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**FIELD METHODS TO MEASURE CONTAMINANT
REMOVAL EFFECTIVENESS OF GAS-PHASE AIR FILTRATION
EQUIPMENT; PHASE 1: SEARCH OF LITERATURE AND PRIOR ART**

By

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FOREWORD

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E. Timothy Oppelt, Director
National Risk Management Research Laboratory

Abstract

Gas-phase air filtration equipment (GPAFE) has been used in HVAC (heating, ventilating and air-conditioning) systems for many years. Traditionally it has been used primarily for controlling odors contained in outdoor air used for building ventilation. Today, because of the emphasis on good indoor air quality (IAQ), GPAFE is being used more and more for the control of indoor gaseous and vaporous contaminants that are known or suspected to affect human health and comfort.

One of the problems facing HVAC design engineers is how to choose a test method to determine the effectiveness of a gas-phase air filtration device. Many different filter systems and test methods are available with differing test protocols, instrumentation types and sensitivities, and costs.

This report, which is the first phase of a two-phase research project, presents the results of a literature search into existing in-field GPAFE effectiveness test methods including required instrumentation and costs.

Contents

Abstract	iv
List of tables	vii
List of figures	viii
Metric Conversions	viii
Acknowledgments	ix
Executive summary	x
1.0 Introduction	1
2.0 Gas-phase air filtration equipment (GPAFE)	3
2.1 Types of GPAFE	3
2.2 Types of Adsorbents	3
2.3 Applications	4
2.4 Performance Variables	5
2.4.1 Bed depth	6
2.4.2 Particle size of adsorbent	6
2.4.3 Void volume	6
2.4.4 Residence time	6
2.4.5 Temperature	6
2.4.6 Relative humidity	7
2.4.7 Flow velocity	7
2.4.8 Contaminant concentration	7
2.5 GPAFE performance under dynamic building operations	8
2.5.1 Relative humidity swing	8
2.5.2 Concentration swing	9
3.0 Existing test methods	9
3.1 Real-time instruments	9
3.1.1 Ozone, sulfur dioxide, and nitrogen dioxide	9
3.1.2 VOCs	10
3.1.3 Corrosive Gases	10
3.1.4 GPAFE test results	10
3.2 Active Sampling methods	12
3.2.1 VOCs	12
3.2.1.1 Evacuated canister	13
3.2.1.2 Solid adsorbent	13

3.2.2	Formaldehyde	15
3.2.3	Nitrogen dioxide	16
3.2.4	Sulfur dioxide	16
3.3	Passive sampling methods	17
3.3.1	VOCs	17
3.3.2	Formaldehyde	19
3.3.3	Nitrogen dioxide	21
3.3.4	Ozone	22
3.3.5	Sulfur dioxide & nitrous acid	22
4.0	An application guide	23
4.1	Ozone, sulfur dioxide, and nitrogen dioxide real-time instruments	23
4.1.1	Air sampling	24
4.1.2	Applications	24
4.2	Active sampling methods	24
4.2.1	GPAFE testing	25
4.2.2	Applications	26
4.3	Passive sampling methods	26
4.3.1	GPAFE testing	27
4.3.2	Handling and shipping	28
4.3.3	Applications	28
5.0	Test methods from GPAFE manufacturers	29
5.1	Remaining carbon tetrachloride activity	29
5.2	TVOC loading analysis	29
5.3	KMNO ₄ content analysis	29
6.0	Recommendations	30
7.0	Scope of phase 2 work	31
7.1	Objectives	31
7.2	Targeted gaseous and vaporous contaminants	31
7.3	Type of building	32
7.4	Type of GPAFE	32
7.5	Sampling methods and programs	32
References		34

List of tables

TABLE 1. GAS-PHASE AIR FILTRATION EQUIPMENT USED IN HVAC SYSTEMS	38
TABLE 2. REAL-TIME INSTRUMENTS FOR COMMON GAS-PHASE CONTAMINANTS IN INDOOR AIR	38
TABLE 3. ACTIVE SAMPLING FOR COMMON GAS-PHASE CONTAMINANTS IN INDOOR AIR	38
TABLE 4. PASSIVE SAMPLING METHODS FOR COMMON GAS-PHASE CONTAMINANTS IN INDOOR AIR	39
TABLE 5. FIELD METHODS FOR GPAFE TESTING-APPLICATION GUIDE ...	39
TABLE 6. PERFORMANCE SPECIFICATION FOR REAL-TIME INSTRUMENT .	40
TABLE 7. STANDARD TEST METHODS FOR ACTIVE SAMPLING -VOCs	40
TABLE 8. STANDARD TEST METHODS FOR ACTIVE SAMPLING - FORMALDEHYDE	41
TABLE 9. STANDARD TEST METHODS FOR ACTIVE SAMPLING - NITROGEN DIOXIDE	41
TABLE 10. STANDARD TEST METHODS FOR ACTIVE SAMPLING - SULFUR DIOXIDE	41
TABLE 11. TEST METHODS FOR PASSIVE SAMPLING - VOCs	42
TABLE 12. STANDARD TEST METHODS FOR PASSIVE SAMPLING - FORMALDEHYDE	42
TABLE 13. TEST METHODS FOR PASSIVE SAMPLING - NITROGEN DIOXIDE	42
TABLE 14. TEST METHODS FOR PASSIVE SAMPLING - SULFUR DIOXIDE	43
TABLE 15. TEST METHODS FOR PASSIVE SAMPLING - OZONE	43
TABLE 16. A LIST OF SUPPLIERS FOR PASSIVE SAMPLERS	44

List of figures

FIGURE 1. TEST METHODS FOR MEASURING GASEOUS CONTAMINANTS IN INDOOR AIR	45
FIGURE 2. A MULTISORBENT TUBE FOR SAMPLING VOCs IN INDOOR AIR (ACTIVE METHOD)	46
FIGURE 3. AN ACTIVE SAMPLING APPARATUS FOR SULFUR DIOXIDE (ASTM D-2914)	47
FIGURE 4. A CARTRIDGE FOR PASSIVE SAMPLING OF NITROGEN DIOXIDE IN INDOOR AIR	48

Metric Conversions

Most measurements in this report are in nonmetric units. Readers more familiar with metric units may use the following conversion factors:

<u>Nonmetric</u>	<u>Multiplied by</u>	<u>Yields Metric</u>
angstrom	0.1	nm
cfm	0.00047	m ³ /s
°F	5/9 (°F-32)	°C
fpm	0.00508	m/s
ft	0.305	m
in.	2.54	cm
lb	0.454	kg
oz	0.0283	kg

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Executive summary

Numerous test methods are commercially available for measuring low level concentrations of gaseous and vaporous contaminants in ambient and indoor air. With appropriate sampling procedures, these methods can be readily used to determine the effectiveness of gas-phase air filtration equipment (GPAFE) in the field.

Categorically speaking, there are three types of test methods; namely, real-time instruments, active sampling followed with an on-site or off-site analysis, and passive sampling followed with an off-site analysis. This report describes these test methods and provides a general guideline regarding the use of these test methods for determining the effectiveness of installed GPAFE in commercial and institutional buildings.

Although real-time instruments are very expensive(>\$10,000), they provide continuous and real-time data to monitor the efficiency and service life of GPAFE. The real-time instruments are commercially available for many gases, including ozone, sulfur dioxide, nitrogen dioxide, formaldehyde, and hydrogen sulfide. The detection limits are typically in the low ppb range. For volatile organic compounds (VOCs), the real-time instruments that can measure a wide range of organic compounds at sub-ppb levels or total VOC at low ppb levels are not available at this time.

The real-time instruments have been used to measure the removal efficiencies of GPAFE against ozone, nitrogen dioxide, sulfur dioxide, and formaldehyde in either laboratory or field studies. However, the users are limited to those research organizations or companies who can afford them and have the resources and expertise to operate them. Although extremely desirable, we do not currently expect that the real-time instruments can be a cost-effective field method for GPAFE testing from the standpoints of building operation and maintenance. To fulfill the needs, the instruments must be improved from their present form (bulky and expensive instruments) to small and low cost sensors with the same or better detection limits.

Active air samplings are the most common methods used today for air samplings. These methods are very accurate and sampling time is typically one to eight hours. Active sampling uses pumps and flow equipment to draw air into sampling tubes. After sampling, the collected contaminants are either analyzed on-site, or sent back for laboratory analysis. The typical accuracy of active sampling methods is $\pm 5-10\%$, and the sensitivity is in a few ppb range. Active sampling test methods are available for VOCs, nitrogen dioxide, oxides of nitrogen, sulfur dioxide, formaldehyde, and many other gases. The active sampling and analysis is usually provided by testing laboratories and consulting firms.

Active sampling methods are recommended for measuring initial efficiency of GPAFE shortly after the installation (for the purpose of performance verification), or checking its efficiency when there is a need to do so (e.g., significant changes in pollutant loads or

design conditions). Since the cost of active sampling and analysis is not inexpensive and sampling time is relatively short (1-8 hours), a good communication and planning among building engineer, testing personnel, and GPAFE manufacturer is essential in terms of the intent of testing, what contaminants should be measured, the expected concentration range of targeted contaminants, the sampling locations, and the timing for sampling. In addition, all the relevant data prior to and during air sampling period should be collected (e.g., flow rate, relative humidity and temperature of airflow through GPAFE) in order to properly interpret the test results over such a short sampling time.

Passive air sampling is the most cost-effective, easy-to-operate test method for monitoring the GPAFE performance. It uses the natural process of diffusion to collect contaminants in the sampler. This straightforward process requires the placement of the passive sampler in a location of interest (a minimum of flow velocity of 25 fpm is required) and the allowance of sufficient time for the sampler to collect an adequate amount of contaminants for analysis. No external devices such as pumps, tubing, flowmeters, calibration kits, or power sources are needed. Most passive samples are small badges or cartridges which can be clipped onto a worker's clothes as a personnel monitor or hung in an indoor space as an area monitor. After sampling, the sampler is sent back to the manufacturer or laboratory for analysis. Passive sampler methods for VOCs, nitrogen dioxide, and formaldehyde have been commercially available for many years. Recently, new techniques have been developed for measuring ozone and sulfur dioxide concentrations, and they are now commercially available. The typical accuracy for passive sampling methods is $\pm 20\text{-}25\%$ for VOCs and $\pm 10\text{-}15\%$ for ozone, nitrogen dioxide, sulfur dioxide, and formaldehyde. The sensitivity is typically in a few ppb range.

