

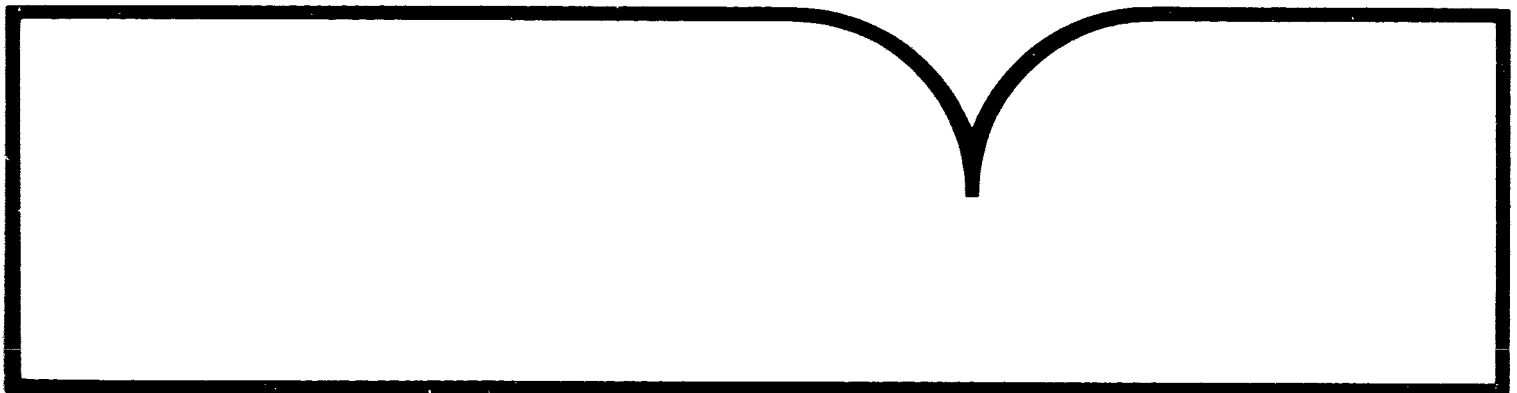
Measurement of Gaseous Emission Rates from
Land Surfaces Using an Emission
Isolation Flux Chamber. User's Guide

Radian Corp., Austin, TX

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MEASUREMENT OF GASEOUS EMISSION
RATES FROM LAND SURFACES
USING AN EMISSION
ISOLATION FLUX CHAMBER

USER'S GUIDE

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SECTION 1

INTRODUCTION

Volatilization of organic compounds from contaminated soil or groundwater into the air represents a major potential source of exposure which has not been assessed. In order to assess this exposure potential, a method is needed to directly measure gas emission rates from contaminated soils and/or groundwater. Additionally, it is recognized that an understanding of the volatilization, transport, and emission processes could lead to a predictive tool for exposure assessment. The information provided by direct measurement and/or predictive modeling will allow state and local regulatory agencies to develop programs to assess and define the need to control gas emissions from area sources contaminated by organic compounds.

The purpose of this User's Guide is to present an approach and protocol, namely the emission isolation flux chamber (or flux chamber) technique, for measuring emission rates of volatile organic compounds from contaminated soils and/or groundwater. Presented is the theory of operation, specifications, sensitivities, method of operation, and data reduction procedures for this technique. It is assumed that the individuals who will use the protocol are, in general, familiar with sample collection and analysis of volatile organic compounds. Also included in this document is a case study that demonstrates the measurement and data reduction processes around a spill site.

The flux chamber technique is applicable to the measurement of emission rates from Resource Conservation and Recovery Act (RCRA) facilities (hazardous waste treatment, and landfill facilities), and from Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) area sources contaminated by losses of volatile organic compounds from spills, from leaking underground storage tanks, from pipelines, and/or from surface impoundments.

