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# SAMPLING APPROACHES FOR THE MEASUREMENT OF VOLATILE COMPOUNDS AT HAZARDOUS WASTE SITES

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## Summary

Sampling approaches suitable for investigating emissions from hazardous waste sites are reviewed. Sampling approaches for measuring volatile compound emission rates and for measuring soil gas concentrations of volatile compounds are each discussed. Discussion of the former category includes emission isolation flux chamber, vent sampling, concentration-profile, transect, and mass balance approaches. Discussion of the latter category includes headspace analysis of soil cores, soil gas probes, and passive samplers. Each approach is described, the applicable equation presented, the researchers cited, and the approach discussed in terms of its utility for emissions investigations.

## Introduction

The potential for release of volatile and sometimes toxic air contaminants exists at uncontrolled hazardous waste sites addressed by CERCLA. These uncontrolled hazardous waste sites can also include landfills and surface impoundments, as well as spills to groundwater occurring from leaking underground storage tanks, pipelines and ponds. Release may also occur at RCRA facilities such as landfills, landtreatment plots and surface impoundments. Emissions of these volatile air contaminants may impact the health and safety of workers on the site, and those residents in the surrounding community. Historically, the only acknowledgement that hazardous waste sites presented a potential air pollution problem was through the many nuisance odor complaints received. More recently, residents in the vicinity of hazardous waste sites have reported symptoms associated with exposure to volatile organic compounds, and concentrations of vapors have been measured at and above the explosive limits in areas where organic compounds have been leaked to groundwater. For these reasons, concern over the air emissions from such sources has increased and as such has presented the need to measure these air pollutants.

The measurement of volatile compounds in ambient air has been dealt with by various researchers, addressing both sample collection and sample analysis. While a knowledge of the concentration of these volatile compounds in ambient air is of interest since it documents the air quality, a

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direct measurement of the emission rate from the source is also desirable. Emission rate information for hazardous waste sites can be used for exposure assessment, assessing air quality impacts under various meteorological conditions and developing suitable control strategies. Additionally, a measure of the volatile compound concentration in the soil and/or waste itself can provide information on the potential for volatile emissions and has even been used as a surrogate parameter for defining the areal extent of contamination in soil.

This article reviews the approaches for measuring volatile compound emission rates and soil gas concentrations at hazardous waste sites. Information is provided on a variety of techniques for making these measurements. The intent of the article is to provide the reader with general information on the techniques rather than provide an exhaustive protocol for a single technique.

## Description of sampling approaches

Sampling approaches for measuring volatile compound emission rates from hazardous waste sites include: (1) emission isolation flux chamber, (2) vent sampling, (3) concentration-profile, (4) transect technique, and (5) mass balance. Each of these techniques provide an emission rate, either through direct measurement or indirectly through measured and calculated values, as opposed to a concentration of the volatile compound in air. Sampling approaches for measuring soil gas concentrations of volatile compounds include: (1) headspace analysis of soil cores, (2) soil gas probes, and (3) passive samplers. These techniques measure a soil gas concentration, as opposed to an emission rate. In either case, the techniques discussed will deal with the approach used to obtain the sample. The procedures for sample collection and subsequent or simultaneous (real-time) sample analysis are not discussed. In most cases, some form of discrete sample collection technique such as gas tight syringe, stainless steel canister, or sorbent cartridge followed by gas chromatographic analysis is appropriate. These procedures have been described by others [1].

### *Emission isolation flux chamber*

The emission isolation flux chamber is a device used to make direct emission rate measurements from land or liquid surfaces such as landfills, spill-sites and surface impoundments. The enclosure approach has been used by researchers to measure emission fluxes of a variety of gaseous species including sulfur and volatile organic species [2—10]. The approach uses an enclosure device (flux chamber) to sample gaseous emissions from a defined surface area. Clean dry sweep air is added to the chamber at a fixed, controlled rate. The volumetric flow rate of sweep air through the chamber is recorded and the concentration of the species of interest is measured at the exit of the chamber. The emission rate is expressed as