Passive sampling is recommended as a routine test method used by building engineers to monitor the removal efficiency and service life of installed GPAFE. Essentially, no training is required except that the proper procedures should be followed regarding sampling locations, sampling time, storage (if necessary), and packaging (for shipping the samplers back to manufacturers and analytical laboratories). In most cases, the shipping can be done by mail, since the samplers are small enough to fit inside an envelope.

It is important to conduct the passive sampling test on a regular basis and to collect all the relevant data that can affect the GPAFE performance. In this manner, test data collected at different periods of service time can be plotted to reliably determine when to change the media used in GPAFE, and to assess the irregular behavior of GPAFE due to the changes in pollutant loads and environmental conditions.

As one would expect, literature data on the use of in-field methods for GPAFE testing are almost non-existent in public domain, especially for passive and active sampling methods. Therefore, it is necessary to conduct Phase 2 of this research project to obtain actual test data using selected test methods. These data will be used to prepare a complete documentation on the test protocols that can be implemented by building engineers to determine and monitor the GPAFE performance.

1.0 Introduction

Gas-phase air filtration equipment (GPAFE) has many applications in heating, ventilation, and air-conditioning (HVAC) systems. In the past, it was used primarily to remove odors from outdoor ventilation air and corrosive gases for protecting valuable artwork in places such as museums. Today, GPAFE has much broader applications. Because of indoor air quality problems in buildings, the use of GPAFE has been expanded to control gases and vaporous contaminants that are known or suspected to affect human health and comfort. Furthermore, the sources of gaseous and vaporous contaminants have been linked more than outdoor ventilation air. More often they are internally generated from building materials and furnishings, human-related activities, cleaning agents.

For the last five years, significant progress has been made towards the effectiveness of GPAFE for IAQ control. Research results from both laboratory and field studies (ref. 1-5) have shown that a well-designed activated carbon adsorber is effective in removing many common indoor contaminants found in buildings, including volatile organic compounds, ozone, sulfur dioxide, and nitrogen dioxide. Furthermore, various chemically-treated and potassium permanganate-based sorbents (ref. 6-7) are shown to have enhanced removal capacities for inorganic gases and certain low molecular weight organic vapors such as formaldehyde and hydrogen sulfide. These research results lead us to believe that GPAFE, when properly designed and applied, can play an important role in improving indoor air quality in commercial, institutional, and public buildings.

In spite of this, information regarding the selection and testing of GPAFE has been largely unavailable. As a result, gas-phase air cleaning is not a control method that can be easily implemented by HVAC engineers at the present time. Many types of GPAFE are available, and each of them performs differently depending upon its bed depth, packaging density, particle size, and extent of bypass. To complicate the subject further, various types of physical and chemical adsorbents are commercially available for use in any given GPAFE. Because these adsorbents use different mechanisms to remove contaminants, they may have different responses to the changes of environmental conditions such as temperature and relative humidity. Although HVAC engineers do not need to know all of these effects in details, they do need application guides and standard test methods to properly select GPAFE in the design stage, and to determine and monitor its performance before and after the installation.

Recognizing these needs, ASHRAE now has two research projects directed towards these efforts. ASHRAE 792-RP (ref. 8) aims towards developing standard laboratory test methods for full-scale (0.6 x 0.6 m) GPAFE. These methods will allow HVAC engineers to properly select GPAFE in the building design stage.

The research project 791-RP has a different purpose. It intends to provide education and information so that an engineer can properly choose, monitor and implement an in-field test scheme for GPAFE. The evaluation will determine the capacities of installed GPAFE to properly benefit the structure and its occupants. The information will be used by HVAC engineers as a guideline to test for gaseous contaminants in the indoor environment before and after installation of the gas-phase air filtration equipment. Also, The research will be used to update the ASHRAE Handbook chapter on contamination control, and will complement in-field use and interpretation of ASHRAE Standard 62-89 and its future version (ref. 9).

As outlined in the Work Statement (ref. 8), the scope of work for Phase 1 is summarized as follows:

- a. Review and summarize pertinent literature regarding in-field testing schemes and equipment for determining the efficacy of installed gas-phase air filtration equipment, with particular emphasis on IAQ.
- b. Obtain information from manufacturers, suppliers, and HVAC contractors regarding available GPAFE, methods of installation, and in-field test methods.
- c. Prepare a list of in-field test methods that may be used by HVAC engineers, including application guideline for each method.
- d. Make recommendations for Phase 2 of this project including budget estimate, man hours, investigator qualifications, and equipment needs for conducting actual testing of installed GPAFE in office buildings.

2.0 Gas-phase air filtration equipment (GPAFE)

2.1 Types of GPAFE

There are two types of GPAFE commonly used in HVAC systems, panel and pleated adsorbers. Their salient features are summarized in Table 1.

The panel adsorber is made of a number of panels arranged in a zigzag configuration within a housing of standard size (0.6 x 0.6 m). Each panel contains granular or pelletized adsorbents, typically 4x8 mesh or 3-4 mm in diameter. The bed depth typically is 2.5 or 5.1 cm, and in some designs up to 7.6 cm. Each standard size adsorber is normally rated at 0.94 m³/s (2000 cfm) airflow rate. These adsorbers can be placed in a multiple holding frame or bolted together to form a bank for handling large air flow rates (up to 22.6 m³/s for side access housing, and front/rear access housing can be used for flow higher than 22.6 m³/s). There is a large variation among the panel type of adsorbers. They differ in packing styles, residence time, amount of adsorbent, in-line depth (flow direction), material of construction, and internal design. It is understood that some of these differences are design variations, intended to meet different application requirements. However, many differences truly reflect the product quality. For example, the extent of adsorbent settling and air leakage between the panel and holder as well as in the housing are the subtle differences in panel adsorbers. These differences can only be detected by actual testing. The pleated adsorber is made of fabric materials in which small sizes (20 mesh or smaller) of adsorbent particles are embedded. This type of material is also available in standard size (0.6 x 0.6 m), typically rated at 0.94 m³/s airflow rate. There is also a large variation among the pleated type of adsorber in terms of adsorbent particle size, the amount of adsorbent, and the method of containing the adsorbent particles in the fabric matrix. Although this type of adsorber does not exhibit adsorbent settling problems, it has its own potential problems, such as uniformity of adsorbent particles in the fibers and blockage of adsorbent surfaces from the binders. Again, these effects on GPAFE performance can not be detected without actual testing.

2.2 Types of Adsorbents

A number of physical and chemical adsorbents are commercially available for use in GPAFE. Since there is no single adsorbent that is effective for all indoor air contaminants, the choice of adsorbent depends primarily on the prevailing contaminants in a given application. In some cases, more than one adsorbent is required.

Activated carbon is the most common adsorbent used in HVAC applications. It uses physical pore-filling adsorption to store VOCs in its micropores (<20 angstroms). The pore-filling adsorption is a phenomenon where the adsorbed molecules are packed so tightly in the micropores that it is in a liquid form. Not all activated carbons have equal adsorption capacity for VOCs, and the difference can be attributed to their micropore size

distributions and internal surface areas. For the control of ppb levels of VOCs, it is advantageous to use activated carbon that is enriched with micropores and ultrafine micropores (<10 angstroms). The micropores are useful in adsorbing high boiling point, large molecular weight VOCs, whereas the ultra fine micropores can adsorb low boiling point, low molecular weight VOCs. Carbon tetrachloride activity (ref. 10) has been the most common method for rating activated carbons for VOCs removal. Due to the anticipated ban of chlorinated hydrocarbons, the ASTM D-28 Committee is currently developing a butane test for replacing the current carbon tetrachloride test.

Activated carbon has also been shown to be effective in removing ppb levels of ozone and sulfur dioxide by means of various chemical and catalytic reactions (ref. 3).

With a few exceptions, activated carbon has very little capacity for adsorbing gases that have boiling points below 0 °C. By impregnating activated carbon with appropriate agent(s), the capacity for removing such contaminants is drastically increased through chemisorption and subsequent reactions. For example; caustic-impregnated activated carbons are used to remove acidic and corrosive gases (e.g., hydrogen sulfides, mercaptans, hydrochloric acid, and nitrogen oxide), acid-impregnated carbons for ammonia and amines, and sodium sulfide-impregnated carbon for formaldehyde. Impregnated carbons are often considered as dual adsorbents because of their ability to remove VOCs via physical adsorption. However, some loss of VOC capacity is expected due to the blockage of impregnates in the micropores.

Another class of adsorbent is potassium permanganate-based material. This material has been used in HVAC industry for years, primarily for odor and corrosion control. It uses oxidation and catalytic reactions to convert certain low molecular weight, and reactive compounds into water, carbon dioxide, and other products which are retained on the interior surfaces. This type of material is known to be effective in removing hydrogen sulfide, sulfur dioxide, low molecular weight mercaptans, and formaldehyde.

Zeolite can also be used to remove VOCs. It is particularly effective with polar VOCs such as alcohols and ketones. However, it is not commonly used in HVAC application because of the cost. Some novel catalysts can be used to remove VOCs and inorganic gases. However, all of them require high temperatures (>150 °C) to achieve high conversion levels.

