

Chapter IP-4

DETERMINATION OF AIR EXCHANGE RATE IN INDOOR AIR

- Method IP-4A - Perfluorocarbon Tracer (PFT)
- Method IP-4B - Tracer Gas

1. Scope

1.1 Method IP-4A is a description of the sampling and analytical protocol for air exchange rate (AER) using perfluorocarbon tubes (PFT) and passive samplers (i.e., capillary adsorption tubes - CATS). This methodology was developed by Brookhaven National Laboratory as an inexpensive way of measuring AER in large-scale field studies. The PFT emitters are utilized indoors to measure the rate of air exchange which occurs over time. This method may be used with multiple PFT source types to allow inter-compartmental flows as well as whole-house AERs to be calculated. The emitters are placed in the dwelling of interest a day in advance of the passive samplers. The source emissions are collected on the passive samplers which are analyzed by a gas chromatograph coupled with an electron capture detector (GC-ECD) for the air exchange rate. If more than one source/sampler is used in a single dwelling, the average of all the calculated AERs is computed.

1.2 Method IP-4B describes the determination of the air exchange rate by the release of sulfur hexafluoride (SF_6) tracer gas. The ambient air is subsequently sampled by commercially available automated syringe samples and analyzed for trace amounts of SF_6 by gas chromatography with electron capture detection or monitored on-site by tracer gas monitors. This concentration-decay technique (also called tracer-gas dilution) has been designated as a standard practice by the American Society for Testing and Materials. In this technique, a small amount of tracer gas is injected into the indoor airspace and thoroughly mixed. Indoor concentrations "decay" with time as the exfiltrating air removes the tracer. The general procedure involves releasing tracer gas at one or more points at sufficient quantities to produce useful initial concentrations. The method of release and quantities involved depend on the internal volume of the structure, the configuration of the air-handling system, estimates of allowable versus useful concentrations, and the sensitivity of the detection system.

2. Applicability

2.1 For some time, it has been a primary focus of the U.S. EPA to compile the missing exposure data needed to complete the risk equation. The data from exposure measurements help to evaluate progress in the efforts to control environmental pollution and provide guidance for modifying approaches to make them more effective. Ultimately, the effectiveness of the regulatory process on reducing pollutant levels may be judged by exposure measurements.

2.2 In addition to measuring mass and elements, total exposure assessment studies should be organized to provide background information on indoor and outdoor air pollutant concentrations. Emphasis should be placed on collecting information on indoor air

pollutant concentrations or the relationship between indoor and outdoor air levels. Air infiltration rates are a critical component in the process of determining the influence of outdoor pollution on indoor concentrations.

2.3 Air infiltration represents an important part of the heating and cooling load of residential, commercial and industrial buildings. The heat loss associated with air leakage through the enclosure of a typical house may be as much as 40% of the total heat load. Considerable energy savings can be realized by reducing the air infiltration in a structure.

2.4 Air leakage is also an important parameter in indoor-outdoor air pollution relationships.

Method IP-4A

DETERMINATION OF AIR EXCHANGE RATE IN INDOOR AIR USING PERFLUOROCARBON TRACER (PFT)

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Method IP-4A

DETERMINATION OF AIR EXCHANGE RATE IN INDOOR AIR USING PERFLUOROCARBON TRACER (PFT)

1. Scope

1.1 This document describes the protocol for the measurement of an integrated air exchange rate (AER) between the outside and inside of detached dwellings over periods ranging from approximately 10 hours to several weeks. Perfluorocarbon tracer (PFT) emitters are utilized indoors to measure the rate of air exchange which occurs over time. This method may be used with multiple PFT source types to allow calculation of both inter-compartmental flows within houses and whole-house AERs.

1.2 The methodology was developed by Brookhaven National Laboratory as an inexpensive way of measuring AER in large-scale field studies. It is currently employed in the Particle Total Exposure Assessment Methodology (P-TEAM) program conducted by the U.S. Environmental Protection Agency (U.S. EPA) and in a 5000 building home measurements study. The Danish Building Research Institute and the Helsinki University of Technology have established analytical labs which offer full AER services. In addition, there are several groups in England who are in the process of establishing AER service facilities.

1.3 The equipment described herein can be utilized to measure air exchange on neighborhood or urban to regional scales. Neighborhood scale monitoring requires measurements to identify the contributions of specific sources. Urban/regional scale measurements would identify important reactant areas.

2. Applicable Documents

2.1 ASTM Standards

D 1356 Definitions of Terms Related to Atmospheric Sampling and Analysis
E 355 Recommended Practice for Gas Chromatography Terms and Relationships

2.2 Other Documents

Ambient Air Studies (1,2)
U.S. EPA Technical Assistance Document (3)

3. Summary of Method

3.1 Air exchange rate (AER) is measured by using the perfluorocarbon tracer (PFT) system. It is designed to measure the integrated rate of exchange of air between the outside and inside of detached dwellings, as well as the exchange between zones in multizone structures. The system is capable of measuring average air exchange rates over periods ranging from about 8 hours to several weeks (4-7).

3.2 Each dwelling can be treated as a single box with AER calculated as if interior partitions are nonexistent or it can be compartmentalized. Perfluorocarbon tracer (PFT) gas is released from one to several locations inside each dwelling chosen to provide uniform PFT dispersion throughout the structure. The tracer gas is allowed to equilibrate in the

dwelling and is then collected inside capillary adsorption tubes (CAT) by diffusion onto activated charcoal spherules. The diffusion rate, and hence the sampling rate, is set by controlling the geometric dimensions of the CAT. The impact of temperature on diffusion rates is generally ignored. Sampling rates are calculated for 25°C. The CAT samplers are located around each dwelling and their PFT burdens are averaged for the calculations. The AER for each home is calculated using laboratory measurements of the collected PFT, field measurements of the structure volumes, and the sampling duration.

3.3 The laboratory analysis (4-7) of PFT collected in the CATs is performed on a gas chromatograph system equipped with an electron-capture detector (GC-ECD). The GC-ECD is first calibrated with PFT standards then a calibration curve is constructed and used to determine the type(s) and amount(s) of PFTs present in the sample.

3.4 For analysis, the samples are thermally desorbed into a 95% nitrogen-5% hydrogen carrier gas stream through a Nafion column to remove water vapor, which can produce an interfering ECD response as well as degrade the ECD performance. The sample then passes through a special catalytic column to oxidize potentially interfering fluorochlorocarbon compounds; it then flows to a precolumn to effect a coarse separation. Sample compounds continue to flow to a Porapak QS adsorbent column trap where earlier eluting compounds pass through; PFTs are retained, and later eluting compounds are vented via a time-programmed switching valve before they reach the QS trap.

3.5 After all PFTs have been trapped, the flow is reversed by a time-programmed switching valve, and heat is electrically applied to the trapping column to release the adsorbed PFTs. The PFTs now flow to a second catalytic column which mimics the first catalytic column, and finally to a main chromatographic column which separates the compounds prior to detection by the ECD. When a compound reaches the ECD, it induces a voltage signal which is sent to a data acquisition/reduction system.

3.6 The detection system consists of a dedicated integrator which receives the signal, transforms it for graphical presentation, and finally calculates concentrations of the unknown PFTs using the stored calibration curve.

3.7 The limit of detection (LOD) for AERs depends on the LOD of the GC-ECD, the sampling rate of the CAT tubes, the sample duration, the emission rates of the PFT sources, the house volume and the true integrated air exchange rate. Most GC-ECD systems can detect PFT quantities as low as 1 picoliter (pL) with 30% precision. The minimum PFT air concentration LOD is controlled by this and the sample exposure time, and the effective sampling rate (4-7).

3.8 The PFT source is inexpensive and reusable. It is small, ready for use as received, and always emitting tracers. The passive sampler (CAT) is also very small and can be located inconspicuously throughout a dwelling. The CATs are reusable providing an analytical check of the remaining PFT background is negligible. The PFT/CATs operate for the desired time without supervision. Additionally, the PFT source has a high affinity for

reaction with electrons and a low atmospheric background which allows analysis by GC-ECD to be carried out with little interference and very low detection limits.

4. Significance

4.1 The measurement of exposure serves as a critical parameter in environmental protection. The data from exposure measurements help to evaluate progress in the efforts to control environmental pollution and provide guidance for modifying approaches to make them more effective. Ultimately, the effectiveness of the regulatory process on reducing pollutant levels may be judged by exposure measurements.

4.2 In the early 1980's the U.S. EPA began to undertake programs to find the missing exposure data needed to complete the risk equation. The application of personal monitors became an effective means to measure the exposures of individuals throughout their daily activities. Besides measuring the individual's exposure to pollutants, the idea to estimate the exposures of entire populations was formulated. Since the measurement of exposures of everyone in a large metropolitan area is expensive, a simpler approach was to combine probability sampling with environmental monitoring. In this manner, the exposures of a representative probability sample of the population could be used to make inferences about exposures of the entire population.

4.3 This initial concept was applied in exposure studies involving volatile organic chemicals (VOC). A number of these studies have now been completed including carbon monoxide personal exposure monitoring. The VOC and carbon monoxide exposure field studies were the beginning of a newly emerging field of total human exposure assessment. However, the need to consider size characteristics and chemical composition in the control of airborne aerosols has been a matter of continuing concern to the U.S. EPA since the establishment of the total suspended particle ambient air quality standards in 1971. More recently, the Science Advisory Board of the U.S. EPA has made a recommendation that calls for exposure assessment studies to assess man's exposure to environmental pollutants, including the determination of sources and their relative contribution to personal exposure.

4.4 In addition to measuring mass and elements, total exposure assessment studies should be organized to provide background information on indoor and outdoor air pollutant concentrations. Emphasis should be placed on collecting information on indoor air pollutant concentrations or the relationship between indoor and outdoor air levels, especially since there has been very little attention given to indoor pollutant concentrations. Air infiltration rates are a critical component in the process of determining the influence of outdoor pollutant concentrations on indoor concentrations.

4.5 The PFT method is less intrusive than alternative methods. The PFT uses a passive sampler which requires no pumps (8-23).

5. Definitions

Definitions used in this document and any user prepared Standard Operating Procedures (SOPs) should be consistent with ASTM D1356. All abbreviations and symbols are defined

within this document at the point of use. Additional definitions, abbreviations, and symbols are provided in Appendices A-1 and B-2 of this compendium.

6. Interferences

6.1 The PFT sources are temperature sensitive. Therefore, careful placement of the sources within a dwelling is necessary. Best results are obtained when the sources are deployed in different areas of a dwelling according to the permeation rates. Haphazard placement will lead to inaccurate measurement (See Section 10).

6.2 The PFT sources and passive samplers measure minute concentrations (ppt), therefore it is very important to keep the PFT containers and the samplers well separated. The samplers are not temperature sensitive, but extreme, abrupt changes in temperature exposure should be avoided. Sampling periods are restricted to a two hour minimum and several months maximum.

6.3 Electron capture detectors are sensitive to halogenated organic compounds. The most important potential interferents in the home are freon-type refrigerants. The GC system is designed to remove these compounds by control of their travel times through the system.

7. Apparatus

7.1 Perfluorocarbon Tracer (PFT) Source - PFT sources as seen in Figure 1 consist of a 6.6 mm inside diameter by 32 mm long cylindrical aluminum shell filled with 0.4 mL of a single PFT liquid and is slightly flared at both ends to facilitate the insertion of an oversized silicone rubber plugs. The PFT liquid takes about two hours to reach equilibrium. A code number is engraved onto the aluminum shell for identification of the PFT source, silicone rubber plug type, and the number of the source (Russell Dietz or ISC Chemicals Ltd., England).

7.2 Capillary Adsorption Tubes (CATs) - CATs are constructed of glass tubes which contain a measured amount of an adsorbent as illustrated in Figure 2. The outside diameter (OD) of the tube is 6.4 mm and it is 6.4 cm long with a 45° taper ground at the ends to about 1/3 the wall thickness (to prevent cutting of "O"-rings in the desorption apparatus). The adsorbent, a granular (small beads) Amborsorb material (usually activated charcoal), is held in place by stainless steel screens (9.5 mm OD; 150 mesh) which are friction-fitted into place. A special PFT impermeable polyurethane cap is used to seal each end of the CAT before and after sampling. An identification number is either hand-engraved using a diamond-tipped vibrator or fired into the glass using powdered lead glass black numbered decals (manufactured by Russell Dietz).

7.3 Gas Chromatograph/Electron Capture Detector (GC-ECD) - Equipped with a Nafion column, two catalytic columns, a pre-column, a QS adsorbent column trap, and a main chromatographic column.

7.4 Computer Integrator - Programmed to receive standard data and produce a calibration curve based on retention times, time windows, minimum areas, type of curves, etc.

8. Reagents

The GC-ECD carrier gas is of the highest quality reagent grade 95% nitrogen - 5% hydrogen carrier gas.

9. PFT Sources Available Commercially

9.1 There are four PFT sources in use today. These are listed below along with the properties which make them appealing for use as a gaseous tracer.

Conservative gaseous tracers

Properties

- Non-depositing
- Low atmospheric background
- Non-scavenged
- Limited industrial use
- Non-reactive
- Sensitively detectable

<u>Perfluorocarbon tracers (PFTs)</u>	<u>Emission</u>		<u>Permeation</u>	<u>Lifetime, yrs.</u>
	<u>Type</u>	<u>Rate</u>	<u>Rate @ 25°C nL/min</u>	
PDCB (P ^a - dimethylcyclobutane)	1	Highest	36-50	2.9-2.1
PMCP (P - methylcyclopentane)	8	Next to highest	40-55	2.6-1.9
PMCH (P - methylcyclohexane)	2	Next to lowest	24-35	4.0-2.7
PDCH (P - dimethylcyclohexane)	3	Lowest	12-20	7.2-4.3

^aP as in PDCB means "perfluoro".

^bnL/min represents nanoliters/minute (10^{-9} /min).

9.2 PFT sources are advantageous over other methods in that they are used as received; they are always emitting tracer and they may be placed in any orientation. They are inexpensive and reusable. The PFT makes use of a passive sampler instead of an active one. Additionally, the PFTs high affinity for reaction with electron and low atmospheric background makes them some of the most sensitive compounds for detection on the ECD.

9.3 Although PFTs are ready for use when purchased, it is important to present how PFTs are made. There are two basic processes that have been used commercially for the production of PFTs, here restricted to the family perfluoroalkylcycloalkanes because they have the maximum response to the ECD. Other perfluoroalkanes and other perfluorocarbons are two or more orders-of-magnitude poorer in detection capability.

9.3.1 One process, cobalt trifluoride catalyzed fluorination, is available from ISC Chemicals Limited in England. The purity of their tracers has been from 85 to 99%, with a limited amount of the other existing and identified PFTs as impurities, generally less than 1%.

9.3.2 The other process for making PFTs is the dimerization of perfluoroalkenes at high pressures (up to 3000 atmospheres) and moderate temperatures (400°C). Originally patented by E.I. DuPont in Wilmington, Delaware, more than 19 years ago, the technique was used at one time to make the PDCB. They abandoned the technology more than five years ago and other small companies can now produce a number of the dimerization products, generally perfluorodialkylcyclobutanes, but at costs up to ten times or more those of the PFTs from ISC. However, the PDCB is a potential continental scale tracer because it has the highest ECD response of any of the PFTs and has a low ambient concentration. Recently, the Flora Corporation in North Carolina has indicated an interest in supplying tracers made by this process.

10. Placement of PFT Sources and Passive Samplers

10.1 Choosing PFT Sources

10.1.1 The choice of PFT source types with zone location is important in multizone structures. Because of the stack effect in all houses, a source placed on the second floor will have a very low concentration in the basement. To improve the precision of its measurement in the basement, the second floor-tracer selected should be one with the highest emission rate and the highest detectability, i.e., the earliest eluting tracer on the gas chromatograph (GC) column.

10.1.2 Thus, the choice for the second floor tracer in a 3-zone study is either Type 1 or Type 8 (see Section 9). The same reasoning extended to the other floors dictates that Type 2 be used on the first floor and Type 3 in the basement, as illustrated in Figure 3. The use of Type 1 in one zone and Type 8 in another zone in a 3-zone building should be avoided because those two tracers elute very close to each other and are therefore difficult to quantify without using special GC conditions. In stacked 4-zone structures, when both Types 1 and 8 must be used, the correct choice for the uppermost zone is Type 1, followed by Type 8 in the next lower zone, Type 2 in the next, and Type 3 in the lowest zone.

10.2 Placement of PFT Sources

Described herein is the placement of sources in family-type dwellings. The AER method can be used for other dwelling types (i.e., industrial, laboratories, offices, etc.).

10.2.1 The PFT sources should be shipped separately from the samplers. Each source shell is engraved with a code, the first number of which identifies it as one of the 4 available PFT types, i.e., type 1, 2, 3 (or TC), or 8.

10.2.2 The sources should be deployed one per every 500 ft² (46.5 m²) of living area. Typically, in a single story ranch-type home, two sources are placed in the living room, dining room, kitchen area and one in each of the bedrooms. The same type of source should be used if the floor is to be treated as a single zone, as shown in Figure 3.

10.2.3 If the house has a basement, a different PFT type should be used since it is a separate but attached zone. For an open (unfinished) basement, one or two sources may be used; if it is divided into rooms, 2 sources should be used. Ignoring the basement by not

including any sources and samplers or using sources of the same type as the main floor, can result in errors in the determination of the living space ventilation rate.

10.2.4 Generally, a PFT source is placed within 0.5 to 1.5 meters of the floor and no closer than 1 meter to an outside wall. For example, it can be taped onto the leg of a table or end table or even on a lower portion of a hanging chandelier.

10.2.5 The emitters are placed in the building at least 8 hours in advance of the samples.

10.2.6 Since the source is sensitive to temperature, it should not be placed within a meter of a heating or cooling source, in direct sunlight or other drafty location such as a window, nor at a location where air would carry the PFT vapors outside or to another zone before they had mixed uniformly within the zone where they were placed.

Note: Since heated air rises and cooled air sinks, the PFT location should be at a vertical location not too far above or below the temperature measurement/control elevation and not be placed above a warm air source (e.g., a lamp or the top of a refrigerator) nor below a cooled air source (e.g., an air conditioner vent or a window sill).

10.2.7 Record the average temperature of the source on the Field Data Sheet illustrated in Figure 4. The daily average room temperature is usually adequate for this purpose, even in the case of one or more daily temperature set-back cycles.

10.2.8 It should be mentioned that the directions included in this method are for a typical dwelling (ACH = 0-2) Table 3 gives the number of sources needed if the building to be monitored is expected to have a higher air change per hour than a normal dwelling, i.e., an office building with higher ventilation.

10.3 Placement of Passive Samplers (CATs)

Note: DO NOT STORE THE SOURCES AND THE SAMPLERS IN THE SAME LOCATION. The sources and samplers should definitely not be shipped in the same container and, ideally, not even shipped on the same day. For example, if transported in the same car or truck, there is a possibility of contamination. During field deployment, the samplers can be placed in the engine compartment or roof rack of a vehicle (effectively outside) while the sources are maintained within the vehicle passenger compartment or trunk. To this end it is generally wise for 1 or 2 passive samplers to remain as controls, that is, to remain unopened, for each series of home infiltration measurements.

10.3.1 One or two samplers are usually deployed in each zone of the home with the same location restriction as the sources and at least 1 to 2 meters from any PFT source or source of air not representative of the room air (e.g., air from the outside or another zone). Thus, the samplers are usually placed near another inside wall location, but at least 2 cm from any wall, and not in a flowing air stream without a shelter such as an envelope or box.

10.3.2 In the bedroom zone of a ranch house or 2-story house, it is prudent to sample in the master bedroom plus one other bedroom; this provides a better average for that zone.

10.3.3 In the family zone, two samplers located as per the two-story diagram, as shown in Figure 3, give an average concentration which is better than just placing one sampler as per the one story diagram.

10.3.4 The samplers are not temperature sensitive, but extremes should be avoided. They can be placed on a table or taped to the leg of a chair or table in any orientation. The samplers have a rubber cap on each end.

10.4 Sampling Start-Up and Shut-Down

10.4.1 To initiate sampling, only one cap must be removed, the one near the numbered end, as seen in Figure 2. The sampler number, location, and time and date sampling commenced must be recorded on the Field Data Sheet shown in Figure 4.

10.4.2 At the end of the designated sampling period (e.g., one day, one week, one month, etc.), cap the sampler and record the time and date sampling ceased on the Field Data Sheet. Verify each CAT ID number upon removal from its sample location. CATs are stored in sealed ziplock bags for transport to the lab.

10.4.3 Record other information as called for on the Field Data Sheet. The volume of each zone of the house should be obtained from inside dimension measurements or estimated from outside lengths and widths, subtracting 1 foot (0.3 m) from each, but using inside ceiling heights. A separate sheet should be used for each home. House floor plan should be drawn to show location of each source and CAT for each sampling event. House Volume should be recorded on house floor plan. These data are needed in conjunction with other information (e.g., from questionnaires) about open windows, presence of fireplaces, window fans, window air conditioners, etc. to assist in interpreting the data.

11. Gas Chromatography with an Electron Capture Detection

11.1 The determination of PFTs collected via either the passive or programmable samplers is accomplished with a gas chromatograph system (Varian Instrument Corp., Floral Park, New Jersey, Model 3700 GC with a Model CDS-111 integrator-controller). The analysis includes thermal desorption, chemical and physical processing, chromatographic separation, and ECD determination of the tracer gas as illustrated in Figure 5.

11.2 Calibration of GC-ECD

11.2.1 Gas standards for calibrating the GC are prepared in the concentration range of 1 to 10,000 pL/L by first preparing 1000 ppm primary standards of PFT in helium (He) either gravimetrically or volumetrically and verifying on a thermal conductivity GC that has been calibrated with pure PFT vapors. These primary standards are then further successively diluted with ultra pure air (Scientific Gas Products, Plainfield, New Jersey) in Spectra-Seal aluminum cylinders (Airco Industrial Gases, Riverton, New Jersey).

Note: Regular steel cylinders have been found to adsorb significant amounts of the higher boiling point tracers (PMCH and PDCH), especially at concentrations of 1 and 10 pL/L, but the Spectra-Seal cylinders showed no adsorption loss (7).

11.2.2 Calibration of the GC is performed by setting flow rates of 5 and 50 mL/min on the gas cylinder standards and passing the flow through consecutive CATS tubes for different durations.

11.2.3 Quantities of from 0.05 to 5000 pL ($\text{pL} = 10^{-12}$) of tracer then are analyzed to calibrate the GC response for each tracer.

11.2.4 The limit of detection (LOD) for AER depends on the LOD of the GC-ECD, the sampling rate of the CAT tubes, the sample duration, the emission rates of the PFT sources, the house volume and the true integrated air exchange rate. It is recommended that GC-ECD systems which can detect PFT quantities at least as low as 1 picoliter with 30% precision be employed. The minimum PFT concentration LOD is controlled by this and the sample exposure time, and the effective sampling rate. For this instrument, the minimum detectable air concentration calculated by:

$$\begin{aligned} (\text{PFT LOD, pL/L}) &= \frac{(\text{Minimum Measurable PFT Amount, pL})}{(\text{Hours Exposed}) \times (\text{Sampling Rate, L/hr})} \\ &= \frac{1 \text{ pL}}{24 \text{ hr} \times 0.00892 \text{ L/hr}} \\ &= 5 \text{ pL/L} \end{aligned}$$

The maximum measurable PFT concentration can be calculated by:

$$\begin{aligned} (\text{PFT Concentration Maximum, pL/L}) &= \frac{(\text{Maximum Measurable PFT Amount, pL})}{(\text{Hours Exposed}) \times (\text{Sampling Rate, L/hr})} \\ &= \frac{270 \text{ pL}}{24 \text{ hr} \times 0.00892 \text{ L/hr}} \\ &= 1260 \text{ pL/L} \end{aligned}$$

Note: The highest PFT concentrations expected in normal dwellings are about 200 pL/L, so the upper limit should be of no consequence. The lowest PFT concentrations may be on the order of 1 pL/L for houses with open windows and fans in use.

11.2.5 The concentration of PFT produced by sources in a home is dependent on the number of PFT sources, their emission rates, the house volume, and the air exchange rate, as outlined by the following equation:

$$C = \frac{n \times S/V}{[n \times S/V]/R}$$

where:

S ~ 1800 nL/hr, PMCH source @ 25°C

n = number of sources

V = house volume, m³

R = air changes per hour (ACH)

The lowest PFT values are expected to be found in large houses with high AER rates. As an example, for a house with the following dimensions:

$$V = 500 \text{ m}^3$$

$$R = 12 \text{ ACH}$$

n = 6 PMCH sources,

the average PFT level is expected to be about 1.8 nL/m^3 . This is about equal to the system LOD. The highest PFT levels will be found in small homes with low AER. As an example, for a house with the following dimensions:

$$V = 150 \text{ m}^3$$

$$R = 0.5 \text{ ACH}$$

n = 6 PMCH sources,

the expected PFT level is 144 nL/m^3 which is well below the system PFT capacity.

11.3 GC-ECD Analysis Protocol

11.3.1 Whether for initial bakeout or for thermal desorption and recovery of sampled PFTs, a special rack with 23 positions should be constructed as illustrated in Figure 4. The resistance heating wire element consists of about 10 turns of 0.8 mm OD (20 gage) nichrome wire (approximately 23 cm in length) such that 4.2 Vac ($\approx 8.5 \text{ A}$ or 36 W) heats the CATS tube to 450°C in 0.5 min and 1.9 Vac ($\approx 3.8 \text{ A}$ or 7 W) holds that temperature for another 0.5 min to effect the sample recovery; power is supplied from a transformer with a secondary rated at 6.3 Vac and 10 A (Essex/Stancor No. P-6308).

11.3.2 The tubes are placed into the rack by slipping through the heating coil (with one rack end removed) until they contact the spring-loaded "O"-ring seal pistons; the removal end, a 25-mm (1-in.) aluminum square stock, is replaced and the eccentric cam compresses the tube ends against the spring-loaded seals. The open 1.59 mm ($1/16 \text{ in.}$) tubing ends are connected to a 24-position Scanivalve rotary valve assembly (Gilian Instrument Corp., Wayne, New Jersey) which has an electrical rotary switch to bring the desorption power to the proper tube.

11.3.2.1 Before the sample is thermally desorbed, the sampler tube is purged with carrier gas (5% H_2 in N_2) for a short period of time to remove any traces of oxygen which otherwise would react with the PFTs during the 400°C desorption recovery. The sample is purged through the precut catalyst as seen in Table 1, the dryer to remove water vapor, and the two precut columns before entering an adsorbent trap. The 10 cm long catalyst bed in the presence of the hydrogen in the carrier gas reduces any chlorofluorocarbon compounds, as well as any remaining oxygen, to their hydrogenated forms, thus rendering these interfering compounds nonelectron-capturing.

11.3.2.2 After the surviving PFTs elute from the precut column, heavier molecular weight constituents still within the column are purged to the atmosphere by reversing the direction of flow. Meanwhile, the eluted PFTs are reconcentrated within a 10 cm long Porapak QS adsorbent trap.

Note: The purpose of the QS trap on the gas chromatograph (GC) is two-fold. First, by not opening the trap until the first PFT eluting from the precut column arrives, some lighter constituents are discarded. Second, after the precut column is backflushed, the trap remains open for 1 min to further purge away light-interfering gases and then is closed.

11.3.2.3 When the Porapak QS trap has been heated to 200°C and opened, the PFTs are flushed through the main catalyst as seen in Table 1 for final cleanup before entering the main column for separation of the PFTs prior to detection in the ECD.

