



Designation: D 5314 – 92 (Reapproved 2001)

Standard Guide for Soil Gas Monitoring in the Vadose Zone¹

This standard is issued under the fixed designation D 5314; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This guide covers information pertaining to a broad spectrum of practices and applications of soil atmosphere sampling, including sample recovery and handling, sample analysis, data interpretation, and data reporting. This guide can increase the awareness of soil gas monitoring practitioners concerning important aspects of the behavior of the soil-water-gas-contaminant system in which this monitoring is performed, as well as inform them of the variety of available techniques of each aspect of the practice. Appropriate applications of soil gas monitoring are identified, as are the purposes of the various applications. Emphasis is placed on soil gas contaminant determinations in certain application examples.

1.2 This guide suggests a variety of approaches useful to successfully monitor vadose zone contaminants with instructions that offer direction to those who generate and use soil gas data.

1.3 This guide does not recommend a standard practice to follow in all cases nor does it recommend definite courses of action. The success of any one soil gas monitoring methodology is strongly dependent upon the environment in which it is applied.

1.4 Concerns of practitioner liability or protection from or release from such liability, or both, are not addressed by this guide.

1.5 This guide is organized into the following sections and subsections that address specific segments of the practice of monitoring soil gas:

Section	
4	Summary of Practice
4.1	Basic principles, including partitioning theory, migration and emplacement processes, and contaminant degradation
4.7	Summary Procedure
5	Significance and Use
6	Approach and Procedure
6.1	Sampling Methodology
6.5	Sample Handling and Transport
6.6	Analysis of Soil Gas Samples
6.7	Data Interpretation
7	Reporting

1.6 *This guide does not purport to set standard levels of acceptable risk. Use of this guide for purposes of risk assessment is wholly the responsibility of the user.*

1.7 The values stated in either inch-pound or SI units are to be regarded separately as the standard. The values given in parentheses are for information only.

1.8 *This standard does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

1.9 *This guide offers an organized collection of information or a series of options and does not recommend a specific course of action. This document cannot replace education or experience and should be used in conjunction with professional judgment. Not all aspects of this guide may be applicable in all circumstances. This ASTM standard is not intended to represent or replace the standard of care by which the adequacy of a given professional service must be judged, nor should this document be applied without consideration of a project's many unique aspects. The word "Standard" in the title of this document means only that the document has been approved through the ASTM consensus process.*

2. Referenced Documents

2.1 ASTM Standards:

D 653 Terminology Relating to Soil, Rock, and Contained Fluids²

D 1356 Terminology Relating to Atmospheric Sampling and Analysis³

D 1357 Practice for Planning the Sampling of the Ambient Atmosphere³

D 1452 Practice for Soil Investigation and Sampling by Auger Borings²

D 1605 Practices for Sampling Atmospheres for Analysis of Gases and Vapors³

D 1914 Practice for Conversion Units and Factors Relating to Atmospheric Analysis³

D 2652 Terminology Relating to Activated Carbon⁴

¹ This guide is under the jurisdiction of ASTM Committee D18 on Soil and Rock and is the direct responsibility of Subcommittee D18.21 on Ground Water and Vadose Zone Investigations.

Current edition approved Nov. 15, 1992. Published January 1993.

² Annual Book of ASTM Standards, Vol 04.08.

³ Annual Book of ASTM Standards, Vol 11.03.

⁴ Annual Book of ASTM Standards, Vol 15.01.

- D 2820 Test Method for C₁ Through C₅ Hydrocarbons in the Atmosphere by Gas Chromatography³
- D 3249 Practice for General Ambient Air Analyzer Procedures³
- D 3416 Test Method for Total Hydrocarbons, Methane, and Carbon Monoxide (Gas Chromatographic Method) in the Atmosphere³
- D 3584 Practice for Indexing Papers and Reports on Soil and Rock for Engineering Purposes²
- D 3614 Guide for Laboratories Engaged in Sampling and Analysis of Atmospheres and Emissions³
- D 3670 Guide for Determination of Precision and Bias of Methods of Committee D-22³
- D 3686 Practice for Sampling Atmospheres to Collect Organic Compound Vapors (Activated Charcoal Tube Adsorption Method)³
- D 3687 Practice for Analysis of Organic Compound Vapors Collected by the Activated Charcoal Tube Adsorption Method³
- D 4220 Practices for Preserving and Transporting Soil Samples²
- D 4490 Practice for Measuring the Concentration of Toxic Gases or Vapors Using Detector Tubes³
- D 4597 Practice for Sampling Workplace Atmospheres to Collect Organic Gases or Vapors with Activated Charcoal Diffusional Samplers³
- D 4696 Guide for Pore-Liquid Sampling from the Vadose Zone²
- D 4700 Guide for Soil Core Sampling from the Vadose Zone²
- D 5088 Practice for the Decontamination of Field Equipment Used at Non Radioactive Waste Sites⁵
- E 177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods⁶
- E 260 Practice for Packed Column Gas Chromatography⁷
- E 355 Practice for Gas Chromatography Terms and Relationships⁷
- E 594 Practice for Testing Flame Ionization Detectors Used in Gas Chromatography⁷
- E 697 Practice for Use of Electron-Capture Detectors in Gas Chromatography⁷