2.3 Applications

For general purpose IAQ in office buildings, GPAFE may be installed in main HVAC systems to control common indoor gas-phase contaminants that are either internally generated or brought in from outdoor ventilation air. To accomplish this, GPAFE is generally located in the mixed-air position of a main air handler to provide cleaned supply air for the spaces it serves. In terms of relative locations, GPAFE is generally found upstream of A/C equipment, and downstream of particulate filters. The GPAFE selection

can be based on required cleanliness level (concentration methods) or equivalent air concept (ref. 11), whichever is appropriate for a particular application. The GPAFE sizing is rather straightforward, and it is commonly based upon airflow rate. That is, one 0.6 x 0.6 m GPAFE for 0.94 m³/s. In some cases, the airflow is derated to enhance the contaminant removal or accommodate the pressure drop limitation.

GPAFE can also be used for odor control. In most cases, odorous gases or vapors are brought in from outdoor ventilation air. Buildings near petroleum refineries may have created additional contaminants such as hydrogen sulfide, chlorine, and mercaptans. Buildings near combustion sources may experience elevated levels of VOCs, nitrogen dioxide, and carbon monoxide. These are considered as special IAQ applications. To eliminate these odors, the solutions often require detailed analysis of contaminants and concentration, and careful selection and sizing of GPAFE.

Whatever the application, GPAFE seldom relies on single-pass efficiency to control indoor contaminants (except treating 100% outdoor air). Instead multiple passes are used to reduce indoor contaminant concentrations in conjunction with recirculation air. It can be shown from a simple steady-state mass balance (ref. 11) that a low efficiency (single-pass) can provide significant cleaning of indoor contaminants if adequate recirculation air is provided. On the other hand, a high efficiency GPAFE may not provide adequate cleaning if the recirculation airflow is very low. Perhaps, this is one of the reasons that there are so many types of GPAFE (heavy, medium, light duties). Most of them are useful products if applied properly.

2.4 Performance Variables

There are many variables that can affect the performance of GPAFE. For the purposes of discussion, we will divide these variables into two groups; design and application variables. Design variables are the parameters that filter manufacturers use to design their GPAFE. These parameters include bed depth, packing density, type of adsorbent, particle size of adsorbent, and residence time at rated flow. Application variables are the parameters at which GPAFE is operated in a HVAC system. These parameters include contaminants and their concentration, temperature, relative humidity, and air flow velocity.

The breakthrough behavior of adsorber under constant conditions is rather straightforward and predictable. Depending upon the relative length between bed depth and mass transfer zone, the adsorber can maintain at near 100% removal levels for a period of time before contaminants start to break through, or contaminants can immediately break through from the adsorber as soon as the flow is introduced (ref.1). If an adsorber is operated at a condition where the bed depth (L) is shorter than the length of mass transfer zone (L'), initial efficiency (single-pass) will be less than 99%, and continuously decreasing with time. When the bed depth is somewhere between $L' < L < 2L'$, initial efficiency will be greater than 99% and remains at >99% for a portion of service time, then decreases with

the remaining service life. When the bed depth is much larger than the length of mass transfer zone (say $L=5L'$), the efficiency is maintained at >99% for most of its service life. This behavior applies to all types of GPAFE and a wide range of contaminants (with the exception of ozone). However, air leakage through GPAFE is not taken into consideration. The mass transfer zone is defined as the length of carbon bed where the concentration of contaminant decreases to, say 1% of its inlet level. Most GPAFE used in HVAC systems are designed with bed depth equivalent to or shorter than the length of mass transfer zone. Therefore, their efficiencies are expected to vary with flow velocity, temperature, and relative humidity. These effects are summarized as follows:

2.4.1 Bed depth - bed depth affects both efficiency and service life of GPAFE. As illustrated above, the effect on efficiency can be understood from the concept of mass transfer zone. The effect on service life is related to the amount of adsorbent in the GPAFE.

2.4.2 Particle size of adsorbent - smaller particle size has faster adsorption rate. However, it does not affect the equilibrium (or saturation) adsorption capacity of adsorbent.

2.4.3 Void volume - void volume is the space between the adsorbent particles in a carbon bed. A carbon bed with higher void volume will have lower efficiency and shorter service life.

2.4.4 Residence time - residence time, when properly defined, is a very useful parameter in characterizing the initial efficiency of an adsorber. It is defined as volume of adsorbent in an adsorber divided by airflow rate passing through the adsorber. Residence time is a lumped parameter of three design variables; bed depth, void volume, and total face area of adsorber. The use of residence time for determining initial efficiency of an adsorber must take adsorbent particle size into consideration. For panel types of adsorber, a residence time of 0.1 seconds is required to cover the mass transfer zone for 4x8 mesh coconut shell activated carbon (ref. 1), which is commonly used in HVAC industry. In general, pleated adsorbers require less residence time to achieve the same efficiency due to the use of smaller particles. When the same adsorbent is used, residence time can also be used as an indicator for service life of an adsorber. An adsorber with longer residence time will have longer service life. The residence time for panel type of adsorber is 0.02-0.1 seconds, and 0.001-0.03 seconds for pleated type of adsorber.

2.4.5 Temperature - the effect of temperature depends on the removal mechanism of GPAFE. For physical adsorption of VOCs, an increase of temperature will result in a decrease of adsorption capacity. On the other hand, temperature can enhance the removal capacity of contaminants when oxidation or catalytic reactions are the principal removal mechanisms. In HVAC systems, air temperature itself is not expected to have a significant effect on GPAFE performance since the variation is generally small. However, a

corresponding change in relative humidity will have a more pronounced effect on the GPAFE performance.

2.4.6 Relative humidity - again, the effect of relative humidity depends on the removal mechanism of GPAFE. For physical adsorption of VOCs, the adsorption capacity of activated carbon can be significantly reduced in the presence of high relative humidity. When relative humidity exceeds 50%, significant adsorption of water vapor can occur in activated carbon. As this happens, the carbon capacity for adsorbing VOCs will be reduced since both water vapor and VOCs are competing for the same adsorption space, or micropore volume. However, the extent of this effect depends on the affinity of water vapor towards the surface of activated carbon relative to VOCs. It has been known that not all activated carbons have the same affinity for water vapor. Based on the VOC loading analysis of in-field carbon samples serving HVAC applications (ref. 2), the VOC adsorption capacity of a coconut shell activated carbon is about 10-15% by weight when water loading is less than 5% (i.e., <50% relative humidity), and 5-10% when water loadings exceed 15% (i.e., >60% relative humidity).

For impregnated carbons or other chemical adsorbents, the effect of relative humidity is specific to the chemistry between impregnate and contaminant. In some systems, relative humidity has a beneficial effect. For example, the adsorbed water can enhance the oxidation reaction of potassium permanganate for hydrogen sulfide removal (ref. 12). In other systems, relative humidity has no effect. For example, the neutralization reaction between caustic-impregnated carbon and hydrogen sulfide is not influenced by the presence of water vapor, except in the extreme cases (ref. 13).

2.4.7 Flow velocity - higher flow velocity will decrease the single-pass efficiency of an adsorber. However, the effect is not a linear relationship. This is a very important point in recirculation air cleaning. In these systems, the increase of airflow will actually result in a net increase of contaminant removal rate. This can be understood by the fact that the contaminant removal rate is determined by the product of recirculation flow rate and single-pass efficiency of adsorber. In recirculation systems, airflow rate will have no noticeable effect on adsorber service life. Increasing recirculation rate will result in high contaminant rate; therefore, lower inlet concentration to the adsorber. The reverse is true for lowering the recirculation flow rate. In both cases, the net result is the same, that is, no noticeable change in contaminant load to the adsorber.

2.4.8 Contaminant concentration - all GPAFE will have a longer service life at lower concentration if all other variables are held constant. However, no GPAFE will have a proportional increase of service life as concentration decreases. This is because the adsorption capacity of any adsorbent decreases, but not in a linear relationship, with decreasing concentration of contaminant. For physical adsorption of VOCs, the extent of this effect depends on boiling point of compound, concentration range, and micropore size distribution of activated carbon (ref. 14). For chemisorption of inorganic gases, the

adsorption capacity of chemical sorbents also may vary with concentration, the extent of the effect depends on gases and environmental conditions (temperature and relative humidity) (ref. 12).

2.5 GPAFE performance under dynamic building operations

We have just discussed the individual effects of various variables on the performance of GPAFE. This information is useful for understanding the basic behavior of GPAFE; however, it does not fully describe the actual performance of GPAFE under dynamic building operations. This is one of the reasons why in-field test methods are needed to determine and monitor the performance of GPAFE in buildings.

Inevitably, GPAFE, after being installed in a building, will be challenged with the everlasting changes in pollutant loads and environmental conditions according to ambient conditions, mode of HVAC operation, occupant activity, and contaminant sources. Among these factors, the most noticeable variables are relative humidity and contaminant concentration. In the following, we will discuss the expected responses of GPAFE under the swings of these two variables, with particular emphasis on VOCs.

2.5.1 Relative humidity swing - since physical adsorption of VOCs is a reversible process, activated carbon may continue to adsorb more VOCs from an air stream or release adsorbed VOCs back to an air stream. This depends on the loading it already has and its saturation adsorption capacities at various relative humidity levels. To illustrate it, let us assume that the saturation capacity is 10% at 50% relative humidity (RH) and 5% at 70% RH. We further assume that a carbon adsorber initially operates at 50% RH, and it has 2% VOC loading after a period of time. After that, RH is suddenly increased to 70%. As a result, a decrease of removal efficiency will occur. However, the carbon will continue to adsorb VOCs since the current VOC loading (2%) is less than its saturation capacity at 70% RH, which is 5%. Let us assume this adsorber continues to operate at 70% RH until the loading reaches its saturation capacity. At this point the adsorber efficiency becomes zero (relative to 70%). After that, the relative humidity is back to 50%. As a result, the adsorber will again adsorb more VOCs since the current loading (5%) is less than the new saturation capacity, which is 10%. Let's say the adsorber continues to operate at 50% RH until the loading reaches its saturation capacity (10%), and the adsorber efficiency becomes zero again (relative to 50%). After that, RH increases to 70%. As a result, the VOCs will desorb, since the current loading (10%) exceeds the new saturation capacity (5%).