11.3.2.4 While this is occurring, the next sample tube can be thermally desorbed and loaded onto the QS trap once it has sufficiently cooled (about 50°C), thus almost halving the overall PFT sample recovery and analysis time by overlapping the stages.

Note: Automation of the sequential analysis of all 23 tubes in either a CATS desorption rack or a BATS lid is accomplished by using the BATS base timing capability to initiate the GC timing sequence as each new tube steps in place. Each analysis, including reporting of the peak areas, takes 10 minutes; 23 tubes are analyzed in just under 4 hours.

11.3.2.5 Figure 5 illustrates the detailed plumbing and valving used to effect the automated chemical and physical processing during the analysis of the PFT samples. Automation occurs through the use of eight external events contained within the integrator-controller. As illustrated in Table 2, one event starts and stops the recorder paper, four events operate the four valves, and three events control the heating of the sampler tube and the Porapak QS trap. Three 6-port (Valco Instrument Co., Houston, Texas, SSAC6T Shaft Seal) and one 4-port (Valco SSAC4UT Shaft Seal) valves with air operators are used. Vespel cone seals are preferred to the Teflon®-filled ceramic type because the latter have been found to bleed contaminants at temperatures above 100°C. With the exception of the sample valve, they are mounted within the GC oven.

11.3.2.6 When the recorder shuts off at 8.01 min, the analysis is complete and the report of the peak areas, which is proportional to the quantity of each tracer, is printed as well as transmitted to a magnetic tape, which can then be processed on a Tektronix 4052 desk top computer. The GC is ready for the repeat of the cycle on a 10 minute frequency. Figure 7 is a typical chromatogram.

12. Calculations

Numerous researchers have proposed models and methods for using tracer gases in the solution of those models for determining the air infiltration rate into a home or building considered as a single, well-mixed chamber or zone. Recently, however, it has been recognized that many larger, more complex buildings, especially those with multiple-zoned HVAC systems and even one- and two-story homes with basements, realistically can only best be represented by models which recognize the building as multiple-connected zones, each of which is well-mixed.

12.1 One-Zone Case

For a building considered as a single, well-mixed zone of known volume, V , containing one type of tracer of known emission rate, $R_s(t)$, such that a tracer concentration, $C(t)$, is measured throughout the house which has an air exfiltration rate of $R_e(t)$, a simple material balance gives:

$$V \frac{dC(t)}{dt} = R_s(t) - R_e(t)C(t) \quad (1)$$

where:

V = volume of the building (constant), m^3

$R_s(t)$ = total tracer source rate (variable), nL/h

$C(t)$ = average tracer concentration in the building (variable), $nL/m^3 \equiv pL/L$

$R_E(t)$ = air exfiltration rate (variable), m^3/h

Equation 1 is a general solution in which it is assumed that the tracer source rate, the tracer concentration, and the exfiltration rate can vary with time; it also was assumed that the tracer concentration is the ambient air, that is, the infiltrating air is negligible, which is always the case for PFT's. Equation 1 then can be solved for various modes of tracer experiments, including tracer decay, constant concentration, and constant emission rate. The PFT sources are designed to provide a constant emission rate source in the building. About 5 to 10 h after deployment, the tracer concentration will become more or less constant, dependent only on slow changes in the exfiltration rate due either to mechanical ventilation or weather changes. For these steady state assumptions [that is, $dC(t)/dt \approx 0$], Equation 1 becomes:

$$\frac{1}{n} \sum_{t=1}^n \frac{R_s(t)}{C(t)} = \frac{1}{n} \sum_{t=1}^n R_E(t) = R_s \frac{1}{n} \sum_{t=1}^n \frac{1}{C(t)} \quad (2)$$

assuming that the source rate is constant, that is $R_s(t) = R_s$, over n periods of concentration. But:

$$\begin{aligned} \frac{1}{n} \sum_{t=1}^n \frac{1}{C(t)} &= \frac{1}{n} \left(\frac{1}{C(1)} + \frac{1}{C(2)} + \dots + \frac{1}{C(n)} \right) \\ &= \frac{1}{n} \left(\frac{C(2)C(3) \dots C(n) + C(1)C(3) \dots C(n) + \dots + C(1)C(2) \dots C(n-1)}{C(1)C(2) \dots C(n)} \right) \\ &\approx \frac{1}{n} \left(\frac{n\bar{C}^{n-1}}{\bar{C}^n} \right) \approx \frac{1}{\bar{C}} \end{aligned}$$

The second term in Equation 2 is the average infiltration rate, \bar{R}_E . Thus:

$$\bar{R}_E \approx \frac{R_s}{\bar{C}} \quad (3)$$

The approximation in Equation 3 is because it was shown that the reciprocal of an average concentration, \bar{C} , which is the quantity that the passive sampler determines, is close to but not identical to the average of reciprocal concentrations.

12.2 Two-Zone Case

Examples of two-zone cases are a two-story house on a slab, a one-story (for example, ranch) with a basement or a crawl space, and any building which is ventilated with two separate HVAC systems. Figure 8 depicts the model for a one-story house (Zone 1) with a basement (Zone 2). Air can infiltrate from outside the house into each zone (R_{11} and R_{12}) and exfiltrate each zone to the outside (R_{E1} and R_{E2}). In addition, air can exchange between the zones in both directions (R_{E12} and R_{E21}). Assuming that a different tracer type is used in each zone (Tracer 1 in Zone 1, etc.), tracer material balances, assuming that steady state pertains and that there is negligible tracer in the outside air, give the following:

Zone 1

$$R_{21}C_{12} - R_{12}C_{11} - R_{E1}C_{11} = -R_{s1} \quad (4)$$

$$R_{21}C_{22} - R_{12}C_{21} - R_{E1}C_{21} = 0 \quad (5)$$

Zone 2

$$R_{12}C_{11} - R_{21}C_{12} - R_{E2}C_{12} = 0 \quad (6)$$

$$R_{12}C_{21} - R_{21}C_{22} - R_{E2}C_{22} = -R_{s2} \quad (7)$$

where:

R_{12} , R_{21} = air exchange rates from Zone 1 to Zone 2 and Zone 2 to Zone 1, m^3/h ,

R_{E1} , R_{E2} = air exfiltration rates from Zones 1 and 2, m^3/h ,

R_{s1} , R_{s2} = rates of tracer sources in each respective zone, nL/h ,
and

C_{11} , C_{21} , C_{12} , C_{22} = concentration of Tracer 1 in Zone 1, etc., nL/m^3 ($\equiv pL/L$).

The concentrations are measured with the passive samplers, and the tracer source rates are known. Thus, the four unknowns, two air exchange rates and two exfiltration rates, can be solved from the four simultaneous equations. The rate of infiltration for each zone then can be calculated from air mass balances:

$$R_{11} = R_{E1} + R_{12} - R_{21} \quad (8)$$

$$R_{12} = R_{E2} + R_{21} - R_{12} \quad (9)$$

The solutions to Equations 4 to 7 can be obtained by solving as two sets of simultaneous equations, noting that R_{21} can be solved from Equations 4 and 5 and R_{12} from Equations 6 and 7. Then R_{E1} and R_{E2} can be obtained from Equations 5 and 7, respectively. The solutions, which are given in the Appendix, also can be obtained, by any standard matrix inversion routine for use on a desktop computer. This is especially useful when the number of zones increases to three or four. Once all the flow rates have been determined, simple

material balances then can be performed for pollutants in the same building. The following equations

$$R_{21}C_{p2} + R_{11}C_{pa} - 2R_{12}C_{p1} - R_{E1}C_{p1} = -R_{p1} + k_1V_1C_{p1} \quad (10)$$

$$R_{12}C_{p1} + R_{12}C_{pa} - R_{21}C_{p2} - R_{E2}C_{p2} = -R_{p2} + k_2V_2C_{p2} \quad (11)$$

where:

C_{p1} , C_{p2} , C_{pa} = concentration of pollutant in Zone 1, Zone 2, and the ambient outside air, respectively,

R_{p1} , R_{p2} = rate of the pollutant source in zone.

k_1 , k_2 = rate of pollutant scavenging in each zone, and

V_1 , V_2 = volume of each zone.

would then give the pollutant net source strength in each zone of the building.

The solutions to the tracer and air material balance equations are:

Two-Zone Case

$$R_{21} = (R_{s1}C_{21})/(C_{11}C_{22} - C_{12}C_{21})$$

$$R_{12} = (R_{s2}C_{12})/(C_{11}C_{22} - C_{12}C_{21})$$

$$R_{E1} = R_{21}(C_{11}/C_{21}) - R_{12}$$

$$R_{E2} = R_{12}(C_{11}/C_{12}) - R_{21}$$

R_{11} and R_{12} are calculated from Equations 8 and 9 in the text.

12.3 Three-Zone Case

A typical example of a three-zone building is a two-story house with a basement. Again, assuming that a different tracer source is used in each zone and that the steady state assumption applies, a set of nine tracer material balance equations can be developed to solve for nine unknown flow terms (three exfiltration flow rates, one from each zone, and six air exchange rate terms, two leaving each zone). A set of three air mass balance equations would provide the three unknown infiltration rates. It is apparent that as the number of zones increases, the matrix solution approach with computer assistance is the only manageable way.

Three-Zone Case

Let:

$$[] = [C_{11}(C_{22}C_{33} - C_{23}C_{32}) + C_{12}(C_{23}C_{31} - C_{21}C_{33}) + C_{13}(C_{21}C_{32} - C_{22}C_{31})]$$

Then:

$$R_{21} = R_{s1}(C_{21}C_{33} - C_{23}C_{31})/[]$$

$$R_{31} = R_{s1}(C_{22}C_{31} - C_{21}C_{32})/[]$$

$$R_{32} = R_{s2}(C_{11}C_{32} - C_{12}C_{31})/[]$$

$$R_{12} = R_{s2}(C_{12}C_{33} - C_{13}C_{32})/[]$$

$$\begin{aligned}
 R_{13} &= R_{s3}(C_{13}C_{22} - C_{12}C_{23})/[] \\
 R_{23} &= R_{s3}(C_{23}C_{11} - C_{13}C_{21})/[] \\
 R_{E1} &= R_{31}(C_{23}/C_{21}) + R_{21}(C_{22}/C_{21}) - R_{13} - R_{12} \\
 R_{E2} &= R_{32}(C_{13}/C_{12}) + R_{12}(C_{11}/C_{12}) - R_{23} - R_{21} \\
 R_{E3} &= R_{13}(C_{11}/C_{13}) + R_{23}(C_{12}/C_{13}) - R_{31} - R_{32} \\
 R_{11} &= R_{E1} + R_{12} + R_{13} - R_{21} - R_{31} \\
 R_{12} &= R_{E2} + R_{21} + R_{23} - R_{12} - R_{32} \\
 R_{13} &= R_{E3} + R_{31} + R_{32} - R_{13} - R_{23}
 \end{aligned}$$

The total ACH in a house is given simply by the sum of the exfiltration rates of all zones divided by the sum of the volume of all zones. (See Section 12.2 entitled "Two-Zone Case" of the text for definition of the terms.)

12.4 N-Zone Case

It is apparent, then, that for N zones, a set of N trace material balance equations can be written to solve for N² unknown flow terms (N exfiltration flow rates, one from each zone, and N(N - 1) air exchange rates, that is, N - 1 leaving each zone to flow to another zone). Also, a set of N air mass balance equations would provide the N unknown infiltration rates.

13. References

1. Hunt, C. M., "Air Infiltration: A Review of Some Existing Measurement Techniques and Data", *Building Air Change Rate and Infiltration Measurements*, ASTM STPJ 719, American Society for Testing and Materials, 1980, 3-23.
2. Card, W. H., et al., "Air Leakage Measurement in a Building by an Infrasonic Method," Technical Report TR-78-1, Final Report National Science Foundation Grants Eng-75-23416 and Computer-Environments, Department of Electrical and Computer Engineering, Syracuse University, Syracuse, NY, January 31, 1978.
3. Riggin, R. M., *Technical Assistance Document for Sampling and Analysis of Toxic Organic Compounds in Ambient Air*, EPA - 600/4-83-027, U.S. Environmental Protection Agency, Research Triangle Park, NC, 1983.
4. *Particle Total Exposure Assessment Methodology (P-TEAM): Pre-Pilot Study*, Vol. I and II, Research Triangle Institute, NC, January 27, 1989.
5. Dietz, R. N., Cote, E. A., Senum, G. I., and Wieser, R. F., "An Inexpensive Perfluorocarbon Tracer Technique for Wide-Scale Infiltration Measurement in Homes", in *Proceedings of International Symposium on Indoor Air Pollution, Health and Energy Conservation*, Amherst, MA, October 13-16, 1981, BNL 30032.

6. Dietz, R. N., and Cote, E. A., "Air Infiltration Measurements in a Home Using a Convenient Perfluorocarbon Tracer Technique", *Environ. Internat.*, 8:419-433, 1982.
7. Dietz, R. N., Goodrich, R. W., Cote, E. A., and Wieser, R. F., "Brookhaven Air Infiltration Measurement System, (BNL/AIMS) Description and Application", Brookhaven National Laboratory, Upton, NY, August, 1983, BNL-33846.
8. Dietz, R. N., Goodrich, R. W., Cote, E. A., and Wieser, R. F., "Application of Perfluorocarbon Tracers to Multizone Air Flow Measurements in Mechanically and Naturally Ventilated Buildings", August, 1984, BNL 35249.
9. Dietz, R. N., D'Ottavio, T. W., and Goodrich, R. W., "Multizone Infiltration Measurements in Homes and Buildings Using a Passive Perfluorocarbon Tracer Method", *ASHRAE Trans.*, 91(2):1761-1776, 1985.
10. D'Ottavio, T. W., and Dietz, R. N., "Errors Resulting from the Use of Single Zone Ventilation Models on Multizone Buildings: Implications for Energy Conservation and Indoor Air Quality Studies", *Ibid*, 1777-1788.
11. Schaap, L., Leaderer, B. P., Renes, S., Verstraelen, H., Tosun, T., and Dietz, R. N., "A Comparison of the Perfluorocarbon and Tracer Gas Decay Methods for Assessing Infiltration Rates in Residences", *Proceedings of the CLIMA 2000 World Congress on Heating, Ventilating, and Air-Conditioning, Vol. 2: Building Design and Performance*, P.O. Fanger, Ed., VVS Kongres-VVS Messe, Copenhagen, 1985, 19-24.
12. Dietz, R. N., D'Ottavio, T. W., and Goodrich, R. W., "Seasonal Effects on Multi-Zone Air Infiltration in Some Typical U.S. Homes Using a Passive Perfluorocarbon Tracer Technique," *Ibid*, 115-121.
13. Leaderer, B. P., Schaap, L., and Dietz, R. N., "Evaluation of the Perfluorocarbon Tracer Technique for Determining Infiltration Rates in Residences," *Environ. Sci. Technol.*, 19(12):1225-1232, 1985.
14. D'Ottavio, T. W., and Dietz, R. N., "Discussion of Radon Transport into a Detached One-Story House with a Basement," *Atmos. Environ.*, 20(5):1065-1069, 1986.
15. Dietz, R. N., Goodrich, R. W., Cote, E. A., and Wieser, R. F., "Detailed Description and Performance of a Passive Perfluorocarbon Tracer System for Building Ventilation and Air Exchange Measurements," in *Measured Air Leakage of Buildings*, ASTM STP 904, Trechsel, H. R., and Lagus, P. L., Eds., American Society for Testing and Materials, Philadelphia, 1986, 203-264.
16. Clausen, G. H., Moller, S. B., Fanger, P. O., Leaderer, B. P., and Dietz, R. N., "Background Odor in Spaces Caused by Previous Tobacco Smoking," *Proceedings of IAQ '86*, ASHRAE, Atlanta, GA, April, 1986, 119-125.

17. Hoogendyk, C. G., Dietz, R. N., D'Ottavio, T. W., and Goodrich, R. W., "Two-Zone Modeling for Air Exchange Rates and NO₂ Source and Decay Rates," BNL 39235, December 1986, Final Report.
18. D'Ottavio, T. W., Dietz, R. N., Kunz, C., and Kothari, B., "Radon Source Rate Measurements Using Multiple Perfluorocarbon Tracers," BNL 39456, February 1987. Presented at Indoor Air '87, Berlin (West), Germany, August 17-21, 1987, *Proceedings of the 4th International Conference on Indoor Air Quality and Climate*, Vol. 2, B. Seifert, et al., Eds., Berlin, 1987, 388-392.
19. Hoogendyk, C. G., Dietz, R. N., D'Ottavio, T. W., and Goodrich, R. W., "Two-Zone Modelling for Air Exchange Rates and NO₂ Source and Decay Rates in a Southern California Residential Indoor Air Quality Study," BNL 39457, February 1987, *Ibid*, 1:333-337.
20. Vercammen, M., Leaderer, B. P., and Dietz, R. N., "Influence of Airflow on the Performance of the Perfluorocarbon Tracer Technique for Measuring Ventilation Rates," *Ibid*, 3:388-392.
21. Dietz, R. N., "Air Infiltration and Mechanical Ventilation Performance of Buildings Determined With a Passive Perfluorocarbon Tracer Technique (Abstract)," BNL 39802, April 1987. To be presented at the Conference "Health Buildings '88," Stockholm, Sweden, September 5-8, 1988.
22. D'Ottavio, T. W., Senum, G. I., and Dietz, R. N., "Error Analysis Techniques for Perfluorocarbon Tracer-Derived Multizone Ventilation Rates," BNL 39867, June 1987, *Bldg. Environ.*, 23(3):187-194, 1988.
23. Dietz, R. N., Goodrich, R. W., D'Ottavio, T. W., Spandau, D. J., and Senum, G. I., "Multiple PFT Tracer-Determined Air Flow and Duct Leakage in a Forced-Air-Equipped Condominium (Abstract)," January, 1988, BNL 40798. To be presented at the 9th Annual Conference on Effective Ventilation, Ghent, Belgium, September 12-15, 1988.
24. Dietz, R. N., "Overview of Tracer Technology Instrumentation for Short-Term and Real-Time Building Ventilation Determinations," March, 1988, BNL 41067, in Technical Note AIVC24, June 1988 101-141.
25. Pellizzari, E. D., Michael, L.C., K. Perritt, Smith, D.J., Hartwell, T.D., and Sebestik, J., "Comparison of Indoor Toxic Air Pollutant Levels in Several Southern California Communities," Draft Final Report, EPA Contract No. 68-02-4544, August, 1988.
26. Lagus, P. L., "Air Leakage Measurements by the Tracer Dilution Method - A Review," *Building Air Change Rate And Infiltration Measurements*, ASTM STP 719, American Society of Testing and Materials, 1980, 36-49.

Table 1. Gas Chromatography Specification and Conditions

Main Column	1.2 m (4 ft) long packed with 0.1% SP-1000 on Carbopack C (Supelco, Inc., Bellefonte, PA)
Precut Columns	1.2 m (4 ft) long Porasil F followed by 0.3 m (1 ft) long of 0.1% SP-1000 on Carbopack C
Column Oven	140°C
Precut Catalyst	10.1 cm (4 in) long packed with palladium (Pd) (1%) on polyethylenimine/SiO ₂ -Royer Pd catalyst (Strem Chemicals, Inc., Newburyport, Mass.); 200°C
Main Catalyst	3.2 cm (1.24 in) long packed similarly; 200°C
Carrier Gas	5% H ₂ in N ₂ at 25 and 20 mL/min, respectively, through the precut and main columns
Porapak QS Trap	10.1 cm (4 in) long packed with Porapak QS
Permeation Dryer	1.2 m (4 ft) long Nafion dryer (Permapure Products Inc., Oceanport, N.J., Model MD-125-48S) located in the top of GC (~35°C)
ECD	180°C

Note: All columns (including catalyst beds and adsorbent trap) are made with 3.2 mm (0.125 in) OD stainless steel tubing.

Table 2. Gas Chromatograph^a Sequence of Events

<u>Event Time, min</u>	<u>Event Code</u>	<u>Event</u>	<u>Event Status</u>
0.00	---	System steps to next sample tube; starts event clock	---
0.01	0.01	Recorder starts	Off
0.01	0.14	QS/sampler heating relay switches to QS trap	On
0.02	0.10	Desorption Power turned on	On
0.02	0.12	High power position	On
0.35	0.13	Low power position	Off
0.50	0.08	Sample in QS trap injected (that is, V4 on)	On
1.60	0.09	V ₄ is off	Off
1.60	0.11	Desorption power turned off	Off
1.62	0.15	QS/sampler relay switches to sampler	Off
2.30	0.06	V ₃ is on	On
4.95	0.04	V ₂ is on	On
5.00	0.02	V ₁ is on	On
5.00	0.10	Desorption power turned on	On
5.00	0.12	High power position	On
5.40	0.13	Low power position (not used for BATS tubes)	Off
5.70	0.08	V ₄ is on	On
7.30	0.11	Desorption power turned off	Off
7.60	0.09	V ₄ is off	Off
7.70	0.07	V ₃ is off	Off
7.75	0.03	V ₁ is off	Off
7.80	0.05	V ₂ is off	Off
8.01	0.00	Recorder off	On

Table 3.
Number of PFT Sources Needed Per Zone to Achieve the
Lower Limit of Detection When the Exposure Time Varies*

Source Type	Hours Exposed				
	8	12	24	48	168 (7 days)
PDCB	13	9	4	2	1
PMCP	11	8	4	2	1
PMCH	18	12	6	3	1
PDCH	37	25	13	6	2

*Assuming:

ACH ≤ 6
 Vol. per zone $\approx 314 \text{ m}^3$ (500 ft² floor space with 8 foot ceilings)
 GC-ECD Limit of Detection $\leq 1 \text{ pL}$
 PFT minimal emission rate

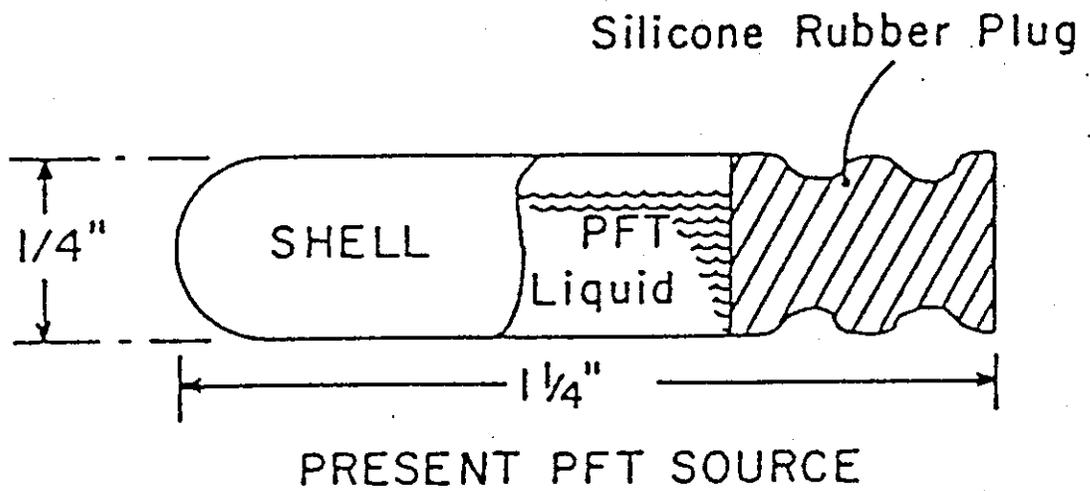


Figure 1. Diagram of the PFT Source Configuration

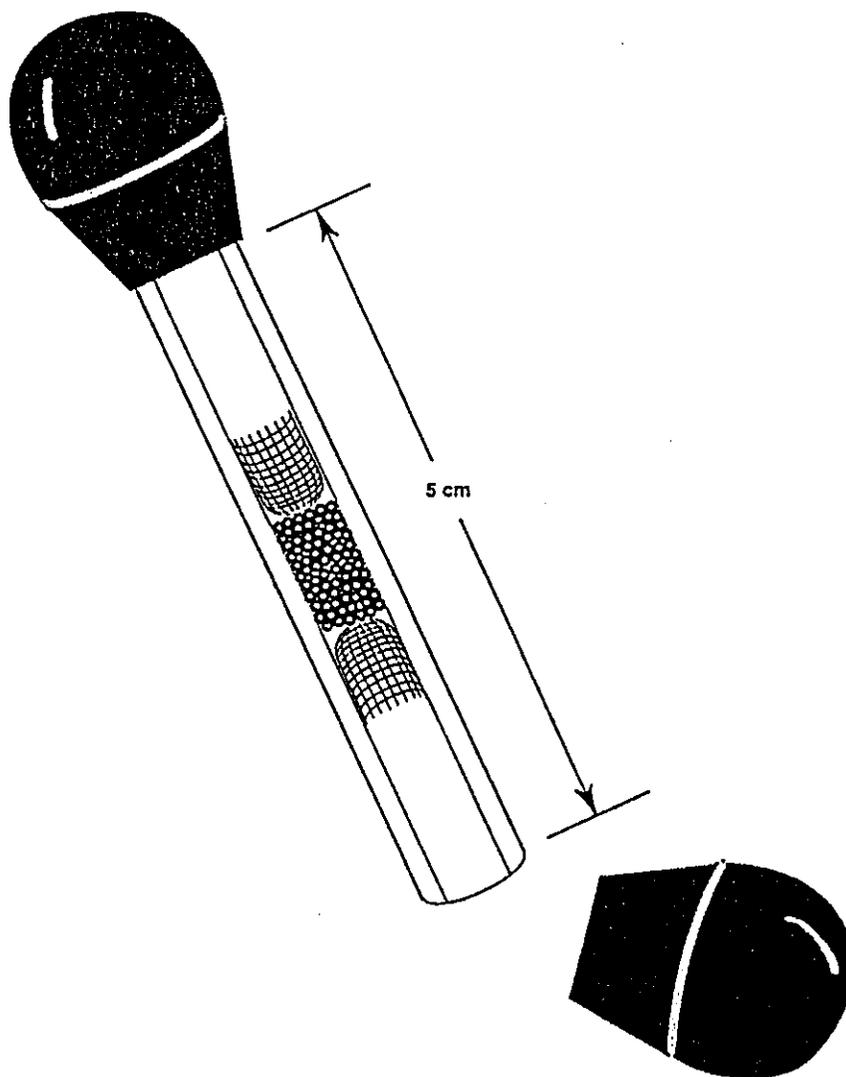
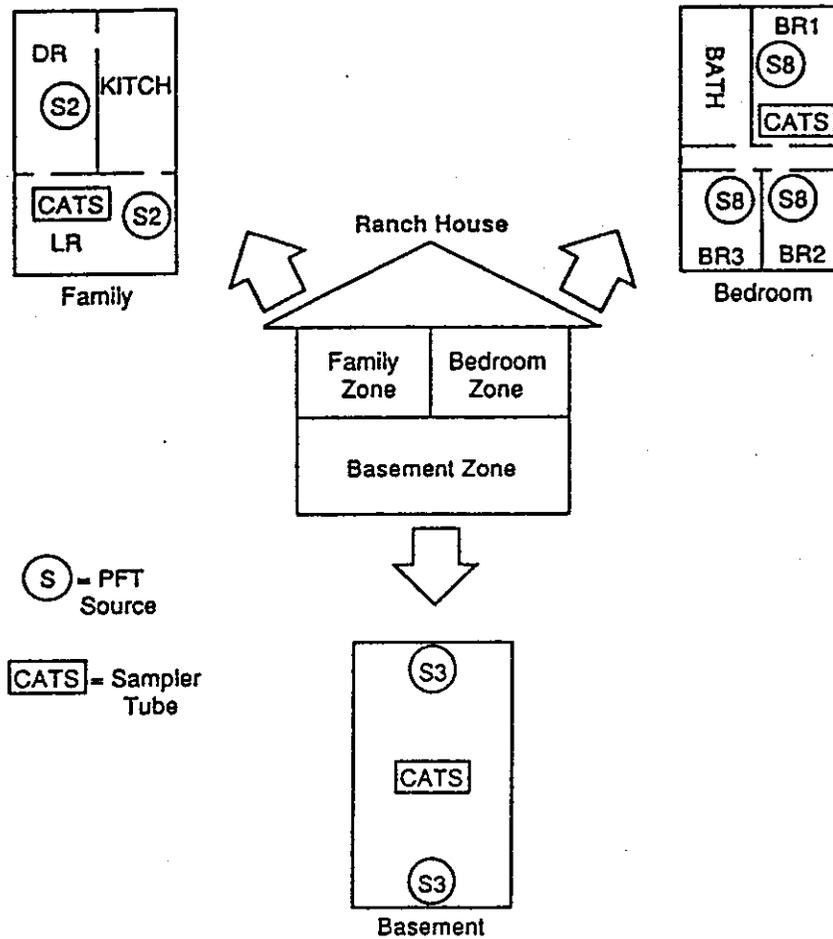


Figure 2. Diagram of a Typical capillary Adsorbent Tube (CAT)

One-Story Ranch Style House with a Basement



Basement Zone

Sources- Place two PTF type 3 sources on opposite ends of the basement. If an obstruction exists, place a source on either side of the obstruction.