$$E_i = C_i R / A \qquad (1)$$

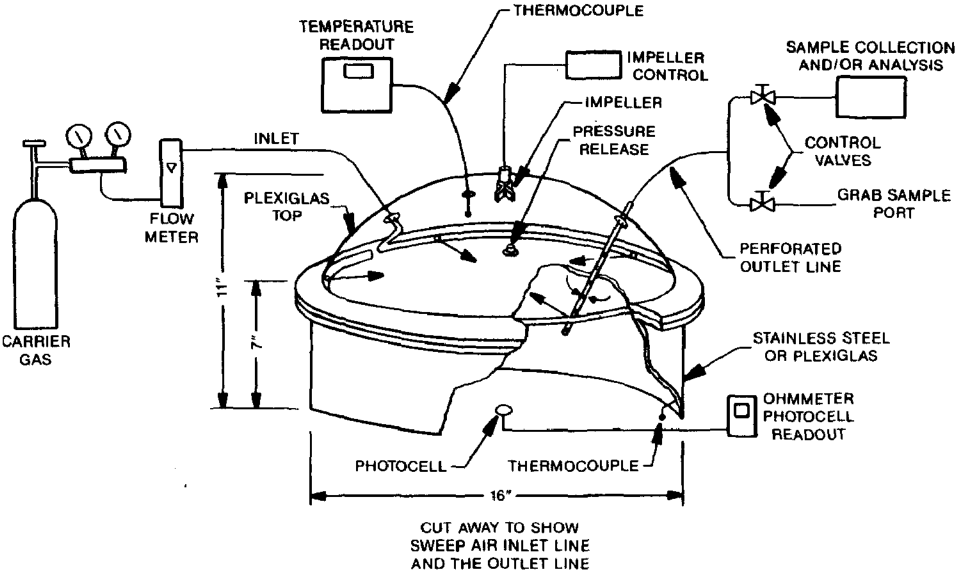

Fig. 1. Schematic diagram of isolation emission flux chamber.

where, $E_i$ = emission rate of component $i$ [$\mu$g/m$^2$ s], $C_i$ = concentration of component $i$ in the air flowing from the chamber [$\mu$g/m$^3$], $R$ = flow rate of air through the chamber [m$^3$/s], and $A$ = surface area enclosed by the chamber [m$^2$]. All parameters in eqn. (1) are measured directly.

A diagram of the flux chamber apparatus used for measuring emission rates from area sources is shown in Fig. 1. The design and operating protocol has recently been validated through extensive testing at a controlled emission source [11]. The sampling equipment consists of a stainless-steel/acrylic chamber, ultra high purity sweep air (normally 5 l/m) and rotameter for measuring flow into the chamber, a thermocouple for measuring the air temperature within the chamber and a sampling manifold for monitoring and/or collection of the species of interest. For wastes containing volatile organic compounds (VOC), concentrations of total hydrocarbons can be monitored continuously in the chamber outlet gas stream using portable flame ionization detector (FID)- and/or photoionization detector (PID)-based analyzers. Discrete samples are collected for subsequent gas chromatographic (GC) analysis once a steady-state emission rate is obtained in the flux chamber (typically within 30 min). The area sources to be measured are typically gridded and a minimum of six measurements made (when possible) to account for spatial variability. Additionally, a single point is selected and resampled as a control point to define temporal variability. Prior to using the chamber, blank and species recovery data are obtained as part of standard quality control procedures for the emission rate measurements. Table 1 presents typical recoveries which can be expected using the flux chamber. The values in Table 1 were generated by introducing a multicomponent gas

