic measuring devices also are available for determining the thickness of the hydrocarbon layer floating on ground water.

- b. Dissolved product (from a well): If free product is detected, analysis of water for dissolved product should be conducted after the free product has been substantially removed from the well. Before collecting a water sample, a well should be purged until temperature, conductivity, and pH stabilize. Often, this will require removal of four or more well volumes by bailing or pumping. Once well volumes are removed and well water is stabilized, a sample can be taken after the water level approaches 80 percent of its initial level. Where water level recovery is slow, the sample can be collected after stabilization is achieved.

Ground-water samples should be collected in a manner that minimizes loss of volatile constituents from the sample. For collecting samples, a gas-actuated positive displacement pump or a submersible pump is preferred. A Teflon or stainless steel bailer is acceptable. Peristaltic pumps or airlift pumps should not be used.

Cross-contamination, which can occur when pumps (or bailers) are transferred from well to well can be avoided by thoroughly cleaning pumps between sampling episodes. Dedicated (i.e., permanent installation) well pumps, while expensive, are often cost effective in the long term and ensure data reliability relative to cross-contamination. If transfer of equipment is necessary, sampling should proceed from the least contaminated to the most contaminated well, if such information is available before sample collection.

Water samples should be collected in vials or containers provided by the analytical laboratory that are specifically designed to prevent loss of volatile constituents from the sample. No headspace should be present in the sample container once the container has been capped. This can be checked by inverting the bottle, once the sample is collected, and looking for bubbles. Sometimes it is not possible to collect a sample without air bubbles, particularly if water is aerated. In these cases, the investigator should record the problem and account for probable error. Cooling samples may also produce headspace (bubbles), but these will disappear once the sample is warmed for analysis.

Samples should be placed in an ice chest maintained at 4°C with blue ice (care should be taken to prevent freezing of the water and bursting of the glass vial). A thermometer with a protected bulb should be carried in each ice chest.

- c. Surface water: Grab samples should be collected in appropriate glass containers supplied by the laboratory. The sample should be collected in such a manner that air bubbles are not entrapped. Semi-solid samples should be collected the same way. The collected samples should be refrigerated (blue ice, 4°C) for transport and analyzed within 7 days of collection (14 days with preservatives).

Exhibit 2 summarizes information on containers, preservation techniques, and holding times for water samples.

Exhibit 2

Required Containers, Preservation Techniques, and Holding Times for Water Samples^{a/}

Test	Container	Preservation	Maximum Holding Time ^{b/}
Purgeable aromatic hydrocarbons (BTEX) Method 8020 or 602	Glass, Teflon-lined septum	Cool, 4°C, <u>0.008%</u> <u>NA2S2O3</u> ^{c/} HCl to pH2 ^{d/}	Analyze within 7 days (max. 14 days if preservative used)
Total petroleum hydrocarbons as gasoline	Glass	Cool, 4°C, <u>0.008%</u> <u>NA2S2O3</u> ^{c/} HCl to pH2 ^{d/}	Analyze as soon as possible (max. 14 days)
Total petroleum hydrocarbons -- diesel fuel oil	Glass	Cool, 4°C	14 days; analyze extract within 40 days

^aModified Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act.

^bSamples should be analyzed as soon as possible after collection. The times listed are the maximum times that samples may be held before analysis and still be considered valid. Samples may be held for a longer period only if the collector or laboratory has data on file to show that the specific types of samples under study are stable for the longer time. Some samples may not be stable for the maximum time period given in the table.

^cShould only be used in the presence of residual chlorine.

^dSample receiving no pH adjustment must be analyzed within seven days of sampling. Sample vials containing hydrochloric acid (HCL) as a preservative should be handled with caution to avoid eye and skin contact.

3. Indoor Air Samples¹

Any contamination found in samples collected to evaluate residential indoor air quality will be compared with the level of that substance in residences outside the impact area (background). The reason for making the comparison against background is two-fold.

First, from the public health perspective, no one should be exposed involuntarily to levels of a potentially harmful material in excess of levels that are characteristic of the individual's community. Determining the basis of comparison requires selecting appropriate sites for collection of background samples. Second, there are no indoor air standards for private places, nor does the state have the statutory authority to set such standards. Without that authority, determining whether cleanup is successful must be made on the basis of local background data.

There are three basic mechanisms by which petroleum products may enter an indoor space: by direct infiltration of product through basement walls by drawing drinking water supply from contaminated sources, and by vapors migrating in the voids in the soil system. The farther an impacted home or other building is from a spill, leak, or other source of contamination, the less likely it is that benzene, toluene, and xylene (BTX) are good indicators for a spill. The distribution of constituents that reaches a given point through vapor migration depends on a wide range of physical, chemical, and biological factors and processes. Consequently, periodic sampling of indoor air that has been impacted by a petroleum spill will not necessarily yield a consistent set of detected compounds or levels of contamination. Indoor air measurements can vary widely in response to changes in weather and to other factors whose effects are not fully understood.

Because of this variation it is necessary to use an analytical procedure that is capable of identifying more of the constituents of petroleum products than simply benzene, xylene and toluene. The sampling and analytical procedures provided with this protocol address 16 compounds that may be expected to be present in petroleum products. These procedures do not cover all constituents that may be of concern, they can be used to test for petroleum, particularly gasoline, in air. Additional methods and further developmental work are required to permit broader identification of other petroleum products.

a. When to Collect Indoor Air Samples

Collection and analysis of indoor air samples should be initiated whenever there is a reasonable expectation that indoor air may be contaminated as the result of a petroleum spill. Historically, sampling has been initiated in response to reports, by residents, of petroleum odors. The wide variety of petroleum products and their various constituents have odor thresholds ranging from tens of parts per billion to hundreds of parts per million. Depending on the particular product and the components of the product that reach a building, significant exposures could occur over long periods of time without any odor being perceived. It is therefore necessary to make judgments based on field conditions as to whether or not reconnaissance sampling for indoor air contamination is necessary. Many of the factors that must be considered in

¹ This material was extracted from the New York State Department of Health, Bureau of Toxic Substance Assessment's Draft Indoor Air Petroleum Sampling and Analysis Protocol (October 1986).

determining whether or not to collect indoor air samples are the same that would be considered in evaluating the spill itself. Primary among these are whether or not there are effective routes of migration or transport between the spill and the receptor and whether or not there is a potential for release and contact and exposure at the receptor. The types of information that may be useful in making these evaluations include:

- # Local hydrology, including direction of ground-water flow, depth to and seasonal variations in ground water as they relate to transport of product and potential for interception at crawl spaces, basements, underground utilities and other sub-surface structures.
- # Local geology, soil characteristics and other physical features that may impact the movement of contaminated ground water, free product or soil vapors.
- # Evidence of migrating free product, contaminated ground water, soil, gas or other manifestations of the presence of contamination.
- # The presence of sewers, waterlines, meter pits or other underground utilities that may represent preferential paths of migration or mechanisms for identifying the extent, magnitude, or impact of a spill.
- # The proximity of residences to the spill and relationship of basements to ground water and local soil conditions.
- # The magnitude and nature of the spill, considering the particular product and its physical and chemical characteristics, and the duration and intensity of the spill and other relevant factors.