Sampler- Place the CATS in the center of the basement or within the largest open area.

Family Zone

Sources- Place two PFT type 2 sources within the two largest rooms.

Sampler- Place a CATS in the largest room.

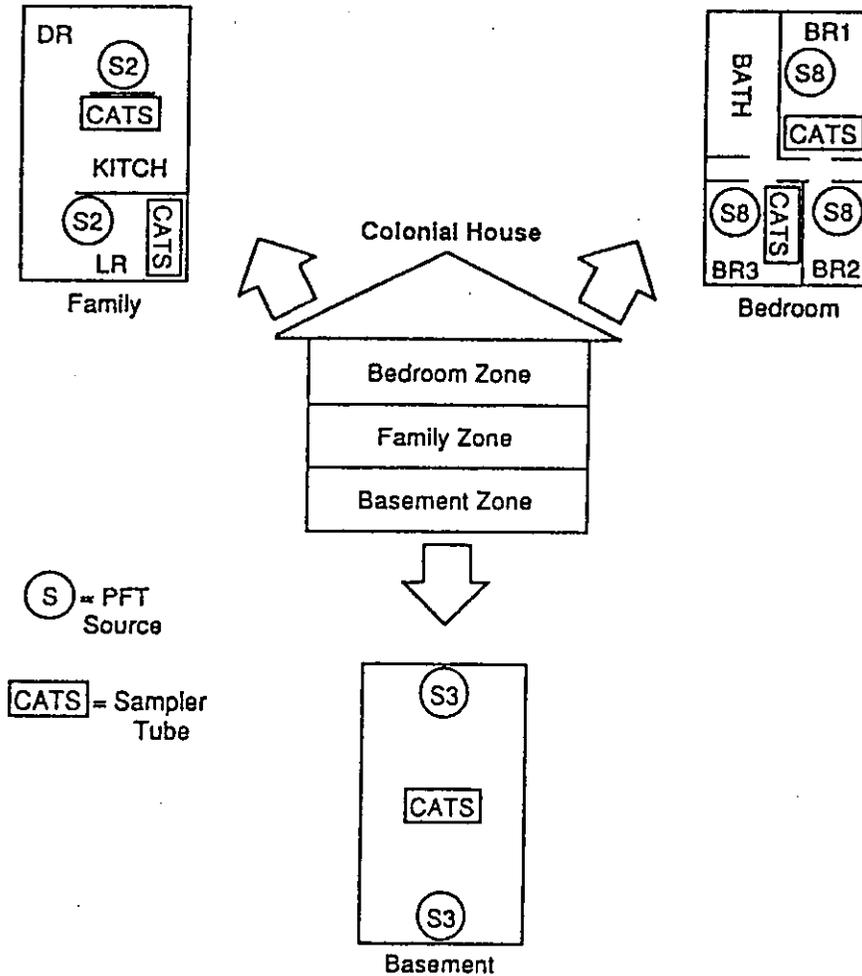
Bedroom Zone

Sources- Place one PFT type 8 source in each bedroom.

Sampler- Place a CATS in the largest bedroom in the zone.

Figure 3A. Placement of PFT Sources

Two-Story Colonial Style House with a Basement



Basement Zone

Sources- Place two PFT type 3 sources on opposite ends of the basement. If an obstruction exists, place a source on either side of the obstruction.

Sampler- Place the CATS in the center of the basement or within the largest open area.

Family Zone

Sources- Place two PFT type 2 sources in the rooms at opposite ends of the zone.

Sampler- Place two CATS in the largest rooms in this zone, towards the center, but away from each other and the sources.

Bedroom Zone

Sources- Place one PFT type 8 source in each bedroom.

Sampler- Place two CATS in the largest bedrooms within this zone.

Figure 3B. Placement of PFT Sources

Project Title _____

House Description

House ID: _____ # of Zones: _____

Circle one

Start Date: / / Start Time: : am pm

Stop Date: / / Stop Time: : am pm

- ___ 1 story
- ___ 2 story
- ___ w/basement
- ___ split level
- ___ w/fireplace
- ___ w/woodstove

Zone #: _____ Zone ID: _____ # of Sources: _____ Source Code: _____

Avg. Temp. (°F): _____ Volume (ft³): _____ # of CATS: _____
(°C): _____ (m³): _____

CATS ID	Room	Item Placed On	Source Location	
			Room	Item Placed On

Zone #: _____ Zone ID: _____ # of Sources: _____ Source Code: _____

Avg. Temp. (°F): _____ Volume (ft³): _____ # of CATS: _____
(°C): _____ (m³): _____

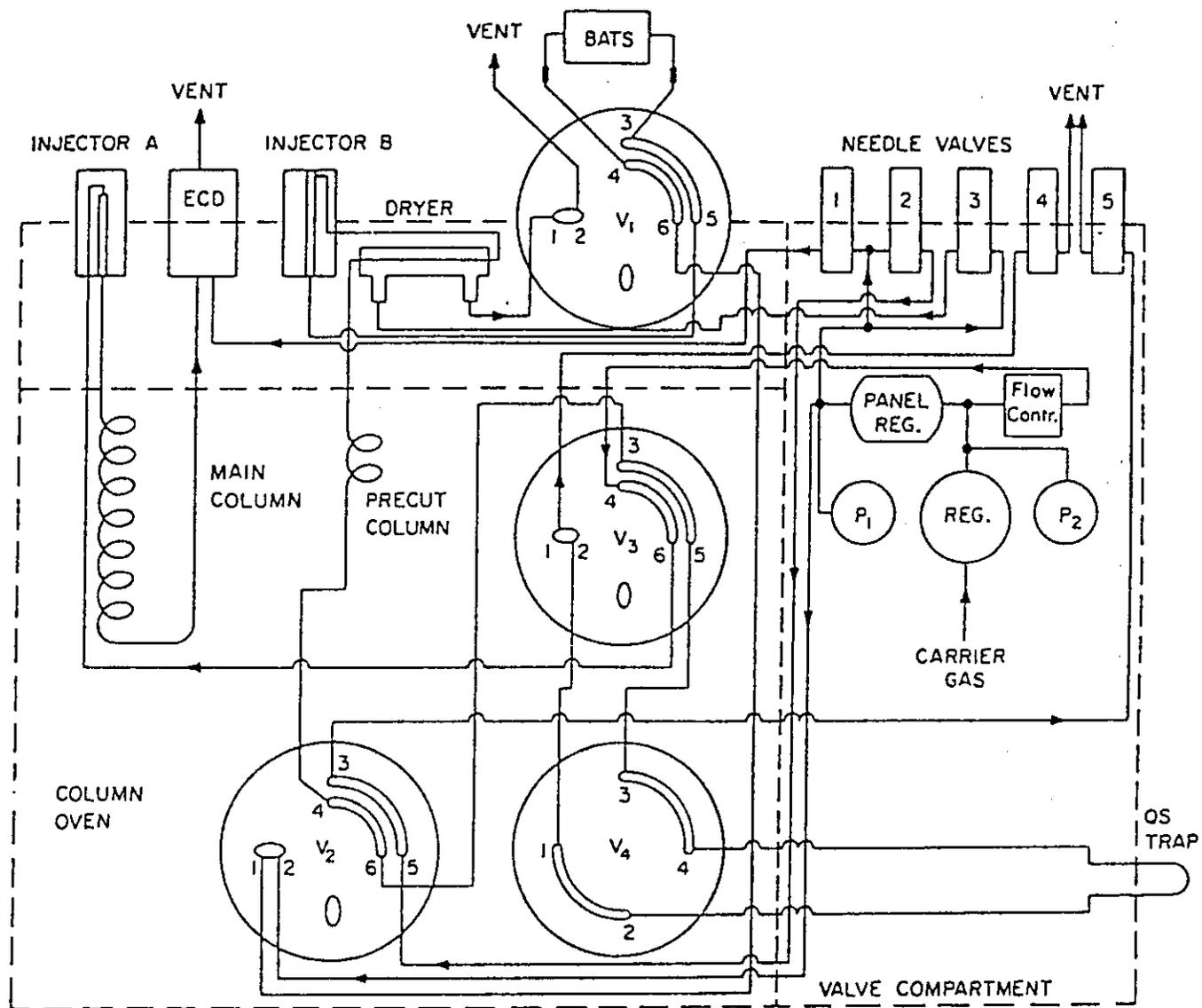
CATS ID	Room	Item Placed On	Source Location	
			Room	Item Placed On

Zone #: _____ Zone ID: _____ # of Sources: _____ Source Code: _____

Avg. Temp. (°F): _____ Volume (ft³): _____ # of CATS: _____
(°C): _____ (m³): _____

CATS ID	Room	Item Placed On	Source Location	
			Room	Item Placed On

Figure 4. Data Sheet



V_1 = The sampler valve.
 V_2 = The precut valve.

V_3 = The flow direction valve.
 V_4 = The Porapak OS valve.

Each is shown in its "ON" position; in the "OFF" position, the valve slots are rotated 90° counterclockwise.

Figure 5. Schematic of Laboratory GC Analyzer

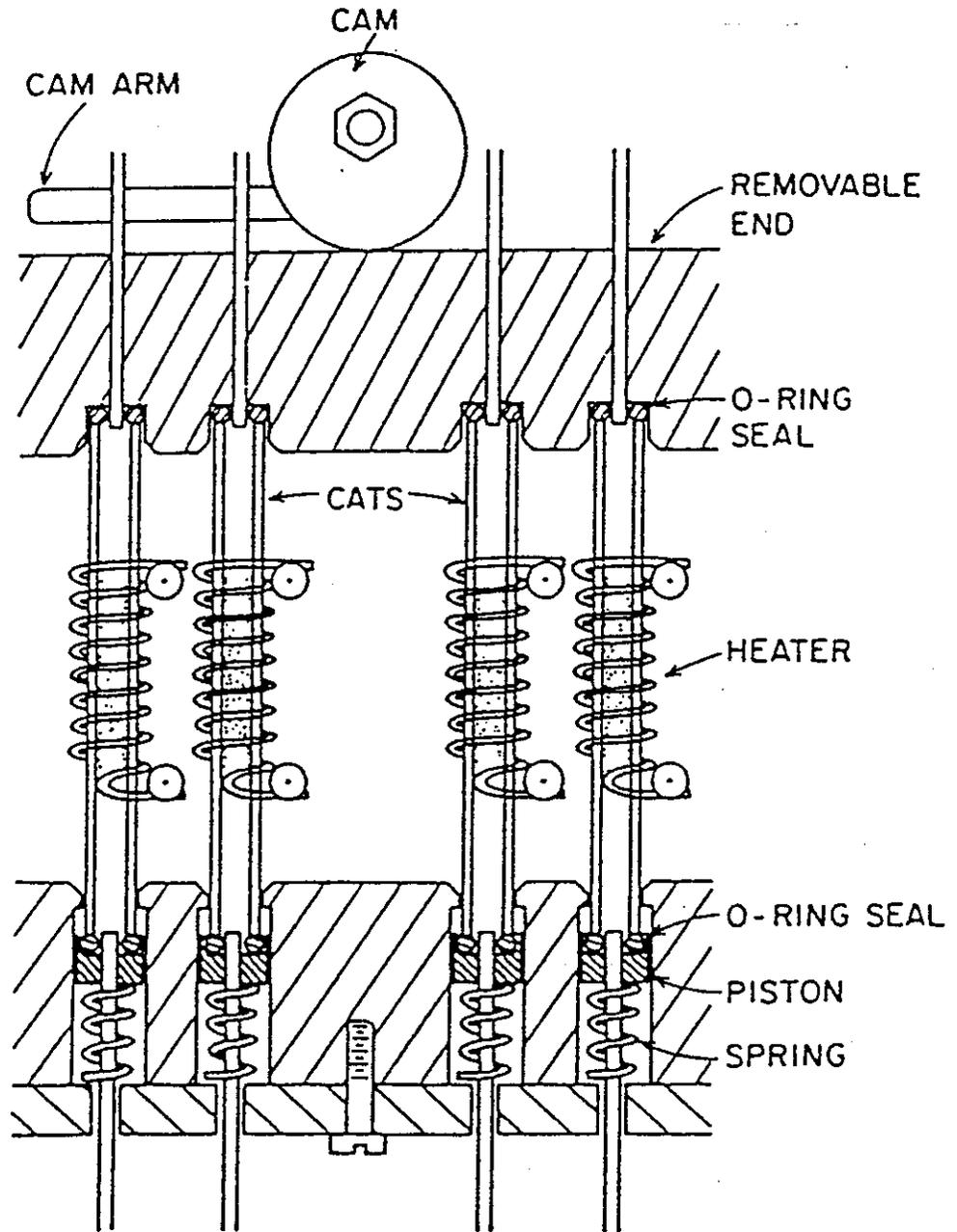


Figure 6. Passive Sampler Thermal Desorption Rack

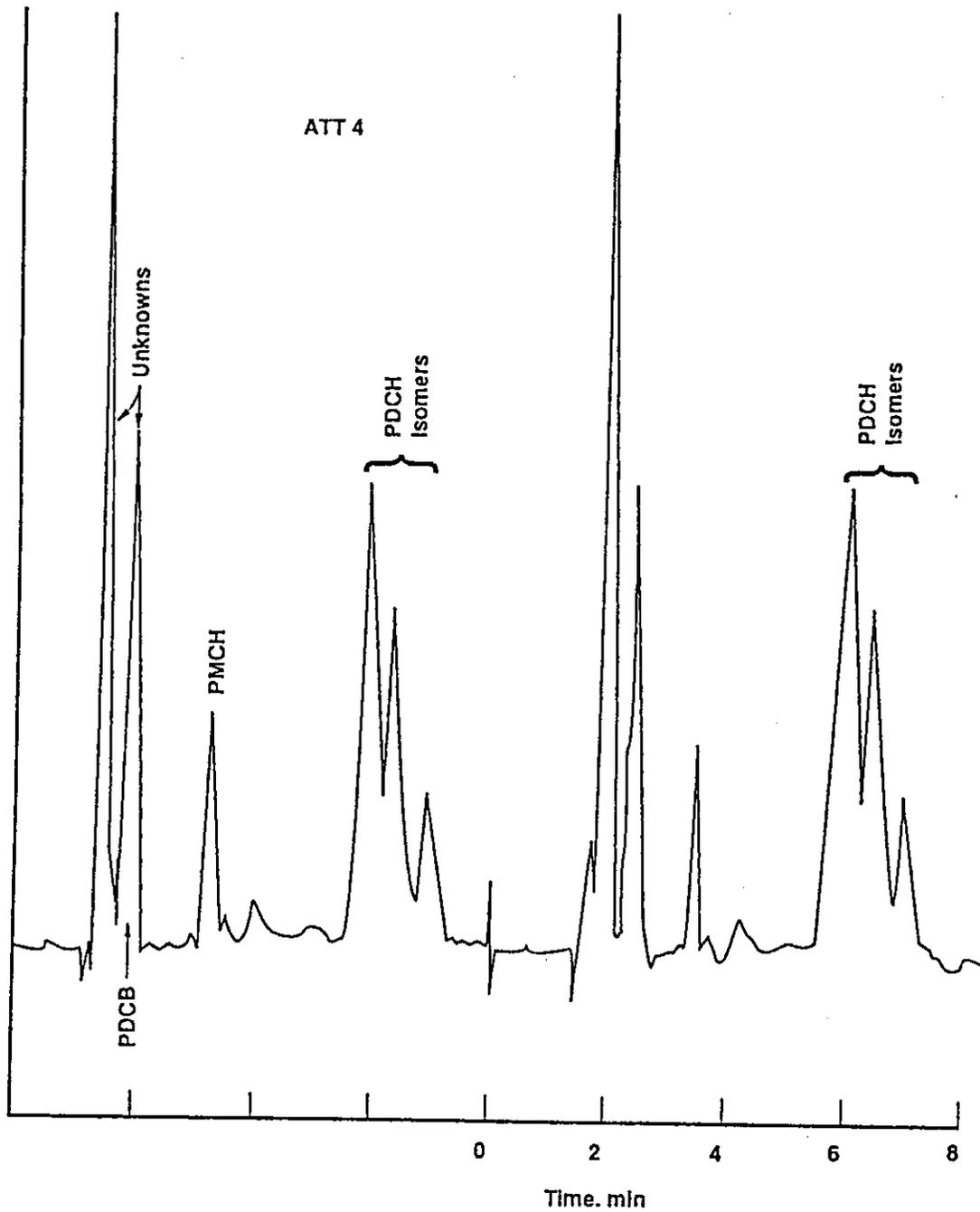
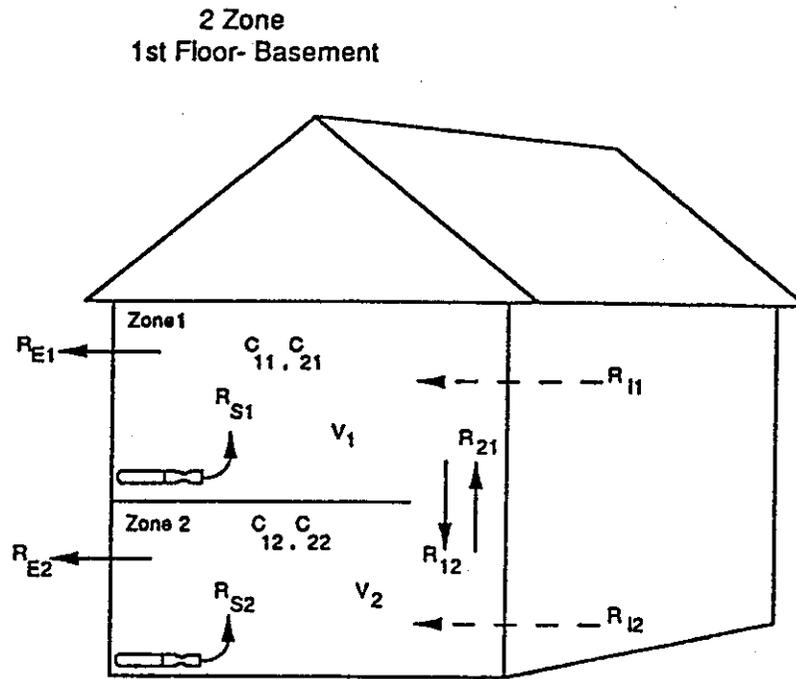


Figure 7. Chromatograms of Two 25-L Ambient Air Samples with the GC Specifications Shown in Table 1. The Unknown Peak after PDCB is PMCP.



R_{11}, R_{12} = Air Infiltration

R_{E1}, R_{E2} = Air Leakage

R_{12}, R_{21} = Air Exchange Between Zones

R_{S1}, R_{S2} = PFT Sources

V_1, V_2 = Zone Volumes

C_{11}, C_{21} = Connection of Tracer 1 in Zone 1

C_{12}, C_{22} = Connection of Tracer 2 in Zone 2

Figure 8. Model Considered for a Two-Zone House

Method IP-4B

DETERMINATION OF AIR EXCHANGE RATE IN INDOOR AIR USING TRACER GAS

1. Scope
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 - 11.1 On Site Monitor Method
 - 11.2 Container Method
12. Sampling
 - 12.1 General Procedures
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 - 12.3 Sampling for Container Method
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18. Acknowledgements
19. References

Method IP-4B

DETERMINATION OF AIR EXCHANGE RATE IN INDOOR AIR USING TRACER GAS

1. Scope

1.1 This document describes the protocol for the measurement for an air exchange rate (AER) between the outside and inside of buildings under natural meteorological conditions by trace gas dilution.

1.2 The tracer gas suggested for this method is sulfur hexafluoride (SF_6). Other tracer gases are available. This document lists other tracers and discusses the advantage of using SF_6 . Occasionally more than one tracer gas may be desired in an application. Situations where it may be advantageous to utilize more than one tracer gas will be discussed.

1.3 To facilitate ease of operation, convenience and accuracy, this method suggests the use of commercially available automated syringe samplers and tracer gas monitors.

1.4 This test method describes a standardized technique for determining air change rate in buildings under natural meteorological conditions by trace gas dilution.

1.5 This test method shall not be used to determine the individual contribution of various building components to the air change rates of a building.

1.6 Use of this test method requires a knowledge of the principles of gas analysis and instrumentation.

1.7 The current state of the art does not possess analytical techniques to extrapolate precisely measured air change rates to meteorological conditions different from those prevailing during measurement.

1.8 This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of whoever uses this standard to consult and establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

2. Applicable Documents

2.1 ASTM Standards

- E741 Determining Air Leakage Rate by Tracer Dilution (1)
- E779 Test Method for Determining Air Leakage Rate by Fan Pressurization
- D1356 Definitions of Terms Related to Atmospheric Sampling and Analysis
- E355 Recommended Practice for Gas Chromatography Terms and Relationships

2.2 Other Documents

- Scientific Publications (2-7)
- U.S. EPA Technical Assistant Documents (8)

3. Summary of Method

3.1 This test method entails introducing a small amount of tracer gas into a structure, thoroughly mixing it, and measuring the rate of change (decay) in tracer concentration. The air change rate can be estimated from the decay rate of tracer concentration with respect to time. On-site meteorological conditions are measured concurrently. In the on-site monitor variant, after the tracer gas has thoroughly mixed, an initial air sample container is filled. The air change rate can be determined from the decay in tracer concentrations.

3.2 A quantity of tracer is released at one or more points in the test building. The amount of tracer released should be sufficient to produce an easily discernible response in the gas measuring instrument. Under no circumstances should the initial tracer gas concentration exceed the Occupational Safety and Health Administration's (OSHA) time weighted average for substances included in the latest OSHA standards.

3.3 Fans or the central air system should be used to circulate the air within the room or structure in order to mix the gas thoroughly. Connecting doors, closet doors, and the like should be opened to allow unobstructed internal air flow. Several minutes should be allowed for mixing.

3.4 Air samples from one central location or several strategic points are collected at timed intervals.

3.5 The tracer concentration of each sample is determined by a gas chromatograph equipped with an electron capture detector.

3.6 The decay in tracer gas concentration as a function of time can be related to the air exchange rate of the building at the place of collection under the current meteorological conditions.

3.7 By repeating this procedure a number of times, it is possible to characterize the effects of climatological (temperature and wind) on structural (wall, windows, floors, ceilings, doors, etc.) factors on infiltration rate.

4. Significance

4.1 Air leakage accounts for a significant portion of the thermal space conditioning load; it can introduce outdoor air contaminants in conditioned indoor air, and it can dilute indoor-generated contaminants, therefore detracting from or providing for occupant comfort.

4.2 Air leakage rates are difficult to predict analytically because they are functions of building tightness and configuration, inside-outside temperature differences, wind speed and direction, quality of workmanship in construction, and numerous other factors.

4.3 This test method describes measurements of air leakage rates. In applying the results of this test method to the design of buildings, consider that the air leakage

characteristics of a structure are affected by building operation, maintenance, and the resistance of the building components to deterioration.

4.4 The tracer dilution method has been proven to be an effective way of measuring the air leakage rate of a structure under field conditions. The measurement of air infiltration using the tracer gas dilution method and on-site gas monitor equipment requires field deployment of equipment and the use of trained technicians. It is possible to take tracer gas samples on site and analyze them at a laboratory facility. The practice of taking container samples can be performed by persons not trained in the operation of the gas monitor equipment.

4.5 As an alternative to the tracer gas method, the fan pressurization method (ASTM Test Method E779) provides an indirect way to relate the air leakage rate or air tightness to the leakage area of a structure. This test method has several differences from the tracer dilution method. It can be used to compare the relative air tightness of several buildings, to identify the leakage source and rate of leakage from different components of the same building envelope, and to determine the air leakage reduction for individual retrofit measures applied incrementally to an existing building.

4.6 When the absolute air leakage rate is needed, the tracer dilution method should be used over a wide range of wind velocities and indoor and outdoor temperature differences. It is best to use the fan pressurization method for diagnostic purposes and resolve the absolute air leakage rate with the tracer dilution method. However, the measuring equipment and techniques are relatively complicated for the tracer dilution method, and the data analysis and correlation are more involved.

4.7 In contrast with the tracer gas dilution method, two other tracer gas techniques are employed:

4.7.1 One is the constant concentration approach in which the tracer gas concentration is maintained essentially constant (order of $\pm 10\%$) in a given volume. The air infiltration rate is determined from how much tracer gas must be injected to maintain the constant concentration. The constant concentration feature is particularly desirable in multi-chamber buildings, since leakage from chamber-to-chamber does not disturb the air infiltration measurement.

4.7.2 The second method is the constant injection method where, as the name implies, tracer gas injection is maintained constant over time.

4.7.3 The governing equations for both constant concentration and constant injection are different from the tracer gas dilution method.

5. Definitions

Definitions used in this document and any user prepared SOPs should be consistent with ASTM D1356. All abbreviations and symbols are defined within this document at the point of use. Additional definitions, abbreviations, and symbols are provided in Appendices A-1 and B-2 of this compendium.

5.1 Air change rate - the ratio of hourly indoor air change and indoor space volume measured in identical volume units (normally expressed in air changes per hour, ACH or ACPH).

5.2 Air leakage rate - the volume of air movement per unit time across the building envelope. This movement includes flow through joints, cracks, and porous surfaces, or combinations thereof. The driving force for such air leakage in service can be either mechanical pressurization and evacuation, natural wind pressures, or air temperature differentials between the building interior and the outdoors, or combinations thereof.

5.3 Building envelope - the exterior shell enclosing the indoor space.

5.4 Exfiltration - air leakage from a building space.

5.5 Indoor space - the volume of a building that exchanges air with outside ambient air. In most cases, this volume is the deliberately conditioned space within a building, generally not including the attic space, basement space, interstitial spaces (such as a double envelope), and attached structures, unless such spaces are connected to the heating and air conditioning system.

5.6 Infiltration - air leakage into a building.

5.7 Natural ventilation - unpowered airflow through intentional building openings such as open windows and vents.

5.8 Tracer gas - a gas that can be mixed with air and measured in very small concentrations, making it possible to detect air movements and measure air changes.

5.9 Ventilation - intentional outdoor air intake through a ventilation system, with mechanical ventilation being that ventilation induced by a mechanical system.

6. Interferences

6.1 SF₆ has a low natural background concentration (typically 0.1 to 0.5 ppt.). One exception to its low natural background, however, can be in the vicinity of electrical power switching equipment which may use SF₆ as an insulating material.