This protocol does not present the vast amount of work that was required to develop this document. Rather, the protocol is a result of literature reviews selecting a measurement technique and field applications demonstrating the technique and developing a data base and validation studies identifying the method of flux chamber operation. References to the other area sources where this technique was applied, the work performed to validate the technique, and the investigations of variables which control the emission process are also given for those individuals desiring further information.

SECTION 2

BACKGROUND

The following subsections discuss the process by which volatile organic compounds are emitted from contaminated land surfaces, the basis upon which the flux chamber technique was selected as an approach for measuring such emission rates, and the principle of the technique.

2.1 Emission Processes

The rate of volatile organic compound (VOC) emissions from contaminated soils is generally believed to be controlled by the diffusion rate of the chemical compound through the air-filled pore spaces of the soil.(1,2,3) The exception occurs when the contaminated material lies on or very near the soil surface. Such is the case when spills occur or immediately after waste is surface-applied to a landtreatment site. In these cases, the emission process will be controlled by the rate of evaporation.

Evaporation is a surface phenomenon, and the parameters that affect the evaporation process are the properties of the waste itself as well as those that have an effect on the air-surface interface (i.e. wind, surface roughness). The important parameters include the volatility or vapor pressure of the waste, ambient meteorological conditions (solar insolation, air and waste temperature, surface wind speed, relative humidity), surface coarseness, and the bulk concentration of the volatile components in the air (although this is usually very low and generally assumed to be negligible).

There are two major types of soil emission processes. Each are treatment dependent. One type occurs in landtreatment facilities and the other at underground facilities such as landfills. In landtreatment applications, the emission rate is generally highly time-dependent. When a fixed amount of waste is applied to the soil surface, it penetrates the soil to a certain depth. The vaporization rate is maximum immediately after waste application, as the material nearest the surface is vaporized and diffuses through a very thin layer of soil. As the waste near the surface is depleted of its VOC content, the volatile material deeper in the soil must diffuse through an increasingly thick soil layer. The soil presents a resistance to VOC diffusion in direct proportion to the VOC depth. Thus, the rate of emissions from the surface decreases with time.

It is common practice in landtreatment to periodically till the soil to provide oxygen for bacterial activity. The tilling effectively mixes the remaining waste in a homogeneous layer near the soil surface. The emission rate is at a maximum immediately following each tilling episode since

volatile waste is again present very near the surface, and resistance to diffusion is at a minimum.

Although also diffusion controlled, the emission process from underground sources such as landfilled waste or material present as a "lens" on the water table has significantly different characteristics than that from surface or near-surface sources. The depth of the emission source is usually quite substantial. Therefore, the emission rate is initially lower due to the resistance to diffusion produced by the column of soil. The initial emission rate is zero, since it takes some time for the volatile material to diffuse through the soil layer. The adsorptive sites on the soil particles must also be initially saturated. Once the emission rate has equilibrated, the rate is relatively constant with time until the underground source is exhausted.

The diffusion process itself through the soil is the same for both types of sources, land treatment (surface) and landfill (underground). Consequently, many of the parameters important to the emission processes are the same, including diffusivity of the VOC in air, soil properties (particle size distribution, soil type, moisture content, particle density, porosity), soil/waste temperature, and volatility of the VOC in the waste. Additional parameters important to the near surface emission processes are the amount of material present in the contaminated soil layer, the initial depth of the contamination, the elapsed time from application (or tilling) and, possibly, ambient conditions such as surface wind speed and relative humidity. The depth of the soil layer above the waste is a very important parameter in the emission process from subsurface sources. Additionally, the adsorptive properties of the soil may also have a significant effect on the emission rate from this latter source type.