3. Terminology

3.1 Definitions of Terms Specific to This Standard:

3.1.1 *capillary fringe*—the basal region of the vadose zone comprising sediments that are saturated, or nearly saturated, near the water table, gradually decreasing in water content with increasing elevation above the water table. Also see Terminology D 653.

3.1.2 *contaminant*—substances not normally found in an environment at the observed concentration.

3.1.3 *emplacement*—the establishment of contaminant residence in the vadose zone in a particular phase.

3.1.4 *free product*—liquid phase contaminants released into the environment.

3.1.5 *free vapor phase*—a condition of contaminant residence in which volatilized contaminants occur in porosity that is effective to free and open gaseous flow and exchange, such porosity generally being macroporosity.

3.1.6 *liquid phase*—contaminant residing as a liquid in vadose zone pore space, often referred to as “free product.”

3.1.7 *macroporosity*—large intergranular porosity with large pore throats, including soil cracks, moldic porosity, animal burrows and other significant void space.

3.1.8 *microporosity*—intragranular porosity and microscopic intergranular porosity with submicroscopic pore throats.

3.1.9 *occluded vapor phase*—condition of contaminant residence in which volatilized contaminants occur in porosity that is ineffective to free and open gaseous flow and exchange, such porosity generally being microporosity; frequently termed dead-end pore space.

3.1.10 *partitioning*—the act of movement of contaminants from one soil residence phase to another.

3.1.11 *soil gas*—vadose zone atmosphere.

3.1.12 *solute phase*—a condition of contaminant residence in which contaminants are dissolved in ground water in either the saturated or the vadose zone.

3.1.13 *sorbed phase*—a condition of contaminant residence in which contaminants are adsorbed onto the surface of soil particles or absorbed by soil organic matter.

3.1.14 *vadose zone*—the hydrogeological region extending from the soil surface to the top of the principal water table.

4. Summary of Guide

4.1 Soil gas monitoring in the vadose zone is a method used to directly measure characteristics of the soil atmosphere that are frequently utilized as an indirect indicator of processes occurring in and below a sampling horizon. Soil gas monitoring is used as a method to suggest the presence, composition, and origin of contaminants in and below the vadose zone. Among other applications, this method is also employed in the exploration for natural resources, including petroleum, natural gas and precious metals. Soil gas monitoring is a valuable screening method for detection of volatile organic contaminants, the most abundant analytical group of ground-water contaminant compounds (1).⁸

4.2 *Basic Theoretical Principles*—The processes indicated by the soil gas monitoring method are partitioning, migration, emplacement and degradation. Partitioning represents a group of processes that control contaminant movement from one physical phase to another, these phases being liquid, free vapor (that is, through-flowing air (2)), occluded vapor (that is, locally accessible air and trapped air (2)), solute and sorbed. Migration refers to contaminant movement over distance with any vertical, horizontal or temporal component. Emplacement refers to establishment of contaminant residence in any phase within any residence opportunity. Degradation is the process whereby contaminants are attenuated by oxidation or reduction in the vadose zone, either through biogenic or abiogenic processes. Soil gas monitoring measures the result of the

⁵ Annual Book of ASTM Standards, Vol 04.09.

⁶ Annual Book of ASTM Standards, Vol 14.02.

⁷ Annual Book of ASTM Standards, Vol 14.01.

⁸ The boldface numbers given in parentheses refer to a list of references at the end of the text.

interaction of these processes in a dynamic equilibrium. Measurement of these processes in static equilibrium is unrealistic.

4.3 The following subsections provide detailed information on partitioning, migration, emplacement and degradation. Subsection 4.4 provides a summary procedure for soil gas sampling. Users of this guide who do not wish to study details of partitioning, migration, emplacement and degradation at this time may skip to 4.4.

4.3.1 Partitioning is the initial step by which contaminants begin to move away from their source. Partitioning occurs in water saturated and unsaturated environments. This group of processes is complex and difficult to quantify when considered in the vadose zone due to the unique makeup of the vadose matrix, i.e. air-filled porosity (microporous and macroporous), pore water, free product, solid-phase soil organic matter, clay and discrete inorganic soil particles. Important individual processes of partitioning are dissolution, volatilization, air-water partitioning, soil-water partitioning and soil-air partitioning (3).