6.2 Tennis balls can contain SF₆ which may pose another possible source of background interference.

7. Apparatus

7.1 This description of apparatus is general in nature, and any equipment capable of performing the test measurements within the allowable tolerances is permitted (see Tables 1 and 2).

7.2 Tracer gas monitor - a device to measure tracer gas used in the study, capable of measuring the tracer gas to within $\pm 5\%$ at any concentration. In this case, a gas chromatograph specifically designed for tracer gas monitoring is described.

7.3 Sampling network - consisting of tubing, tubing junctions, a pump, and possibly an aspirator. This network is used to draw samples from remote locations within a structure, blend them, and bring the blended sample to a convenient place for analysis. In general, it is best to avoid plasticized tubing, such as vinyl, and use copper, stainless steel, or possibly polypropylene or nylon. The technician should be aware that surface absorption within the sampling network can be a major source of confusion in any concentration decay measurement.

7.4 Sample containers - non-absorbent, inert, low-permeability containers (such as sample bags, syringes with needle caps, or plastic bottles) used to collect and store air samples from buildings under test. With this method syringes are utilized because of air volume accuracy and ease of injection into the chromatograph.

7.5 Pump - non-contaminating air sample pump, either manual or powered, used to fill sample containers. Plastic bottles can be filled by hand squeezing. With this method a commercially available automatic syringe sampler is utilized.

7.6 Syringes - disposable syringes may be used as sample containers if sealed or to inject gas samples when the gas monitor is a gas chromatograph. A plastic bottle containing tracer gas or tracer gas/air mix can also be used.

7.7 Circulating fans - used to circulate air within a structure, capable of circulating air over 360°. Oscillating or hassock fans are preferred. Such fans are normally unnecessary in buildings with ducted forced air systems.

7.8 Meteorology stations - portable, that records wind speed and direction, outside temperature, and (if available) relative humidity, is used to obtain on-site meteorological data.

7.9 Barometer - a device to measure local barometric pressure is useful. If one is not available, barometric pressure from the nearest weather station is obtained for the time during which measurements are performed. These data are corrected for any elevation difference between the weather station and the test structure.

7.10 Tracer gas - a cylinder or container of gas chosen from those listed in Tables 1 and 2 is necessary as a source of the tracer used in the test. On this method SF₆ is used.

7.11 Timing device - a clock, watch, chronometer, or similar device suitable for measuring elapsed time and time intervals.

8. Reagents and Materials

8.1 Tracer gas - pure form SF₆.

8.2 Nitrogen gas - high purity reagent gas as the electron capture detector carrier gas.

9. Safety Precaution

The maximum allowable concentration in air for each of the tracer gases that have been used for tracer dilution air leakage measurements is provided in Tables 1 and 2. Do not

exceed this concentration under any circumstances. Good experimental practice is to ensure that the maximum allowable concentration of the particular tracer is less than this maximum by at least a factor of four. The initial tracer gas concentration must not exceed under any circumstances the OSHA time-weighted average for substances included in the latest OSHA-controlled gases list.

10. Tracer Gas Technology

10.1 General

The implementation of tracer gas technology provides quantitative information concerning air mass or pollutant transport and dispersion which cannot be readily obtained in any other manner. Applications that have used this technology include:

- Meteorological tracing and atmospheric diffusion studies.
- Isolation of the contribution of a specific emitting source from other local sources.
- Large distance plume tracking and impact assessment.
- Determination of the transport and dispersion characteristics of a locale prior to new facility construction to assess potential new source impact on air quality.
- Examination of pollutant species dispersion, depletion or conversion.
- Characterization and assessment of gaseous effluents from nuclear generating stations.
- Evaluation of highway air pollutant emission factors in the vicinity of a major highway in an urban area.
- Studying of air movement within or around an enclosed volume for ventilation studies.
- Validation and correlation of ambient air quality advection and dispersion models.
- Infiltration measurements in structures to quantify convective energy losses.
- Assessment of mine ventilation and air flow characteristics.
- Prediction of smoke movement in building fires.
- Characterization of air transport/communication and earth media permeability assessment in underground structures.

10.2 SF₆ Tracer Gas

10.2.1 Sulfur hexafluoride is a colorless, tasteless, incombustible gas, with an inertness resembling nitrogen, unchanged even at the softening temperature of hard glass and unaffected by water or caustic potash. This gas possesses excellent properties for use as a voltage insulation.

10.2.2 SF₆ is considered to be one of the most desirable tracers. It possesses one of the highest electron capture responses (it can be detected down to 10⁻¹² parts SF₆ per part air - 1 ppt); and it has a low natural background concentration (typically 0.1 to 0.5 ppt).

Other factors which make SF₆ the ideal tracer gas are:

- Non-toxic, non-allergenic, non-radioactive, colorless and odorless.
- Gaseous at ambient temperatures.
- Chemically inert and thermally stable for atmospheric applications.
- Capable of rapid and controlled atmospheric release from a point or area source.

- Amenable to conventional sample collection techniques.
- Commercially available.

10.2.3 One exception to its low natural background, however, can be in the vicinity of electrical power switching equipment which may use SF₆ (or Freon C-318) as an insulating material. Tennis balls contain SF₆. Thus, in any tracer release/monitoring study, care must be taken to determine whether there are background concentrations, potential tracer gas interferences or contamination prior to performing the tracer release.

11. Release of Tracer Gas

11.1 On Site Monitor Method

11.1.1 The assumption underlying the tracer gas measurement of air change rate is that for perfect mixing with steady air flow, the loss rate of tracer gas concentration conforms to the exponential dilution law; that is, the loss rate or dilution of an escaping gas is proportional to its concentration. Mathematically, this assumption leads to Equation 1.

$$C = C_0 \exp(-It) \quad (1)$$

where:

- C = tracer gas concentration at time, t
 C₀ = tracer gas concentration at time = 0
 I = air change rate
 t = time

11.1.2 Injection and Mixing of Tracer Gas - At one or more points in the test structure, release an amount of tracer gas sufficient to produce an easily discernible response in the gas-measuring instrument. The location of release is governed by the location of air handling system(s) or mixing fans in a structure with no air-handling system. This release can be done with a gas-tight syringe or a plastic bottle filled with tracer gas.

11.1.3 In a building with ducted forced air system(s), operate the main fan(s) continuously. Introduce tracer gas into the main supply or return duct(s), preferably in the vicinity of the main fan(s).

11.1.4 Leaks in the ductwork system may produce an incremental increase in the air leakage rate. Two methods to assess this leakage are:

11.1.4.1 After beginning a test, as in 10.3.3, operate the main fan(s) only for initial mixing and shortly before sampling.

11.1.4.2 Use portable fans for mixing after initiating a test as in 10.3.3. Perform the remainder of the test as in 10.3.5.

11.1.5 In a building without central heating and air conditioning system(s), release the tracer gas at one or more points within the structure. Use fans to circulate the air and mix the gas. Take care not to affect the pressure distribution within the structure. Open all doors connecting contiguous living spaces.

11.2 Container Method

11.2.1 Injection of Tracer Gas - A predetermined quantity of the tracer gas is initially injected into the building so that the initial concentration of the tracer gas is below the safety limits listed in Tables 1 and 2 and within the optimum detection range of the gas monitor used. Graduated syringes can be used for this injection. These can be prepared before the test or filled from a bottle of compressed tracer gas at the site. The injection is accomplished by slowly walking around inside the structure, injecting gas into each room in a quantity approximately proportional to the volume of the room. The graduation on the syringe greatly aids in this process. A sample container with tracer gas/air can be used in a similar manner.

11.2.2 Mixing Tracer Gas in Dwelling - A waiting period of approximately $\frac{1}{2}$ to 1 h should then be allowed for proper mixing of the tracer gas. For a building with a forced air heating system, the fan on the furnace can be turned on to assist in the mixing. Experience in dwellings without an air system suggests that natural convection currents will mix the tracer gas well. This is also true for each floor of the building (if the doors between rooms are open). In multi-story structures there seems to be higher on the upper floors. This is probably due to natural convection currents caused by rising warm air. Circulating fans can be used to assist mixing of the tracer gas.

12. Sampling

12.1 General Procedures

Collecting of SF₆ samples during periods of gaseous release may be performed by several techniques. The current state-of-the-art in this topical area encompasses:

- Grab samples (syringes)
- Sequential instantaneous samples
- Portable bagged samples (time-averaged)
- Sequential bagged samples at fixed sites (time-averaged)
- Spatially-averaged bagged samples from mobile platforms (automobiles, vans, aircraft)
- Limited semicontinuous sampling (frontal chromatography)
- Continuous detector sampling
- Time-averaged samples - evacuated containers

12.2 Sampling for On Site Monitor Method

12.2.1 Before taking gas samples, allow at least 30 minutes for mixing.

12.2.2 To test for homogeneity in tracer gas concentration, take samples from a number of building spaces. When concentrations differ by less than 5% of the average concentration measured within the structure, begin monitoring the decay of tracer concentration. In a residential structure, two or more samples from widely separated locations are required. In multi-story structures, two widely separated samples per floor are required.

12.2.3 Tracer samples may be measured at a single location by taking individual samples (grab samples) at a number of distinct locations, or by drawing samples from a number of locations through a common network (multi-point sampling).

12.2.4 When multi-point sampling is used, place sensors at strategic points within the test structure and feed to a central measuring terminal. For methods that analyze air with a single measurement device, use a sampling network to bring blended air to the analyzer. A diagram of a sampling network and a sampling junction are shown in Figures 1 and 2. Note that if the dilution rate in different rooms or floors is different, samples drawn by this method yield air leakage rates slightly less than the true average rate. For example, if one of the rooms or floors is leaking air at twice the rate of the other (1 ACPH and 0.5 ACPH), analysis of the blended samples of the two will lead to an air leakage rate estimate about 4% lower than the true average rate.

12.3 Sampling for Container Method

12.3.1 Filling Initial Sample Containers - After adequate mixing of the tracer gas, an initial air sample container is filled for each floor of living space. If it is suspected that certain volumes of the building are not in perfect communication with each other, then separate air sample containers should be filled for each volume. This is accomplished by walking around the floor, filling the sample container by means of a small pump, or hand squeezing a plastic sample bottle or syringe. This will provide an integrated sample. The important criterion is that the air sample container must be filled slowly, thus ensuring that an integrated sample is obtained.

12.3.2 Label each air sample container as follows: Identification of the building (address), time of injection, time of sample, section of building from which sample was taken (first floor, basement, etc.), meteorological conditions, and indoor temperature. A suitable alternative procedure is to record these data on a log sheet and identify the samples by numbers corresponding to log entries.

12.3.3 Decay of Tracer Gas - Wait 1 hour for the tracer gas concentration to decay. Note the activities of occupants and the operating mode of mechanical equipment during this period.

12.3.4 Fill Sample Containers - Repeat the procedure in 11.3.3 at known intervals to obtain two or more additional samples of air for each floor of the building.

12.3.5 The procedures 12.3.1 through 12.3.4 are graphically shown in Figure 3.

12.4 Sampling for the Container Method with Automatic Syringe Samplers

12.4.1 A brief overview of the latest techniques used in the collection of air samples during tracer gas experiments indicates an evolution from simple, manual sampling to programmable, automated sample collection using advanced, multi-station samplers. The design and operation of microcomputer controlled sequential syringe samplers provides reliability, efficiency, and portability at a moderate cost.

12.4.2 In order to meaningfully interpret data from pollution monitoring programs, the accuracy, reliability, and reproducibility of sampling and measuring techniques become major areas of concern. Additional demands placed on sampling programs include

minimizing personnel and equipment requirements to meet specific measurement tasks, and low maintenance and replacement costs. Typical areas of interest are indoor residential and work atmospheres (Small, 1983; Spengler and Sexton, 1983; Berglund and Johansson, 1982), industrial environments, and studies concerned with transport and fate of air pollutants.

12.4.3 An automatic sampler commercially available from Scientific Instrumentation Specialists (Moscow, Idaho 208-882-3860) contains an advanced timing system which allows automatic collection of twelve sequential, time-averaged gas samples. Rack and pinion gears driven by a stepper motor mechanically actuate each syringe. In operation, the syringe plunger remains stationary while the rack and pinion drive gradually extends the syringe body. At the end of travel, the syringe needle drives into a silicone septum, and power transfers to the next syringe. A digital clock, controlled by a quartz crystal oscillator governs the operation of the sampler. The overall time accuracy is better than + 0.001% and the station-to-station sampling time reproducibility is about + 0.01%. The time base interval (2-8 minutes) is internally selectable. An operator can pre-program the unit up to 15 days ahead of the actual operation, locate it on a suitable site, and leave it unattended. The sampler will start collecting sequential, time-averaged samples (each ranging from 2 minutes to several hours) at the pre-selected time, and upon collection of each sample, seal the syringe needle to prevent diffusion or sample contamination. The unit can be very quickly turned around for another sampling cycle. A rechargeable battery, which allows up to 50 hours of continuous operation, assures portability. An optional 115/230V A/C power supply kit is available. The unit is enclosed in a sturdy aluminum case, secured with two key locks, and easily portable by one person as the overall weight is approximately 13.5 kg, as illustrated in Figure 4.

12.4.4 For collection of SF₆ air samples, polyethylene, glass, or stainless steel syringes are recommended.

12.5 Sampling Method for Large Buildings

12.5.1 Residential infiltration measurements utilizing tracer gas are relatively straightforward to accomplish. Generally, a small amount of tracer gas is released in the structure and either the central heating system or a few optimally placed fans are used to assure a homogeneous tracer gas concentration in the structure. After this, the decay in tracer gas concentration as a function of time is monitored. In the case of electronegative gases such as SF₆ and the halocarbons, the monitoring instrument of choice is a gas chromatograph equipped with an electron capture detector. By repeating this procedure a number of times, it is possible to characterize the effects of climatological (temperature and wind) and structural (walls, windows, floors, ceilings, doors, etc.) factors on the infiltration rate.

12.5.2 Approaches are not so straightforward for large buildings. The sheer volume of the building indicates that a simple tracer release/sampling operation may not provide data which are valid for the structure as a whole. Two general approaches, however, can be undertaken. If one is more concerned about the relative contribution of a given floor to total structure infiltration (as would be the case in deciding on a retrofitting program), it

is generally sufficient to perform measurements in a manner similar to that for residential structures for each floor. An anomalously high ACPH for a given floor would imply that retrofitting should concentrate on this floor.

12.5.3 A useful improvement of this established technique is the use of multiple tracer gases to characterize air exchange between the floor immediately above and below the floor being studied. By releasing three different tracer gases on three consecutive floors and monitoring their relative concentration decays with time on all three floors, one can completely characterize infiltration across the floor ceiling and external envelope of the middle floor. This technique is identified as the "sandwich approach" and depicted in Figure 5.

12.5.4 On the other hand, to characterize the total infiltration of a large structure, it is necessary to provide a tracer supply and sampling network. In this technique (identified as the "simultaneous approach"), each floor is provided with the same tracer gas and sampled independently of all other floors. As shown in Figure 6, flexible tubing is run to each floor generally through the heating/ventilating of air-conditioning ducting or the service channel in a particular building. Sampling and gas injection are performed at one central location within the structure. Actual installation details are strongly dependent on the physical characteristics of each individual building.

12.5.5 The "simultaneous approach" allows one to obtain individual decay rates for each floor at approximately the same time. Suitable averaging then provides the average infiltration rate for the structure, thereby allowing one to study systemic variations in infiltration rate due to temperature, wind, or other factors.

13. Analytical System

13.1 Samples analyzed for SF₆ during tracer release projects use gas chromatographs with an electron capture detector. In practice these instruments should be measurement-specific units optimized for SF₆ or other selected gaseous tracers.

13.2 The SF₆ concentration can be determined by on-site monitors or in the laboratory by transporting the air sample in a suitable container.

13.3 If the automatic syringe samples (Section 11) are utilized, the samples can be injected directly into the gas chromatograph.

13.4 Any gas chromatograph with an electron capture detector can be utilized, however, tracer gas monitors specifically optimized for sulfur hexafluoride are commercially available from Systems, Science and Software (S-Cubed, La Jolla, CA; Telephone: 619/453-0060).

13.4.1 Tracer gas monitors designed and manufactured by Systems, Science and Software (S-Cubed) are capable of providing measurements of unusual sensitivity (few ppt for SF₆). Parts per trillion identification allows remote detection with a minimum of tracer gas discharge. A unique feature of the S-Cubed tracer gas monitors is the use of a gated LED display which outputs values characteristic only of the tracer gas being monitored. Spurious, anomalous, or additional chromatographic peaks are not outputted; hence, confusion over the identity of a given peak cannot occur.

13.4.2 Functionally, the monitor is a measurement specific gas chromatograph with an electron capture detector. This type of detector utilizes the high electron affinity of gases with halogen group elements to provide a measurable signal. Sulfur hexafluoride is such a gas and is an ideal tracer because it is transported and dispersed exactly as other atmospheric gases.

13.4.3 The heart of the instrument, as discussed previously, is the GC column. It separates the various gaseous components of a sample by selectively slowing down some gases relative to others. The column can be thought of as a device to elute the distinct components in a gas sample in a definite order. In the case of monitoring for SF₆ only, the column material is 5A Molecular Sieve (synthetic zeolite). Columns constructed with this material possess the unique property that SF₆ is eluted prior to oxygen. In making low level tracer determinations, this property allows easy identification of a small SF₆ peak due to the absence of an uncertain baseline disturbed by the relatively high amplitude signal corresponding to an oxygen peak.

13.4.4 For field tracer gas projects, the S-Cubed Model 215AUP Environmeter has been repeatedly selected to serve as the primary instrument. The reasons for this choice in preference to other units are:

- Instrument is designed and built for field atmospheric tracing applications (Unit is not a converted or modified laboratory bench GC).
- Monitor is portable and self-contained (power supply, carrier gas and signal output display are on-board).
- Unit has range selectable capability; peak-holding digital display of signal output is directly related to SF₆ concentration.
- Rotary shear valve with a constant volume sample loop insures consistent and reproducible sample loadings with syringe injection (grab samples) or use of a remote sampling wand.
- Monitor contains printed circuit electrometer and pulse drive circuitry for low noise electronic functions, reliability and ruggedness.
- Unit is optimized for detection of SF₆ over the range 10⁻⁹ to 10⁻¹² parts SF₆ per part air.
- Detector cell design (concentric foil and collector geometry), ionization source (tritiated-titanium foil) and pulse drive circuitry provide three decade linear dynamic range. (Unit does not require pulse counting or other output signal conditioning).
- Unit is easily operated by non-professional personnel; it does not require operation by or supervision of an analytical chemist.
- Individual calibration curves for each operating range are provided with the unit.
- Unit complies with U.S. Nuclear Regulatory Commission or Agreement States health safety requirements for sealed radioactive sources; no film badges required.
- Transfer, possession and use of unit authorized under a general distribution radiation license. (Eliminates customer filing for a specific radiation license).

14. Calibration

14.1 State the method of calibration of the gas analyzer. If the analyzer is not provided with a manufacturer's calibration, perform an actual calibration. Use standard mixtures of at least two different concentrations in the range anticipated in an actual test, unless manufacturer's specifications allow single point calibration.

14.2 Instrument calibration should be performed on a regular basis, i.e., monthly, weekly or when in the field on a daily basis (pre- and post-test measurements). This activity uses calibration gases (SF₆ in dry nitrogen or pre-purified air). Six calibration standards are used at the analyzer manufacturing site when the initial calibration curve is generated. For field use, one, or at most two, calibration concentrations are all that are required. A mid-range standard, or two standards spanning the measurement range of interest is sufficient in most cases. However, if six point calibration is desired, gases could be maintained in the following SF₆ concentrations: 5×10^{-9} , 1×10^{-9} , 5×10^{-10} , 5×10^{-11} , 1×10^{-11} , and 5×10^{-12} . Supplementing this activity, daily pre- and post-test ambient background measurements should be made in the release area to ascertain the magnitude of this condition on the specific tracer gas being released.

15. Calculations

15.1 Calculations for On Site Method

15.1.1 Rearrange Equation 1 (Section 11.1.1) as follows:

$$I = (1/t)\ln(C_0/C) \quad (2)$$

where:

C = measured time-dependent concentration

C₀ = concentration at t = 0

I = air change rate

t = time

Equation 2 is the starting point for several means of calculating air change rate from concentration and time measurements.

15.1.2 Graphical Method - Plot the natural logarithm of concentration on a linear scale against time in hours on a linear scale. The measurements should fall on a straight line with time, provided the air change rate remains constant. Scatter of points is expected and a straight line may have to be faired in the "best fit" sense. A minimum of three points over 1 hour should be used to determine this straight line.

15.1.2.1 On the straight line determined in 14.1.2, choose two points with coordinates (C₁, t₁) and (C₂, t₂) where C₁ is the concentration at time i. Calculate I, the air change rate, as follows:

$$I = (\ln C_2 - \ln C_1)/(t_2 - t_1) \quad (3)$$

This technique is shown in Figure 7.

15.1.2.2 This graphical method lends itself well to field study of the data, since it is easy to plot the log of concentration as a function of time. It is less sensitive to errors in concentration than other methods. It has the further advantage that a graph provides a visual display of any departures in the exponential decay law. So long as the data fall on a reasonably straight line, one has confidence that the data obtained are valid within the assumptions necessary for the validity of the tracer dilution method. One caveat that should be observed during any measurement interval is that the data points used in determining an air leakage rate should encompass the mean winds observed during the course of the measurement.

15.1.2.3 When many data points are obtained, a least-square computer program is used to calculate a "best fit" to the straight line.

15.1.3 Finite Difference Method - Calculate the air change rate after each sampling using the finite difference form of Equation 2 as follows:

$$I = L/V = 1/(t_{i+1} - t_i) \ln C_i/C_{i+1} \quad (4)$$

where:

L = leakage rate

V = room volume

t_i = time at "i"th interval

C_i = tracer concentration at "i"th sample interval

For measurement over N sampling intervals, form a mean and standard deviation as follows:

$$\text{Mean } I = \bar{I} = (1/N) \sum I$$

$$\text{Standard Deviation} = S_1 = \sqrt{[\sum I^2 - (\sum I)^2/N]/[N - 1]}$$

The air change rate, $I = L/V$, is "best fit" to the sample values of this parameter. The best fit for I is the mean, and is determined from the test data in accordance with Equation 5. This finite difference method has the advantage of simplicity, but it is very sensitive to errors in concentration or to the effects of poor mixing, especially when short sampling intervals are used.

15.1.4 Decay Time Method - Concentration decay usually occurs quickly; this allows for a rapid means of estimating I. For example, with time measured in minutes, the time for one half the initial concentration to decay is noted as $t_{1/2}$ and the I estimate is given by $41.59/t_{1/2}$. Similar ratios are given for other decay fractions and are shown in Table 3. These ratios are simply computed for C/C_0 ratios of 3/4, 2/3, 1/2, etc. The measurer has to record the time that a desired ratio is encountered.

15.2 Calculations for the Container Method

Determination of Tracer Gas Concentration - Tracer gas concentrations are determined in an off-site laboratory using gas monitor equipment. The air leakage rate I is then

determined from Equation 2. For periods from 1 to 2 hours, Equation 2 is an accurate relation for determining the air exchange.

16. Records and Reports

The report should include the following information. Include as much of this information as possible to facilitate comparison with other data at a later time.

16.1 Measurement Characterization

- Air Mixing - method of initial mixing and method of maintaining mixing during the measurement if one is used
- Air Sampling - location of sampling site, sample interval, initial sample time, and method of sampling
- Tracer Gas - type, initial concentration, method of introduction
- Detector - type and method of calibration
- Type of Calculation - finite difference, decay time, graphical, least square.

16.2 Meteorological Conditions

- Location and height of meteorological measurement
- Wind speed and direction (both maximum and average)
- Temperature and measurement technique
- Barometric pressure and measurement technique
- Relative humidity or wet bulb temperature

16.3 Test Space Characterization

- Structure Type - residential, commercial, industrial, other
- Location of structure relative to other structures (give type) and roadways
- Location of structure relative to surrounding terrain (give type, that is, gullies, mountain, mounds, cliffs, etc.)
- Structure orientation and elevation relative to other structures, roadways and surrounding terrain
- Windows - type, dimensions, number, and location in test space
- Walls - interior and exterior
- Leakage - noticeable areas
- Location of chimneys, vents, and other such specified opening
- Type and capacity of heating, ventilation, and air-conditioning systems

16.4 Test Space Operating Characteristics

- Doors - open or closed
- Windows - open or closed
- HVAC System - on or off
- Vent Fans - on or off
- Special Circumstances or Characteristics During Test - occupied, unoccupied, ingress, egress

- Indoor temperature and measurement technique
- Relative humidity and measurement technique

17. Performance Criteria and Quality Assurance

17.1 General

17.1.1 At present, insufficient data exist for purposes of precision and accuracy determination. A reasonable estimate of the uncertainty in a given air change rate determination is about 10% or less.

17.1.2 Note that the air change rate is a strong function of indoor-outdoor temperature difference and wind speed and direction. When interpreting or comparing air change rate data, the fact that a pressure and temperature dependence does exist should be considered. It can have a strong effect on the results.

17.1.3 Integral to all SF₆ tracer gas acquisition, release, field sample acquisition and tracer gas analyses, established quality control methods should be applied. This activity reflects: use of SF₆ and carrier gases which conform to manufacturers' specification; use of components and materials that are compatible with SF₆; use of standardized field operating procedures; and, the comprehensive documenting of test data.

17.2 Instrumentation

17.2.1 Automatic syringe sampler - The sequential tracer gas samplers have proven extremely effective and reliable in a variety of atmospheric tracer field studies. The samplers have been used to collect fifteen minute, thirty minute, sixty minute, or longer average air samples in a number of different environments. Data return rates of 92%, 95%, and 97% have been reported. These results and investigations are good indicators of the usefulness, flexibility, and reliability of the samplers. In particular, the high degree of success (>90% in all documented cases) points to the reliability of the sequential syringe samplers.

17.2.2 Tracer Gas Monitors

17.2.2.1 To complement the comprehensiveness of the gas chromatographic measurements, instrument calibration runs should be performed on a regular basis, i.e., monthly, weekly, or when in the field on a daily basis (pre- and post-test measurements). This activity uses calibration gases (SF₆ in dry nitrogen or pre-purified air). Section 14 discusses calibration. Supplementing this activity, daily pre- and post-test ambient background measurements should be made in the release area to ascertain the magnitude of this condition on the specific tracer gas being released.

17.2.2.2 In practice, the SF₆ analyses from the 1-hour time-averaged sequential samplers are tabulated. The results of analysis for the instantaneous grab samples are recorded on the field test sheets, i.e., aligned to site, location, and time listings. In addition, all gas chromatographic analyses (sample measurements, background concentration tests and calibration runs) are generally recorded on strip charts (chromatograms).

18. Acknowledgements

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19. References

1. American Society for Testing and Materials, "Standard Test Method for Determining Air Leakage Rate by Tracer Dilution," E741-83, Philadelphia, PA, 1983.
2. Nagda, N. L., Fortmann, R. C., Koontz, M. D., and Rector, H. E., "Air Infiltration and building Factors: Comparison of Measurement Methods," Paper number 86-16.1, presented at the 79th Annual Meeting of the Air Pollution Control Association, Minneapolis, MN, 1986.
3. Lagus, P. L., "Characterization of Building Infiltration by the Tracer-Dilution Method," *Energy*, 2:461, 1977.
4. Lagus, P. L., "Air Leakage Measurements by the Tracer Dilution Method - A Review," *Building Air Change and Infiltration Measurements*, ASTM STP 719, C. M. Hunt, J. C. King, and H. R. Treschel, eds., American Society for Testing and Materials, 1980, pp.36-49.