An understanding of the emission processes and the important parameters is necessary in the measurement of emission rates from soil surfaces and in the proper interpretation of the test results. As an example, the emission rate from a source is affected by rain since the porosity and, hence, the diffusion rate are reduced with increasing moisture content of the soil. Thus, emission rates immediately after a rainfall will be lower than those from drier soils and may take substantial periods of time to return to the emission rate prior to the rain.(4) Emission rates may vary with the time of day and season, as a result of changes in ambient and soil/waste temperatures.(4) Emission rates from soil areas containing fissures can be higher and much less homogeneous than those from unfractured areas. Thus, considerable care must be taken in planning and implementing a measurement program to determine representative emission rates from such soil surfaces.

2.2 Measurement Techniques

Based on a literature review (5), the techniques for determining gas emissions rates from land surfaces contaminated with organic compounds can be divided into three approaches: indirect measurements, direct measurements, and laboratory simulations. Indirect techniques typically require measurements of ambient air concentrations at or near the site. These

measurements are related to the surface area of the area source and local meteorological conditions using a dispersion model to determine an emission rate. The second approach is to directly measure emission rates using for example the flux chamber. The third approach is to create an emission source in the laboratory and model the emissions by various techniques for application to field sites. These three approaches were compared for precision, accuracy, and sensitivity. Other considerations included applicability, complexity, manpower requirements, and costs.

The most promising technique for measuring gas emission rates from land surfaces was determined to be the emission isolation flux chamber technique. The advantages are:

- o lowest (most sensitive) detection limit of the methods examined;
- o easily obtained accuracy and precision data;
- o simple and economical equipment relative to other techniques;
- o minimal manpower and time requirements;
- o rapid and simple data reduction; and
- o applicable to a wide variety of surfaces.

2.3 Flux Chamber Operation

The flux chamber technique has been used by researchers to measure emission fluxes of sulfur, nitrogen, and volatile organic species (6,7,8,9,10). The approach uses a flux chamber (enclosure device) 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 calculated as:

$$E_i = Y_i Q/A \quad (2-1)$$

where: E_i = emission rate of component i (mass/area-time),
 Y_i = concentration of component i in the air flowing from the chamber (mass/volume),
 Q = flow rate of air into the chamber (volume/time),
 A = surface area enclosed by the chamber (area).

All parameters in Equation 2-1 are measured directly.

Most of the emission rate assessments are of area sources much larger than the enclosed surface area of the flux chamber (0.130 m^2). In these

cases, an overall emission rate for the area source is calculated from multiple measurements based on random sampling and statistical analysis.

SECTION 3

MEASUREMENT OF GASEOUS EMISSION RATES FROM LAND SURFACES USING AN EMISSION ISOLATION FLUX CHAMBER - PROPOSED METHOD

3.1 Applicability and Principle

3.1.1 Applicability

The flux chamber technique is applicable to the measurement of emission rates from Resource Conservation and Recovery Act (RCRA) facilities such as hazardous waste landtreatment and landfill facilities. This technique is also applicable for emission rate measurements from Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) waste sites such as areas contaminated by losses of volatile organic compounds from spills, from leaking underground storage tanks, from pipelines, and/or from surface impoundments.

3.1.2 Principle

Gaseous emissions are collected from an isolated surface area with an enclosure device called an emission isolation flux chamber (or flux chamber). The gaseous emissions are swept through an exit port where the concentration is monitored and/or sampled. The concentration is monitored and/or sampled either continuously (i.e., "real-time") or discretely. Real-time measurements are typically made with portable total hydrocarbon analyzers and are useful for relative measurements (i.e., the determination of flux chamber steady-state operation, zoning). Discrete samples are taken when absolute measurements are necessary (i.e., steady-state concentrations, emission rate levels). The emission rate is calculated based upon the surface area isolated, the sweep air flow rate, and the gaseous concentration measured. An estimated average emission rate for the area source is calculated based upon statistical sampling of a defined total area.