In summary, the adsorber efficiency will respond to the change of relative humidity, but the effect is reversible. In order to minimize this effect, the residence time of an adsorber must be long enough so that the mass transfer zone is significantly shorter than the bed depth of adsorber.

Certain chemical adsorbents are expected to be affected by the swing of relative humidity. However, the desorption of contaminants (negative efficiency) is unlikely since chemisorption is an irreversible process.

2.5.2 Concentration swing - the concentration swing follows the same principle we have just discussed. However, the effect is expected to be less pronounced as compared to relative humidity swing. Generally speaking, a significant change in concentration is required to cause a noticeable effect. However, these conditions may occur during a building operation. An example of this is high concentration emission of VOCs during a painting activity. In these situations, a carbon adsorber may work as a capacitor to reduce the peak concentration. This is to say, a carbon adsorber that has no capacity left for removing ppb levels of VOCs, can still be very effective to remove ppm of VOCs. On the other hand, the desorption of VOCs may occur when clean air passes through a carbon adsorber which is previously saturated with ppm level of VOC. However, the extent of desorption is highly related to carbon particle size.

3.0 Existing test methods

There is a variety of methods and techniques available to measure the presence and concentrations of gaseous and vaporous contaminants in indoor environments. Methods commonly used for indoor air testing include the modified OSHA methods, the EPA test methods for ambient air quality measurements (ref. 15 and 16), the NIOSH methods for non-industrial indoor environments (ref. 17 and 18), and ASTM test methods for indoor environments (ref. 19).

These test methods may be classified into three basic categories; real-time or on-line instruments, active sampling methods, and passive sampling techniques. Although all of these methods can be directly applied to the testing of gas-phase air filtration equipment (GPAFE), the selection of methods often depends on cost of testing and application needs. The representative equipment used for these test methods are shown in Figure 1.

3.1 Real-time instruments

Table 2 summarizes the real-time instruments for measuring common indoor gaseous contaminants.

3.1.1 Ozone, sulfur dioxide, and nitrogen dioxide - the real time instruments for monitoring ppb levels of ozone, sulfur dioxide, and nitrogen dioxide are well-developed. These instruments provide excellent reliability, accuracy, detection limit, and data acquisition and communication capability. Since they are contaminant-specific, three individual instruments are required to measure the concentrations of ozone, sulfur dioxide, and nitrogen dioxide. The continuous measurement of ppb levels of ozone is based on the absorption of ultraviolet radiation at 254 nm wavelength. The measurement of sulfur

dioxide is commonly based on pulsed fluorescence technique, and nitrogen oxides (NO_x) is based on chemiluminescence technique. The operation principles of these real-time instruments are available from the manufacturers (ref. 20) and will not be discussed here.

3.1.2 VOCs - real-time instruments for measuring a wide range of VOCs at sub-ppb levels or total VOCs (TVOC) at ppb levels are not available at this time. However, some real-time instruments can provide excellent detection limits for specific classes of organic compounds. Semiconductor gas sensors and Fourier transform infrared remote sensing appear to be the emerging technologies for detecting ppb levels of VOCs. Semiconductor gas sensor (ref. 21) is a tiny catalytic converter, measuring the change in conductivity as organic vapors are converted to carbon dioxide and water. These semiconductor-based sensors are currently marketed as IAQ sensors for building control. However, major efforts will have to be made before it can be used for GPAFE testing, namely; internal calibration with a standard VOC, an internal compensation for relative humidity and temperature effects, and an order of magnitude improvement in detection limit. Fourier transform infrared remote sensing (ref. 22) has demonstrated its applicability for measuring ppb levels of many individual VOCs in office buildings.

3.1.3 Corrosive Gases - these wall-mounted or hand-held sensors (ref. 23) were developed to determine the corrosion potential of controlled environments where computers and electronic equipment are located to control a manufacturing process. These sensors measure the film thickness of copper or silver via the change of resonance frequency on the quartz crystal microbalance (QCM). Each copper or silver-plated crystal has a natural resonance frequency based on its mass. As corrosion films form on the crystal, the mass increases by the reactions between corrosive gases and copper (or silver). As a result, the resonance frequency decreases. By using proper conversion factors, the corrosion rates thus can be determined. The amount of corrosion formed film thickness depends upon the nature of contaminant, concentration of corrosive contaminant, exposure time, and environmental factors such as humidity and temperature. The ISA (Instrument Society of America) Standard S71.04 (ref. 24), provides four environmental classes (G1, G2, G3, and GX) according to the film thickness on a copper coupon. In each environmental class the maximum allowable concentration is specified for each corrosive gas such as hydrogen sulfide, ozone, chlorine, sulfur dioxide, nitrogen dioxide, and ammonia.

3.1.4 GPAFE test results - Real-time instruments have been used for GPAFE testing. Battelle (ref. 7) conducted laboratory testing on a full-scale (0.6 x 0.6 m) GPAFE for ozone, sulfur dioxide, nitrogen dioxide, and formaldehyde. The test was conducted in a duct under controlled conditions. Before introducing the challenging gases into the test duct, the test air was cleaned with prefilters, both particulate and gas phase, to establish an acceptable background level. All of the challenging gases were injected at sample port upstream of GPAFE at constant concentrations. The sulfur dioxide and nitrogen dioxide were supplied from high pressure cylinders. Flow of these gases was metered through mass flow controllers and passed through 0.63 cm teflon tubing to the injection port at

very low flow rates so that their respective concentrations were in the desired ppb levels in the test duct. Ozone was introduced by passing a metered flow of approximately 500 cc/min of ultra-high purity air through an electrical discharge ozone source, and then into the test air. Formaldehyde was introduced as a dilute aqueous solution by means of a syringe drive, through a heated probe which caused vaporization of the formaldehyde solution. The standard deviations of challenging concentration generated by the above-mentioned methods were 6.7-13% for ozone, sulfur dioxide, and nitrogen dioxide, and 24% for formaldehyde.

The flow rate of test air was also maintained at a constant level ($0.47 \text{ m}^3/\text{s} \pm 1\%$) using a blower with a variable speed motor. The temperature and relative humidity were not controlled. However, since the room air was used, the variations of temperature and relative humidity were small ($18\text{-}20^\circ\text{C}$ and $50\text{-}55\%$, respectively) during the test period. The GPAFE tested was of carbon impregnated filter type (contains 3-5 kg 20x60 mesh impregnated carbon). A total of seven filters arranged in series were used to treat $0.47 \text{ m}^3/\text{s}$ air flow.

The sulfur dioxide concentrations upstream and downstream of the GPAFE were continuously monitored by Thermo Environmental Model 43-S, which is a high-sensitivity version of the Thermo Environmental Model 43-A. The detection limit is 0.1 ppbv. Ozone was monitored by the Thermo Environmental Model 49 with a detection limit of 1 ppbv. Both instruments are designated by the EPA as an equivalent method used for measuring ambient pollutants (ref. 25). The LMA-3 monitor (ref. 26) was used for nitrogen dioxide. This is a relatively new instrument which provides extremely high sensitivity for nitrogen dioxide in a compact and rugged package. Formaldehyde was monitored by Battelle-developed instrument (ref. 27), which has been used for extensive sampling of indoor and outdoor air. The performance of the GPAFE was continuously monitored for 80 hours.

As one would expect, these instruments have proven to be valuable tools in monitoring the GPAFE performance under dynamic conditions. Since they are real-time instruments, any effects on GPAFE performance resulting from changes in environmental conditions (temperature, airflow, and relative humidity) and challenge concentrations, can be instantaneously detected. For example, about 50 hours into the test, the relative humidity suddenly dropped to about 40% as a cold front passed through the test site, bringing cold and dry air into the region. As the relative humidity dropped to 40%, there was a corresponding increase of SO_2 concentration downstream of GPAFE. At a later time, the downstream SO_2 concentration returned back to the previous level when relative humidity is adjusted to within the test conditions (50-55%). This instance demonstrates that a real-time instrument is a valuable tool in monitoring the GPAFE performance, especially in environments where frequent variations in environmental conditions as well as pollutant load are expected. If not for the real time instruments, the sudden increase of SO_2 downstream concentration might have been interpreted as a breakthrough, instead of what turned out to be a spike as a result of humidity change.

Since 1990, Weschler et al., (ref. 3) at Bellcore has been conducting an on-going study to monitor the performance of GPAFE in a quite large clean room. A total of 12 activated carbon adsorbers were installed in the air-handling unit servicing the cleanroom. Each adsorber contains 12 panels arranged in a zigzag configuration within a housing, and each panel contains 3.4 kg of virgin coconut shell carbon rated at 60% carbon tetrachloride activity. The air-handling unit treats only outside air; no recirculation air passes through the unit. The air flow through this unit is 10.2 m³/s. Filters with ASHRAE dust spot rating of 30% were installed upstream of the carbon adsorbers, and filters with ASHRAE dust spot rating of 85% were installed downstream of the carbon adsorbers.

Three gas-phase contaminants were monitored: ozone, selected VOCs and sulfur dioxide. Only the measurements of ozone and sulfur dioxide will be discussed here (the VOCs measurements will be discussed in Section 4.3). Ozone concentrations were measured with an ultraviolet (UV) photometric analyzer (254 nm; sensitivity: 1 ppb; precision: $\pm 1\%$ or 1 ppb, whichever is greater), sulfur dioxide concentrations were measured with a pulsed fluorescent analyzer (range: 0 to 500 ppbv; sensitivity: 1 ppbv; precision: $\pm 1\%$ or 1 ppbv, whichever is greater).

Since ozone and sulfur dioxide are outdoor pollutants in this test site, the indoor and outdoor concentrations were measured, and the effectiveness of the carbon adsorber is expressed as indoor/outdoor concentration ratio.

After one year of continuous service, the test results indicate that the I/O concentration ratio for ozone remains to be 0.1. This ratio was 0.7 prior to the installation of the carbon filters. After three years service, the ozone I/O ratio increased to 0.2-0.25. For sulfur dioxide, the I/O ratio is less than 0.1 after 17 months of the installation, and the I/O ratio is independent of outdoor sulfur dioxide concentration.