TABLE 1

Compounds tested in the emission isolation flux chamber and the measured % recovery

| Compound | % Recovery | Compound | % Recovery |
|---|---|---|---|
| Total $C_2$ | 100 | 3-Methylhexane | 106 |
| Total $C_3$ | 108 | 2,2,4-Trimethylpentane | 106 |
| Isobutane | 109 | n-Heptane | 103 |
| 1-Butene | 108 | Methylcyclohexane | 103 |
| n-Butane | 106 | Toluene | 103 |
| *trans*-2-Butene | 107 | Ethyl benzene | 94.7 |
| *cis*-2-Butene | 109 | *m*- and *p*-Xylene | 88.5 |
| Isopentane | 112 | *o*-Xylene | 97.3 |
| 1-Pentene | 105 | n-Nonane | 99.4 |
| 2-Methyl-1-butene | 124 | n-Propylbenzene | 95.5 |
| n-Pentene | 103 | *p*-Ethyltoluene | 92.5 |
| *cis*-2-Pentene | 105 | 1,3,5-Trimethylbenzene | 93.5 |
| Cyclopentene | 105 | 1,2,4-Trimethylbenzene | 88.7 |
| Isohexane | 107 | 2-Methyl-2-butene | 103 |
| 3-Methylpentane | 106 | Methyl mercaptan | 107 |
| Methylcyclopentane | 105 | Ethyl mercaptan | 107 |
| Benzene | 106 | Butyl mercaptan | 101 |
| 1,2-Dimethylpentane | 105 | Tetrahydrothiophene | 115 |

standard into the flux chamber at a known rate, operating the flux chamber in typical fashion and collecting the exit gas for analysis.

A modified design of the emission isolation flux chamber has also been used to measure emission rates during coring of wastes. The downhole flux chamber is placed down a hollow stem auger in the same manner as a core sampler. This technique makes it possible to measure emission rates from waste bodies which may be exposed during remedial action activities.

### *Vent sampling*

Methods for measuring emissions from ducted sources are well documented [12]. This approach can be applied to landfill vents or vents for storage tanks. The approach requires that the volumetric flow rate of the gas be determined, typically as measurements of velocity and duct cross-sectional area, and that the gas concentration be measured. The emission rate from the vent can then be calculated as

$$E_i = C_i U A \tag{2}$$

where, $E_i$ = emission rate of component $i$ [µg/s], $U$ = gas velocity through vent [m/s], and $C_i$ = concentration of component $i$ in vent gas [µg/m$^3$]. All parameters in eqn. (2) are measured directly.

Under certain circumstances, the gas flow rate from a vent may be either intermittent or so low that accurate measurement of the gas flow is not possible. In such cases, the vent emission rate may be measured directly using the flux chamber. The chamber would be placed directly over the vent and any open space between the vent and chamber sealed.

*Concentration-profile*

The concentration-profile (C-P) technique was developed by L.J. Thibodeaux, C. Springer and others at the University of Arkansas under a U.S. Environmental Protection Agency cooperative agreement [13]. The C-P technique, as developed by Thibodeaux, has been used to estimate emission rates of volatile species from wastewater treatment ponds [13—16] and more recently from land treatment facilities [16,17]. The C-P approach is an indirect sampling technique predicated upon experimental measurements of wind velocity, volatile species concentration and temperature profiles in the boundary layer above the waste body. These measurements are used to estimate the vertical flux of the volatile species as:

$$E_i = \left( \frac{D_i}{D_{\mathrm{H_2O}}} \right)^n S_v S_i K^2 / \phi_m{}^2 S_c \qquad (3)$$

where, $E_i$ = emission rates (flux) of organic species $i$ [g/cm$^2$ s], $D_i$ = molecular diffusivity of organic species $i$ in air [cm$^2$/s], $D_{\mathrm{H_2O}}$ = molecular diffusivity of water vapor in air [cm$^2$/s], $K$ = von Karman's constant, $S_v$ = logarithmic slope of the air velocity profile [cm/s], $S_i$ = logarithmic slope of the concentration-profile for organic species $i$ [g/cm$^3$], $\phi_m$ = Businger wind shear parameter, $S_c$ = turbulent Schmidt number, and $n$ = exponent for diffusivity ratio.

The term $(\phi_m{}^2 S_c)^{-1}$ represents an atmospheric stability correction factor and is expressed as a function of the Richardson number. The function is an empirical correlation which corrects the estimated emission rate for water vapor to measured values under various atmospheric stabilities. For this reason, the correction factor is valid only under specific meteorological conditions. The molecular diffusivities of water and many organic species are available in the open literature [18,19]. Diffusivities for those compounds for which values are not available, and for compound classes or total hydrocarbons must be estimated.