3.2 Precision, Accuracy, Sensitivity, and Range

3.2.1 Precision

Single chamber precision (i.e., repeatability) of the method is approximately 5 percent at measured emission rates of 3,200 ug/min·m². Variability between different flux chambers (i.e., reproducibility) is approximately 9.5 percent within a measured emission rate range of 39,000 to 65,000 ug/min·m². (4)

The reproducibility results were determined from a bench-scale study. The tests were designed to eliminate temporal variations from the flux chamber reproducibility. However, using the same bench-scale facility, a test design was not possible for measuring flux chamber repeatability without bias from temporal variations. As a result, the repeatability tests were performed in the laboratory. The differences therefore between the stated emission rates for repeatability and reproducibility reflect the differences in laboratory simulated emission rates and those measured from the bench-scale facility.

3.2.2 Accuracy

Flux chamber recovery (Section 3.6.1.4.2) results show a recovery range of 77 percent to 124 percent. Table 3-1 lists measured recoveries for a number of compounds tested. The average recovery for the 40 compounds tested is 103 percent.

Flux chamber emission rate measurements made on the soil cells range from 50 percent to 100 percent of the predicted emission rates. That is, the measured emission rates can be expected to be within a factor of one-half of the "true" emission rates.(4) The flux chamber accuracy based upon both the recovery tests and predictive modeling ranges from 50 percent to 124 percent.

3.2.3 Sensitivity

The sensitivity of this method depends on the detection limit of the analytical technique used. When discrete samples are collected using gas canisters and analyzed by gas chromatographic methods, the estimated emission rate sensitivity is $1.2 \text{ ug/min}\cdot\text{m}^2$ for an analytical detection limit of 10 ppbv benzene. When emission rates are measured in a continuous (real-time) method, the estimated sensitivity is $124 \text{ ug/min}\cdot\text{m}^2$ for an analytical detection limit of 1 ppmv benzene.

3.2.4 Range

The range of this method depends upon the analytical technique used. High level emission rates are analyzed by introducing proportional amounts of gas sample to the analyzer. Using this technique, high level emission rates of $120,000 \text{ ug/min}\cdot\text{m}^2$ have been measured.(4) Low levels are limited by the sensitivity of the analytical technique. Gas chromatographic techniques have been used to measure low level emission rates of $1.2 \text{ ug/min}\cdot\text{m}^2$ for measured concentrations of 10 ppbv benzene.

3.3 Interferences

3.3.1 Flux Chamber Method

Impurities in the sweep air and/or organic compounds outgassing from the transfer lines and acrylic chamber top may cause background contamination. The emission isolation flux chamber must be demonstrated to be free

TABLE 3-1
 COMPOUNDS TESTED IN THE EMISSION ISOLATION FLUX CHAMBER
 AND THE MEASURED PERCENT RECOVERY

Compound	Percent Recovery*	Compound	Percent 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
t-2-butene	107	Ethyl benzene	94.7
c-2-butene	109	mtp-xylene	88.5
Isopentane	112	c-xylene	97.3
1-pentene	105	n-nonane	99.4
2-methyl-1-butene	124	n-propylbenzene	95.5
n-pentane	107	p-ethyltoluene	92.5
n-pentene	103	1,3,5-trimethylbenzene	93.5
c-2-pentene	105	1,2,4-trimethylbenzene	86.7
Cyclopentene	105	2-methyl-2-butene	103
n-hexane	95.1	Methyl mercaptan	107
Isohexane	107	Ethyl mercaptan	107
3-methylpentane	106	Butyl mercaptan	101
Methylcyclopentane	105	Tetrahydrothiophene	115
Benzene	106	Trichloroethylene	77.1
1,2-Dimethylpentane	105	Ethylene dichloride	103

*Section 3.8.2

from significant (<10 percent of expected measured concentrations) levels of such contamination under the measurement operating conditions by running method blanks. Background levels above this limit will significantly bias the flux chamber measurements. Typical values measured with a real-time analyzer (OVA) range from 0 to 2 ppmv exit gas concentration.

Cross-contamination can occur whenever high level and low level samples are sequentially analyzed. To reduce the likelihood of cross-contamination, the chamber should be purged between samples with ultra high purity air and followed with running a method blank until typical values are achieved.