3.2 Active sampling methods

Various active sampling methods are available for measuring ppb levels of concentrations of many inorganic gases and organic vapors. These methods employ sorption tubes or canisters and pump to collect air samples. Subsequently, the sorbent tubes/canister are either analyzed at the test site, or sent back to a testing laboratory for contaminant analysis. Active sampling methods are often used by building researchers, consultants, and analytical labs for IAQ investigation and diagnostics. Table 3 lists the active sampling methods for various gases and vapors.

3.2.1 VOCs - there are three basic techniques for active sampling of airborne VOCs; solvent impingers, evacuated canisters with cryogenic trapping, and solid adsorbents. Solvent impingers are seldom used due to their lack of sensitivity. Therefore, only the last two sampling methods will be discussed:

3.2.1.1 Evacuated canister - ASTM D 5466 (ref. 28) describes a standard testing method for VOC sampling using evacuated canister technique. The canister sampling can be done in pressurized or subatmospheric modes. A sample of air is drawn through a sample train comprising components that regulate the rate and duration of sampling into a precleaned and pre-evacuated passivated canister. After the air sample is collected, the canister is transported to a laboratory for analysis. Upon receipt at the laboratory, the canister is attached to a pressure gauge to measure the final canister pressure. The water vapor collected in the canister may be removed by a Nafion dryer. Before the analysis, The VOCs collected in the canister are concentrated in a cryogenically-cooled trap. The cryogen is then removed and the temperature of the trap is raised. The VOCs are revolatilized and separated by a GC column, then detected by a mass spectrometer.

This sampling method is applicable to concentration of VOCs ranging from the detection limits of GC/MS used to 300 ppb by volume. Above this concentration, the sampling requires dilution with dry ultra high purity nitrogen or air. This sampling method is particularly well suited for the collection and analysis of complex VOC mixtures and is not subject to high volatility limitations. Subatmospheric pressure sampling may be used to collect grab samples (duration of 10 to 30 seconds) or time-integrated samples (duration of 12 to 24 hours) taken through a flow-restrictive inlet (for example, mass flow controller, vacuum regulator, or critical orifice). Pressurized sampling is used when long-term integrated samples or higher volume samples are required. The sample is collected in a canister using a pump and flow control arrangement to achieve a typical 103-206 kPa (15-30 psig) final canister pressure. For example, a 6-L evacuated canister can be filled at 7.1 cm³/min for 24 h to achieve a final pressure of about 144 kPa (15 psig).

For those applications where a membrane dryer is used, difficulties may arise in sample analysis if moisture accumulates in the dryer. This problem can be eliminated by a cleaning procedure that periodically heats the dryer to about 100 °C while purging with high purity air. Contamination may occur in the sampling system if canisters are not properly cleaned before use. Additionally, all other sampling equipment (for example, pump and flow controllers) must be thoroughly cleaned to ensure that the filling apparatus will not contaminate samples. In addition, sufficient system and field blank samples shall be analyzed to detect contamination as soon as it occurs. Instructions for cleaning the canister and certifying the field sampling systems are described in ASTM D 5466-93 Section 11.1 and 11.2 (ref. 28). Collection of pressurized samples in humid environments may result in condensation of water in sampling canisters. This water may prevent the recovery of polar compounds from the canister.

3.2.1.2 Solid adsorbent - the active sampling of VOCs can be accomplished by means of adsorption on porous materials such as activated charcoal, tenax, carbon molecular sieves, or graphitized carbon black using an adsorbent tube and a small portable sampling pump. The sampling procedure involves the collection of air sample into the adsorbent tube at a known rate through the pump for a fixed period of time. Then the tube with collected VOCs is sent back for GC (gas chromatography)/MS (mass spectrometry) analysis.

The most common adsorbents used in sampling VOCs are activated charcoal and tenax. The size of charcoal tube ranges from 100/50 to 800/400 mg, which means that the tube is divided into two sections with the front section containing 100 to 800 mg of activated charcoal and the back section containing 50 to 400 mg of activated charcoal. The 100/50 mg tube is most frequently used in sampling VOCs. Although activated charcoal is effective in collecting various VOCs, the collection efficiency can be affected by moisture present in the air sample. It is known that moisture level (>60% relative humidity) can reduce VOC adsorption capacity by as much as 50%, especially for low boiling point compounds. The other problem is sampling polar and reactive organic compounds, some of which may undergo chemical reactions on the charcoal surfaces to form other species. In addition, the thermal desorption of high boiling point compounds is not always quantitative. Tenax, on the other hand, is a chemically inert material and effective in sampling high boiling point compounds, but ineffective for sampling low boiling point VOCs (<70-80 °C). Tenax also suffers moisture effect, perhaps to a lesser extent than activated charcoal.

To collect a wide range of organic compounds in indoor environments, a multisorbent tube that contains several complementary materials should be used. One such sampler which contains a combination of Tenax-TA, Ambersorb XE-340, and activated charcoal has been used to characterize indoor VOCs in office buildings (ref. 29). Another kind of multisorbent tube (Figure 2) has also been used for sampling VOC in a product emission study (ref. 30) This multisorbent tube contains carbotrap (graphitized carbon black, 12 m²/g), carbotrap (graphitized carbon black, 100 m²/g), and carbonsieve S-111 (carbon molecular sieve, 800 m²/g).

After VOCs are collected in a sorbent tube, the collected VOCs must be recovered before being injected into GC/MS for analysis. Solvent extraction and high temperature desorption are the two most common methods used for the recovery of collected VOCs from the sampler. The identification and quantification of VOCs is done by GC/MS analysis. For analysis, the GC with a mass-spectrometric detector can be set to operate in the full scan mode or SIM mode. The GC/MS is set up for automatic and repetitive analysis. The system is comprised of a GC with a capillary or equivalent column for gas separation. The system also includes computer and software for data acquisition, reduction, and reporting. The column equipped in GC separates a VOC mixture as each compound elutes from the column at different times. This column separation is operated based on the principle of physical adsorption. As the VOC mixture passes through the column, the compounds will break through from the column in the order of increasing boiling point and decreasing order of polarizability of compound. The identification of compound is done by the retention time of the peak associated with each compound. This compound identification is often aided by a library database. When operated in full scan mode, qualitative identification can be confirmed and quantitative identification can be made for targeted compounds. The presence of other compounds not on the analytical target list may also be determined qualitatively. Full scan mode limits sensitivity to the range of 1 to 5 ppb by volume for most applicable compounds. In the SIM mode,

detection limits can be a factor of 10 or lower, approaching the same sensitivity as a GC multidetector system. However, SIM flexibility is limited because the MS is programmed to acquire data for a limited number of ions characteristic of targeted compounds while disregarding other acquired information. Therefore, the GC/MS-SIM procedure provides quantitation of a restricted targeted compound list of VOCs.

3.2.2 Formaldehyde - both EPA (ref. 31) and ASTM (ref. 32) provide standard test methods for determination of formaldehyde and other carbonyl compounds in air. Both methods are similar and use active sampler methodology. The method, specific to formaldehyde, can with some modifications, also detect many other types of aldehydes and ketones. This method uses an absorbing agent, 2,4-dinitro-phenylhydrazine (DNPH) to collect formaldehyde. By reacting with DNPH in an acidic environment, formaldehyde is readily converted to a stable DNPH derivative. This derivative is analyzed using high performance liquid chromatography (HPLC), equipped with an ultraviolet (UV) absorption detector operating at 360 nm. Formaldehyde or other carbonyl compounds in the sample are identified and quantified by comparison of their retention time and peak height, or peak areas with those of standard solutions.

The test begins with drawing a known volume of indoor air through a prepacked silica gel cartridge coated with acidified DNPH, at a sampling rate of 0.5 -1.2 L/min. for an appropriate period of time. After sampling, the sample cartridges are capped and placed in borosilicate glass culture tubes with polypropylene caps. The capped tubes are then placed in a friction-top can containing a pouch of charcoal and returned to the laboratory for analysis. Alternatively, the sample vials can be placed in a thermally-insulated box with appropriate padding for shipment to the laboratory. The cartridges may either be placed in cold storage until analysis, or immediately washed by gravity fed elution of 6 cm³ of acetonitrile from a plastic syringe reservoir to a graduated test tube or a 5 cm³ volumetric flask. The elute is then diluted to a known volume and refrigerated until analysis.

The DNPH method is suitable for determination of formaldehyde in the concentration range of low ppb to low ppm. It can be used for long-term (1-24 hour) or short-term (5 to 60 min) sampling of indoor air for formaldehyde. The sampling flow rate usually ranges between 0.5 and 1.2 L/min.

This test method has been used by two different laboratories to make over 1500 measurements of formaldehyde and other aldehydes in ambient air for the EPA Urban Air Toxics Program (UATP), conducted in 14 cities throughout the United States. The precision of 45 replicate HPLC injections of a stock solution of formaldehyde-DNPH derivative over a two-month period has been shown to be 0.85% relative standard deviation. Triplicate analysis of each of twelve identical samples of exposed DNPH cartridges provided formaldehyde measurements that agreed within 10.9%. The absolute percent differences between collocated duplicate sample sets from the 1988 UATP program were 11.8% for formaldehyde.

3.2.3 Nitrogen dioxide - the active sampling of nitrogen dioxide in indoor or ambient air is often accomplished by a colorimetric method based on the Griess-Saltzman reaction. ASTM D 1607 (ref. 33) describes such an active method.

For air sampling, assemble a fritted-tip bubbler (absorber) along with a mist eliminator, flow meter, pump, and mist eliminator. The fritted-tip bubbler contains 10 mL of absorbing agents (prepared by dissolving 5 g of anhydrous sulfanilic acid in one liter of water containing 149 mL glacial acetic acid). Draw an air sample through it at the rate of 0.4 L/min, long enough to develop sufficient color (about 10 to 60 min.). Measure the total air volume sampled, temperature and pressure (for air volume correction, if necessary). After sampling, development of the red-violet color is complete within 15 min at room temperature. Transfer to a stoppered cuvette and read in a spectrophotometer at 550 nm, using distilled water as a reference. If colors are too dark to read, unexposed adsorbing agent may be used to dilute the colors. Then multiply the measured absorbance by the dilution factor.