Information developed from the initial field investigation will be evaluated to determine if indoor air sampling is required and to what extent. In the absence of direct information, such as reports of petroleum odors, the decision to sample must be based on the judgment of the investigating parties. If any combination of technical factors indicate there is a reasonable potential for indoor air contamination, a program of monitoring should be initiated. Obvious factors that must be considered may include a high or fluctuating ground-water table, porous or granular soil, unsealed or wet basements, natural or man-made conduits for subsurface flow of petroleum and the proximity and nature of the spill.

b. Sampling Design and Frequency

When sampling is initiated it will be done for one of two reasons: to evaluate known impacts or to monitor to detect possible indoor air contamination. In the first instance, design of the sampling program is relatively easy: focus on the impacted homes. It is more difficult to design a sampling strategy for the second case. In either case, background data will be required for comparison with measurements taken in the impacted or potentially impacted homes or businesses.

In those cases where a direct impact is known, the principal decisions that must be made are when to sample and how many samples to collect. Collection of samples in cases where there is evidence of an impact is important, if for no other reason but to establish, by measurement, the link between the spill and the receptor. It is also necessary to establish the baseline for both impact and background. The frequency of follow-up sampling will be

dictated by the local circumstances and will require continuous re-evaluation and up-dating of information. In the case of a large spill, where obvious contamination has occurred but the major plume has not reached the location of concern and there is no one using the facility, it is possible that less frequent sampling will be required. On the other hand, if someone is using the impacted space and the relation to the source is uncertain, more frequent sampling will be required. The presence or absence of specific mitigating activities such as recovery operations or air purifiers will also be a consideration. In general, the initial sampling will be more frequent and, as data are developed, the frequency would be reduced. Realistically, the time frame is in terms of months.

In the case where monitoring is initiated to detect the migration of a plume, the guidance is less specific. The sampling design must be flexible based on evaluation of the available field data. Sampling should be initiated as soon after the spill as is reasonably possible for two reasons. The most important reason is that, while direct evidence of contamination, such as odor, may not be present, the presence of contamination may be determined as a result of sampling. Early initiation of sampling is also important to establish a specific baseline against which future samples can be evaluated. Frequency of sampling will be dictated, again, by the field conditions and the results of the initial sampling. If the first samples show evidence of contamination, follow-up will be required sooner than if the initial samples were clean. In the case of the presence of contamination, the first follow-up samples should be collected within a month and subsequent samples collected on a longer term basis. Where contamination was not present the follow-up sample may be taken after a longer period. The times in either case must be flexible depending on the particular circumstances.

c. Number of Samples

The number of samples collected will be dictated by the magnitude of the spill and the number of locations known to be impacted or potentially impacted. When a small number of homes or businesses are involved (up to about five), all locations must be sampled. As the number of affected locations increases, the total number of sample locations may need to be increased, but not all of the locations need be sampled. Consideration may also be given to alternating sample locations. The important consideration is establishing a sampling strategy that will yield data that can be used to devise a plan for responding to the contamination that is discovered.

Whenever indoor air samples are collected in response to a petroleum spill, samples must also be collected to establish background levels in the local community for the same constituents of concern. Airborne levels of the compounds that make up the various petroleum products vary considerably depending on local conditions. Since there is such wide variation among expected levels from place to place and since evaluations of indoor air petroleum contamination will be based on background levels, this sampling is critical. The background sample locations should be within the community of concern and be as similar to the test homes as is practical. It is not expected that the similarity will be perfect, but every effort must be made to obtain a sufficient number of comparable background homes to properly represent the impacted community.

The number of background samples collected during any given sampling episode will depend on the number of test locations being sampled according to the following table (for air):

<u>Test Samples</u>	<u>Background Samples</u>
1 - 5	1 - 3
6 - 10	4 - 6
> 10	30-60% of # test samples

The number of background samples are given as a range, reflecting, among other things, the problems with identifying acceptable locations for background samples. In order to have data that are "comparable," it is necessary to impose what may appear to be restrictive conditions on the activities in background homes during collection of samples. In order to obtain comparable data, the investigation must create the most comparable conditions possible. The primary concern is to close up the building to the maximum extent possible. This can presumably be accomplished overnight, causing a minimum impact on those who own or occupy the space. Other requirements that may significantly interfere with individual use, but may also impact the quality of data, are use of heating and air conditioning equipment and cooking. Restriction of these and other activities are necessary to permit collection of data that are representative of uncontrollable factors and represent consistent conditions in all houses that are to be compared. The preferred requirements for selections acceptable for background sampling locations are provided in Exhibit 3. From time to time, as new data become available, the requirements for the test and control houses will be modified to make the sample collection and data analysis more effective.

Before initiating sampling at any location, the Indoor Air Quality Residential Questionnaire (Exhibit 4) must be completed. The purpose of the questionnaire is to ensure that every location is evaluated consistently and to provide all the necessary information to characterize the home where sampling will take place.

When sampling is initiated the sampling protocol described in Exhibit 5 must be followed. Samples collected from each location should include one from the basement, two from the living or use space, and one outdoor ambient sample. When two or three sample locations are close to one another, a single outdoor ambient sample may be used. Blank samples must be provided at the rate of one for each sampled house or building and one for each ambient sample. Duplicate analyses are required at each sample location in addition to splits being supplied for 20 percent of the samples.