A diagram of a C-P sampling system used is shown in Fig. 2. The sampling equipment consists of the following: a four-meter mast with a wind direction indicator, wind speed sensors, temperature sensors, and air collection probes spaced at six logarithmic intervals; a continuous real-time data collection system; a thermocouple for measuring water temperature; and water sampling equipment.

Prior to sample collection, meteorological conditions are monitored to determine compliance with the necessary meteorological criteria. Once acceptable meteorological conditions are documented, the sample collection period is initiated. During the sample collection period, wind speed, air temperature, water temperature, and relative humidity are measured.

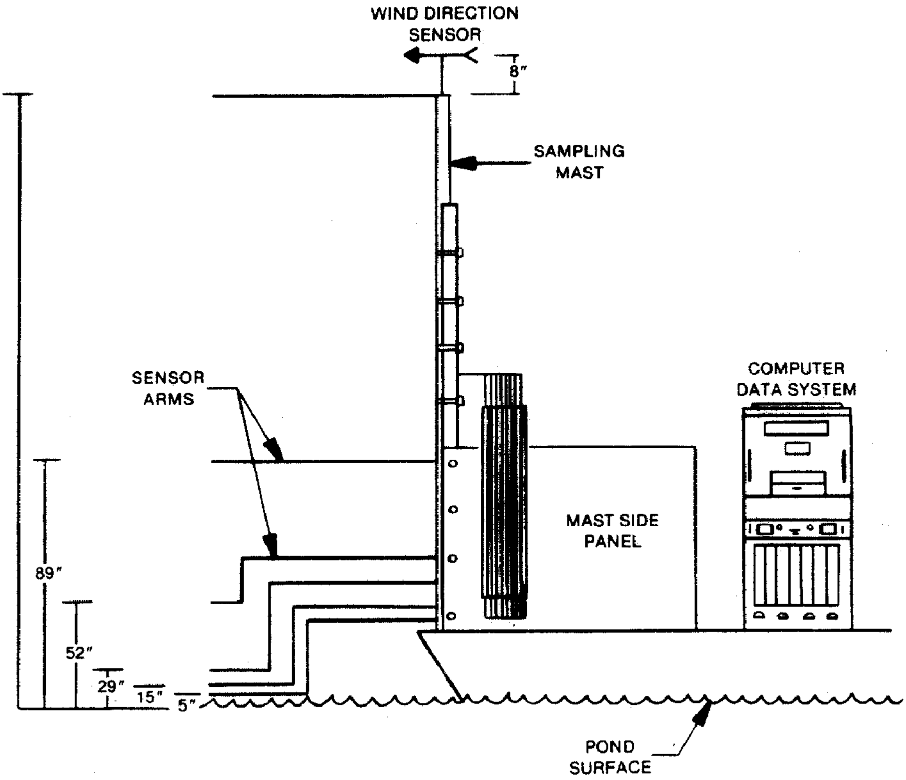

Fig. 2. Mast sample collection system for concentration-profile sampling.

Since any volatile compound emissions will have been diluted in the ambient air by the time they are measured by the CP approach, the sample collection and analytical systems must have much lower limits of detection and lower background contaminants than those used with the flux chamber.

*Transect technique*

The transect technique is an indirect emission measurement approach which has been used to measure fugitive particulate and gaseous emissions from area and line sources [16,20]. Application of this technique include landfills, surface impoundments and waste handling operations. Horizontal and vertical arrays of samplers are used to measure concentrations of volatile specie(s) within the effective cross-section of the fugitive emission plume. The volatile specie(s) emission rate is then obtained by spatial integration of the measured concentrations over the assumed plume area

$$E_i = uA_s \iint_{A_p} C_{i(h,w)}\,\mathrm{d}h\mathrm{d}w \tag{4}$$

where, $E_i$ = emission rate of component $i$ [$\mu$g/m$^3$ s], $u$ = wind speed [m/s], $C_i$ = concentration of component $i$ at point $(h,w)$, corrected for upwind