5. Deuble, J. L., "Atmospheric Gas Technology Techniques and Applications," Technical Bulletin 79-5, Systems, Science and Software, LaJolla, CA.
6. Krasnec, J. P., "Instrumentation of Sampling and Characterization of Toxic Gaseous and Some Particulate Air Pollutants," Paper number 524, presented at the Pittsburgh Conference, Atlantic City, NJ, 1986.
7. Krasnec, J. P., and Denning, D. E., "Application of Automated, Multi-Station Sequential Samplers in Atmospheric Tracer Studies," presented at the 7th World Clean Air Congress, Sydney, Australia, 1986.
8. Riggin, R. M., *Technical Assistance Document for Sampling and Analysis of Toxic Organic Compounds in Ambient Air*, EPA - 600/4-83-027, U.S. Environmental Protection Agency, Research Triangle Park, NC, 1983

Table 1. Gases and Techniques for Tracer Dilution Method (1)

<u>Tracer</u>	<u>Measuring Apparatus</u>	<u>Maximum Allowable Concentration in Air (vol/vol)</u>	<u>Maximum Detectable Concentration, ppm</u>	<u>Toxicology</u>
Hydrogen	Katharometer	4% (lower explosive limit)	200	nontoxic
Helium	Katharometer		300	nontoxic
Carbon monoxide	infrared absorption	50 ppm	5	combines with hemoglobin to produce asphyxia
	gas chromatograph with gas flame ion detector		0.4	
Carbon	infrared absorption	5000 ppm	1	nontoxic
	thermal conductivity detector		70	
Sulfur hexafluoride	electron capture gas chromatograph	1000 ppm	0.000002	nontoxic
Nitrous oxide	infrared absorption	25 ppm	1	nontoxic
Ethane	flame ionization detector	3% (lower explosive limit)	5	nontoxic
Methane	infrared absorption	5% (lower explosive limit)	5	nontoxic

Table 2. Atmospheric Constituents (1)

<u>Compound</u>	<u>Average Tropospheric Background Concentrations, ppm</u>	<u>Typical Indoor and Urban Ambient Concentrations, ppm</u>	<u>Anthropogenic Sources</u>
H ₂	0.5	0.5	---
He	5.2	5.2	---
CO	0.1	5-50	combustion
CO ₂	320	30-5000	combustion
N ₂ O	0.3	0.3-several ppm	combustion
Ethane	1.5 x 10 ⁻³	0.1	incomplete combustion
Methane	1.5	2-5	incomplete combustion
SF ₆	10 ⁻³	10 ⁻⁵	telephone switching stations

Table 3. Decay Ratios to Compute ACPH

<u>Concentration Ratio</u>	<u>Decay Time, min.</u>	<u>I. ACPH</u>
3/4	$t_{3/4}$	$17.26/t_{3/4}$
2/3	$t_{2/3}$	$24.33/t_{2/3}$
1/2	$t_{1/2}$	$41.59/t_{1/2}$
1/3	$t_{1/3}$	$65.92/t_{1/3}$
1/4	$t_{1/4}$	$83.18/t_{1/4}$
1/8	$t_{1/8}$	$124.77/t_{1/8}$

To Collection Device
on Continuing Monitor

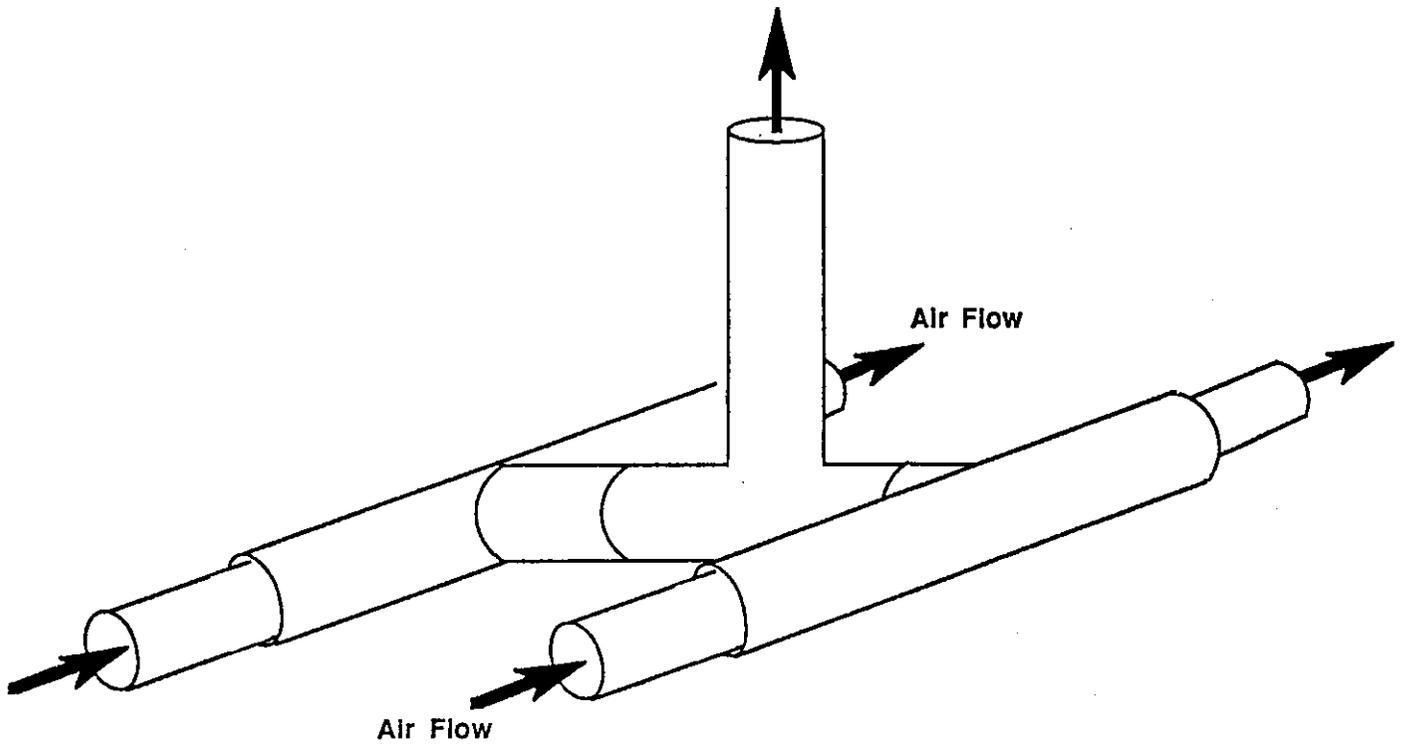


Figure 1. Four-Point Sampling Junction

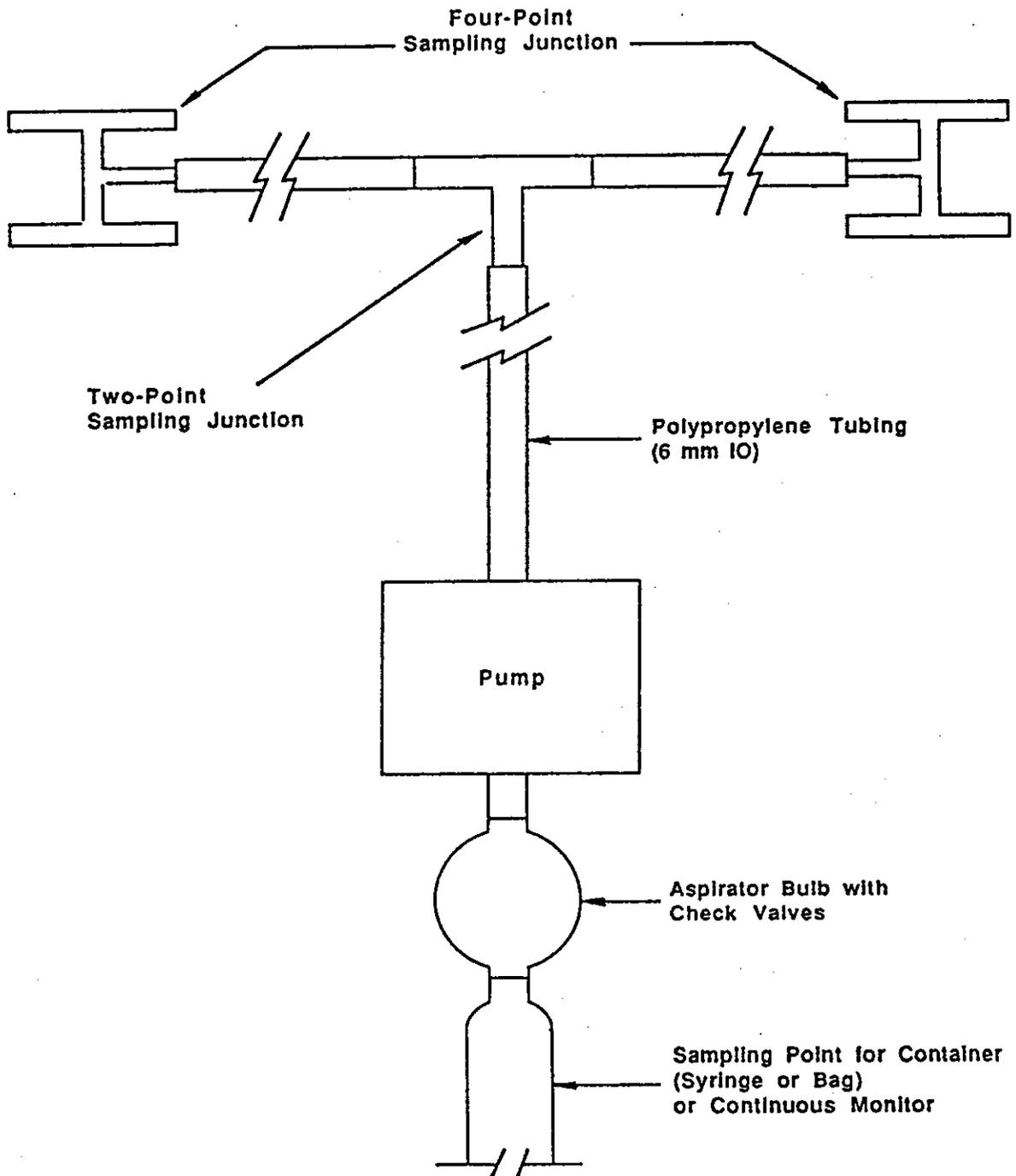


Figure 2. Symmetrical Light-Point Sampling System

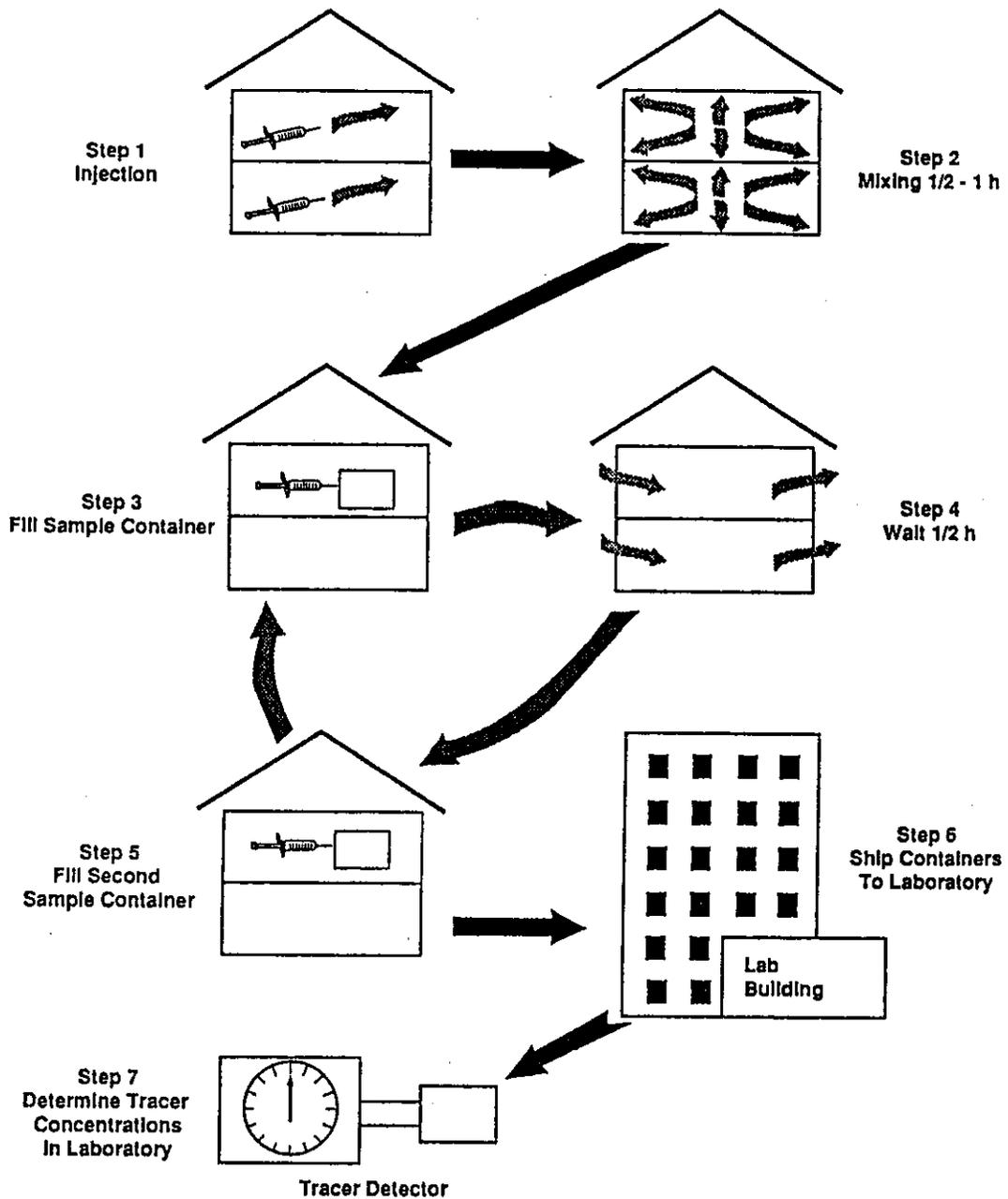


Figure 3. Procedure for Measuring Air Leakage Rate Using Sample Containers

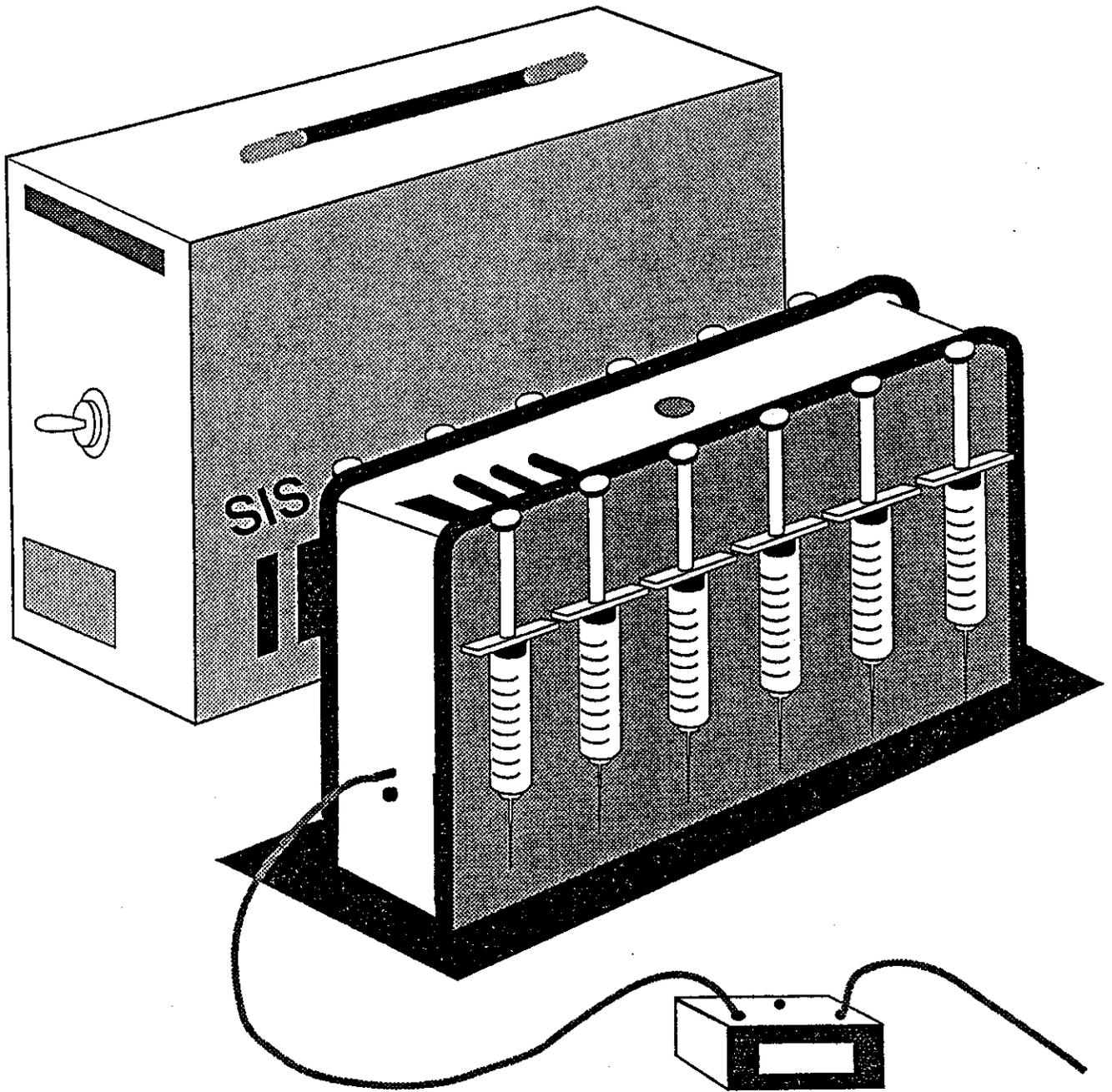


Figure 4. SIS Series 12A Multi-Station Sequential Environmental Gas Sampler

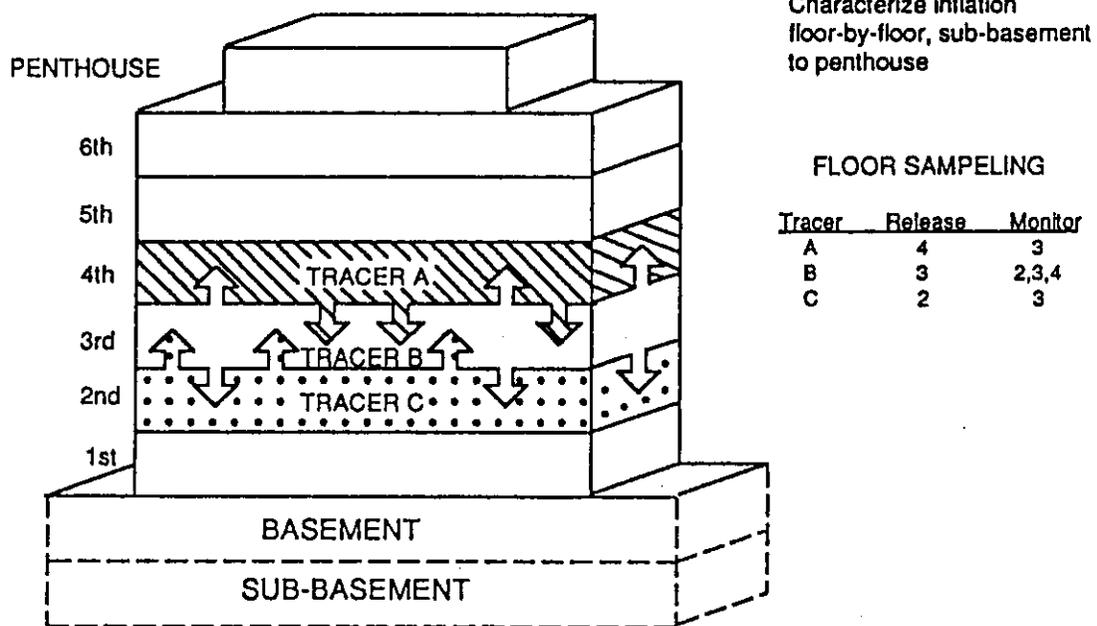


Figure 5. Multiple Tracer "Sandwich Approach" for Characterizing Air Infiltration in High-Rise Buildings

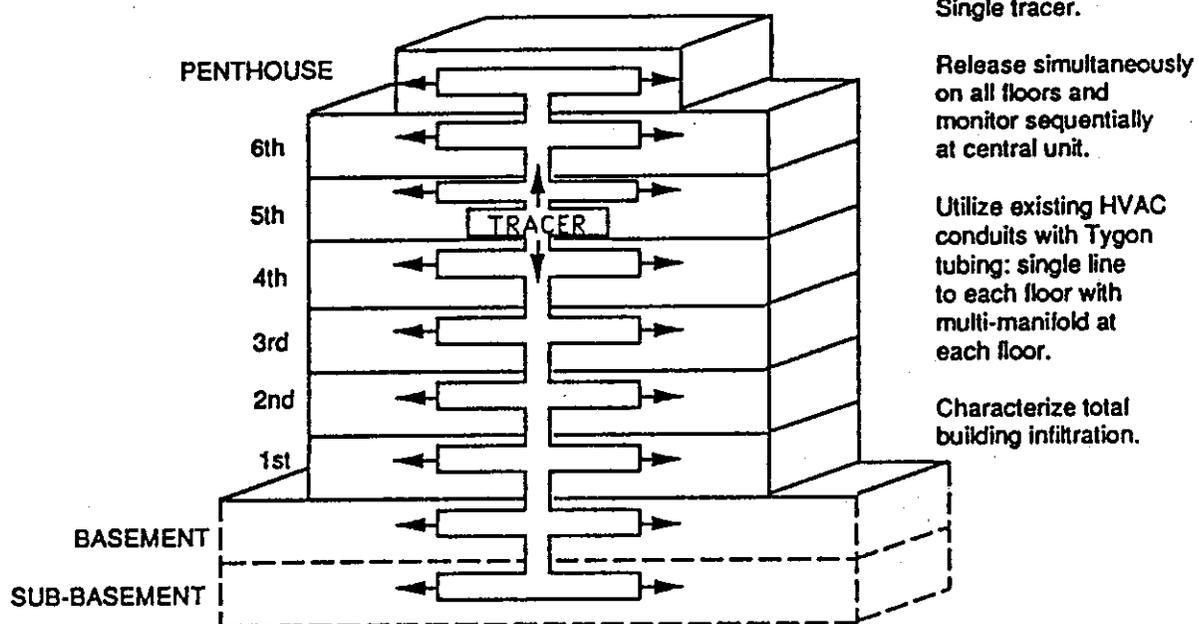
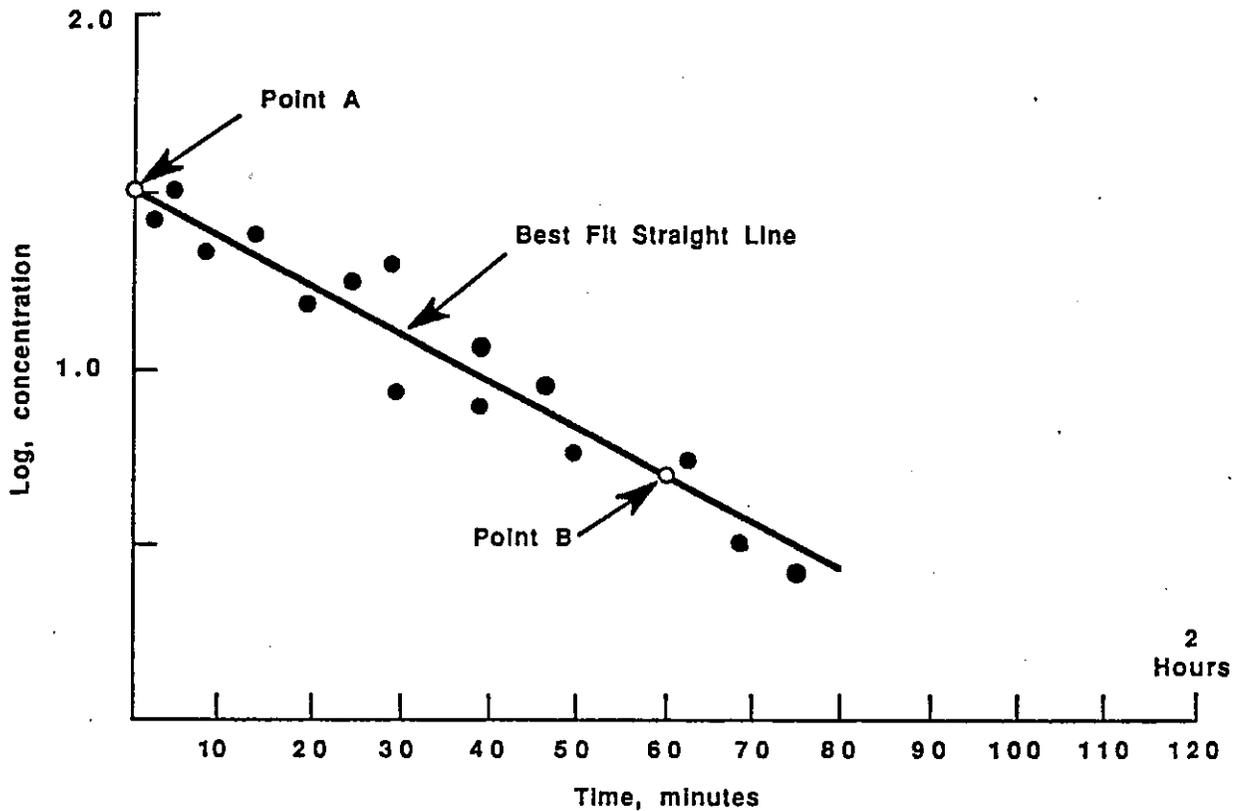


Figure 6. Single Tracer "Simultaneous Approach" for Characterizing Air Infiltration in High-Rise Buildings

4



- Data Points (Natural Logarithm of Concentration Values)
- Concentration Points 60 Minutes Apart

For $C_A = 5$ and $C_B = 2$; the exact ACH = 0.916

Graphically

$$\begin{aligned}
 \text{ACH} &= \ln C_A - \ln C_B \\
 &= 1.6 - 0.7 \\
 &= \underline{0.9}
 \end{aligned}$$

Point A = Start
 Point B = 60 Minutes

Figure 7. Graphical Determination of Air Change Rate

Chapter IP-5

DETERMINATION OF NITROGEN DIOXIDE (NO₂) IN INDOOR AIR

- Method IP-5A - Continuous Luminol Monitor
- Method IP-5B - Palmes Diffusion Tube
- Method IP-5C - Passive Sampling Device

1. Scope

This document describes three methods for determination of NO₂ in indoor air. An active sampling device and two passive sampling devices are discussed. The monitoring of nitrogen dioxide (NO₂) at sub-ppm and low-ppb levels is of primary concern in indoor, nonindustrial locations such as the home. The trend toward much more airtight homes which began during the energy crisis of the early 1970s has caused concern among health experts about increased levels of NO₂ in indoors. Nitrogen dioxide is a combustion product found in houses mostly due to gas or wood burning stoves, heaters and/or fireplaces. Hazardous concentrations can occur in closed environments such as kitchens and family rooms where ventilation is minimal.