The analytical procedure that should be used is provided in Exhibit 6. This tentative procedure, Volatile Organics in Air, updated January 1986, provides analytical response to 16 of the components that have been associated with petroleum products. The list is far from comprehensive but includes:

benzene	tert-butylbenzene
toluene	1,3,5-trimethylbenzene
o,m,p-xylenes	1,2,4-trimethylbenzene
ethylbenzene	p-cymene
cumene	cyclopropylbenzene
styrene	sec-butylbenzene
n-propylbenzene	A-butylbenzene

Completion of sampling using these protocols will provide a basis for developing consistent and comparable data.

Exhibit 3

Selection of Houses for Background Indoor/Outdoor Air Sampling

Houses for background sampling, which number one half the number of houses studied as impacted homes, will be selected using the following criteria and sampled to obtain background air levels for the study.

Houses selected for the background survey should have the following similar characteristics to the houses under study:

1. age
2. type of construction
3. air exchange rate (tightness of house)
4. heating system
5. location of garage (attached or detached)
6. setting (urban, suburban, rural, etc.)

Factors that would eliminate a house from being selected include:

1. Houses that are near obvious sources of air contamination (i.e., gas station, petroleum product storage areas, highways, etc.)
2. Houses where unusual or excessive use or storage of petroleum products occurs.

For a minimum of 12 hours prior to air sample collection, the following preparations should be implemented:

DO NOT

- # open any windows, fireplace flues or vents
- # operate ventilation fans
- # smoke in the house
- # paint
- # use gas stoves, fireplace, or any combustion equipment
- # operate or store automobile in attached garage
- # allow containers of gasoline or oil to remain within the house or garage area (houses using oil-fired furnaces exempted).

AVOID

- # cooking by any means
- # changing indoor air temperature by any means (furnace or air conditioner)

Household Sampling Considerations

- a. Indoor and outdoor air sampling should be done concurrently
- b. Use of house during sampling period should be limited

Exhibit 3

Selection of Houses for Background Indoor/Outdoor Air Sampling (continued)

- c. An Indoor Air Quality Residential Questionnaire should be completed for each house.
- d. Sample locations:
 - 2 - indoor locations (high-use areas) on the first floor
 - 1 - basement location
 - 1 - ambient sample: upwind and away from the immediate vicinity of the house and roadway
(NOTE: Ambient sampling can be reduced to one sample per each group of three houses if all of the houses are being sampled concurrently.)

Sample Collection

- a. All samples are to be collected in duplicate for each sampling location. Note: Those samples that are to be split between laboratories are to be collected in quadruplicate (2 per laboratory).
- b. A sample bulk per house and each outdoor location is required. The end caps should be removed from the cartridge. The cartridge is then to be placed in the cartridge connection on the sampling equipment, recapped, and placed in the cooler with the other samples.

QA/QC Requirements (see analytical method, Volatile Organics in Air, in Exhibit 6)

- a. All blanks are to be analyzed.
- b. 20% of all samples taken are to be split with WCL&R DOH under DEC spill contract.
- c. Duplicate analyses are required for one sampling location in each home (include in this the associated outdoor sample).

Exhibit 4
Indoor Air Quality Residential Questionnaire

Date Prepared: _____

Prepared By: _____

Title _____

Complete the following Questionnaire for Each Household Sampled:

RESIDENCE OCCUPANTS

1. OCCUPANT
- A. Name: _____
- B. Address: _____

- C. County: _____
- D. Home Phone No. _____
- E. Office Phone No. _____

2. OWNER OR LANDLORD
- A. Name: _____
- B. Address: _____

- C. Phone No. _____

3. ALL CURRENT HOUSEHOLD OCCUPANTS

	<u>Name</u>	<u>Age</u>	<u>Sex</u>	<u>Smoker?</u> <u>Yes or No</u>	<u>Occupation</u>
A.	_____				
B.	_____				
C.	_____				
D.	_____				
E.	_____				
F.	_____				
G.	_____				
H.	_____				

Exhibit 4
Indoor Air Quality Residential Questionnaire
(continued)

Circle the Appropriate Response:

CHARACTERISTICS OF RESIDENCE

4. RESIDENCE TYPE

	<u>Single-Family Dwellings</u>	<u>No. of Bedrooms</u>	<u>No. of Floors</u>
A. Ranch	_____	_____	_____
B. Raised Ranch	_____	_____	_____
C. Split Level	_____	_____	_____
D. Colonial	_____	_____	_____
E. Mobile Home	_____	_____	_____
F. Other (Specify) _____	_____	_____	_____

	<u>Multiple-Family Dwellings</u>	<u>No. of Bedrooms</u>	<u>No. of Floors</u>
G. Apartment	_____	_____	_____
H. Duplex	_____	_____	_____
I. Other (Specify) _____	_____	_____	_____

5. RESIDENCE LOCATION

- A. Urban Industrial
- B. Urban Non-industrial
- C. Suburban
- D. Rural
- E. Other (Specify) _____

6. RESIDENCE AGE _____ Years

INSIDE POLLUTION SOURCES

7. HEATING SYSTEMS

- | | |
|------------------------|-----------------------------|
| A. Hot Air Circulation | E. Heat Pump |
| B. Hot Water Radiation | F. Unvented Kerosene Heater |
| C. Steam Radiation | G. Other (Specify) _____ |
| D. Electric Baseboard | |

Exhibit 4
Indoor Air Quality Residential Questionnaire
(continued)

8. LOCATION OF HEATING SOURCE

- A. Basement
- B. Living Area
- C. Other (Specify) _____

9. HEATING SYSTEM FUEL TYPE

- A. Natural Gas
- B. Fuel Oil
- C. Electric
- D. Wood
- E. Coal
- F. Solar
- G. Other (Specify) _____

10. HEAT DISTRIBUTION

- A. Ducts
- B. Radiators
- C. Other (Specify) _____

If ducts are used, are they lined or covered with an insulating material, if so, what type? _____

11. COOLING SYSTEM

- A. Central Air Conditioning
- B. Window Air Conditioning Units
- C. Other (Specify) _____

If air conditioning is present, specify location and capacities.