4.3.2 Dissolution is the process whereby volatile contaminants move between the liquid phase (free product) and the solute phase (dissolved in water). At equilibrium, the product of the mole fraction of a particular compound in the liquid phase and the activity coefficient of that compound in the liquid phase is equal to the product of the mole fraction of that compound in the solute phase and the activity coefficient of that compound in the solute phase. This process is more clearly described by the following expression:

$$X_I^L \Gamma_I^L = X_I^W \Gamma_I^W \quad (1)$$

where:

X_I^L = the mole fraction of compound (I) in the liquid (L) phase (free product),

X_I^W = the mole fraction of compound (I) in the solute (W) phase (dissolved in water),

Γ_I^L = the activity coefficient of compound (I) in the liquid (L) phase (free product), and

Γ_I^W = the activity coefficient of compound (I) in the solute (W) phase (dissolved in water).

Dissolution equilibrium is therefore influenced by concentration of the subject compound in both the free product contaminant mixture and water. The most common practical application of expression (Eq 1) in soil gas monitoring is in hydrocarbon detection. Simplification of (Eq 1) is achieved by the following:

assume:

$$\Gamma_I^W = 1/S_I$$

where:

S = the solubility of compound (I) in water

and:

$\Gamma_I^L = 1$, acceptable for hydrocarbons (3),

then:

$$X_I^W = X_I^L S_I \quad (2)$$

4.3.2.1 Dissolution equilibrium is impacted by the presence of liquid phase cosolvents, such as gasoline additives, at low concentrations in liquid phase mixtures. This change in dissolution equilibrium can enhance the solubility of certain liquid

phase components in water beyond what is indicated by partitioning coefficient data generated in the laboratory. This can have significant impact on downstream concentrations of the contaminant(s) in the soil atmosphere.

4.3.2.2 The effects of temperature upon dissolution equilibrium are generally insignificant for aliphatic hydrocarbons between 15 and 50°C (4), the temperature range from which most soil gas samples are recovered. However, temperature effects upon dissolution equilibrium can be significant for other common families of contaminant compounds within similar temperature ranges (5). These effects must be considered when planning or interpreting the results of a soil gas survey.

4.3.2.3 Dissolution equilibrium is altered by changes in water salinity. Modest decreases in the solubility of contaminants in water are to be expected with increases in salinity of the solution.

4.3.2.4 The rate of dissolution is strongly dependent upon the partitioning coefficient of the particular contaminant of interest and the amount of mixing of the liquid phase and water (3). For example, partitioning of a particular contaminant into ground water is accelerated by frequent water level fluctuations within a contaminated capillary fringe. The downstream implications for subsequent partitioning of the contaminant from the solute to the vapor phase for eventual soil gas recovery are obvious.

4.3.3 Volatilization is the process during which volatile contaminants move between the liquid phase (free product) or solute phase and a vapor phase, either the free vapor phase or the occluded vapor phase or both. Contaminant mixtures can contain compounds with a considerable range of vapor pressures that can contribute contaminants to the soil atmosphere by volatilization. This atmosphere will exhibit a composition similar to that of the parent contaminant but lacking in those constituents with the lowest vapor pressures. The likelihood of the presence of a particular contaminant introduced into the soil atmosphere by volatilization can be estimated by considering the partial pressure of that contaminant in a vapor phase. This partial pressure is equal to the product of the mole fraction concentration of the subject component in the liquid contaminant solution, the activity coefficient of the subject component and the vapor pressure of the pure component. This concept is more clearly expressed as follows:

$$P = X_I \Gamma_I P^o \quad (3)$$

where:

P = the partial pressure of the subject contaminant compound in the vapor phase,

X_I = the mole fraction concentration of contaminant (I) in the liquid contaminant solution,

Γ_I = the activity coefficient of the subject contaminant in the liquid contaminant solution, and

P^o = the vapor pressure of the pure component.

4.3.3.1 The quantity of contaminant volatilized into a vapor phase and the rate of that process is strongly dependent upon temperature. Rate of volatilization is also controlled by the rate of transport of contaminant vapors from the liquid phase-vapor phase interface (3). This rate is probably higher when macroporous flow paths are available for vapor phase transport, and is promoted by a number of driving forces. These are

concentration gradient, density gradient between soil atmosphere and contaminant-saturated soil atmosphere, convection currents related to temperature gradient, barometric pressure pumping and introduction of water onto the liquid phase-vapor phase interface.