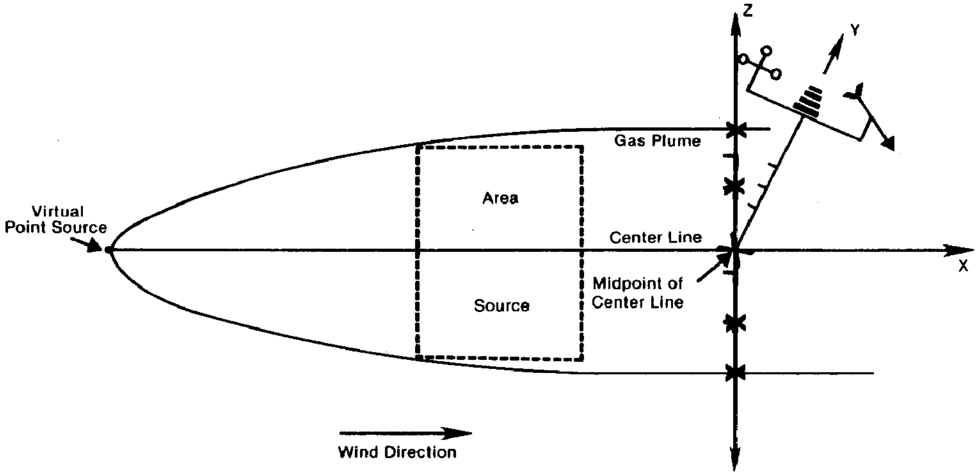

**Fig. 3. Example of transect technique sampling.**

background [$\mu g/m^3$], $h$ = vertical distance coordinate [m], $w$ = horizontal distance coordinate [m], $A_S$ = surface area of emitting source [$m^2$], and $A_P$ = effective cross-sectional area of plume [$m^2$].

A diagram of a transect sampling system used is shown in Fig. 3. The sampling equipment consists of a central 3.5 m mast having three equally spaced air sampling probes and single wind direction, wind speed, and temperature sensors at the top, and five 1.5 m masts with single air sampling probes. The central mast is aligned with the expected plume centerline. Two masts are placed at equal spacings on each side of the central mast and one mast is used to collect air samples at an upwind location. The spacing of the associated masts are selected to cover the expected horizontal plume cross-section, as defined by observation and/or profiling with a real-time total hydrocarbon (THC) analyzer.

Prior to sample collection, meteorological parameters are monitored to determine if acceptable sampling conditions existed. Following documentation of acceptable meteorological conditions, sampling is initiated. As with the C-P technique, sample collection and analytical systems must have lower detection levels and background contaminants than with the flux chamber. During the sampling period, meteorological parameters are monitored.

### *Mass balance*

Theoretically, emissions rates or losses from any process can be estimated from an accurate mass balance. For example, if all input and outlet streams for a surface impoundment or tank are precisely characterized with regard to flow rates, composition, and physical properties, any difference between the total known amount of material entering the system and that known to be leaving, would be losses or emissions. This can be expressed as

$$\text{Mass losses} = \text{mass in} - \text{mass out} \tag{5}$$

Other examples of where a mass balance approach has been used for measuring emission rates include waste transfer operations and solvent recovery operations.

In practice, precise measurement of material volumes, flow rates, and characteristics are often difficult to obtain. Most flow rates and material rate measurements in chemical processing are made in terms of volume. Thus, fluid densities must be known to convert volumetric measurements to mass flows. A liquid material balance can be expressed as

$$E_i = L_j W_{i,j} P_j - L_k W_{i,k} P_k \tag{6}$$

where, $E_i$ = emissions (losses) of component $i$ [lb], $L_j$ = volume of input stream $j$ [gal], $L_k$ = volume of output stream $k$ [gal], $W_{i,j}$ = weight fraction of component $i$ in input stream $j$, $W_{i,k}$ = weight fraction of component $i$ in outlet stream $k$, and $P_j$, $P_k$ = density of liquid streams $j$ and $k$, respectively [lb/gal].

All parameters in eqn. (6) are measured. Difficulties in making accurate measurements and the fact that the losses are typically a small percentage of the "mass in" and "mass out" make this approach difficult to apply with good results.