Exhibit 4
Indoor Air Quality Residential Questionnaire
(continued)

12. Is a humidifier used in the household? _____

If yes, specify type and location. _____

13. Specify all type(s) of air treatment provided: (e.g., furnace filter, electrostatic precipitator, ozonator, etc.)

14. INSULATION

- A. Fiberglass
- B. Urea-Formaldehyde Foam
- C. Cellulose
- D. Polyurethane
- E. Asbestos
- F. Rock Wool
- G. Vermiculite
- H. Other (Specify) _____

Specify type of insulation used in each location listed below, if applicable, and the thickness, and whether the insulation is exposed (if there is no insulation write None):

	<u>Type</u>	<u>Thickness (ins.)</u>	<u>Visibly Exposed</u> <u>Yes or No</u>
Outside Walls	_____	_____	_____
Roof Rafters	_____	_____	_____
Attic Floors	_____	_____	_____
Crawl Space	_____	_____	_____
Other	_____		

Exhibit 4
Indoor Air Quality Residential Questionnaire
(continued)

15. OTHER CONSERVATION MEASURES

- A. Storm Windows Installed
- B. Storm Doors Installed
- C. Weatherstripping
- D. Polyethylene Sheeting (Windows)
- E. Caulking
- F. Other (Specify) _____

16. General Description of Building Condition Related to Air Tightness.

17. MATERIALS PRESENT IN HOUSEHOLD

- A. Plywood
- B. Framing Lumber
- C. Particle Board
- D. Fiberboard
- E. Brick or Masonry Stone
- F. Wall to Wall Carpeting
- G. Draperies
- H. Other (Specify) _____

18. APPLIANCES & FIXTURES PRESENT IN HOUSEHOLD

	<u>Appliance</u>	<u>Type (Gas, Elec.)</u>	<u>Location</u>
A.	Refrigerator	_____	_____
B.	Range	_____	_____

Exhibit 4
Indoor Air Quality Residential Questionnaire
(continued)

- C. Oven _____
- D. Microwave Oven _____
- E. Freezer _____
- F. Washer _____
- G. Dryer _____
- H. Water Heater _____
- I. Other _____

19. Is there a workshop, hobby or craft area in the resident? _____

If yes - specify type, location, use, and list all chemicals, solvents, draft/art supplies used, and where stored.

20. Is there a basement at this resident? _____

Basement is finished _____ unfinished _____

Is there seepage _____ flooding _____ of water within the basement area? _____

21. Is there a garage on the premises? _____. Is it enclosed and attached to the house or separate? _____

Is a vehicle normally parked in the garage? _____

22. Are any pets kept within the residence? _____

If yes, specify type and number _____

23. Has the building ever had a fire? _____

If yes, what section of the house? _____

Exhibit 4
Indoor Air Quality Residential Questionnaire
(continued)

24. List all household consumer chemical products - disinfectants, cleaning agents, solvents, detergents, etc., and where stored in residence.

- | | |
|-----------|-----------|
| 1. _____ | 11. _____ |
| 2. _____ | 12. _____ |
| 3. _____ | 13. _____ |
| 4. _____ | 14. _____ |
| 5. _____ | 15. _____ |
| 6. _____ | 16. _____ |
| 7. _____ | 17. _____ |
| 8. _____ | 18. _____ |
| 9. _____ | 19. _____ |
| 10. _____ | 20. _____ |

25. List all flammable liquids or materials, paints, pesticides, fungicides, insecticides, etc., and where stored in household.

- | | |
|-----------|-----------|
| 1. _____ | 11. _____ |
| 2. _____ | 12. _____ |
| 3. _____ | 13. _____ |
| 4. _____ | 14. _____ |
| 5. _____ | 15. _____ |
| 6. _____ | 16. _____ |
| 7. _____ | 17. _____ |
| 8. _____ | 18. _____ |
| 9. _____ | 19. _____ |
| 10. _____ | 20. _____ |

26. Has the house ever been fumigated? If yes, describe type and location of treatment? _____

Exhibit 4
Indoor Air Quality Residential Questionnaire
(continued)

WATER SUPPLY

27. Source of Water:

- A. Public Water Supply
- B. Drilled Well
- C. Driven Well
- D. Dug Well
- E. Other (Specify) _____

28. Well Specifications:

- A. Well Diameter _____
- B. Well Depth _____
- C. Depth to Bedrock _____
- D. Feet of Casing _____
- E. Grouted or Ungouted _____
- F. Well Capacity _____

29. Water System:

- A. Type of Pump _____
- B. Well Yield _____
- C. Type of Storage Tank _____
- D. Size of Storage Tank _____
- E. Type of Treatment _____

30. Water Quality:

- A. Taste and/or odor problem? _____
If so, describe _____
How long has the taste and/or odor been present? _____
- B. Scale or staining problems? _____
If so, describe _____

Exhibit 4
Indoor Air Quality Residential Questionnaire
(continued)

31. Describe soil type at resident location. _____

32. Waste Disposal
- A. Public Sewer
 - B. Septic Tank
 - C. Leach Field
 - D. Other (Specify) _____
 - E. Distance to Well _____
 - F. Type of Septic Tank Additive Used

POTENTIAL OUTSIDE AIRBORNE SOURCES OF POLLUTION

33. Residential Emissions
- A. Wood - Burning Fireplace or Stove
 - A. Coal - Burning Stove
 - C. Dry Exhaust
 - D. Other (Specify) _____

34. Kitchen Fan is:
- A. Vented to the Outside
 - B. Recirculating to Kitchen
 - C. Other (Specify) _____

35. Describe type, location, and distance of industry nearest to residence.

Exhibit 4
Indoor Air Quality Residential Questionnaire
(continued)

36. Describe type, location, and distance of commercial establishment nearest to residence.

37. Describe type, location, and distance from residence of nearest landfill or dump sites nearest to residence.

38. Remarks (include any information that may be pertinent to detecting source of household contamination).

39. Floor plan of residence - on the following page, draw a floor plan of the household sampled. Include North/South orientation, location of well and waste disposal system, location of heating and water systems within residence.

Exhibit 5
**Air Sample Collection Techniques for Aromatic Hydrocarbons,
Chlorinated Hydrocarbons, and Related Volatile Organic Compounds**

1. Scope and Application

This procedure may be used to collect indoor and outdoor air samples for the purpose of measuring the concentrations of benzene, toluene, xylenes, chlorinated hydrocarbons, and related volatile hydrocarbons, and as an estimate of gasoline contamination.