The use of a transparent chamber may result in gas and surface warming due to greenhouse effects. The degree of gas and surface warming are dependent upon the outside air temperature. For outside air temperatures of 28°C, a temperature gradient between the inside flux chamber air and outside air increases from 9°C at 5 τ (30 minutes) to 30°C 2.5 hours later. Such heating is minimized by the use of short sampling times.

As a result of the greenhouse effect, condensation may occur when monitoring moist surfaces. Condensation should be recorded when observed and dried from chamber surfaces and lines between sample runs. Condensation could reduce exit gas concentrations of water soluble compounds.

The emission rate process from soils enclosed by the flux chamber could be suppressed as the internal VOC vapor phase concentration increases. Emission rate suppression is avoided by increasing the sweep air flow rate. Suppression is not a significant factor until flux chamber entrapped vapor concentrations are greater than 10 percent of the equilibrium vapor phase concentration. The equilibrium vapor phase concentration is determined from the headspace concentration measurements of a soil sample. This concern applies only when sampling highly concentrated and volatile waste.

3.3.2 Emission Process

Ground moisture resulting from either rain, heavy dew, etc. has a definite effect upon the emission rate from land surfaces. Ground moisture accumulation from trace amounts of rain (≤ 0.01 inches) have little or no effect, whereas ground moisture resulting from a rainfall of 0.30 inches of water has been observed to decrease emission rates by 90 percent.(4) At this level of precipitation, seven days of hot, sunny weather were required before the gas emission rates returned to values equal to that before the rain. As such, emission rate measurements made on soils recently experiencing an elevated ground moisture content would be biased. Emission rate measurements will be below those made at normal soil moisture levels.

3.4 Apparatus and Materials

3.4.1 Flux Chamber and Supporting Equipment

A diagram of the flux chamber and supporting equipment is shown in Figure 3-1. The flux chamber materials and specifications are listed in