When sampling is conducted with fritted-tip bubblers, this test method is valid for determining nitrogen dioxide concentrations between 4 and 10 mg/m³ (0.002 and 5 ppm). The standard deviation of results obtained from a single analyst on separate samples from the same flowing air stream is $0.524 C^{1/2}$ (C from 10 to 400 µg/m³). Where C is concentration of nitrogen dioxide in µg. The standard deviation of single analyses, obtained from different laboratories taking separate samples from the flowing air stream is $0.517 + 1.27 C^{1/2}$ (C from 16 to 400 µg/m³).

For high concentration applications (>5 ppm), the active sampling of nitrogen dioxide can be accomplished using the phenol-disulfonic acid colorimetric procedures (ref. 34).

3.2.4 Sulfur dioxide - the active sampling for sulfur dioxide is also commonly carried out by colorimetric methods (see Figure 3). Sulfur dioxide is absorbed by aspirating a measured air sample through a tetrachloromercurate (TCM) solution, resulting the formation of a dichlorosulfonatomercurate complex. After the absorption is completed, any ozone in the solution is allowed to decay. The liquid is treated first with a solution of sulfamic acid to destroy the nitrite anion formed from the absorption of oxides of nitrogen present in the atmosphere. It is treated next with solutions of formaldehyde and specially purified acid-bleached pararosaniline containing phosphoric acid to control pH. Pararosaniline, formaldehyde, and bisulfite anion react to form the intensely colored pararosaniline methyl sulfonic acid.

In a 1-hour sampling, add 10 mL of TCM solution to a midjet impinger and insert it into the sampling system (see Figure 3). Collect the sample at approximately 0.5 L/min for 1 hour, using either a critical orifice or a needle valve to control flow. Shield the absorbing reagent from direct sunlight during and after sampling by covering the impinger to prevent deterioration. Keep the temperature of the absorbing solution below 25 °C. If the sample must be stored before analysis, maintain the temperature at 5 °C in a refrigerator. The 24-

hour sample procedure is similar to 1-hr sampling, except for the difference in amount of TCM solution (50 mL) and flow rate (0.2 L/min).

This test method is applicable in determining sulfur dioxide concentrations ranging from approximately $25 \mu\text{g}/\text{m}^3$ (0.01 ppm) to $1000 \mu\text{g}/\text{m}^3$ (0.4 ppm). The limit of detection, corresponding to twice the standard deviation, is $4 \mu\text{g}/\text{m}^3$ in a 24-hr sample, or $7 \mu\text{g}/\text{m}^3$ in a 1-h sample.

3.3 Passive sampling methods

Passive sampling techniques use a natural process called diffusion to collect air contaminants into the sampler. This collection process is done without any external devices such as pump, battery or tubes. Driven by the concentration difference, diffusion brings gaseous or vaporous contaminants from air into the sampler, and the contaminants are collected by the adsorbent or chemical reagent in the sampler. After a period of sampling time, the samplers are sent to testing laboratories and the collected contaminants are recovered and analyzed. Table 4 summarizes the passive sampling methods for various gaseous and vaporous contaminants.

The passive sampling methods were originally developed for monitoring the worker's exposure in industrial settings, and the sampling guidelines provided by manufacturers are geared towards OSHA and ACGIH (American Conference of Governmental Industrial Hygienists) standards. However, with some modifications in sampling time, these passive sampling methods are equally applicable to indoor air quality applications in commercial and institutional buildings.

3.3.1 VOCs - the passive VOC sampler generally consists of a diffusion screen (white film), a spacer, and a charcoal (activated carbon) sorbent pad assembled in a disk shaped plastic holder. The sampler can be clipped to the worker's lapel or pocket near the breathing zone to measure personal exposure, placed in a particular location to measure the VOC concentration in that space, or placed upstream and downstream of GPAFE to measure the removal efficiency.

Each VOC sampler comes sealed in an aluminum can. Sampling begins by removing the monitor from the can and recording the time. After sampling, the white film on the face of the monitor is removed and replaced with an impermeable cap; the time is again recorded. Samplers are typically analyzed soon after sampling. During the sampling period, the monitor should be placed at a location with adequate air movement (at least 25 fpm). Stagnant air at the face of the sampler will result in nonrepresentative sampling.

The sampling time of VOC passive monitor depends upon the VOC concentrations in air. For the compliance of OSHA or ACGIH standards in industrial environments, typical sampling time is 8 hours, chosen to be consistent with the TWA values (8-hour work day). However, for indoor air quality applications in commercial and institutional buildings, the

sampling time is typically extended to one-four weeks. The reason for this is that the VOC concentration is at least three orders of magnitude lower than the concentrations encountered in industrial applications.

After the completion of sampling, the collected VOCs in the samplers are desorbed using the extraction method. In most cases, carbon disulfide is used. Typically, this extraction procedure is conducted by placing the charcoal pad in a vial into which 1-2 mL carbon disulfide is added, then the vial is gently vibrated for 30-60 mins to desorb VOCs from the charcoal pad. After the extraction, a 1 or 2 μL aliquot is injected into GC/MS for VOC analysis.

The VOCs data from the GC/MS analysis are reported as the weights (μg) of individual organic compounds that are collected during air sampling. By knowing the sampling rate, sampling time, recovery coefficient, and the weight collected, the concentration of a particular compound can be calculated.

The validity of passive organic monitors for indoor air applications has been studied extensively. Cohen et al. (ref. 35) conducted a set of controlled chamber experiments to validate the passive samplers (3M OVM (Organic Vapor Monitor) 3500) for five compounds (chloroform, benzene, heptane, perchlorethylene, and dichlorobenzene), two concentration levels (10 and 100 $\mu\text{g}/\text{m}^3$) and two relative humidity levels (20 and 70%). Shield and Weschler (ref. 36), conducted a field study by using passive sampler (3M OVM 3500) to monitor VOCs concentrations in telephone switch offices (New Jersey). The results of these two studies indicated that the accuracy of passive VOC samplers is typically $\pm 25\%$ with 95% confidence level. One interlaboratory study was conducted in Europe by De Bortoli et al. (ref. 37), where the OVMs were exposed for four days to concentrations of butanol, xylene, pinene, and decane from 25 to 1500 $\mu\text{g}/\text{m}^3$. Except for butanol and pentanol all deviations between the passive and active measurement were less than 21 percent. The deviation between the predicted value and the passive measurement ranged between -34 and +15 percent for all compounds except butanol and pentanol. The errors arise from the loss of contaminants during collection and recovery. The study conducted by Seifert and Abraham (ref. 38) has shown that the 3M OVM passive samplers can be used as valid sampling techniques for a wide range of VOCs. This group exposed the samplers in a chamber for a 2-week period and measured concentration that varied from predicted by between 1 and 22 %.

Based on the analysis of blank sample, Shield and Weschler (ref. 36) assessed that the detection limit would be 0.06 $\mu\text{g}/\text{m}^3$ for compounds with boiling point higher than 175 $^{\circ}\text{C}$. This is based on the assumption that a value three times the blank value is required for unambiguous detection. This detection is low enough to allow passive sampling technique to measure the indoor concentration of most organic compounds.

Passive VOC samplers have been used to monitor the removal efficiencies of GPAFE in the field. In the Weschler study (ref. 3), selected VOCs were measured using passive

samplers (3M OVM 3500, accuracy: 25%, reproducibility: 13% of the mean value, sensitivity: 0.06 $\mu\text{g}/\text{m}^3$).

For measuring VOCs removal efficiencies, three replicate passive samplers were placed upstream of the carbon adsorber, and another three samples downstream of the carbon adsorber. The single pass efficiency of adsorber is calculated from the difference in concentration measured upstream and downstream of the carbon adsorber. For subsequent collection periods, the samplers were positioned identically. The sampling time is 4-6 weeks. Prior to the VOC analysis, each passive sampler was spiked with an internal standard and then extracted with 1 mL of carbon disulfide solution. Organic compounds contained in the extract were separated and identified using standard GC/MS procedures.

The single-pass efficiencies of the carbon adsorber for selected VOCs are in the range of 60-90% after one year of continuous service (ref. 36).

3.3.2 Formaldehyde - ASTM D 5014-94 (ref. 39) describes a standard test method for measurement of formaldehyde in indoor air using passive sampler methodology. In this method formaldehyde is collected in a diffusion tube and analyzed by a colorimetric method using 3-methyl-2-benzothiazolinone hydrazone hydrochloride (MBTH).

During sampling, formaldehyde is absorbed into a 0.05% aqueous solution of MBTH contained in a glass vial, which comes with a septum cap that retains a Knudsen disk. During air sampling the vial is inverted to establish contact between the absorbing liquid and the Knudsen disk. Formaldehyde diffuses from the ambient atmosphere into the MBTH solution through the Knudsen disk at a constant rate. After collection, the resulting azine is oxidized by a ferric chloride-sulfamic acid solution to form a blue cationic dye in acidic medium. The concentration of the blue cation is measured by colorimetry at 628 nm. The concentration of formaldehyde is computed from the amount of formaldehyde collected divided by the product of the diffusion rate and the time of exposure.

At heart of this test method lies the Knudsen disk, which provides a constant sampling rate of formaldehyde. This disk is also a gas barrier that prevents the interference of other aldehyde compounds. The Knudsen disk is made of polytetrafluoroethylene membranes of 0.07 mm thickness and 0.02 μm pore sizes. Using the prescribed sampler, the Knudsen disk allows the ambient atmosphere to be sampled for formaldehyde at a constant rate of approximately 11.6 mL/min independent of air flow velocity ranging from 0.13 to 1.3 m/s (25 to 250 ft/min). The sampling rate normally is provided by the supplier of the Knudsen disks, but may also be determined experimentally in accordance with the procedures described in ASTM D5014-94, Section 10.3.