### *Headspace measurements*

The concentrations of volatile compounds in the soil gas can be obtained by analyzing the headspace gas from samples collected in subsurface structure or from soil cores. Sampling the headspace in existing subsurface structures is a simple technique that can yield valuable information regarding the levels of volatile compounds in the soil gas. The technique involves collecting grab samples or using a portable hydrocarbon analyzer to measure the headspace concentration in monitoring wells, storm sewers, utility vaults, or other subsurface structures. The results obtained may provide information regarding the extent of any contaminant plume and assist in identifying health and safety considerations for subsequent investigative work.

The headspace gas or extracted solids of a soil waste core can also be analyzed to determine volatile compound concentrations. To obtain a sample to measure the headspace, an undisturbed core is collected using an auger or by driving a tube into the ground. The sample is then sealed in a sample container with minimal headspace.

Soil cores can be obtained using a variety of equipment as illustrated by the U.S. EPA's recent review [21]. A number of researchers have applied this technique to detecting volatile compounds in soil gases at various subsurface levels [22—29].

The primary limitation of this headspace technique is that it is better suited for measuring adsorbed organics rather than free organics in the interstitial pore spaces [29]. This implies that the technique would be better applied for coring into wastes rather than a soil overburden or cover. Another limitation to this technique is the possible loss of volatile hydro-

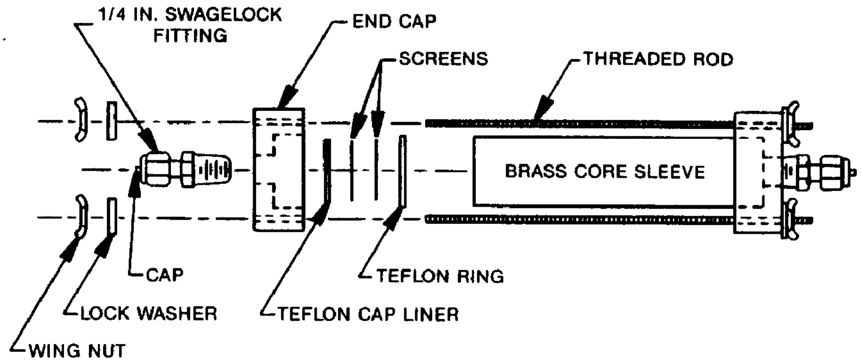

**Fig. 4. Soil core sample sleeve.**

carbons when the sample is removed form the ground or transferred for analysis. Sample exposure to the atmosphere has been successfully avoided by capping the soil core tubes [29,30]. Hanisch and McDevitt [29] reported a technique used at several hazardous waste sites. The core sampler used (Fig. 4) consists of a brass core sleeve which is pressed into the soil to a sufficient depth to fill the sampler but not compress the sample. After excess soil is removed, the sleeve is sealed with a Teflon-lined cap. The samples are stored at room temperature. Headspace gas is removed from the core by a syringe and analyzed by GC.

### *Ground probes*

Ground probes can be used to collect samples of soil gas in-situ at varying depths to determine the concentration of volatile compounds. A variety of ground probe designs and operations have been used by researchers [31—46]. In most applications, however, investigators used the ground probes to obtain information regarding the presence of species or relative differences in concentrations, as opposed to an accurate measure of the soil gas concentration. As such, the technique has been used quite extensively to detect and map the areal extent of subsurface contamination. This is accomplished by assuming that the volatile compounds can serve as an indicator of the subsurface contamination. The approach has proven useful for mapping groundwater contamination by gasoline and chlorinated solvents, as well as for determining the effectiveness of ground vapor ventilation systems.