2. Applicability

2.1 In the past, active sampling devices have been the method of choice for collection of NO₂ from indoor air. More specifically, Compendium Method IP-5A uses a real-time, direct measurement monitor to detect the presence of NO₂ involving the detection of fluorescent energy emitted from the reaction of NO₂ with a Luminol solution (5-amino-2,3-dihydro-1,4 phthalazine dione). As illustrated, real-time, direct measurement monitors are active sampling devices that require a mechanical pump to move the sample to the collection medium. Consequently, the sampling devices require some form of power to drive the pump and are usually heavy and bulky in appearance.

2.2 In recent years, interest has been increasing in the use of diffusion-base passive sampling devices (PSDs) for the collection of NO₂ in indoor air. PSDs are more attractive for indoor air because of their characteristics of small size, quiet operation (no pump), and low unit costs.

2.3 Real-time monitors have been used more at fixed monitoring stations, thus not always reflecting the actual concentration of pollutants that people come in contact with in their daily lives.

2.4 Since the PSDs are lighter and smaller than the real-time monitors, they can be worn by the person or in close proximity to where people spend most of their time, thus enabling epidemiologists to better attribute health effects of NO₂ to indoor air concentration.

2.5 Compendium Method IP-5B and Method IP-5C use the diffusion principle for monitoring NO₂ in indoor air. Method IP-5B uses the Palmes tube, while Method IP-5C utilizes the passive sampling device (PSD).

Method IP-5A

DETERMINATION OF NITROGEN DIOXIDE (NO₂) IN INDOOR AIR USING A CONTINUOUS LUMINOX MONITOR

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Method IP-5A

DETERMINATION OF NITROGEN DIOXIDE (NO₂) IN INDOOR AIR USING A CONTINUOUS LUMINOX MONITOR

1. Scope

1.1 Nitrogen dioxide (NO₂) is a combustion product found in houses mostly due to gas or wood burning stoves, heaters and/or fireplaces. Hazardous concentrations can occur in closed environments such as kitchens, and family rooms where ventilation is minimal.

1.2 Described herein as a method by which nitrogen dioxide can be sampled and analyzed in the air. The detection of NO₂ by chemiluminescence takes place between gas and liquid phases whereby the contact of NO₂ gas with a solution of Luminol causes direct oxidation of the solution.

1.3 The following method describes an instrument using chemiluminescence detection for the determination of NO₂.

2. Applicable Documents

2.1 ATSM Standards

D1605 Sampling Atmospheres for Analysis of Gases and Vapors
D1356 Definitions of Terms Related to Atmospheric Sampling and Analysis
D1357 Planning the Sampling of the Ambient Atmosphere

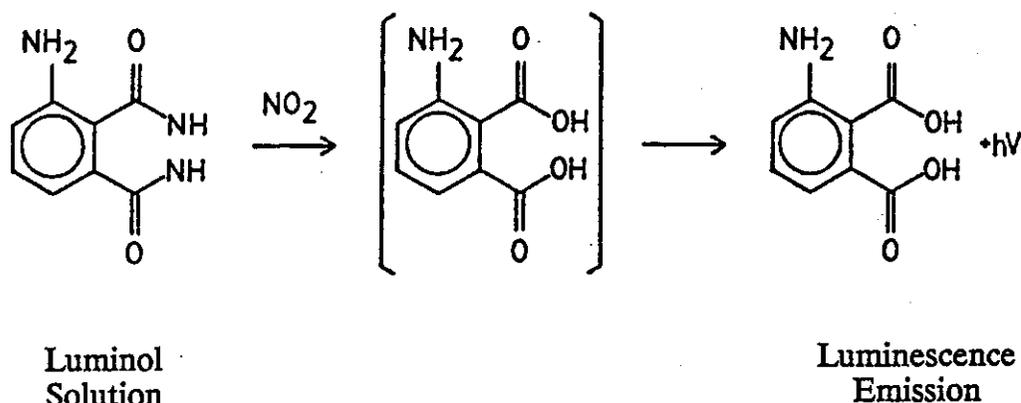
2.2 Other Documents

U.S. Environmental Protection Agency Technical Assistance Document (1)
Laboratory and Indoor/Ambient Air Studies (2-10)
Other Documents (11-12)

3. Summary Of Method

3.1 The instrument monitors NO₂ gas concentrations by the real-time, direct measurement of the fluorescent energy emitted from the reaction of NO₂ with Luminol solution (5-Amino-2,3 dihydro-1,4 phthalazine dione).

3.2 The LMA-3 NO₂ analyzer operates by detecting the fluorescent energy produced when NO₂ reacts with a solution of Luminol. In operation, sampled air is drawn through the instrument and across a fabric wick wetted with the Luminol solution. The solution is continuously replenished at the top of the wick and removed at the bottom by a small peristaltic pump. If the sampled air contains NO₂, the Luminol solution is oxidized, producing fluorescent energy according to the reaction shown on the next page.



3.3 To detect the release of energy ($h\nu$) from the reaction, a photomultiplier tube (PMT) is positioned to view the central portion of the wick. The signal from the PMT is directly proportional to the NO_2 concentration in the sampled air. Unlike other chemiluminescent NO_x detectors, the Luminol monitor measures NO_2 directly without prior conversion of NO_2 to NO . The operational block diagram for the LMA-3 NO_2 analyzer is illustrated in Figure 1.

3.4 A 500-mL polypropylene bottle serves as a reservoir to supply fresh Luminol solution continuously through the instrument. The solution is moved from the reservoir to the reaction chamber by a peristaltic pump operating at about 0.05 mL/min. The wick material is kept saturated while 1.5 L/min of sample air is drawn over the surface where reaction takes place. The emitted light from the reaction of NO_2 and Luminol is measured by a photomultiplier tube situated in front of the chamber. After leaving the wick material, Luminol is transported via the peristaltic pump into a reservoir for spent solution. Sample air drawn from the chamber and exhausted to the rear of the instrument by a small air pump.

4. Significance

4.1 Nitrogen dioxide is a reactive gas product of combustion. Household combustion sources include gas stoves, gas heating, wood burning stoves, furnaces and fireplaces. NO_2 levels in indoor air are usually equal to or lower than outdoor levels. But if combustion sources are present, then NO_2 levels can exceed outdoor concentrations. The National Ambient Air Quality Standard (NAAQS) for NO_2 for a 24-hour average is $100 \mu\text{g}/\text{m}^3$ (~53 ppb).

4.2 Numerous investigations have documented that NO_2 concentrations may be substantially greater indoor in homes that have unvented combustion sources. Specifically, increase levels of NO_2 may be encountered in homes with gas heating, gas stoves with pilot lights and cigarette smoke.

4.3 NO₂ has been known to cause acute lung damage at high concentrations. Concentrations at five parts per million (ppm) can cause respiratory distress. However, data on health effects of NO₂ at concentrations commonly encountered in the residential environment (500 ppb to 1 ppb) is unknown. In experimental models at these NO₂ levels, reduced efficiencies of lung defense mechanism, effects on mucociliary clearance, alveolar macrophages and the immune system have all been documented (13-14).

4.4 Consequently, the need exists for a continuous, extrasensitive NO₂ analyzer which is reliable, accurate, portable and suitable for indoor air measurements.

4.5 Historically NO₂ has been determined by colorimetric methods, and chemiluminescence methods using catalytic oxidation whereby the catalytic converter converted NO₂ to NO. In turn, NO would react with ozone and cause measurable chemiluminescence. Consequently NO would interfere with NO₂ analysis.

4.6 By using Luminol in an alkaline solution, gaseous NO₂ at atmospheric pressure reacts with the Luminol to also produce chemiluminescence. This reaction has little NO interference.

4.7 Consequently, Scintrex Ltd. applied this technology to a continuous NO₂ analyzer capable of monitoring down to the low ppb range. Recently, the monitor was extensively evaluated (10). Table 1 outlines the results of the laboratory evaluation.

5. Definitions

Note: Definitions used in this document and any user prepared SOPs should be consistent with ASTM Method D1356. All pertinent abbreviations and symbols are defined within this document at point of use.

5.1 Chemiluminescence - the emission of radiation from a molecule which, after being in a vibrationally excited state, returns to its ground state.

5.2 Fluorescence - the process by which electromagnetic radiation of one spectral region is absorbed and radiated as nonthermal radiation at other wavelengths, usually longer.

5.3 Luminol - a modified solution of Luminol (5-amino-2, 3-dihydro-1,4 pthalamine dione), NaOH, Na₂SO₃ and alcohol dissolved in deionized water.

5.4 Precision - the ability of an analyzer to produce a uniform response with repeated measurements under identical conditions. The analyzer's precision is estimated by the standard deviation of a set of measurements at a uniform pollutant concentration.

5.5 Interferents - Any chemical compound which produces a response in or change of response in the analyzer is an interferent. Widely occurring compounds which may interfere include water vapor (H₂O), CO₂, oxygen (O₂), ozone (O₃) and peroxyacetyl nitrate (PAN). These compounds are known to quench various fluorescent and photochemical processes.

5.6 Limit of detection (LOD) - a limit of detection is defined as the minimum signal that may be distinguished from the background signal with a given confidence level. An LOD equal to three standard deviations of the signal for clear air (6) has been accepted.

5.7 Noise - noise (7) is the standard deviation of twenty-five consecutive measurements of zero air taken at two-minute intervals.

5.8 Lower detection limit (LDL) - lower detection limit (7) is specified as "the minimum pollutant concentration which produces a signal of twice the noise level."

5.9 Drift - drift (7) is specified as the difference between two measurements taken at the beginning and end of a specific test period (12-hour or 24-hour period).

6. Interferences

6.1 Historically, ozone has been reported in the literature (7,8) as an interference as a quenching agent to the ultraviolet light given off from the chemical reaction. An O₃ trap has been added to the analyzer to eliminate this interference.

6.2 PAN has been documented (7,9) as an interference in instruments employing the Luminol reaction. Reported relative response of the LMA-3 analyzer has been both qualitative and less than quantitative. A recent laboratory evaluation (10) indicated an average relative interference response of 0.62.

6.3 In a recent laboratory test (10), the LMA-3 analyzers illustrated measurable interference from CO₂ of 1 to 2 ppb at an NO₂ concentration level of 25 ppb (or a 5 to 7% error).

6.4 Oxygen is an effective quencher of fluorescent and photochemical reactions. Although the O₂ concentration in indoor air is largely constant and no O₂-dependent effect should be seen in the measurements, possible problems could exist during calibration. Laboratory evaluation (10) has indicated an analyzer response variation of approximately ±0.6 ppb at an NO₂ concentration of 26.5 ppb (or 2% of the total response of the LMA-3 analyzer). Consequently, indoor air levels of O₂ should be contained as part of the calibration gas mixtures.

6.5 Water is a common interference for many fluorescent analyzers. In a recent study (10), results indicated an analyzer response variation of approximately -7 ppb at a concentration of 25 ppb of NO₂ (or a 29% error). However, since indoor air normally has a constant relative humidity, this should not affect monitor response during sampling. However, if calibration gases contain no moisture, then an error can be introduced into the analytical system. Each calibration point generated should contain approximate levels of water representing the indoor air parcel being sampled.

7. Apparatus

7.1 Sampling and Analysis

7.1.1 Chemiluminescent NO₂ monitor - Scintrex Ltd., 222 Snidercroft Rd., Concord, Ontario, Canada, L4K1B5, 416-669-2280, LMA-3 Part No. 856 000 or equivalent.

7.1.2 Rechargeable battery - back-up one 12 volt 1.5 amp-hr. gel cell. or 115 or 220 volt AC battery, best source.

7.1.3 Tubing - tubing for the liquid pump, 9.8 cm long for the waste line, 8.9 cm long for the feed line, Scintrex Ltd., 222 Snidercroft Rd., Concord, Ontario, Canada, L4K1B5, 416-669-2280, Part No. 856 019 or equivalent.

7.1.4 Wick - wick for the monitor, Scintrex, Ltd., 222 Snidercroft Rd., Concord, Ontario, Canada, L4K1B5, 416-669-2280, Part No. 856 020 or equivalent.

7.1.5 Air line trap - trap protects the air pump from liquid infiltration, best source.

7.1.6 Filter cartridge - Scintrex Ltd., 222 Snidercroft Rd., Concord, Ontario, Canada, L4K1B5, 416-669-2280, Part No. 200 213 or equivalent.

7.1.7 2 liter external reservoir kit - to reduce replenishing Luminol solution (optional), Scintrex Ltd., 222 Snidercroft Rd., Concord, Ontario, Canada, L4K1B5, 416-669-2280, Part No. 856 018 or equivalent.

7.1.8 Carrying case - for portable operation, Scintrex Ltd., 222 Snidercroft Rd., Concord, Ontario, Canada, L4K1B5, 416-669-2280, Part No. 856 014 or equivalent.

7.1.9 Calibrator - portable calibrator for LMA-3 monitor (optional). Provides a continuous supply of purge gas and a stable constant temperature environment for permeation device(s), Scintrex, Ltd., 222 Snidercroft Rd., Concord, Ontario, Canada, L4K1B5, 416-669-2280, LC5-3 Luminol Calibration Source or equivalent.

7.1.10 Data logger - portable calibration controller (optional). Provides accurate dilutions of a gas standard using mass flow controllers and mixing chambers, Scintrex, Ltd., 222 Snidercroft Rd., Concord, Ontario, Canada, L4K1B5, ~~416-669-2280~~, LCC-3 Luminol Calibration Controller or equivalent.

7.2 Calibration

7.2.1 Flowmeters and controllers - In order to obtain an accurate dilution ratio, in the dilution method used for calibration, the flow rates must be regulated to 1% and be measured to an accuracy of at least 2%. The meter and controller can be two separate devices, or combined in one device. The user's manual for the meter should be consulted for calibration information. Additional information on the calibration of flow devices can be found in the Quality Assurance Handbook (15). If the calibration system uses the same type of flow meter (e.g. bubble flow meter, rotameter, mass flow meter, etc.), then no correction to standard temperature and pressure (STP) need to be made.

7.2.2 Mixing chambers - A chamber constructed of glass, Teflon®, or other nonreactive material, and designed to provide thorough mixing of NO₂ and diluent air for the dilution method.

7.2.3 Output manifold - The output manifold should be constructed of glass, Teflon®, or other nonreactive material, and should be of sufficient diameter to insure an insignificant

pressure drop at the analyzer connection. The system must have a vent designed to insure atmospheric pressure at the manifold and to prevent indoor air from entering the manifold.

8. Reagents and Material

8.1 Luminol Solution

8.1.1 The Luminol solutions used by the LMA-3 NO₂ analyzer contains additives which enhance the response to NO₂, and reduce interferences from other gases such as ozone.

Note: The Luminol solutions are weakly basic and should be handled accordingly. Avoid contact with the eyes or prolonged contact with the skin. Wash with water after contact with the skin.

8.1.2 A variety of Luminol solutions have been formulated to give linear responses over different concentration ranges.

Note: The information supplied with each bottle will outline the range of linearity, rejection ratio for the ozone response as well as the PAN (peroxyacetyl nitrate) response for all of the available formulations at that time.

8.2 Calibration Gas

Note: In a recent laboratory test (10) O₂, CO₂ and water vapor were determined to cause interference to the monitor output; therefore, it is important to calibrate the LMA-3 analyzer with calibration mixtures containing indoor levels of these species. 

8.2.1 Zero-air source - A source of dry zero-air that is verified to be free of contaminants that could cause detectable responses from the NO₂ analyzer will be needed. The zero-air must contain <0.1 ppb NO₂.

8.2.2 Calibration standard - NO₂ standards must be traceable (16) to a National Institute of Standards and Technology - Standard Reference Material (NIST-SRM) or a NIST/EPA approved commercially available Certified Reference Material (CRM). The NO₂ standards must be in air unless the dilution method is used. For dilution, NO₂ in nitrogen may be used if the zero-air contains O₂, CO₂ and H₂O similar to indoor air. An acceptable protocol for demonstrating the traceability of commercial cylinder gas to an NITS-SRM or CRM cylinder gas is provided in Section 14, reference 17. In order to establish a calibration curve and determine linearity of the LMA-3 analyzer, the calibration gas cylinder should correspond to 10, 20, 40, 60, and 80% of monitor full scale.

8.2.3 Span gas - pressurized cylinder containing NO₂ concentration corresponding to 80% of full scale, best source.

8.2.4 Flow control valves - used to regulate gas cylinder flow rate to analytical system, best source.

8.2.5 Multistage pressure regulators - standard two-stage, stainless steel diaphragm regulators with pressure gauges for gas cylinders.

8.2.6 Tubing - Polypropylene tubing to connect analyzer to gas cylinders when calibrating, zeroing, and spanning the instrument.

8.2.7 Thermometer - used to measure monitoring area temperature.

8.2.8 Barometer - capable of measuring barometric pressure of monitoring area.

9. Sampling System

9.1 Description

The LMA-3 NO₂ analyzer is contained in an instrument housing approximately 15" x 8" x 8" (20 x 22 x 38 cm). The instrument can be operated continuously on 110 VAC or for 2 to 3 hours with the assistance of an onboard battery. The monitor can operate at a range of either 0 to 20 or 0 to 200 ppbv, and can be connected to a strip-chart recorder or data acquisition system for permanent record of the NO₂ measurements.

9.1.1 Front Panel Controls (see Figure 2)

9.1.1.1 The power switch turns on the power to the electric and the liquid pump motor. When it is ON (upper position) the yellow LED above it will be illuminated.

9.1.1.2 The air pump switch turns on the air pump if the power is ON. A yellow LED indicates that the air pump is ON.

9.1.1.3 The backflush momentary push button initiates the backflush cycle. During the backflush, waste Luminol is pumped into the wick area to rinse out any residue, then it is pumped away. The cycle takes about 5 minutes. During this time the red LED above the backflush switch will light up. No readings may be taken during this period.

9.1.1.4 The battery charger is active any time the unit is plugged into line current. The yellow "battery charge" LED should be illuminated under this condition.

9.1.1.5 The battery low red LED indicates two warning conditions. If the unit is operating from the battery and the voltage drops below 11.6 volts, the LED will be illuminated. Secondly, if the unit is plugged in and the current acceptance of the battery exceeds 100 mA, the LED will come ON. The LED may be illuminated for a few minutes each time the unit is plugged into line current. This does not indicate a fault. It will stay ON for an extended period if the battery has been substantially discharged. If the unit is put into battery service before the light goes out, a full three hours of use should not be expected.

9.1.1.6 The three-position time constant switch is used to select 0.3, 1.0 or 3.0 seconds as the time constant for the last amplifier. The setting of 0.3 seconds provides the least amount of signal damping and is suitable for most applications. The slower settings may be selected if it is desirable to damp out noise in the signal originating from fluctuations in the NO₂ concentration, or from the instrument when measuring very low NO₂ mixing ratios.

9.1.1.7 The zero control is used to bring the displayed or output signal to zero when there is no NO₂ present.

9.1.1.8 The span control sets the photomultiplier tube high voltage (PMT HV) and hence the gain of the light detection system. It is used to change the displayed value or output voltage when a calibration source of known mixing ratio is introduced to the instrument.

9.1.1.9 The BNC type output connector provides an output voltage for use with a chart recorder or other data acquisition system. Each volt at this output corresponds to

100.00 in the display range 200, or to 10.000 in the display range 20. The output voltage extends to 5 volts even though the display shuts down above values of 2 volts.

9.1.1.10 This is a two-position toggle switch for selection of either 0 to 20 ppbv or 0 to 200 NO₂ range. This display is 4.5 digits so that the last decimal place represents 1 pptv when the instrument is in the 20 range. This display shows a single "+" sign at the left hand side when the input to the digital panel meter is above its acceptable range.

9.1.1.11 This is a three-position momentary toggle switch by which the input to the digital panel meter is chosen. If the unit is properly calibrated in the normal center position (signal), the NO₂ mixing ratio is continuously displayed. When the toggle is lifted up, the battery voltage is displayed. In order to give a true voltage reading, the battery charger is off line while this switch is held in the upper position. If the battery low light was ON due to high current acceptance, it will go out when the battery voltage is checked. When the toggle is held down, the photomultiplier high voltage will be displayed. The normal operating range for the photomultiplier is -400 to -800 volts.

9.1.1.12 The signal overload red LED indicates two fault conditions. If the light is ON steadily, then the first amplifier is overloaded. The second fault indication occurs when there is severe overloading at the first amplifier. The signal overload light will flash. This will usually be the result of the light leaking into the system from improper assembly after servicing.

9.1.2 Rear Panel Controls (see Figure 3)

9.1.2.1 These fittings are provided so that the user may attach larger fluid reservoirs for longer unattended use. They are not connected when the instrument leaves the factory.

9.1.2.2 Fittings are provided on the back panel for connecting tubing to and from the instrument. They are compression type fittings constructed on stainless steel with teflon ferrules. Suitable tubing sizes are 0.25 inch or 6 mm outside diameter.

9.1.2.3 Two access hole through the back panel are provided just below the Air Out connector. They are provided to make servicing of the wick area easier. These are normally closed with press-in chrome plated hole plugs.

9.1.2.4 This connector permits the external control of two of the LMA-3's functions: 1) operation of the air pump and 2) initialization of the backflush sequence. In addition, the circuit to the air pump indicator may also be controlled through this connector. The pin assignments are as follows:

- Air pump live (A)
- Air pump return (B)
- Air pump LED live (C)
- Air pump LED return (D)
- LMA-3 supply (9.2 Volts) (E)
- LMA-3 ground (F)
- Ground for backflush trigger (H)
- Input for backflush trigger (J)

When external control is not desired, the "shorting plug" must always be installed. The shorting plug connects pins A to B, C to D and H to J. For external control of functions

within the LMA-3 it is recommended that optical isolators or relays be used in order to avoid having to tie the grounds of the LMA-3 and the driving electronics together.

The following external functions are possible:

- Air pump control - Opening and closing the contact between pins A and B will turn the air pump OFF and ON, provided the air pump switch that is located on the front panel is turned ON.
- Air pump indicator control - Opening and closing the contact between pins C and D will turn the air pump LED OFF and ON provided the air pump switch that is located on the front panel is turned ON.
- External backflush control - For control of the backflush trigger, wire the switching device as follows: 1) pin E through a 100 k ohm resistor to normally open, 2) pin F through a 100 k ohm resistor to common, 3) pin H to common, and 4) pin J to normally closed. The switch may be held high between 20 microseconds and 10 seconds before going low again. This will put 4.6 Volts down pin H to trigger the backflush cycle. The front panel backflush control will still be usable if this wiring is used.

9.1.2.5 The BNC type output connector is provided for the convenience of the operator. It carries exactly the same signal as the Output connector on the front panel.

9.1.2.6 The power cord receptacle also carries the instrument's main fuse and a supply voltage selection card. Locate the power receptacle on the rear of the instrument. Slide the plastic window to the left to expose the fuse and voltage selector. Observe the number showing on the small circuit board which is now visible. This number should indicate the nominal value of the power supply to be used (i.e. 120 or 240 volts). If it does not indicate the proper voltage, pull it out and re-orient it so that the desired figure shows when the board is re-installed. There are also positions which indicate 100 or 220 volts. These are not used on this instrument. If they are selected, the power circuits will be supplied as if 120 had been selected (for 100) or if 240 had been selected (for 220). The instrument is shipped with the voltage selector in the 120 position and a 0.2 amp slo-blow fuse installed. To inspect or change the main fuse, pull the small lever marked "Pull Fuse".

Note: If 240 volt service is required the main fuse must be changed to 0.1 amp slo-blow. Four spare fuses are supplied with the instrument, two of each value. Once the proper voltage selection and fusing have been verified, the plastic window may be slid to the right and the power cord inserted in the receptacle.

9.1.2.7 The LMA-3 may be operated from lead-acid type batteries of larger capacity than the rechargeable batteries built-in to the instrument. The nominal voltage of the external battery should be 12 volts. When the plug is pushed into the jack, the internal battery is disconnected from the power circuit and the external battery takes its place. If the external battery is of much higher capacity, then the built-in battery charger will not provide enough current to recharge the battery in a reasonable amount of time. For this reason, large external batteries should be recharged separately.

Note: When connecting an external battery, make sure the LMA-3 is turned OFF and is not plugged in to line current. First, clamp the jaws onto the external battery (red to positive and black to negative) and then plug the cable into the back of the LMA-3.

9.1.3 Inside display area - The inside display area contains several distinct functional areas. They are:

- Detection assembly
- Liquid/air handling components
- Power supplies/signal processing

9.1.3.1 The detection assembly contains the photomultiplier tube (PMT), the air passage and wick plates and the liquid and air fittings.

9.1.3.2 Air passage plate - The function of this plate is to direct the sample air onto the wick. The air passage plate incorporates a window which admits light to the PMT detector. The air pathway in the plate is convoluted in order to stop ambient light from reaching the PMT detector.

9.1.3.3 Wick plate - The wick plate is fastened directly to the air passage plates. The wick itself consists of a strip of absorbent material held to the plate by bars at the top and bottom. The liquid fittings project from the left side of the detector assembly. The upper fitting carries a slow continuous feed of the Luminol solution to the top of the wick and the lower fitting carries away the expended solutions to a waste bottle. The air fittings face the rear of the instrument. The upper AIR IN fitting is oriented upwards to facilitate the attachment of the PFA Teflon® air tubing by means of a teflon compression fitting. The lower AIR OUT fitting is a simple nipple over which the tygon outlet tubing is pressed.

9.1.3.4 Liquid/air handling components - The miniature air pump is attached to the top right side of the instrument frame. The pump draws air through the air passage circuit and then exhausts the sampled air through the AIR OUT fitting located in the rear panel. A trap is provided in the air line to protect the air pump from liquid that may escape from the detector assembly as well as from particulates in the sample air. The trap is located between the detector assembly and the air pump and consists of two stages, a liquid trap and a particulate trap. The liquid trap is a round chamber, mounted high on the inside wall of the LMA-3, which captures by means of gravity any large amounts of liquid in the air line. The second trap is a disposable cartridge air filter, located beneath the liquid trap, which captures any particulates in the air being sampled. The liquid pump is a two-channel peristaltic pump, mounted on the left portion of the center bulkhead. When the power is turned ON, the roller assembly can be seen to rotate at approximately 3 rpm. The direction of the rotation coincides with the direction of the liquid flowing through the tubing. The liquid lines can be traced quite easily. It can be observed that the liquid lines run from the Luminol supply bottle, through one side of the pump, to the top fitting on the wick plate, then from the bottom fitting on the wick plate to the other side of the pump, and finally to the waste bottle.

9.1.3.5 Power supplies/signal processing - The main power supplies are controlled from the sealed power supply section that can be seen in the left rear corner of the case. Housed inside are two printed circuit boards. The power circuit board provides voltages

for logic circuits, power for running the motors, charging the battery, and supplying the photomultiplier high voltage circuitry. The second board carries the main power transformer with its secondary fuse and the timer circuit for controlling the air and liquid pump motors during the backflush operation. The backup battery is located underneath the rear chassis and cannot be seen from above. Any time the unit is plugged in to line current, the battery is automatically charged.

9.1.3.6 Signal processing - The remainder of the electronics lie forward of the center bulkhead. One printed circuit board is devoted to the high voltage power supply for the photomultiplier while the other carries the signal generation and temperature compensation circuits. The normal switches, potentiometers and indicator lights are found in this area as well as the self-contained liquid crystal digital voltmeter attached to the front panel.

9.2 Operating Procedures

9.2.1 Installation

9.2.1.1 Install the instrument in an upright position.

Note: The instrument can be operated continuously on an angle of up to 30 degrees from vertical in any direction. It can also tolerate momentary tipping in any direction of up to 60 degrees from vertical.

9.2.1.2 Before operating, ensure that the air INLET and OUTLET parts on the back panel, are not obstructed.

9.2.2 Internal Reservoir (see Figure 4)

9.2.2.1 Confirm that the instrument is turned OFF and unplugged.

9.2.2.2 Remove the top cover of the instrument.

9.2.2.3 Working with one bottle at a time, pull the tubing from the top of the bottle and remove the bottle from the instrument.