FIGURE 3-1
 A CUTAWAY DIAGRAM OF THE EMISSION ISOLATION FLUX CHAMBER AND
 SUPPORT EQUIPMENT

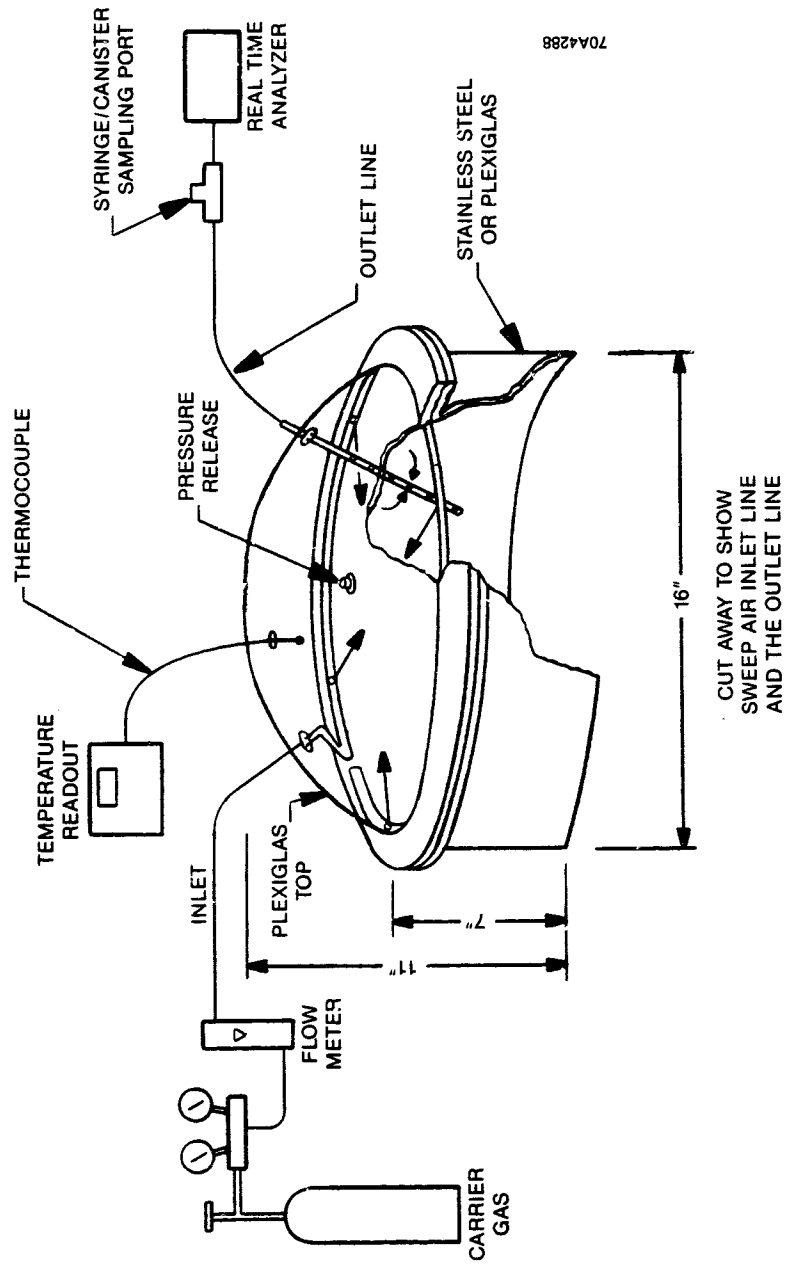


Table 3-2. A construction diagram of the flux chamber is shown in Figure 3-2.

The sweep air carrier gas should be dry, organic free air equal to or better than commercial ultra high purity grade (<0.1 ppmv THC). A gas flow meter with no internal rubber parts and adjustable within the range of 1-10 L/min should be used to control gas flow. Temperature measurements should be made with an accuracy of $\pm 1.0^{\circ}\text{C}$. A fine-wire thermocouple with electronic readout is recommended. Caution should be taken to avoid any contact of a thermocouple with metal. This would give inaccurate air temperature readings. A pressure release port is required to avoid pressure build-up inside the flux chamber during operation. This port should never be blocked. For system blanks, a clean Teflon™ sheet should be used to provide a clean surface for the flux chamber.

3.4.2 Discrete Sample Collection

Discrete grab samples should be collected with air-tight, inert containers. For on-site analysis, 100 ml precision lock, glass syringes are recommended. Glass plungers are recommended over Teflon™ tip plungers. If Teflon™ tip plungers are used, then special controls must be followed to avoid cross-contamination (Section 3.7.1.1). For samples to be transported or to be stored for periods longer than 1 hour, 2L stainless steel gas canisters are recommended.

3.4.3 Analysis

3.4.3.1 Real Time

Analyzer

For real-time, continuous monitoring of the exit gas concentration, analyzers with precision of ± 10 percent of the measured value and a detection limit of 1 ppmv are recommended.

Calibration Gases

The portable, real-time analyzers will require the following levels of calibration gases:

- o High-Level Gas: Concentration within 50 percent to 90 percent of the span value (maximum expected concentration or upper limit of instrument linear range).
- o Low-Level Gas: Concentration less than or equal to 0.01 percent of the span value.
- o Zero Grade Gas: Ultra high purity (UHP) air (<0.1 ppmv THC).

The calibration gas for these analyzers can be the same as that used for the on-site discrete analyzer (Section 3.4.3.2.2).