2. Summary of Method

The above-mentioned volatile organic compounds are adsorbed onto Porapak N contained in sampling cartridges. The compounds are desorbed from the cartridges with prepurified methanol and analyzed by gas chromatography using a photoionization detector and/or an electron capture detector. Analysis is performed as described in the Toxicology Institute method "Volatile Organics in Air" (Exhibit 6).

3. Sample Collection Apparatus

- 3.1 Vacuum pump, Gast 1531-107B-G288X, or equivalent, capable of maintaining at least 20" Hg vacuum.
- 3.2 Rotameter, range 0 to 2 liters per minute, calibrated for air against a primary standard (e.g., 1 liter bubblemeter), having a rubber bung or equivalent connector to fit the Porapak N cartridge, and gum rubber tubing for connecting the rotameter to the cartridge. (Such as Gilmont Instruments, Inc. rotameter, Cat. #F-1260, size 2, 401 Great Neck Road, Great Neck, NY 11021.)
- 3.3 Sling psychrometer for measuring temperature and relative humidity at the site.
- 3.4 Adhesive labels for identifying cartridges.
- 3.5 Porapak N cartridges (80-100 mesh), see Analytical Toxicology Institute method "Volatile Organics in Air" (Exhibit 7) for cartridge preparation.
- 3.6 Sample Identification forms for indoor and outdoor sampling.
- 3.7 Caplugs, size 7/32" SC for capping ends of Porapak N cartridges, Caplugs Division, Protective Closures Co. Inc., Elmwood Avenue, Buffalo, NY.
- 3.8 Ring Stand Supports and clamp holders.
- 3.9 1/4" plastic tees or four-way connectors (crosses).
- 3.10 Tygon tubing, 3/16" I.D. and 1/4" I.D. with 1/8" wall.

4. Sample Collection Procedures

- 4.1 Sample identification forms must be filled out for each site where samples are collected. Measure temperature and relative humidity at the sampling site.

Exhibit 5

Air Sample Collection Techniques for Aromatic Hydrocarbons, Chlorinated Hydrocarbons, and Related Volatile Organic Compounds (continued)

- 4.2 Attach a label to each cartridge indicating name, site identification, and cartridge number (1, 2 or 3). Samples should be collected in triplicate to ensure that a back-up sample is available for analysis in case of field or laboratory accident, and for verification of results.
- 4.3 Remove the two red Caplugs from each Porapak N cartridge and keep them in a clean container while the cartridges are being used to collect air samples. Attach the sampling manifold (see Exhibit 8) to a clamp and ring stand support, about three feet above the floor or ground. Attach the cartridges to the sampling manifold using 3/16" I.D. Tygon tubing as in Exhibit 9.
- 4.4 Turn on the vacuum pump. Record the start time.
- 4.5 Measure the initial air flow rate using a calibrated rotameter, and record it on the sample data sheet (Exhibit 10). Disconnect the rotameter while sampling. Be sure that the cartridge is positioned as shown in Exhibit 11, with the Porapak N section nearest to the air inlet of the cartridge.
- 4.6 A total of at least 20 liters but not more than 25 liters of air should be sampled.

The required sampling time may be determined from the following equations:
minimum time required:

$$T_{\min} = \frac{20}{R}$$

where: T_{\min} = sampling time required to pass 20 liters of air thru the cartridge (in minutes)

R = initial air flow rate, in liters per minute

maximum time required:

$$T_{\max} = \frac{25}{R}$$

where: T_{\max} = sampling time required to pass 25 liters of air thru the cartridge (in minutes)

R = initial air flow rate, in liters per minute

- 4.7 At the end of the collection period, measure and record the final air flow rate. Record the stop time.

Exhibit 5

Air Sample Collection Techniques for Aromatic Hydrocarbons, Chlorinated Hydrocarbons, and Related Volatile Organic Compounds (continued)

4.8 Recap the labeled Porapak N cartridge ends with the red Caplugs and return the labeled cartridges to the laboratory along with the sample identification form, and a field blank cartridge. The blank cartridge is treated in the following manner: Label the cartridge "Field Blank." Remove the red Caplugs. Replace the red Caplugs and return this cartridge to the laboratory along with the samples.

5. Air Volume Calculations

5.1 Calculate the total sampling time in minutes.

5.2 Calculate the average air flow rate in liters per minute.

5.3 Air volume collected

$$V = \frac{\text{LPM} \times M}{1000}$$

where: V = air volume collected, in cubic meters.
LPM = sampling rate, in liters per minute.
M = time sampled, in minutes.
1000 = conversion factor to convert liters to cubic meters.

6. References

R. Narang, manuscript in preparation, NYSDOH, DL&R, Toxicology Institute, ESP Albany, NY.

Exhibit 6
Volatile Organics in Air

1. Scope and Application

1.1 This method covers the determination of both aromatic and halogenated volatile organic compounds in air.

1.2 This method is applicable to the determination of the following compounds in air:

Electron Capture Detector (ECD)
or Hall Detector (HECD)

Photoionization Detector (PID)

chloroform

1,1,1-trichloroethane

trichloroethene

carbon tetrachloride

bromodichloromethane

1,1,2-trichloroethane

tetrachloroethene

1,2-dibromoethane

bromoform

1,1,2,2-tetrachloroethane

benzene

toluene

chlorobenzene

o,m,p-xylenes

o,m,p-chlorotoluenes

1.3 The method may be extended to the compounds listed below. However, validation of accuracy and precision for each additional compound is necessary.

ECD/HECD

o,m,p-dichlorobenzenes

cis-1,3-dichloropropene

dibromochloromethane

trans-1,3-dichloropropene

1,2-dichloroethane

trans-1,2-dichloroethane

1,1-dichloroethane

1,1-dichloroethene

PID

o,m,p-dichlorobenzenes

ethylbenzene

cumene

styrene

n-propyl benzene

tert-butyl benzene

bromobenzene

1,3,5-trimethyl benzene

1,2,4-trimethyl benzene

p-cymene

cyclo propyl benzene

sec-butyl benzene

n-butyl benzene

1.4 Detection limits are 1 ug/m³ for chlorinated organics by ECD, 10 ug/m³ for chlorinated organics by HECD, and 10 ug/m³ for aromatics by PID. These detection limits are achievable when the optimum volume of air in cubic meters is collected and breakthrough volumes have not been exceeded. (See 1.5).