4.3.4 Air-water partitioning is the process by which volatile contaminants move between the solute phase and a vapor phase, either the free vapor phase or the occluded vapor phase or both. For dilute solutions, air-water partitioning is controlled by Henry's law, which states that the vapor pressure of a volatile compound above a dilute aqueous solution of that compound is equal to the product of the Henry's law constant and the mole fraction of that compound in the aqueous solution. Henry's law may be represented as:

$$P_I = kX_{I(aq)} \quad (4)$$

where:

- P_I = vapor pressure of compound (*I*) above a dilute aqueous solution of (*I*),
- k = the Henry's law constant for compound (*I*) at a given temperature, and
- $X_{I(aq)}$ = the mole fraction of the subject contaminant compound in the aqueous solution.

Care must be exercised in using Henry's law to approximate contaminant vapor pressures because of unknowns related to the concentration of contaminants in solution and the contribution of other partitioning processes. Some available literature pertaining to soil gas surveying places emphasis on Henry's law constant at 25°C and atmospheric pressure as a primary controlling factor in determining the suitability of a particular volatile contaminant to the soil gas monitoring method. Such emphasis may be inappropriate when, for example, free product is the source of contaminant vapors or when contaminants have not reached ground water. Care must also be exercised in noting the units in which Henry's law constants are expressed, as these vary from source to source. Volatile but very highly water soluble compounds behaving according to Henry's law may not be detectable in soil gas because of their persistence for residence in the solute phase (6).

4.3.5 Soil-water partitioning is the process by which volatile contaminants move between the sorbed phase and the solute phase. This process is generally underestimated in its importance to the success or failure of contaminant recovery by soil gas sampling, especially when utilizing the majority of active soil gas sampling techniques generally available to field personnel.⁹ There is uncertainty with respect to factors controlling soil-water partitioning, creating doubt as to the reliability of soil sorption data in most applications. Problems with soil sorption data include variability in measurement protocols, the variable nature of organic matter in soils, the effect of dissolved organic matter, unusual pH effects and the effect of salinity, among others (3).

4.3.5.1 The contribution of soil-water partitioning to contaminant phase residence equilibria is strongly controlled by sorbed contaminant concentration in soil, soil makeup, vadose

zone pore water content, and soil porosity configuration. Important variables in soil makeup are the quantity, type and distribution of clay in soil and the quantity, type and distribution of soil organic matter. These variables impact the surface area available to sorptive processes, that is, the storage capacity of the soil for contaminants in the sorbed phase, and the pH of the sorption environment. Variations in vadose zone pore water content directly affect the storage capacity of the soil for contaminants in the solute phase. Soil porosity configuration, principally microporosity versus macroporosity, is critical to the rate of soil-water partitioning due to the contrast in surface area between micropores and macropores and the related storage capacity of this porosity for both pore water and sorbed contaminants.

4.3.6 Soil-air partitioning is the process by which volatile contaminants move between the sorbed phase and a vapor phase, either the free vapor phase or the occluded vapor phase or both. Like soil-water partitioning, this process is underestimated in its importance to the recoverability of contaminants by many soil gas sampling techniques. In vadose zone horizons with very low pore water contents, soil-air partitioning can yield vapor phase contaminant composition that differs from free product composition. In vadose zone horizons with higher pore water content, the responsibility for this compositional inconsistency is shared, largely with soil-water partitioning. In wet soil conditions, threshold soil water content values exist for trapped soil atmosphere content to become significant (7), suggesting that responsibility for this compositional inconsistency can be largely attributed to occluded phase residence. Additional important variables are soil clay content, type and distribution, and soil organic matter content, type and distribution. Studies have demonstrated significant impact of soil organic matter and clay content on volatile organic compound emissions from soils (8). Due to the strong control on vapor phase contaminant content by the soil-air partitioning process, it is unreasonable to expect soil contaminants with high affinity for sorption to be efficiently recovered by most soil gas sampling techniques.

4.4 Migration of contaminants in the vadose zone, that is, unsaturated flow, is highly complex and is controlled by soil characteristics, contaminant composition and contaminant phase (9). Migration through unsaturated matrix can occur through a variety of diffusion, dispersion and mass transport mechanisms which behave in a manner unique to saturated flow.

4.4.1 A major division in migratory behavior of contaminants is defined by their solubility or immiscibility in water. Contaminants are often introduced into the soil as liquid mixtures, the components of which immediately begin to partition into other phases upon soil entry. Contaminants that establish soil residence behind a migratory front change in composition with distance from their point of entry. As contaminant migration continues, pathways for individual components can become divergent, such that the composition of the liquid mixture continues to change as migration proceeds. Eventually, migration of liquid mixtures may reach ground water. This can be retarded if the contaminants partition

⁹ See 6.2 for a discussion of active soil gas sampling techniques.