9.2.2.4 The Luminol fluid may then be emptied or replenished as appropriate by removing the lid from the bottle.

Note: The "feed" bottle sits in the well closest to the front and the "waste" bottle sits to the rear.

9.2.2.5 Replace the bottle and push the tubing back onto the fitting.

9.2.2.6 Proceed with the second bottle as described above.

9.2.2.7 Replace the instrument cover and tighten the cover fastener located on the rear panel.

9.2.3 External Reservoirs

Note: An external reservoir kit is commercially available. To install the external reservoirs, the following sequence of steps are outlined below.

9.2.3.1 Confirm that the instrument is turned OFF and unplugged.

9.2.3.2 Loosen the instrument cover fastener located on the rear panel and slide the cover off.

9.2.3.3 Loosen the fittings on top of the standard liquid bottles so that the black plastic fitting may be pulled out.

9.2.3.4 Remove the standard bottles from the instrument.

9.2.3.5 Plug the black tubes into the bulkhead fittings on the rear panel and finger tighten the fitting caps.

9.2.3.6 Tubes from the external reservoirs are attached to the LIQUID IN and LIQUID OUT fittings on the rear panel.

Note: The liquid lines should be kept as short as possible and very small inner diameter so that fresh solution will reach the wick quickly after liquid changes and so that the backflush cycle will operate correctly.

9.2.3.7 Replace the instrument cover and tighten the cover fastener located on the rear panel.

9.2.4 Powering the Unit and Sampling

9.2.4.1 If line current is available, plug the LMA-3 into the power source. The yellow battery charge light emitting diode (LED) should be illuminated.

Note: Because the battery is charged with a "float" voltage, the unit may be safely left plugged into the power source without damaging the battery.

9.2.4.2 Turn the power switch ON. The yellow LED above the switch should be illuminated. The digital panel meter will also be activated and will show a four digit number approximately equal to zero.

9.2.4.3 Insure that the liquid pump motor is operating. In operation, the loading on the pump is uneven as a result of the work involved in compressing the pump tubing with each successive roller.

Note: The motor will sound alternately as if it is straining then running free. This is normal as long as the rotation does not significantly slow during the high load periods. The rotation speed of the pump should be approximately 3 rpm. After the liquid pump has been operating for about 10 minutes, you should be able to see plugs of liquid traveling down the waste tubing to the waste bottle.

9.2.4.4 Turn ON the air pump switch.

Note: You should now hear a fairly loud buzzing noise. This noise may be muffled by attaching a short length of one-quarter inch plastic tubing to the AIR OUT port. Tubing (preferably 0.030" wall x 0.25" OD teflon) may also be attached to the AIR IN port to deliver sample gas from a remote location or to muffle the air pump noise. Figure 5 illustrates the air flow through the LMA-3 NO₂ analyzer.

9.2.4.5 Check the battery voltage and photomultiplier tube high voltage (PMT HV) using the momentary DISPLAY SELECT switch. The battery voltage should be between 11.6 and 13.5 volts depending upon its state of charge. The PMT HV will normally be in the -400 to -800 volt range.

9.2.4.6 Select the appropriate DISPLAY RANGE and TIME CONSTANT. Where the NO₂ levels are very low, or if fast fluctuations in the signal are undesirable, choose a longer time constant setting.

9.2.4.7 Operate the instrument for 30 minutes in order to insure stable operation, then commence sampling at designated location.

9.2.5 Backflushing

9.2.5.1 As the LMA-3 operates, a certain amount of evaporation takes place in the reaction cell. Eventually this action leaves a solid residue which can block the detector window and reduce the readings. Recent field studies (10) have demonstrated that the LMA-3, when operated continuously for several days, will provide erratic responses. To eradicate the residue and erratic responses, a backflush cycle has been incorporated into the LMA-3 to dissolve and flush the residue into the waste bottle. The backflush cycle should be performed on a daily basis.

9.2.5.2 When the BACKFLUSH switch is pressed the backflush cycle will commence, shutting down the air pump and reversing the liquid pump at a higher than normal rate. This action draws liquid from the waste bottle and pumps it into the air passages. After about 2 1/2 minutes, the liquid pump returns to the normal direction of rotation at high speed. This quickly empties the air passages of liquid. After another 2 1/2 minutes, the liquid pump returns to its normal speed and the air pump restarts.

9.2.5.3 Backflush the system each time the reservoir is refilled (about every three days during continuous operation, or if a decrease in sensitivity is observed). Backflushing is recommended every 24 hours if the instrument is to be operated without daily calibration.

9.2.5.4 Ensure there is at least one-half inch of liquid in the waste bottle.

9.2.5.5 Place the three-way switch in the BACKFLUSH mode for about two minutes. The red LED above the BACKFLUSH button will remain lit during the cycle.

Note: If for any reason the instrument power is turned OFF during a backflush cycle, make sure that the AIR PUMP switch is in the OFF position before turning the power back ON. Run the instrument in this mode (normal liquid flow, air pump OFF) for at least 6 minutes before putting the air pump back ON or initiating another backflush.

9.2.5.6 When the fluid lines are full and the reaction chamber flooded, place the three-way switch in the PRIME position for approximately 2 minutes to clear sampling lines of fluid.

9.2.5.7 Return the three-way switch to the NORMAL position.

9.2.5.8 The LMA-3 signal will take 10 to 30 minutes to return to normal after a backflush operation.

Note: The backflush cycle should be initiated, whenever any of the conditions listed below are met:

- Each time the reservoir is refilled, or
- If a decrease in sensitivity is observed, or
- Daily if the analyzer is operated continuously.

10. Analytical Systems

10.1 System Description

10.1.1 The analytical system consists of a reducing agent, Luminol solution, with NO₂ gas acting as an oxidizing agent. A microphotometer measures the relative transmittance of the fluorescent energy emitted from the oxidation reaction of the Luminol.

10.1.2 A photomultiplier tube serves as the microphotometer by viewing the reaction site which is a cloth wick saturated in Luminol solution upon which the gas liquid reaction occurs.

10.1.3 The signal from the wick provides a measure of the NO₂ mixing ratio.

10.1.4 The signal is inputted to an analog to digital converter, a liquid crystal digital (LCD) voltmeter, and onto an LCD screen.

10.1.5 The analog can also be inputted to a strip recorder or to data acquisition instrumentation.

10.2 Systems Performance Criteria

10.2.1 Calibration - Calibrate the NO₂ air monitor every time the Luminol solution is changed or if the monitor has not been used for twelve or more hours.

10.2.2 Manual Zero and Span Calibration

10.2.2.1 Prior to operating the analyzer, an initial calibration must be performed. The following provides procedures to measure NO₂ concentrations in indoor air using the NO₂ LMA-3 continuous monitor.

Note: Follow the manufacturer's detailed instructions when calibrating a specific analyzer.

10.2.2.2 Assemble the analyzer as discussed in Section 9.2.4.

10.2.2.3 Connect zero gas to the analyzer at the AIR IN port.

10.2.2.4 Open the gas cylinder pressure valve.

10.2.2.5 Adjust the secondary pressure valve until the secondary pressure gauge reads approximately 5 psi more than the desired delivery pressure.

Note: If the air flow is pressurizing the unit, a "T" connection can be used to direct excess air to the atmosphere. Connect one end of the "T" to the AIR IN port and leave the other end open to the atmosphere.

10.2.2.6 Set the sample flow rate as read by the rotameter (read the widest part of the float) to the value that is to be used during sampling (2 Lpm is recommended).

10.2.2.7 Let the zero gas flow long enough to establish a stable trace. Allow at least 5 minutes for the analyzer to stabilize.

10.2.2.8 Adjust the zero control knob until the trace corresponds to the line representing 5% of the strip chart width above the chart zero or baseline. The above is to allow for possible negative zero drift. If the strip chart already has an elevated baseline, use it as the zero setting.

10.2.2.9 Let the zero gas flow long enough to establish a stable trace. Allow at least 5 minutes. Mark the strip chart trace as adjusted zero.

10.2.2.10 Disconnect the zero gas.

10.2.2.11 Connect the span gas with a concentration corresponding to approximately 80% of full scale, depending upon the Luminol solution, to the "T" connection.

Note: The calibration gas should contain O₂, CO₂ and H₂O in concentrations expected in indoor air.

10.2.2.12 Open the gas cylinder pressure valve. Adjust the secondary pressure valve until the secondary pressure gauge reads approximately 5 psi more than the desired pressure.

10.2.2.13 Set the sample flow rate, as read by the rotameter, to the value that is to be used during sampling, which should be approximately 2 Lpm.

10.2.2.14 Let the span gas flow until the analyzer stabilizes.

10.2.2.15 Adjust the span control until the deflection corresponds to the correct percentage of chart, as computed by:

$$\text{Correct percentage of chart} = [C_s(\text{ppb})]/[C_f(\text{ppb})] \times 100 + 5 \% \text{ zero offset}$$

where:

C_s = concentration of NO_2 span gas, ppb

C_f = full scale reading of analyzer, ppb

As an example where the % zero offset is 5 and the correct percentage of chart for the span gas of 40 ppb would be:

$$40 \text{ ppb}/50 \text{ ppb} \times 100 + 5 = 85$$

10.2.2.16 Allow the span gas to flow until a stable trace is observed. Allow at least 5 minutes. Mark the strip chart trace as adjusted span.

10.2.2.17 Disconnect the span gas.

10.2.2.18 Repeat Section 10.2.2.8 through Section 10.2.2.17 and if no readjustment is required, go to Section 10.2.3. If a readjustment greater than 1 ppb is required, repeat Section 10.2.2.8 through Section 10.2.2.9.

10.2.2.19 Lock the zero and span controls.

10.2.2.20 Record final zero and span potentiometer setting.

10.2.3 Multipoint Calibration

10.2.3.1 A multipoint calibration is required when the analyzer is first purchased, the analyzer has had maintenance which could affect its response characteristics, or when results from the auditing process show that the desired performance standards are not being met.

10.2.3.2 A multipoint calibration required calibration gases with concentrations corresponding to approximately 10, 20, 40, 60, and 80% of full scale. The calibration gases should be certified to be within $\pm 2\%$ of the stated value and purchased in high pressure cylinders with inside surfaces of a chromium-molybdenum alloy of low iron content or other appropriate linings. The cylinders should be stored in areas not subject to extreme temperature changes nor exposed to direct sunlight.

Note: Each span gas cylinder should contain O_2 , CO_2 and H_2O in concentrations expected in indoor air.

There are two acceptable methods for dynamic multipoint calibration of the LMA-3 analyzer. They are:

- the use of individual certified standard cylinders of NO_2 for each concentration needed, and
- the use of one certified standard high concentration cylinder of NO_2 , diluted as necessary with zero-air, to obtain the various calibration concentrations needed.

The equipment needed for calibration can be purchased commercially, or can be assembled by the user as illustrated in Figure 6. When a calibrator or its components are being purchased, certain factors must be considered:

- traceability of the certified calibration gases to an NIST-SRM (16,17) or a NIST/EPA-approved commercially available Certified Reference Manual (see Section 8.2),
- accuracy of the flow-measuring device or devices (rotameter, mass flow meter, bubble meter),
- maximum and minimum flows of dilution air and calibration gases, and
- ease of transporting the calibration equipment from site to site.

10.2.3.3 For an individual cylinder multipoint calibration, assemble the monitor and calibration system as illustrated in Figure 6.

10.2.3.4 Perform a manual zero and span calibration as in Section 10.2.2 and record the adjusted zero and span concentrations and their respective chart values.

10.2.3.5 Connect the span gas with a concentration value corresponding to 80% of full scale to the analyzer system.

10.2.3.6 Open the gas cylinder pressure valve until the secondary pressure gauge reads approximately 5 psi more than the desired pressure.

10.2.3.7 Set the sample flow rate as read by the rotameter (read the widest part of the float) to the value to be used when sampling, normally 2 Lpm.

10.2.3.8 Let the span gas flow long enough to establish a stable trace on the strip chart recorder; allow a least 5 minutes. Mark the chart trace as an unadjusted span.

Note: No adjustments are made at this point.

10.2.3.9 Disconnect the span gas.

10.2.3.10 Connect zero gas to the analyzer.

10.2.3.11 Open the gas cylinder pressure valve and adjust the secondary pressure valve until the secondary pressure gauge reads approximately 5 psi more than the desired pressure.

10.2.3.12 Set the sample flow rate as read by the rotameter to the value that is used when sampling, usually 2 Lpm.

10.2.3.13 Let the zero gas flow long enough to establish a stable zero trace on the strip chart recorder; allow at least 5 minutes. Mark the chart trace as an unadjusted zero.

10.2.3.14 Repeat Section 10.2.3.5 through Section 10.2.3.13 for each of the calibration gases with concentrations corresponding to approximately 60, 40, 20 and 10% of full scale in that order.

10.2.3.15 Fill in the information required and construct a calibration curve of analyzer response as percent of chart versus concentration in ppb. Draw a best fit, smooth curve passing through the zero and minimizing the deviation of the remaining upscale points from the curve. The calibration curve should have no inflection points, i.e., it should either be a straight line or bowed in one direction only. Curve fitting techniques may be used in constructing the calibration curve by applying appropriate constraints to force the curve through the zero. This procedure becomes quite involved; however, the most frequently used technique is to graph the curve (see Section 10.2.3.28 through Section 10.2.3.30).

10.2.3.16 Recheck any calibration point deviating more than ± 1.0 ppb NO_2 from the smooth calibration curve. If the recheck gives the same results, have the calibration gas reanalyzed. Use the best fit curve as the calibration curve.

10.2.3.17 For a dynamic dilution multipoint calibration, assemble the analyzer and dynamic dilution system as illustrated in Figure 6.

10.2.3.18 Adjust the zero air flow from the dilution system to the analyzer. The flow must exceed the total demand of the analyzer connected to the output manifold to ensure that no ambient air is pulled into the manifold vent.

Note: Zero and calibration gases should contain O_2 , CO_2 and H_2O in concentrations expected in indoor air.

Note: In lieu of connecting analyzer to manifold, one may fill Tedlar® bags with generated standards to be sampled by the LMA-3 NO_2 analyzer.

10.2.3.19 Allow the analyzer to sample the zero air until a stable response is obtained; adjust the analyzer zero control to within ± 0.5 ppb of zero base line.

Note: Offsetting the analyzer zero adjustment to +5% of scale is recommended to facilitate observing negative zero drift. On most analyzers this should be done by offsetting the recorder zero.

10.2.3.20 Determine the 80% of monitor full scale. Example: For an analyzer with an operating range of 0 to 50 ppb, the 80% value would be:

$$0.80 \times 50 = 40 \text{ ppb}$$

10.2.3.21 Adjust the NO_2 flow from the standard NO_2 cylinder to generate a NO_2 concentration of approximately 80% of the monitor full scale. Measure the NO_2 flow and record.

10.2.3.22 Measure the dilution air flow and record.

10.2.3.23 Calculate the generated NO_2 standard by the following equation:

$$(\text{NO}_2)_{\text{gen}} = [(\text{NO}_2)_{\text{std}}(Q_{\text{NO}_2})]/[Q_{\text{dil}} + Q_{\text{NO}_2}]$$

where:

$(\text{NO}_2)_{\text{gen}}$ = concentration of NO_2 generated, by dilution, ppb

$(\text{NO}_2)_{\text{std}}$ = concentration of NITS-SRM or CRM NO_2 gas standard, ppb

Q_{NO_2} = flow rate of NO_2 standard, L/min

Q_{dil} = flow rate of dilution air flow, L/min

Note: If wet test meter or bubble meter is used for flow measurement, the vapor pressure of water at the temperature of the meter must be subtracted from the barometric pressure.

Note: If both the NO_2 and the zero-air flow rates are measured with the same type of flow meter (e.g. bubble flow meter, rotameter, mass flow meter, wet test meter, etc.) correction to standard temperature and pressure (STP) is not necessary. However, if this is not the case, then the flow of NO_2 gas and dilution gas must be corrected to STP by the following equation:

$$Q_{\text{NO}_2} = (Q_1) [(P_{\text{bar}}/760)(298/T + 273)]$$

where:

Q_{NO_2} = flow rate of NO_2 standard corrected to STP, L/min

Q_1 = uncorrected flow rate of NO_2 standard, L/min

P_{bar} = barometric pressure, mm Hg

T = temperature of gas being measured, °C

10.2.3.24 Allow the analyzer to sample until the response is stable; adjust the analyzer span until the required response is obtained, and record the NO_2 recorder response. After the zero and 80% points have been set, without further adjusting the instrument, generate four approximately evenly spaced points between zero and 80% by increasing the dilution flow (Q_{dil}) or by decreasing the NO_2 flow (Q_{NO_2}). For each concentration generated, calculate the NO_2 concentrations and record the results for each point.

Note: If substantial adjustments of the span control are necessary, recheck the zero and span adjustments by repeating Section 10.2.2.

10.2.3.25 Construct a calibration curve of monitor response as percent of chart versus concentration in ppb. Draw a best fit, smooth curve passing through the zero and minimizing the deviation of the remaining upscale points from the curve. The calibration curve should have no inflection points, i.e., it should either be a straight line or bowed in one direction only. Curve fitting techniques may be used in constructing the calibration curve by applying appropriate constraints to force the curve through the zero. This procedure becomes quite involved; however, the most frequently used technique is to graph the curve.

10.2.3.26 Recheck any calibration point deviating more than $\pm 1.0 + 0.02 C_c$ ppb from the smooth calibration curve. If the recheck gives the same results, have that calibration gas reanalyzed. Use the best fit curve as the calibration curve.

10.3 Analytical Procedure

The analytical procedure is concurrent with the operating procedures. Therefore, it is recommended to follow procedures outlined in Section 9.2 and Section 10.2 for analysis.

11. Systems Maintenance

11.1 Periodic Maintenance

Proper maintenance is necessary for successful monitor performance. Periodic maintenance should be performed to reduce equipment failure and maintain calibration integrity of the instrument. Instrument calibration should be checked on a schedule established after the analyzer has operated for a period of time. The sensitivity and linearity should also be checked. These instrument checks should be done at least on an annual basis. However, when any component (i.e., detector or pump) is changed, the linearity and selectivity of the instrument should be confirmed. The settings of the zero and span controls of instruments which operate continuously should be checked as often as required. A log of these settings and a service and repair log should be kept to assist in evaluating maintenance difficulties.

11.2 Routine Maintenance

Regular checks of the instrument and its operation are mandatory. Even though a system may provide excellent quality data initially, without routine maintenance and system checks the quality of the data will degenerate with time. Follow all routine maintenance procedures specified in the manufacturer's instruction manual.

11.2.1 Sampling system - The sampling system to which the analyzer is connected must be checked at regular intervals according to a maintenance schedule based on the components used in the specific application. Sampling system maintenance normally includes the following steps:

- checking the entire system for leaks and proper flow rates,
- cleaning and/or renewing sample system components,
- ensuring that calibration cylinders are shut off when not in use,
- ordering filled and assayed cylinders at intervals which include ample lead time to ensure continuous supply of calibration gas,
- checking operation of pumps, recorders, motors, timers and other commercial components by referring to manufacturer's instructions,
- checking and/or cleaning the entire sampling system, including the sample cell in the analyzer, when abnormal sample conditions occur, such as when slugs of water, dirt or oil are introduced.

11.2.2 Daily servicing - Automatic 80% full scale span (40 ppb) and zero precision checks should be performed utilizing the instrument's automatic zero/span standardization feature (if so equipped) and individual secondary standard gases of NO_2 in air with the above concentrations. In addition, backflushing should be performed daily, immediately before daily zero/span precision check.

11.2.3 Each visit servicing - Verify that the zero and span potentiometer settings are at the proper position. Likewise, verify that the sample flow is correct. Plot the daily zero, precision check, and span values on their respective days. If any of the zero and span values exceed 5% of stated value, perform a manual zero and span check and adjust the analyzer to the correct zero and span values using the front panel zero and span potentiometer, respectively. If there is insufficient range in the span potentiometer, a multipoint calibration must be performed.

11.2.4 Weekly servicing - Perform a leak check weekly and whenever the loosening or tightening of a fitting is involved in maintenance procedures. Using an individual cylinder, introduce a 20% of full scale (10 ppb) intermediate span gas at ambient pressure upstream of the sample pump as a precision check. Maintain the same excess flow each time the manual precision check is performed. The manual precision check should be within 10% of value. If not, investigate the cause and initiate repairs.

11.2.5 Biweekly servicing - Field evaluation (10) of the LMA-3 illustrated erratic results when the pump tubing was not changed at approximately two-week intervals. Therefore, changing of pump tubing biweekly will eliminate this source of analytical error.

11.2.6 Cleaning - Clean the upper chamber when there is an accumulation of liquid in the chamber or if large amounts of residue plug the cartridge filter.

Note: Usually minute amounts of liquid can evaporate, but if liquid stays in the chamber it may leak into and ruin the air pump.

Disassemble the trap as follows:

11.2.6.1 Confirm that the instrument is turned OFF and unplugged.

11.2.6.2 Loosen the instrument cover fastener, located on the rear panel, and slide the cover off.

11.2.6.3 Remove the "feed" and "waste" bottles from the instrument.

11.2.6.4 Remove the two phillips head retaining screws from the outside of the case and pull away the panel. The upper side trim panel on the air pump side of the instrument must be removed.

11.2.6.5 Pull the air tubes off of the trap. Separate the filter cartridge from the upper chamber.

11.2.6.6 Remove the two flat head screws which hold the chamber to the side of the instrument case. Lift the chamber out of the instrument.

11.2.6.7 Observe and note the relative positions of the air tubes and the mounting holes before disassembling the chamber.

11.2.6.8 Unscrew the two black end pieces from each other.

Note: It may be necessary to soak the unit in water to loosen the chemical residues that can bind the pieces to the center tube.

11.2.6.9 After cleaning the chamber, re-assemble it. The ends should be screwed together firmly by hand. Check the relative positions of the tubes. As mounted in the instrument, the longer black tube should point straight upwards and the short tube should point towards the front of the instrument. Adjust end pieces or switch them accordingly.

11.2.6.10 Reassemble in the reverse order of disassembly.

Note: Pass tygon tubing through the clamp on the side panel, and make sure the tubing rises sharply from the detector assembly.

12. Standard Operating Procedures (SOPs), Quality Assurance (QA) and Performance Criteria

Required quality assurance measures and guidance concerning performance criteria that should be achieved by each user are summarized and provided in the following section.

12.1 Standard Operating Procedures

12.1.1 SOPs should be generated by the users to describe and document the following activities in their laboratory:

- assembly, calibration, leak check, and operation of the specific sampling system and equipment used,
- preparation, storage, shipment, and handling of the sampler system,
- purchase, certification, and transport of standard reference materials, and
- all aspects of data recording and processing, including lists of computer hardware and software used.

12.1.2 Specific stepwise instructions should be provided in the SOPs and should be readily available to and understood by the personnel conducting the monitoring work.

12.2 Quality Assurance Program

The user should develop, implement, and maintain a quality assurance program to ensure that the sampling system is operating properly and collecting accurate data. Established calibration, operation, and maintenance procedures should be conducted on a regularly scheduled basis and should be part of the quality assurance program. Calibration procedures and operation procedures in Section 9.2, and maintenance procedures in Section 11 of this method and the manufacturer's instruction manual should be followed and included in the QA program. Additional QA measures (e.g., trouble shooting) as well as further guidance in maintaining the sampling system should be provided by the manufacturer.

12.2.1 Precision Check

12.2.1.1 A periodic precision check is used to assess the data. A one-point check on the analyzer is carried out at least once every 2 weeks at a NO_2 concentration between 8 and 10 ppb.

12.2.1.2 The analyzer must be operated in its normal sampling mode, and the precision test gas must pass through all filters, scrubbers, conditioners, and other components used during normal ambient sampling. The standards from which the precision check test concentrations are obtained must be traceable to a NITS-SRM or a commercially available CRM; the standards used for calibration may be used for the precision check. They must conform to specifications outlined in Section 8.2.

Note: All gas standards should contain O_2 , CO_2 and H_2O in concentrations expected in indoor air.

12.2.1.3 Connect the analyzer's sample inlet line to a precision gas source that has a concentration between 8 and 10 ppb NO_2 and that is traceable to a NITS-SRM or a CRM as illustrated in Section 9.2.3. If a precision check is made in conjunction with a zero/span check, it must be made prior to any zero and span adjustments.

12.2.1.4 Allow the analyzer to sample the precision gas for a least 5 min or until a stable recorder trace is obtained.

12.2.1.5 Record this value and mark the chart as "unadjusted" precision check.

12.2.1.6 The expected response of the LMA-3 analyzer should be within 10% of the precision calibration gas standard.

12.2.2 Performance Audit

12.2.2.1 An audit is an independent assessment of the accuracy of data generated by an analyzer.

12.2.2.2 Independence is achieved by having the audit performed by an operator other than the one conducting the routine field measurements and by using audit standards, reference materials, and equipment different from those routinely used in monitoring.

12.2.2.3 The audit should be an assessment of the measurement process under normal operations, that is, without any special preparation or adjustment of the system. Routine quality assurance checks conducted by the operator are necessary for obtaining and reporting good quality data, but they are not to be considered part of the auditing procedure.

12.2.2.4 Proper implementation of an auditing program will ensure the integrity of the data and assess the accuracy of the data.

12.2.2.5 A performance audit consists of challenging the continuous analyzer with known concentrations of NO₂, containing O₂, CO₂ and H₂O in concentrations expected in indoor air, within the measurement range of the analyzer. Known concentrations of NO₂ can be generated by using individual cylinders for each concentration (see Section 10.2.3) or by using one cylinder of a high NO₂ concentration and diluting it to the desired levels with zero-air (see Section 10.2.3.17). In either case, the gases used must be traceable to a NIST-SRM or a commercially available CRM.

12.2.2.6 A dynamic dilution system must be capable of measuring and controlling flow rates to within $\pm 2\%$ of the required flow. Flow meters must be calibrated under the conditions of use against a reliable standard such as a soap bubble meter or a wet test meter; all volumetric flow rates should be corrected to STP at 25°C (77°F) and 760 mm Hg (29.92 in Hg); but if both the NO₂ and the zero air flow rates are measured with the same type device at the same temperature and pressure, the STP correction factor in the audit equations can be disregarded.

12.2.2.7 The analyzer should be challenged with at least one audit gas of known concentration from each of the following concentrations within the measurement range of the analyzer being audited:

<u>Audit Point</u>	<u>NO₂ Concentration Range, ppb</u>
1	3 to 7
2	8 to 12
3	18 to 22
4	28 to 32
5	38 to 42

The difference in NO₂ concentration (ppb) between the audit value and the measured value is used to calculate the accuracy of the analyzer.

12.2.2.8 All measurement of audit concentrations should fall within $\pm 10\%$ of the audit value as a precision check.

12.3 Performance Criteria

12.3.1 Specific performance criteria have been discussed and are outlined in Table 1.

12.3.2 The lower detection limit of the method is 5 ppt_v.

12.3.3 The sensitivity of the method is 1 second for a 20% change in NO₂ mixing ratio.

12.3.4 The precision of the method is linear up to about 5 ppm, provided that a flow rate of 0.1 mL/min is maintained through the system.

13. Method Safety

This procedure may involve hazardous materials, operations, and equipment. This method does not purport to address all of the safety problems associated with its use. It is the user's responsibility to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to the implementation of this procedure. This should be part of the user's SOP manual.