This test method allows field measurement of formaldehyde in indoor air at concentrations from 0.01 to 17 mg/m^3 (0.008 to 14 ppm) using sampling times between 15 mins and 24 hours. A 24-hour sampling time is recommended to measure time-weighted average

formaldehyde concentration ranging from 0.01 to 0.2 mg/m³ (0.008 to 0.16 ppm, v/v) in offices and residences. An 8-h sampling time allows measurement ranging from 0.03 to 0.6 mg/m³ (0.025 to 0.5 ppm, v/v). The test method is suitable for both area and personal monitoring. In addition, this test method allows sampling and quantification of formaldehyde under field conditions with the aid of a portable field colorimeter, without any laboratory support.

The MBTH method of analysis was checked for reproducibility by three different laboratories. The results agreed within $\pm 5\%$. During the development of this test method, five independent sets of ten samplers were each exposed to laboratory test atmospheres of formaldehyde between 0.1 and 1 mg/m³ for 4-h periods. A linear relationship between the formaldehyde concentration and the amount collected by the sampler was observed. The mean coefficient of variation and bias determined for the five sets of data were 5.0 and 1.2%, respectively. Additional experiments examined the effect of air velocity impinging upon the sampler. Four independent sets of twenty devices were each exposed to face velocities between 0.13 and 1.3 m/s (25 and 250 fpm). The MCV (mean coefficient of variation) and the mean bias for these data were 4.1% and 2.1%, respectively.

This test method has also been checked in field study (ref. 39). In this study, the samplers were exposed to formaldehyde concentrations between 0.05 and 0.5 mg/m³ for 5-hr periods in a carpeted room with gypsum board walls. Reference samplers were collected over 30-min periods at approximately 45 min intervals following the procedure recommended in NIOSH P&CAM 125. The mean bias and MCV were -4.8 and 7.3%, respectively, leading to an OSA (overall system accuracy) of $\pm 19.8\%$.

There is another type of passive test method for formaldehyde. This formaldehyde sampler is a badge-shaped device used for either personal or area monitoring. Bisulfite-impregnated adsorbent is used to collect formaldehyde (convert formaldehyde to a less volatile product). It is known that this test method is liable to humidity effects since the reaction between formaldehyde and bisulfite is sensitive to water vapor. For this reason, it will be advisable to use the badge equipped with an additional section for controlling relative humidity during sampling.

This passive method, with the incorporation of humidity control, has been tested to determine the interference effect of other compounds such as isopropyl alcohol and phenol. The test results indicated that isopropyl alcohol does not interfere with the formaldehyde measurements. However, the presence of phenol will interfere with the formaldehyde measurements. At similar concentrations, the presence of phenol causes approximately a 20% reduction in the level of formaldehyde reported by the monitors. This interference effect can be corrected by increasing the concentration of chromotropic acid in the analytical procedure from 1% to 5%. It is recommended that the 5% chromotropic acid be used in the analysis whenever phenol is suspected of being present during the formaldehyde sampling period. The reliable quantitation level in the analytical procedure is 3.6 μg . With the sampling rate of this monitor at 4.52 μg per ppm-hr, this is equivalent to sampling 0.1 ppm in 8 hours.

3.3.3 Nitrogen dioxide - the nitrogen dioxide passive sampling method was first developed by Palmes in 1976 (ref. 40), and the sampling tube he developed is often referred to by others as the Palmes Tube. As a matter of fact, Dr. Palmes pioneered the passive sampling techniques for sulfur dioxide in 1973 (ref. 41), then developed the technique for nitrogen dioxide.

The Palmes tube is made of acrylic tubing with a length of 7.1 cm and an inside diameter of 0.95 cm (the area/length ratio is 0.1 cm). The collecting media is triethanolamine (TEA), which is coated on stainless steel grids (40 x 40 per inch mesh and 0.25 mm diameter wire). Three of these wafer-shape stainless steel grids coated with TEA were stacked at the bottom of a 1.27 x 1.27 cm sleeve type low density polyethylene cap. This cap was then fixed at one end of the tube, holding the TEA coated screens in position. The device is designed simply to be used in the field, light weight (7 g) and unbreakable. It is designed to be worn with the exposed end of the tube in downward position since diffusion is independent of gravity. In addition, wearing the sampler open end down would keep dust or water from falling into the open end of the tube. A schematic diagram of a personal NO₂ sampler is shown in Figure 4.

The TEA coating involves three steps; cleaning of stainless steel (dipping into ultrasonic bath, rinsing with distilled water, and drying in an oven at 125 °C), dipping into a 50% volume/volume solution of TEA in acetone, and evaporating of acetone (first, excess TEA/acetone solution was removed by placing on absorbent paper, then acetone was evaporated by allowing 15 minutes waiting time). This procedure gave an average TEA loading of 0.95 mg/screen. This is equivalent to 6.4 μmole TEA per screen or 19 μmole for the three screens used in each sampler. This represents a very large amount capacity for NO₂ collection considering that quantities of NO₂ to be collected are often less than 100 nanomoles.

The amount of NO₂ collected in a TEA-coated screen was determined by a colormetric method. After the sampling, the TEA-coated screen is transferred from the sampling tube to a glass-stoppered graduate in which the adsorbing solution was added to a volume of 55 mL. After vigorous shaking for about 30 seconds (allows a few minutes for solid to settle), 10 mL of the solution was then transferred to another glass-stoppered graduate. Before the absorbance measurements, 10 minutes was allowed for complete color development. The amount of NO ion was measured using the standard curve prepared from a standard NO₂ ion solution. The absorbing solution was made of sulfanilamide, NEDA, and hydrogen peroxide. The standard solution was produced by dissolving 0.15 grams of reagent-grade sodium nitrite in distilled water, and diluted to 1 liter. This solution contained 100 μg of NO₂ (ion) per milliliter.

The accuracy of this method is about ±10-15%, and the sensitivity is in a few ppb range.

3.3.4 Ozone - the passive method for sampling indoor ozone has been developed recently (ref. 42-43), and is now commercially available. This technique is based on the oxidation reaction of nitrite (NO_2) to form nitrate (NO_3^-). The passive ozone sampler is a barrel-shaped device with a clip. The sampler contains two glass-fiber filters coated with potassium carbonate (K_2CO_3) and sodium nitrite (NaNO_2). After nitrate is formed from the oxidation reaction of nitrite, the amount of nitrate is determined by using ion chromatography. The average ozone concentration is calculated from the measured nitrate concentration and a known sampling rate. This technique has been validated by controlled laboratory tests at typical ambient ozone concentrations (40 ppb to 100 ppb) under relative humidities and temperatures varying from 10 to 80% and 0 and 40 °C, respectively. The limit of detection for the passive sampler is 17 ppb for 12 hour measurements and the precision is $\pm 9.8\%$ at lower concentration and $\pm 7\%$ at higher concentrations (ref. 42).

This sampling method has also been verified in a field study (ref. 42). In this study, indoor and outdoor samples were collected from 23 non-smoking households. All homes were located within residential neighborhoods. Monitoring was conducted at each home for 5-day period. In each home, indoor samples were collected over 12 hours for all daytime periods at various locations, such as main activity rooms (at least 1 meter from walls), window air conditioners, and other ventilation devices, (1.2 meter above the floor to avoid effects from turbulence). Outdoor ozone concentrations were measured using passive samplers placed outside homes, at least 1 meter from walls, trees, and other large subjects. Outdoor ozone sampling time was 24 hours.

For method validation purposes, ozone concentrations were also measured at a stationary ambient monitoring (SAM) site using an UV photometric ambient ozone analyzer, in addition to the passive ozone samplers. The UV analyzer is designated as an equivalent method for ambient ozone measurements by the U.S. EPA. The lower detection limit for the UV analyzer is 2 ppb with a precision of 2 ppb. Daytime ozone concentrations measured by the continuous monitor at the SAM site ranged from 28 to 92 ppb, with a mean of 55 ± 15 ppb. The collected daytime passive samplers measured ozone at levels ranging from 31 to 95 ppb, with a mean being 56 ± 16 ppb. Nighttime ozone concentrations measured by the passive samplers also ranged from 3 to 40 ppb, with a mean of 19 ± 9 ppb. The relative error of the passive sampler measurements was calculated to be 15% for daytime and 25% for nighttime samples. The higher relative error for nighttime samples may be due to the low nighttime ozone concentrations; it represents an absolute uncertainty of only 5 ppb.

3.3.5 Sulfur dioxide & nitrous acid - the monitor consists of a polystyrene cartridge closed on one end and covered on the other by a diffusion barrier made of Gore-tex membrane. The cartridge is 3.8 cm in diameter and attaches to surfaces by a metal clip. The passive monitors are assembled in a clean air hood. The cartridge contains a 37 mm sodium carbonate treated glass fiber filter which is the collecting medium for the nitrous acid (HONO) and sulfur dioxide (SO_2). After the sampling, the monitor is analyzed by ion chromatography.

This passive monitor (ref. 44) was tested in an environmental chamber for the effect of humidity (25-80%), and over a limited range of HONO (40-110 ppb), SO₂ (180-250 ppb) concentrations, and sampling times (2-43 hours). To validate this passive sampling technique, continuous monitoring (EPA equivalent test protocols) instruments were used as reference to compare the concentration measured by the passive monitor.

For nitrous acid, the sampling rate is 100 mL/min (± 14.8), and the limit of detection based on the ion chromatography analysis is 7.1 nmoles HONO, equivalent to 29 ppb-hr. For sulfur dioxide, the sampling rate is 41 mL/min (± 3.4), and the limit of detection is 52.6 ppb-hr. (requires at least one hour sampling time if the concentration is 52.6 ppb, and 10 hours if the concentration is 5.26 ppb). For both gases, excellent agreement was found between concentrations measured by the reference instrument and passive sampling technique, although the accuracy is higher for sulfur dioxide than nitrous acid ($\pm 20\%$ for nitrous acid and $\pm 10\%$ for sulfur dioxide). Relative humidity was found to have no significant effect on the sampling rate of either gas.