TABLE 3-2
FLUX CHAMBER MATERIALS SPECIFICATIONS

Item	Description	Specification
Carrier Gas Lines: Inlet/Outlet	Teflon™ (clear)	1/4" OD, 5' to 8' long, thin walled, 1/4" stainless steel fittings
Sweep Air Wrap Perforation ^a	Stainless Steel four equidistant holes jetting direction	1/4" OD, 54" long, perforated hole No. 1 (nearest input), 5/64" ID, holes No. 2-4, 3/32" ID, axially, horizontally
Fittings ^b	Stainless steel Stainless steel	1/4" bulkheads with teflon washers for chamber penetration 1/4" cap to seal wrap line end
Thermocouples Air (1)	Fine wire K type	36" long, bead tip, teflon coated (extensions optional), penetrate flux chamber 3", support with 1/4" bulkhead with septa
Flux Chamber: Base	Stainless steel column	16" ID x 7" tall, welded to a support ring flange
Support ring flange	Stainless steel	16" ID x 20" OD x 1/4" thick
Dome	Acrylic four holes Inlet/outlet Air temperature Pressure release	Spherical, 4" displacement at center, 16" ID at seal, 2" lip for seal, 1/4" thick, molded Equidistant, 4" from aluminum gasket 1/2" ID with 1/4" stainless steel bulkhead 1/2" ID with 1/4" stainless steel bulkhead 13/16" ID with 3/4" stainless steel bulkhead
Seal Dome to Base	Top gasket Dome lip	Aluminum 16" ID, 20" OD, 1/4" thick Below aluminum gasket is the acrylic lip of dome

(Continued)

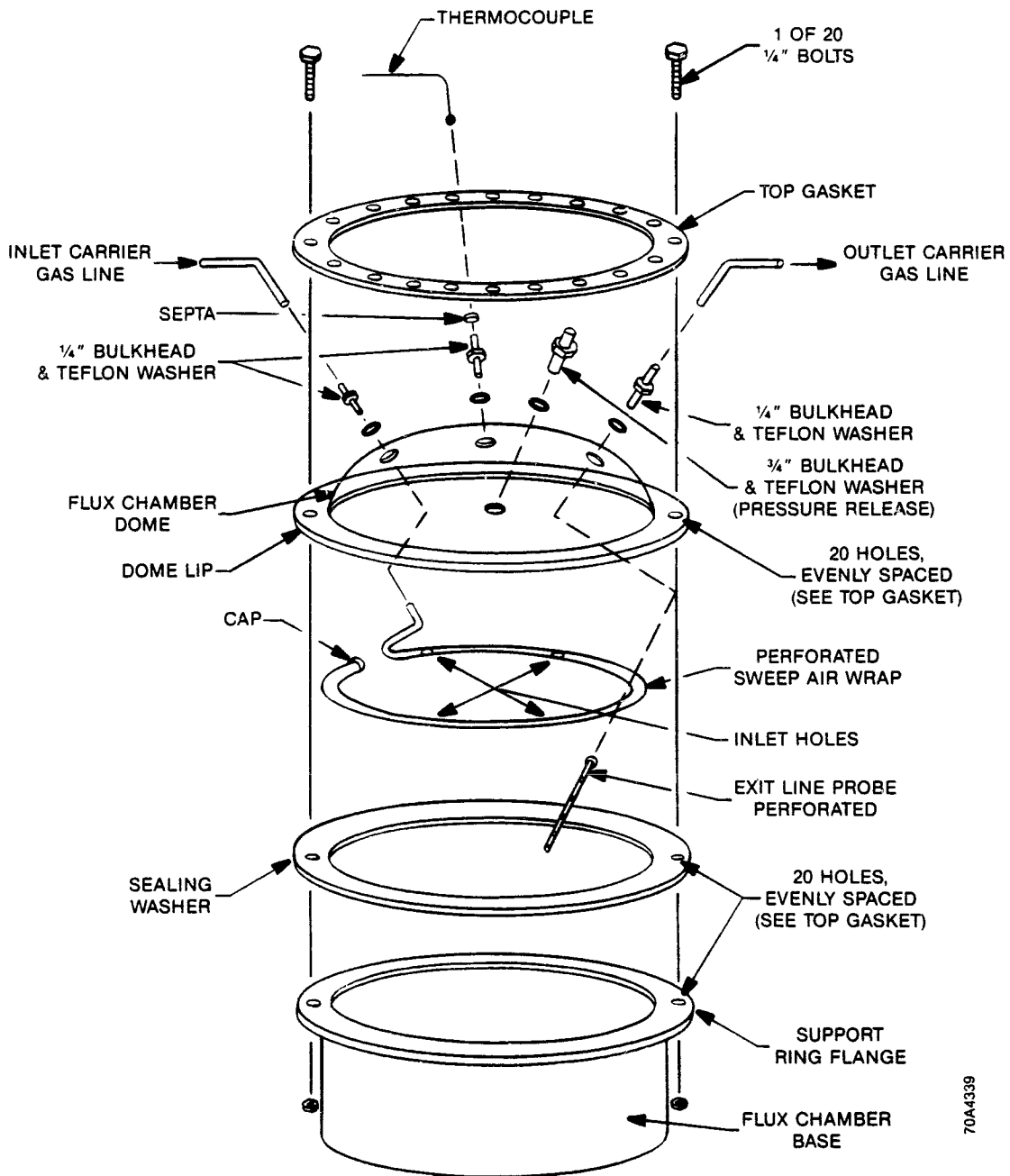
TABLE 3-2
(Continued)