14. References

1. Riggin, R. M., *Technical Assistance Document for Sampling and Analysis of Toxic Organic Compounds in Ambient Air*, U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Research Triangle Park, NC, 27711, EPA-600/4-83-027, April, 1980.
2. Bubacz, D. K., and Pleil, J. D., *Real-Time Measurement of Ambient NO₂: Calibration System Design and Preliminary Evaluation of the Luminox LMA-3 NO₂ Monitor*, Northrop Services, Inc., Environmental Sciences, Research Triangle Park, NC, 27707, 1986.
3. Bubacz, D. K., Daughtrey, E. H., Pleil, J. D., and Kronmiller, K. G., "Luminox Measurements of Ambient NO₂," *Proceedings of the 1987 EPA/APCA Symposium on Measurement of Toxic and Related Air Pollutants*, Air Pollution Control Association Publication No. VIP-8, 1987.
4. Rickman, E. E., Jr., and Wright, R. S., *Interference of Nitrogenous Compounds on Chemiluminescent Measurement of Nitrogen Dioxide*, Research Triangle Institute, Report No. RTI/3180/24-01F, 1986.
5. Winer, A. M., Peters, J. W., Smith, J. P., and Pitts, J. N., Jr., "Response of Commercial Chemiluminescent NO-NO₂ Analyzers to Other Nitrogen-Containing Compounds," *Environmental Science and Technology*, 18:1118-1121, 1974.
6. Schiff, H. I., Mackay, G. I., Castledine, C., Harris, G. W., and Tran, Q., "A Sensitive Direct Measurement NO₂ Instrument," *Proceedings, 1986 EPA/APCA Symposium on Measurement of Toxic Air Pollutants*, pp. 834-855, April, Raleigh, NC, 1986.
7. Wendel, G. J., Stedman, D. H., Cantrell, C. A., and Damrauer, L., "Luminal-Based Nitrogen Dioxide Detector," *Analytical Chemistry*, 55:937-940, 1983.
8. Maeda, Y., Aoki, K., and Munemori, M., "Chemiluminescence Method for the Determination of Nitrogen Dioxide," *Analytical Chemistry*, 55:307-311, 1980.
9. Sickles, J. E., II, McClenny, W. A., and Paur, R. J., *Sampling and Analytical Methods Development for Dry Deposition Monitoring*, U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Research Triangle Park, NC, 27711, EPA-600/4-87-011, September, 1987.

10. Rickman, E. E., Groen, A. H., Wright, R. S., and Sickles, J. E., "Laboratory and Field Evaluation of Extrasensitive SO₂ and NO₂ Analyzers for Acid Deposition Monitoring," U.S. Environmental Protection Agency, Quality Assurance Division, Research Triangle Park, NC, 27711, RTI/3999/18-04F, Draft, May, 1989.
11. *LMA-3 Luminox Operation Manual*, Scintrex Ltd., 222 Snidercroft Rd., Concord, Ontario, Canada, L4K1B5, 416-669-2280, January, 1987.
12. *Manual on Indoor Air Quality* (Sections 4 and 6), Lawrence Berkeley Laboratory, Berkeley, CA, February 1984, Electric Power Research Institute, EPRI-EM-3469.
13. Dawson, S. V., and Schencker, M. B., "Health Effects of Inhalation of Ambient Concentrations of Nitrogen Dioxide," *Am. Rev. Respir. Dis.*, 120:281, 1979.
14. Morrow, P., "Toxicological Data on NO₂: An Overview," *J. Toxicol. Environ. Health*, 13:205, 1984.
15. *Quality Assurance Handbook for Air Pollution Measurement Systems, Volume II - Ambient Air Specific Methods*, U.S. Environmental Protection Agency, Quality Assurance Division, Research Triangle Park, NC, 27711, EPA-600/4-77-0272, May, 1987.
16. National Institute of Standards and Technology (NIST) Catalog of Standard Reference Materials, NIST Special Publication, NIST, Gaithersburg, MD, 1989.
17. *A Procedure for Establishing Traceability of Gas Mixtures to Certain National Bureau of Standards Standard Reference Materials*, U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Research Triangle Park, NC, 27711, EPA-600/7-81-010, January, 1981.

Table 1. Laboratory Performance Parameter Results of the LMA-3 NO₂ Extrasensitive Monitor Evaluation

<u>Performance Parameter</u>	<u>Results</u>
Mean Noise	0.003 ppb
Mean Precision (0% FS)	0.003 ppb
Mean Precision (20% FS)	0.040 ppb
Mean Precision (50% FS)	0.065 ppb
Mean Precision (80% FS)	0.105 ppb
Limit of Detection	0.009 ppb
Lower Detection Limit	0.005 ppb
Mean Daily Zero Drift	-0.00 ppb
Mean Daily Span Drift (20% FS)	-1.3%
Mean Rise Time	1.8 min
Mean Fall Time	0.2 min

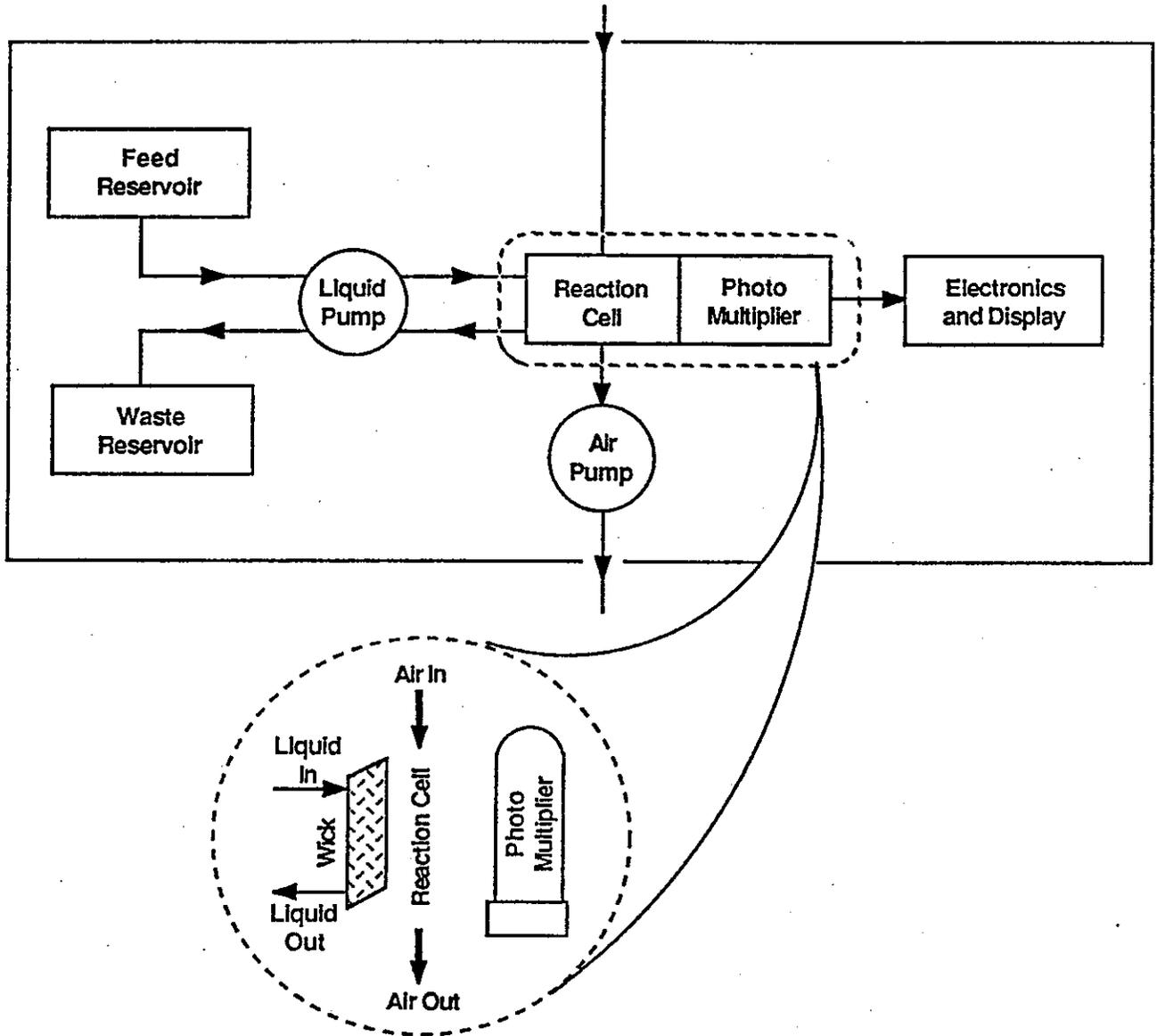


Figure 1. Operational Block Diagram of the LMA-3 NO₂ Analyzer

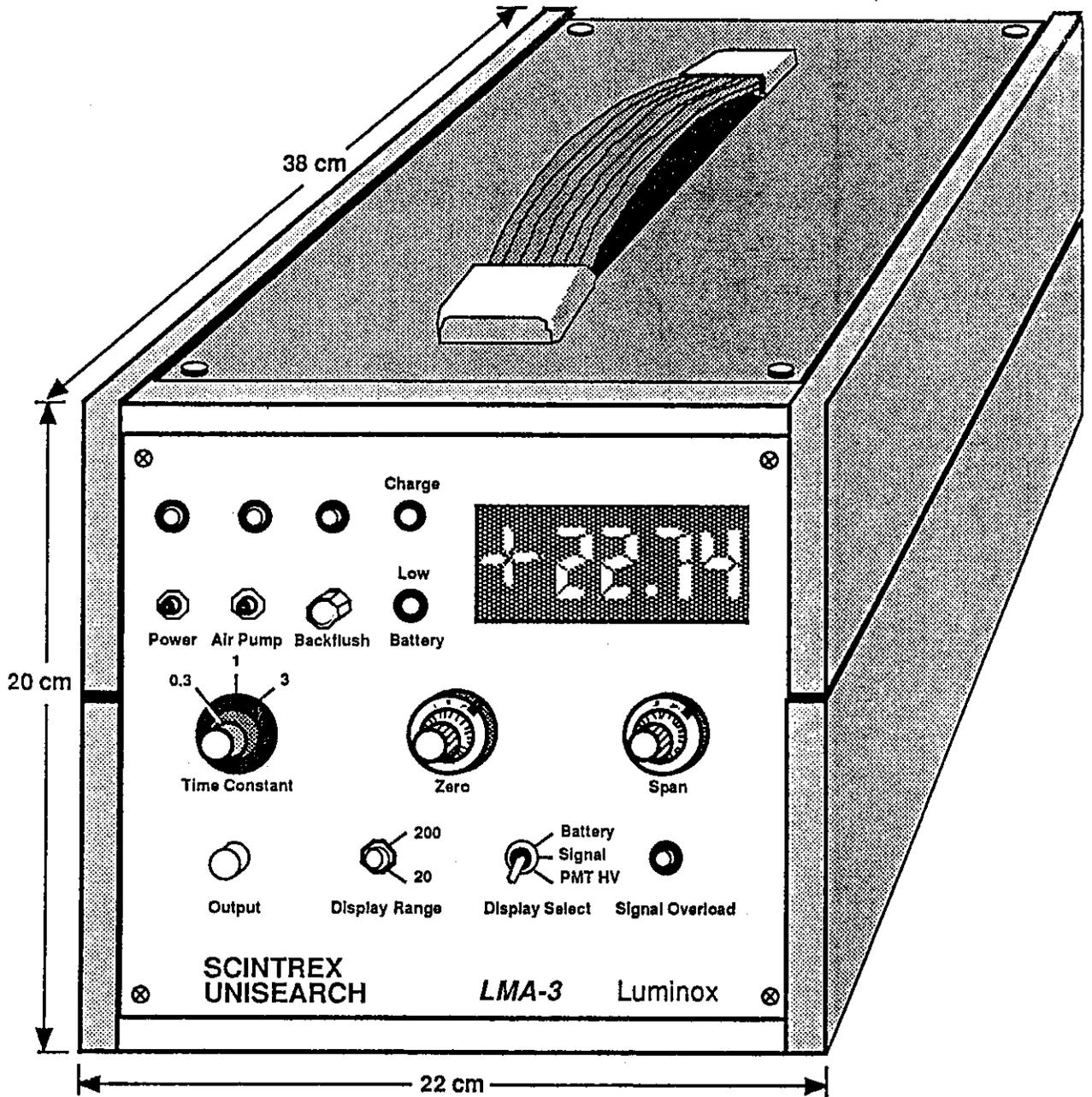


Figure 2. Front View LMA-3 NO₂ Analyzer

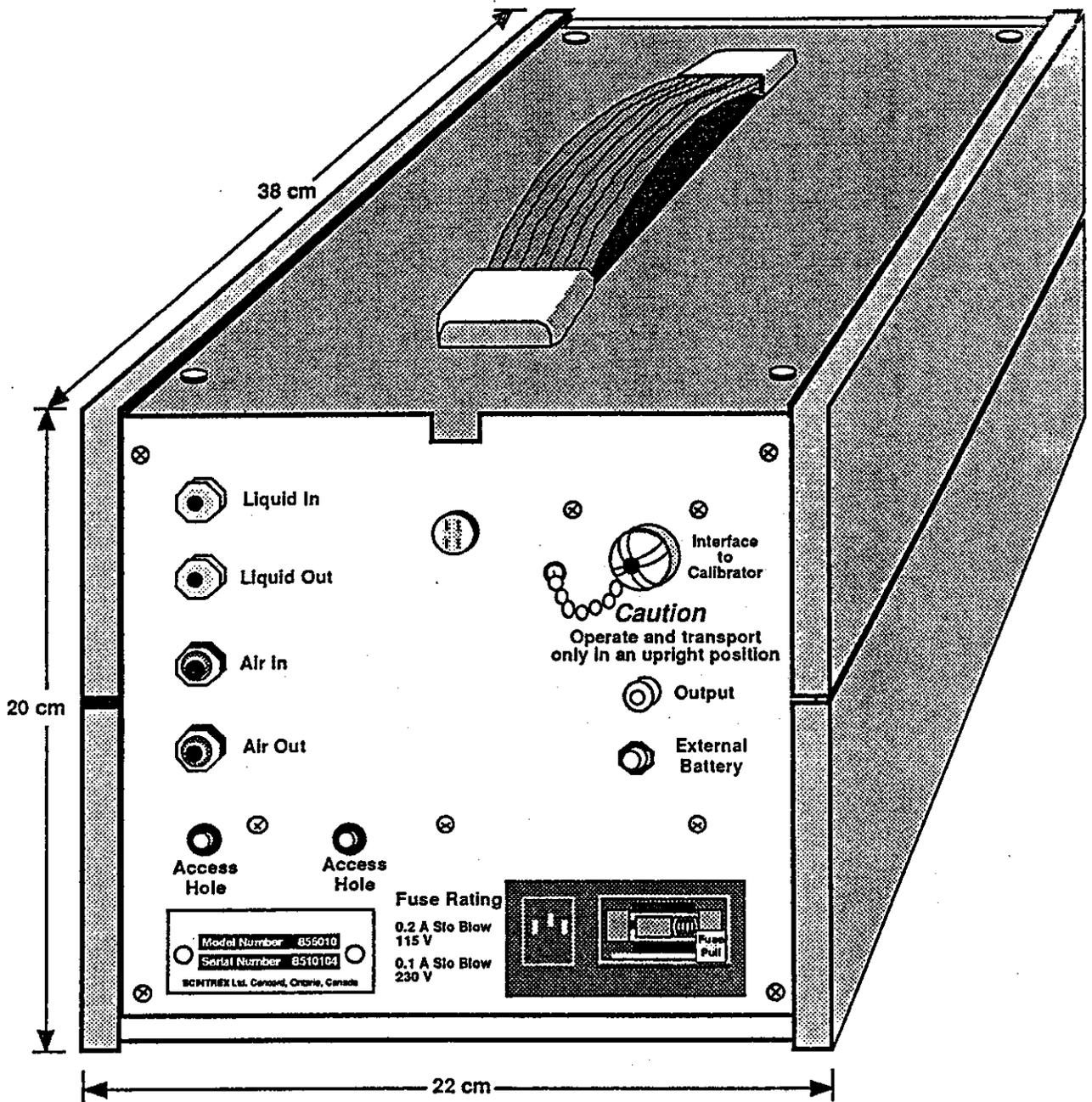


Figure 3. Back View LMA-3 NO₂ Analyzer

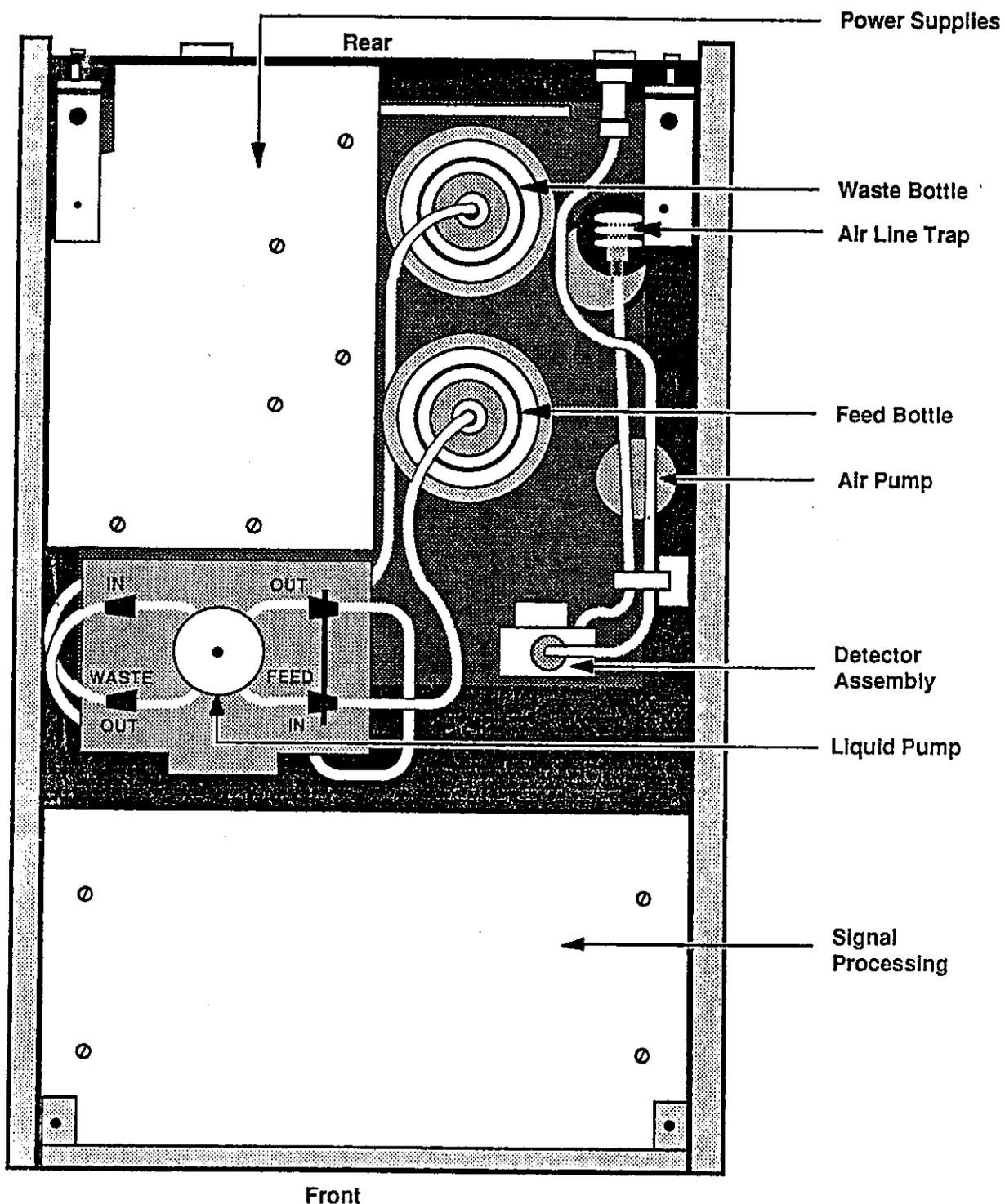


Figure 4. Top View LMA-3 NO₂ Analyzer

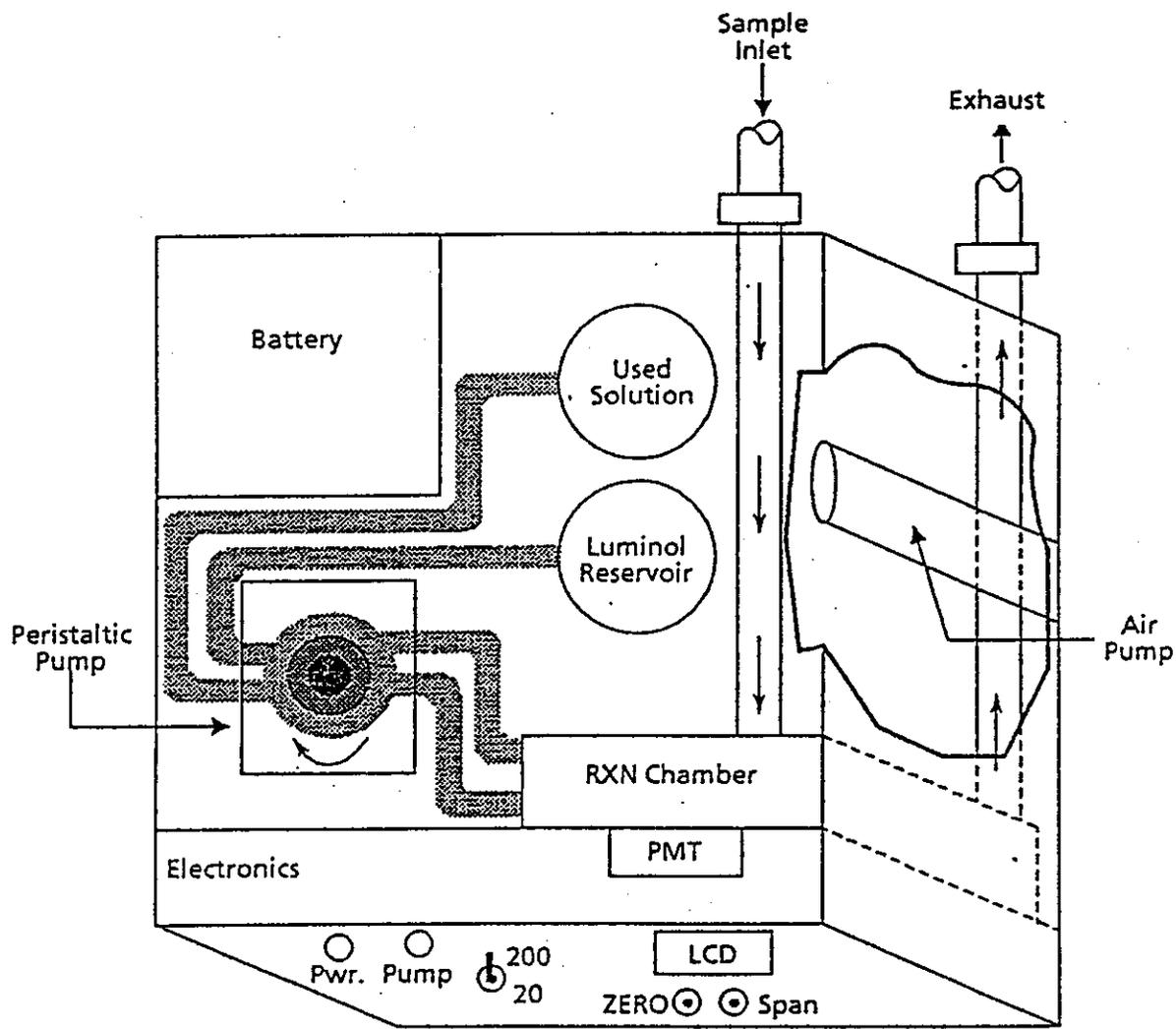


Figure 5. Sample Air through the LMA-3 NO₂ Analyzer

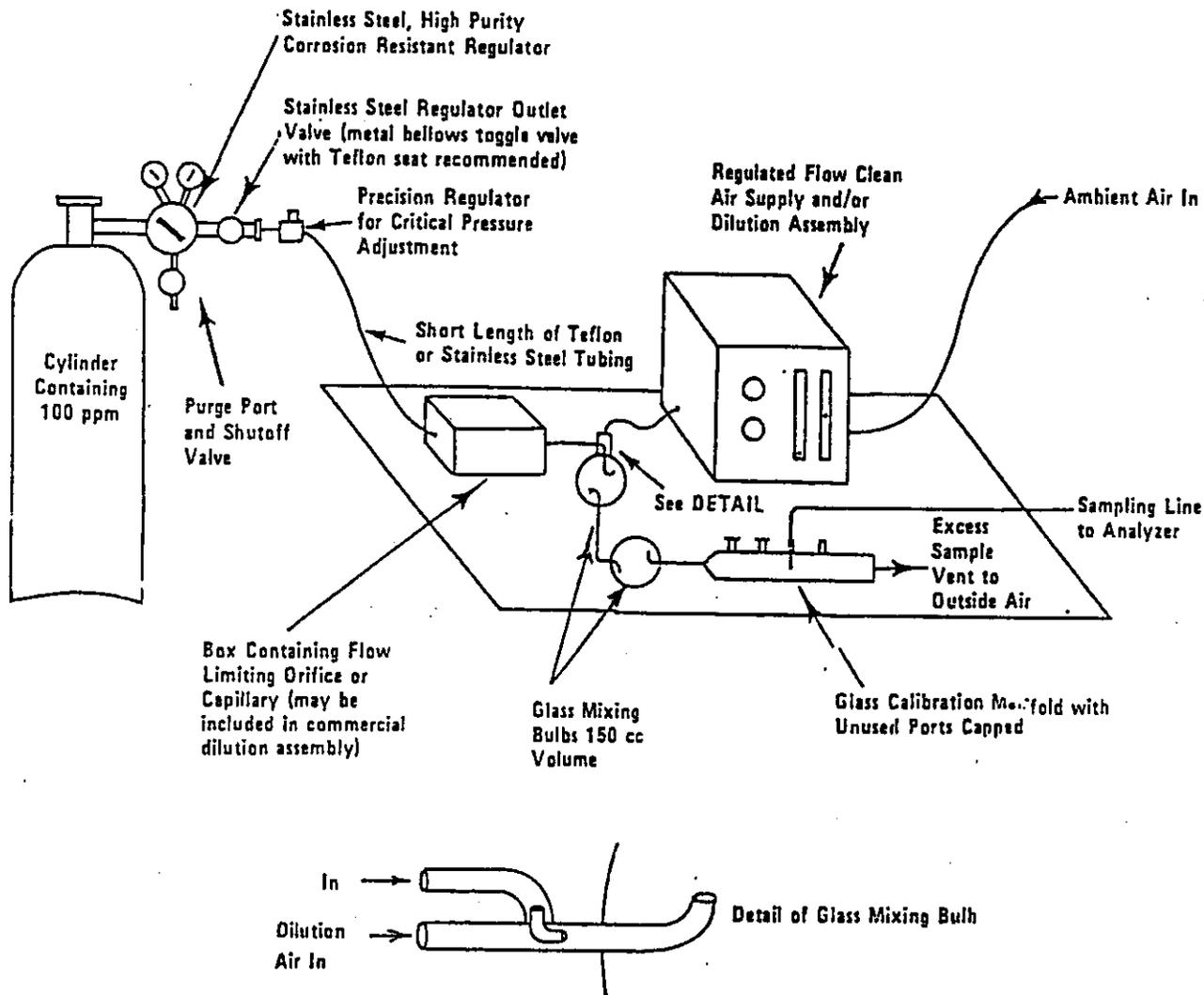


Figure 6. Assembly for Dilution of NO₂ from Cylinder for Use in Calibration or Span Check



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