An example of a ground probe is shown in Fig. 5. In general, the probes are made-up of a tube with a drive head to allow the probe to be driven into the ground. A variety of drive mechanisms have been used including manual (sledge hammer or post driver), pneumatic or sliding weight. When being inserted from the surface, ground probes are typically used at depths from 1 to 3 m. However, they can be placed at greater depths by first drilling a pilot hole to within 1.5 m of the desired depth, driving the ground probe and then backfilling the hole around the ground probe. Once in place, soil gas enters the probe through a series of holes or openings. Investigators have operated

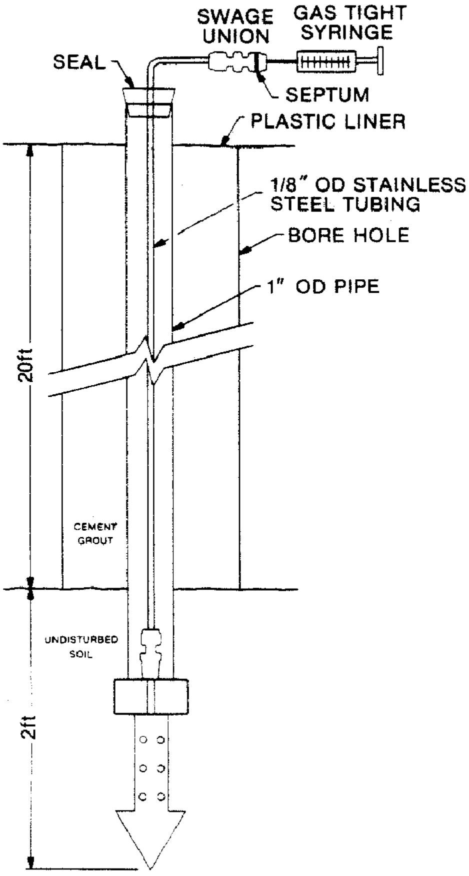

Fig. 5. Schematic diagram of vapor sampling probe.

the ground probes in both static and dynamic modes. In the dynamic mode, soil gas is pumped through the ground probe using a vacuum pump. By pumping soil gas through the ground probe, the soil gas equilibrium is more than likely disrupted. This may result in the measured concentration from the ground probe changing with time, if the soil gas is removed from the soil pore space at a rate faster than which it can be replenished. In the static mode, the ground probe is allowed to equilibrate with the soil gas, and a small volume withdrawn for analysis. If the ground probe is to be used as a static device, it is best to have minimal dead-space, since this will improve the ability of the system to equilibrate with the soil gas. The subsequent analysis is basically a headspace analysis.

### *Passive samplers*

Passive samplers can be used to detect volatile compounds alone or with other techniques, like ground probes. Passive samplers rely upon diffusion of the compound to bring it into contact with the sample collection device, rather than sampling a known volume of gas. For this reason, it is difficult to correlate the concentration of the compound measured to the concentration of the compound in the soil gas. Probably the most common passive sampler used for detecting volatile compounds is the Petrex technique [47—50], although a variety of passive dosimeters have been used in conjunction with headspace sampling and ground probes [38, 51- 53].

The Petrex technique, which has a patent pending uses a thin ferromagnetic (Curie-point) wire coated with an activated charcoal. The wire is placed in a glass tube and buried 0.15—0.30 m below the surface for several weeks. When the sample is retrieved, the wire is placed in a vacuum chamber, heated and the desorbed compounds analyzed by Curie-point mass spectrometry. The procedure cannot be used in frozen or saturated soils, but has minimal effects from rain or other varying meteorological conditions. The technique has been used for oil exploration as well as investigations of hazardous waste sites.

## Conclusion

A variety of approaches exists for measuring both emission rates and soil gas concentrations at hazardous waste sites. In choosing an approach an investigator must first determine the end use of the data. Soil gas measurement techniques can provide measurements of the concentration of a compound in the soil, but cannot be used to determine exposure to workers or homeowners bordering a site. A decision also should be made regarding the accuracy of the measurement which will be acceptable. Many of the techniques for measuring soil gas concentrations are best suited for detecting the presence of a compound rather than accurately measuring the concentration in the soil gas.

Very few of the approaches described here have undergone rigorous validation of the technique. For this reason, it is important that the users of the techniques be familiar with environmental sampling and include appropriate provisions for defining the quality of the data collected. Recently, the emission isolation flux chamber approach underwent validation tests at a controlled emission source. A specific protocol for design, construction and operation has been developed as a result of this testing. The protocol is undergoing peer review prior to being released by EPA.

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