1.5 The breakthrough volume of the collection system is generally independent of analyte concentration. If testing is to be done for those compounds listed in Section 1.2 as ECD/HECD, the maximum sampling volume may not exceed 25

Exhibit 6
Volatile Organics in Air
(continued)

liters. If testing is to be done only for those compounds listed in Section 1.2 as PID, the maximum sampling volume may not exceed 40-50 liters. The breakthrough volume has not yet been determined for those compounds listed in Section 1.3

2. Summary of Method

Volatile organic compounds are trapped on Porapak-N by passing a known volume of air through a cartridge containing this material. Volatiles are eluted from the cartridge with a known volume of methanol. Aliquots of the methanolic eluate are injected into a gas chromatography system using electron capture detector (ECD) or Hall detector (HECD), and photoionization detector (PID).

3. Interferences

3.1 Solvents, glassware, and associated equipment may produce artifacts leading to misinterpretation of gas chromatographic tracings. All reagents and glassware must be demonstrated to be free from interferences under the conditions of analysis. In particular, the eluting solvent (methanol) is a frequent cause of interference and purification or cleanup may be required. The Porapak N cartridges are also an occasional source of contamination.

3.2 The gas chromatographic technique may produce peaks from substances that coelute. For absolute identification, mass spectral confirmation is necessary. It should be noted that HECD is more specific than ECD for halogenated compounds, therefore HECD provides a greater probability of correct qualification than does ECD.

4. Apparatus and Materials

4.1 Porapak N - 80/100 mesh, T.M. - Supelco Corp.

4.2 Serum vials, 10 ml, with Teflon-lined caps

4.3 Pasteur capillary pipets

4.4 Glass tubing - Pyrex 1/4 inch x 10 inch

4.5 Pump - Gast (T.M.) carbon vanes oil-less Model #1531-107-288 or equivalent

4.6.1 Column for Hall

Carbopak B, 60/80 mesh with 1% SP-1000 packed in an 8 ft. x 0.1 inch I.D. stainless steel or glass column with helium carrier gas at 40 ml/min flow rate. Column temperature held at 45°C for 3 minutes, programmed at 8°C/min to 220°C, held for 18 minutes.

Exhibit 6

Volatile Organics in Air (continued)

4.6.2 Column for PID

5% SP-1200 + 1.75% Bentone-34 on 100/120 mesh Supelcoport packed in a 6 ft. x 0.082 inch I.D. stainless steel or glass column. Carrier gas is helium at a flow rate of 30 ml/minute. Temperature program sequence: 50°C for 2 minutes, then program at 4°C/min. to 110°C, hold until all compounds have eluted (20 minutes is suggested).

NOTE: Whenever column is not being used and is attached to PID, maintain it at the upper temperature of the program (90°C). Condition new Benton/SP-1200 columns at 120°C for several days with helium before connecting to the detector.

4.6.3 Column for ECD and/or PID

15% SF-96 OV-225 on Chromasorb WAW-DMCS, 6 ft. x 1/4 inch O.D. glass column with argon/methane carrier gas for ECD at a flow rate of 30 ml/min. Operate at 60°C isothermally.

- 4.7 Manifold for collection of duplicate samples
- 4.8 Polyethylene "tees", "crosses," and Tygon tubing
- 4.9 Calibrated rotameter
- 4.10 Manifold - for purging cartridges in a conditioning oven
- 4.11 Polyethylene caps (Caplugs) for 1/4 inch glass tubing
- 4.12 Glass wool - silanized, methanol washed

5. Reagents, Solvents, and Standards

- 5.1 Methanol - may need to be prepurified (see methanol cleanup)
- 5.2 Standards - reference grade for all compounds of interest
- 5.3 Standard stock solutions
 - 5.3.1 Prepare standard stock solutions at least every four weeks.
 - 5.3.2 Place about 9.8 ml of methanol into a ground-glass-stoppered 10 ml Class A volumetric flask.
 - 5.3.3 Allow the flask to stand unstoppered about 10 minutes or until all alcohol wetted surfaces have dried.
 - 5.3.4 Weigh the flask to the nearest 0.1 mg.

Exhibit 6

Volatile Organics in Air (continued)

5.3.5 For compounds that are liquids at room temperature: using a 100 ug/l syringe, immediately add 2 or 3 drops of the standard to the flask, then reweigh. Be sure that the drops fall directly into the methanol without contacting the neck of the flask.

5.3.6 For compounds that are solids at room temperature: using a clean spatula, immediately add a few crystals of the standard to the flask, then reweigh. Be sure that the crystals fall directly into the methanol.

5.3.7 Dilute the solutions from 5.3.5 and 5.3.6 to volume, stopper, then mix by inverting the flask several times.

5.3.8 Transfer the solution to a dated and labelled screw-cap vial with a Teflon liner.

NOTE: Because of the toxicity of many of the compounds, it is recommended that primary dilutions be prepared in a hood. It is further recommended that a NIOSH-approved toxic gas respirator be used when the analyst handles high concentrations of such materials.

5.3.9 Calculate the concentration from the net gain in weight. Calculate the concentration taking into account the percent purity of the original standard compound.

5.3.10 Store the solutions at 4°C.

5.4 Mixed Standard Solution(s)

It is suggested that the individual stock solutions be diluted into a combined working solution in the range of 1-10 ng/ul, depending upon the detector used and the limit of detection desired.

5.5 Argon/Methane - 95%/5%

5.6 Helium

6. Calibration

6.1 The working solution(s) prepared in Section 5.4 can be used to either prepare a calibration curve or to bracket the samples by either injecting varying volumes or by preparing additional concentrations of analytes.

6.2 Each day the gas chromatographic systems are operated, demonstrate, through the use of calibrating standards, that the gas chromatographic system is functioning properly.