Item	Description	Specification
	Sealing washer	Teflon, 16" ID, 20" OD, 1/32" thick
	Bottom gasket	Stainless steel support ring
	Fasteners	20, 1/4" bolts equidistant around lip
Volume	With 1" soil penetration	0.03 m ³ (30L)
Surface Area	Enclosed by chamber	0.130 m ²
Exit Line Probe	Teflon™	1/4" OD, 6" long, stainless steel fitting, perforated
Perforation	2 rows of holes	3/32" ID, 5 holes per row, 1" separation, rows are positioned orthogonally

^aAvoid placement of exit line probe in jetting path of sweep air inlet holes

^bAll fittings are manufactured by Swagelok® or equivalent manufacturer (bulkheads use Teflon™ washers for sealing)

FIGURE 3-2
EXPLODED VIEW OF THE FLUX CHAMBER



70A4339

Quality Control (QC) Gas

The portable, real-time analyzer will require a quality control (QC) gas concentrated to fall within the span range. The QC gas for this analyzer can be the same as that used for the on-site discrete analyzer.

3.4.3.2 Discrete

Analyzer

The analyzer should be sensitive with low detection limits. For on-site analysis of grab samples, instrumentation having precision of ± 5 percent of the measured value with a detection limit of 1 ppm is recommended. Analyzers with injection loops are recommended to reproduce the sample volumes injected. For off-site analysis, instrumentation with precision of ± 30 percent at detection limits of 1 ppbv are recommended.

Calibration Gases

The concentrations and composition of the calibration gases to be used will vary depending on the species of interest. Preferably, the following gas concentrations should be used for each species of interest:

- o High-Level Gas: 90 percent of the span value.
- o Mid-Level Gas: Average expected concentration.
- o Low-Level Gas: 0.01 percent of the span value.
- o Zero Grade Gas: Ultra high purity (UHP) air, (<0.1 ppmv THC).

Alternatively, a high-level gas may be used with a dilution system to generate the lower level gas concentrations. A dilution system is recommended that meets or exceeds that described in Section 6.2.1.1 of Method 18 of 40 CFR Part 60. If multicomponent species are analyzed, then on-site calibration gases should be benzene or hexane. To identify and quantitate multicomponent responses when a single component (benzene or hexane) is used for calibration, a library of normalized responses relative to the single component calibration gas must be employed. This does not guarantee all species of the multicomponent will be identified. If specific identification and quantitation are not required, then quantitation and identification should be made relative to the calibration gas.

QC Gas

The discrete analyzer will require a QC gas that has a concentration within the span range.