Exhibit 6
Volatile Organics in Air
(continued)

7. Quality Control

- 7.1 Sample collection must be carried out in duplicate (or triplicate) with individually calibrated cartridges.
- 7.2 Since flow rates may vary considerably from one cartridge to the next, it is important to attempt assurance of uniform packing by visual inspection for loose Porapak N. In a further check of proper packing, sample throughput rate will be checked at the beginning and end of sampling. If this rate differential is more than 10%, the cartridge should be discarded.
- 7.3 At least two field blank cartridges must be carried to and from the sampling site and must be transported along with the actual cartridges for samples.
- 7.4 Each batch of Porapak N cartridges will be checked for contamination by gas chromatographic analysis of methanol eluate. If contamination is detected the entire batch of cartridges must be rejected. 10% of each batch should be tested in this manner.
- 7.5 Methanol will be checked by gas chromatographic analysis for contamination on each day samples are eluted.
- 7.6 Duplicate sample analyses should be performed on 10% of samples collected or a minimum of one per analysis batch.
- 7.7 Standards
 - 7.7.1 Standards must be analyzed daily.
 - 7.7.2 Concentrations of standards analyzed will be such that peak areas obtained will approximate those in samples.
 - 7.7.3 Standards must contain all analytes that are present in samples.
- 7.8 Spikes

With each group of samples to be eluted, a spike must be tested. This is done by adding a methanolic solution of selected analytes to a Porapak N cartridge. Elution is performed following the procedure in Section 8.3. Spiked recovery should be calculated and appropriate quality control limits determined. Spiked recoveries not meeting the designated QC limits should be immediately investigated, with elution of duplicate sample cartridges being recommended.

8. Procedure

8.1 Sample Cartridge Preparation

- 8.1.1 Porapak N is added to a glass column and conditioned overnight at 180°C with helium or nitrogen as a carrier gas.

Exhibit 6
Volatile Organics in Air
(continued)

8.1.2 A 4 inch column of Porapak N is then inserted into a 10 inch x 1/4 inch borosilicate glass tube and is held in position by methanol-washed, silanized glass wool plugs. The Porapak N should be at one end of the glass tube, not in the center. This now constitutes a cartridge.

8.1.3 Cartridges are attached to a manifold in an oven and heated at 160°-180°C for 30-45 minutes, with carrier gas (He or N) following at approximately 20 ml/min.

8.1.4 Cartridges are capped when cool enough to handle. Store cartridges in a contamination-free area.

8.1.5 Following sample collection and solvent elution, cartridges may be reused if reconditioned as outlined in section 8.1.3.

8.2 Sample Collection

8.2.1 Cartridges are attached to the sampling manifold using Tygon tubing for connection between the cartridge and the GAST vacuum pump. Polyethylene "X" connectors are used to collect replicate, parallel samples. Flow rates are measured in the field using a laboratory calibrated rotameter and are measured both before and after sampling. Flow rates of 0.3 to 0.5 liters per minute are generally observed with the collection volume being appropriate for the analytes of interest (see 1.5). A critical orifice is not usually necessary because the resistance of the cartridge itself limits the flow rate.

8.2.2 Cartridges are kept capped until sample collection. After sampling the caps are replaced on the cartridges and the cartridges are either placed in screw-capped test tubes with Teflon liners or wrapped tightly in aluminum foil. Cartridges should be refrigerated at 4°C immediately after sample collection and transported to the laboratory promptly. Analysis should be performed as soon as possible after collection. A maximum holding time of 14 days is recommended.

8.3 The methanol elution of a cartridge is performed by clipping the cartridge in a vertical position with the lower end at about the 2 ml graduation of the collection tube. Methanol is added to the top of the cartridge and elution proceeds until 1.5 ml (or other known volume) of eluate has been collected. Once elution is begun, it must be completed without allowing the top of the Porapak N to be exposed to the air.

8.4 Blanks, spikes, and replicates should be eluted using the procedure in Section 8.3.

Exhibit 6
Volatile Organics in Air
(continued)

8.5 Gas chromatographic analysis is performed on eluates using conditions detailed in Sections:

8.5.1 Hall (HECD) detector

8.5.2 Photoionization (PID) detector

8.5.3 Electron capture (ECD) detector and/or PID

9. Calculations

9.1 Calculations are performed using the general formula:

$$\text{Concentration in air in ug/m}^3 = \frac{A}{B} \times \frac{C}{D} \times \frac{E}{F}$$

A = Area (or peak height) of sample peak

B = Area (or peak height) of standard peak

C = ng of standard represented by B

D = Volume of sample injected in ul

E = Final volume of eluate in ml

F = Sampling volume in cubic meters (m³)

9.2 If the analyst uses a calibration curve the following equation may be used:

$$\text{Concentration in Air in ug/m}^3 = \frac{A \times B}{C}$$

A = Concentration in eluate in ug/ml

B = Final volume of eluate in ml

C = Sampling volume in cubic meters (m³)

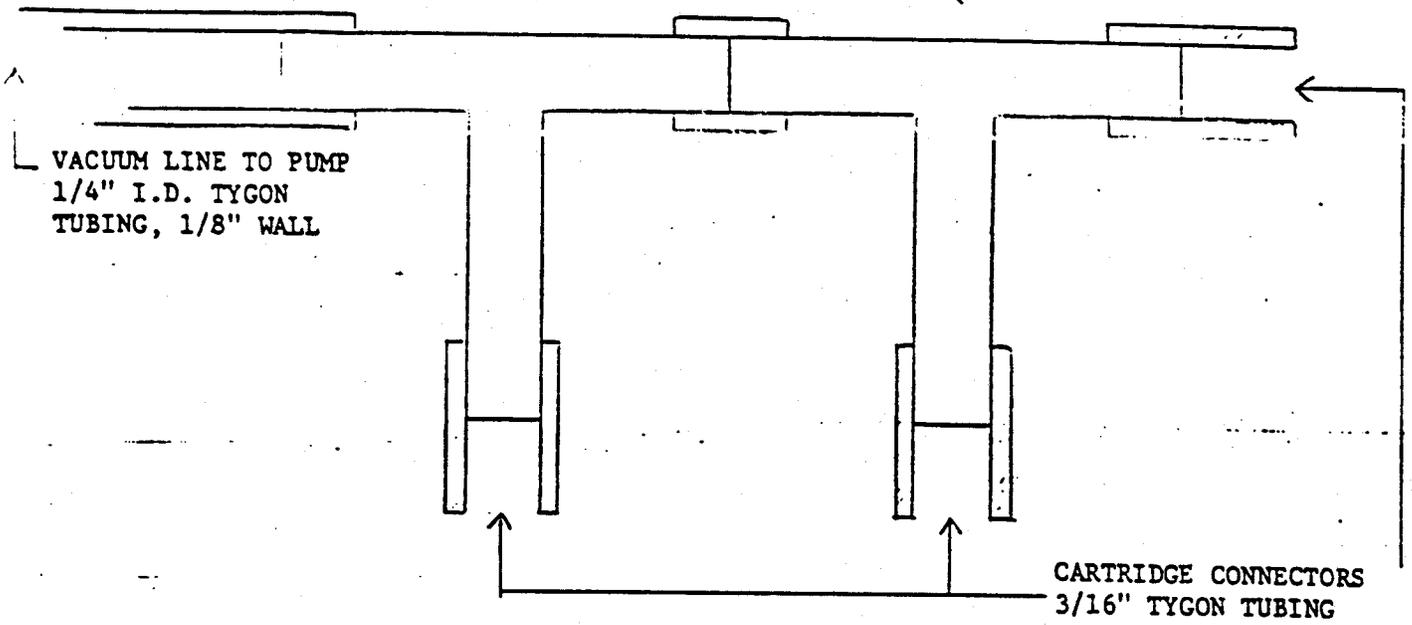
10. References

- 10.1 Van Tassel, S., Amalfitano, N., and Narang, R.S., "Determination of Arenes and Volatile Halo-organic Compounds in Air at Microgram/Cubic Meter Levels by Gas Chromatography". Analytical Chemistry, November 1981.
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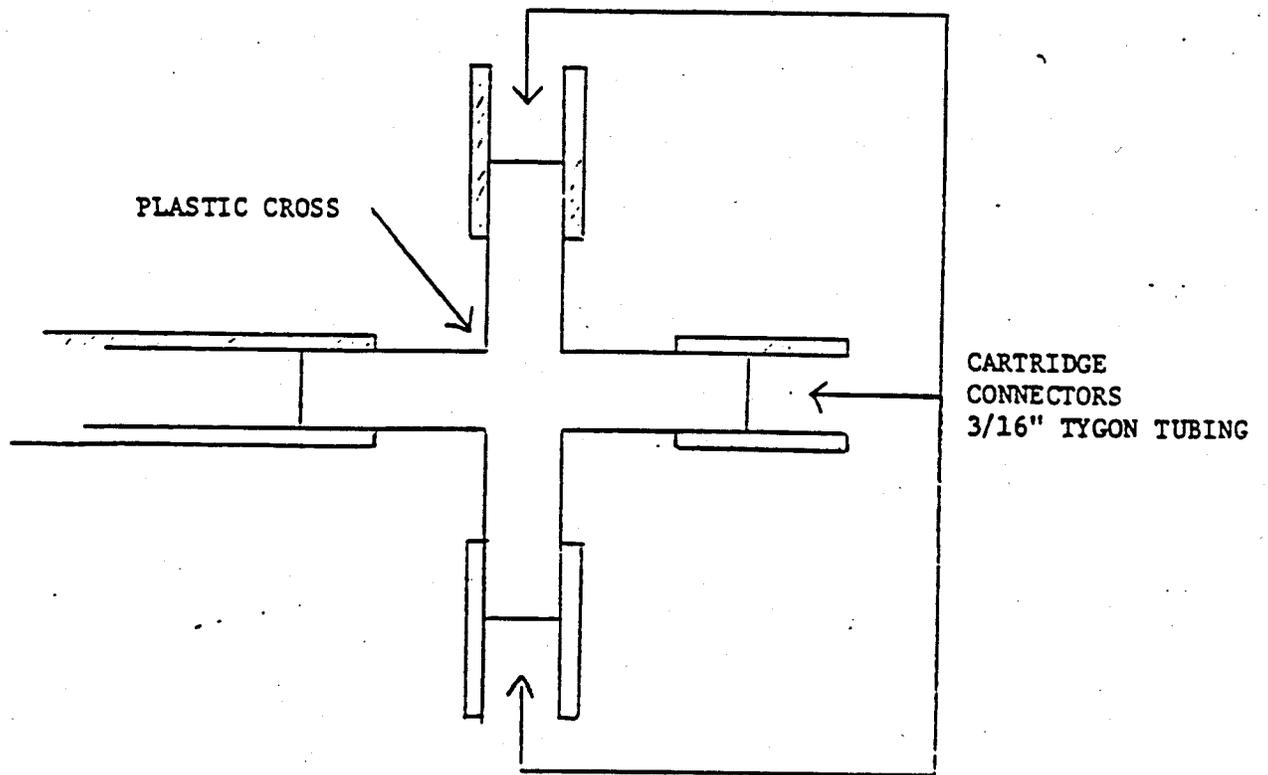
Exhibit 7

Sample Manifolds

PLASTIC TEES



A. TEES



B. CROSS

Exhibit 8

Sample Data Sheet

USE I.D. # (AS LOCATED ON PROJECT MAP): _____

OCCUPANT: _____

ADDRESS: _____

DATE COLLECTED: _____

COLLECTED BY: _____ ROTAMETER I.D. # _____

CARTRIDGE Shape, Size* Identification Number	Time Start	Time Stop Run	Total Time Reading (Min)	Initial Rotameter Reading (COB)	Final Rotameter Rate (COB)	Average Flow Volume (LPM)	Total Air (M ³)
Acc.#							

Long or Short (Lengths)

Remarks _____

SITE TEMPERATURE: _____

ODOR INTENSITY AND TYPE: _____

HUMIDITY (SLING PSYCHROMETER): _____

BASEMENT WALL CONDITION: _____

(PLEASE COMPLETE INFORMATION ON REVERSE SIDE)

Exhibit 8

**Sample Data Sheet
(continued)**

OTHER OBSERVATIONS: _____

WEATHER ON SAMPLING DAY: _____

LAST PREVIOUS RAINFALL AND DURATION: _____

APPROX. AGE OF HOUSE: _____

DEHUMIDIFIER IN USE? _____

MAP: _____

LOCATION OF FACILITIES IN BASEMENT (BEDROOMS, PLAYROOMS,
LAUNDRY AREA) _____

LOCATION OF SUMP AND SAMPLER (Including Height of Sampler) _____

LOCATION WINDOWS AND VENT FANS, IF PRESENT _____

Exhibit 9

Assembled Sample Collection Equipment