4.0 An application guide

The selection of field methods for GPAFE testing depends largely upon the application needs and cost. For this purpose, Table 5 compares various types of test methods in terms of capability, sampling requirements, availability, and cost. Furthermore, information regarding the sampling procedures for GPAFE testing, accuracy, and detection limit for each test method will be provided in this section. It must be stressed that with the exception of real-time instruments, the methods outlined in this section have not been verified or demonstrated for GPAFE testings.

4.1 Ozone, sulfur dioxide, and nitrogen dioxide real-time instruments

As discussed previously, the unique advantage of using real-time instruments for GPAFE testing is that they provide near real-time data. This is especially useful if users would like to investigate the effects of contaminant concentration and environmental conditions (e.g., relative humidity, airflow rate, and temperature) on the removal efficiency of GPAFE under dynamic conditions.

The real-time instruments for ozone, sulfur dioxide, and nitrogen dioxide are well-developed, and these monitors provide excellent reliability, accuracy, detection limit, and data acquisition and communication capability. The continuous measurements of ppb levels of ozone are based on the absorption of ultraviolet radiation at 254 nm wavelength. The measurements of sulfur dioxide are commonly based on pulsed fluorescence technique. NO-NO₂ is based on chemiluminescence technique. The performance specifications of these real-time instruments can be obtained from the manufacturers, and should meet the performance specifications in Table 6.

4.1.1 Air sampling - sampling of outdoor or indoor air should be conducted in accordance with the guidelines provided by EPA and ASTM (ref. 44-47). For ozone sampling, special attention should be given to ensure accurate measurements. The sampling tubes should be made of inert material (e.g., PTFE fluorocarbon), and the sampling line should be short and direct, preferably not more than 5 m in length. Since ozone in ambient air can easily be created and destroyed under direct exposure to bright sunlight via a series of photochemical reactions, the air sampling points should be in a shady location or protected from direct exposure to bright sunlight. When the sampling air is hot and humid, neither the sample line nor its path through the instrument should be cooled to the condensation point, since ozone is soluble and rapidly destroyed by condensate. Situations in which the analyzer will be exposed to rapid and frequent changes of ambient temperature should be avoided. Many instruments compensate for slow changes in ambient temperature, but do not respond well to the rapid changes often found in small air monitoring stations, which may exceed 1 °C/min.

The removal efficiency of GPAFE can be determined by sequential sampling upstream and downstream of GPAFE through the use of a three-way valve. Due to the concentration differences before and after GPAFE, adequate purging should be provided to prevent memory effect before switching the sampling valve, or the initial data after switching the sample valve should be ignored. The upstream location should be 2-3 inches from the GPAFE and the downstream location should be 8-10 feet away from GPAFE.

4.1.2 Applications - although real-time instruments are ideal for monitoring the removal efficiency and service life of GPAFE, the cost is prohibitive for building engineers to use for general purpose IAQ applications.

These instruments are primarily used for ambient air quality monitoring (e.g., EPA), for laboratory evaluation of GPAFE, and for monitoring of a critical environment or process. Although not used extensively, these instruments have been used as a reference to validate active or passive sampling techniques. They have also been used to control the concentration of targeted contaminants in conjunction with building DDC control and the use of appropriate GPAFE.

4.2 Active sampling methods

Active air samplings are the most common methods used today for air sampling. These methods are very accurate and sampling time is relatively short, typically one to eight hours. This method provides integrated concentration data over the sampling period of time. Therefore, one can not use this method to investigate the performance of GPAFE under dynamic conditions.

Active sampling uses pump and flow equipment to draw air into the sampling tubes. After sampling, the collected contaminants are either analyzed on the test sites, or sent back to

laboratories for analysis. Active sampling test methods are available for VOCs, nitrogen dioxide, oxides of nitrogen, sulfur dioxide, formaldehyde, and many other gases. These methods are summarized in Tables 7-10. The active sampling and analysis are usually provided for by testing laboratories and consulting firms.

4.2.1 GPAFE testing - since the sampling time of active methods is rather short, it is essential to have a good communication and planning among building engineer, testing laboratory, and GPAFE manufacturer in terms of the intent of testing, the contaminants to be measured, an expected concentration range of targeted contaminants, sampling locations, and timing for sampling. In addition, all the relevant data prior to and during air sampling period should be collected (e.g., flow rate, relative humidity and temperature of airflow through GPAFE) in order to properly interpret the test results over such a short period of sampling time.

A guide for GPAFE testing is suggested as follows:

- a. Prior to the sampling, calibrate the sampling system including pump, flow regulator, tubing to be used.
- b. Follow manufacturer's instructions on air sampling procedures.
- c. For measuring removal efficiency of GPAFE, the sampling points, both upstream and downstream of GPAFE, should be in the locations where the airflow is well mixed, and as close to GPAFE as possible. Generally, the distance is 5-15 cm upstream of GPAFE, and 2.4-3 m downstream of GPAFE. For large GPAFE installation, duplicate samplings may be required to obtain a good average upstream and downstream concentration.
- d. For measuring removal efficiency of GPAFE, simultaneous air sampling should be conducted at upstream and downstream location of GPAFE, especially when sampling time is short.
- e. Sampling volumes (or time) - The minimum sample volume (time) is governed by the detection limit of the analytical method, and the maximum sample volume is determined by the capacity of media used to collect the contaminants. Due to the concentration difference between upstream and downstream of GPAFE, larger sampling volume (higher flow rate or longer sampling time) may be required at downstream locations to ensure the amount of contaminant collected is well above the detection limit of the analytical method.
- f. A sample flow rate of less than 10 mL/min should not be used. Calculations based upon diffusion coefficient for several compounds indicate that sampling at less than 10 mL/min may not give accurate results.

g. It is recommended that at least one sampling tube should be presented for analysis as a field blank with every 10 or 15 samples. The purpose of the field blank is to check if the sampling tubes are contaminated prior to and during the sampling. If a field blank shows contamination, results from the field blank should not be used to correct sample results, and the samples taken during the test must be assumed to be contaminated.

h. During air sampling, collect all the relevant data that can affect the GPAFE performance such as temperature, relative humidity and airflow rate.

4.2.2 Applications - since the cost of active sampling and analysis is expensive and sampling time is relatively short (1-8 hours), active sampling methods are recommended to be used for measuring initial efficiency of GPAFE shortly after the installation (for the purpose of performance verification), or checking its efficiency when there is a need to do so (e.g., significant changes in pollutant loads or design conditions). The active sampling method should also be used when there is a reason to believe that the installed GPAFE is no longer working (e.g., smelling odors). Active sampling is unsuitable for use as a routine field method for monitoring the service life of GPAFE due to the number of tests required and associated cost over the life time of GPAFE. The cost of a single test is at least a few hundred dollars.

4.3 Passive sampling methods

Passive air sampling is the most cost-effective, easy-to-operate test method for air sampling. Since this technique uses a natural process called diffusion to collect contaminants on the sampler, all that is required is to place the passive sampler in a location of interest and allow sufficient time for the sampler to collect an adequate amount of contaminants for analysis. It does not require any external devices such as pump, tubing, flow meter, calibration kit, or power source. The passive sample is often in the form of a badge or cartridge, which can be clipped onto a worker's clothes as a personnel monitor or hung in an indoor space as an area monitor. After sampling, the sampler is sent back to the manufacturer or laboratory for analysis.

Passive sampling is generally less accurate than either real-time instruments or active sampling methods due to the loss in contaminant collection and recovery. In addition, the required sampling time is longer. In spite of this, passive sampling appears to be the most attractive method for monitoring GPAFE performance due to its low cost and ease of sampling.

It is important to conduct the passive sampling test on a regular basis and to collect all the relevant data that can affect the GPAFE performance. By doing so, test data collected at different periods of service time can be plotted to reliably determine when to change GPAFE, and to assess the irregular behavior of GPAFE due to the changes in pollutant loads and environmental conditions.

The passive sampling methods for VOCs, nitrogen dioxide, and formaldehyde have been available for many years. New techniques have been developed for measuring ozone and sulfur dioxide concentrations, and they are now commercially available. These methods are summarized in Table 11-15. A list of manufacturers and suppliers for passive samplers are given in Table 16.

Most test protocols developed for passive sampling of low levels of inorganic gases (ozone, sulfur dioxide, formaldehyde, and nitrogen dioxide) in indoor air may be directly applied to measure VOC efficiency of GPAFE without significant modifications. However, for VOCs, the test protocol must be simplified in terms of compound selection for analysis since it is impractical to track down all the individual compounds in a complex VOC mixture. To simplify the analysis and reduce the cost, compound selection for VOCs will be discussed in Section 7.

4.3.1 GPAFE testing - a guide for GPAFE testing is suggested as follows:

- a. Open the sampler container at the time sampling is to be initiated.
- b. Follow the manufacturer's instruction for air sampling procedures.
- c. Ensure that the air velocity at the sampler position is above the minimum velocity recommended by the manufacturer (typically 0.13 m/s). Avoid sampling stagnant areas such as against walls or in corners of rooms.
- d. Follow manufacturer's instruction for sampling time. The minimum sampling time is governed by the sampling rate and the sensitivity of the analytical method. The maximum sampling time is determined by the sampling rate and the removal capacity of media used to collect contaminants. Due to the concentration difference between upstream and downstream of GPAFE, larger sampling volume (higher flow rate or longer sampling time) may be required at downstream locations to ensure the amount of contaminant collected is well above the detection limit of the analytical method.
- e. Since the accuracies of passive sampling for concentration measurements typically are $\pm 15 - \pm 25\%$ depending upon type of gases to be measured, a minimum of two samplers should be placed both upstream and downstream of GPAFE in order to obtain a good average value. Theoretically, the errors in efficiency measurements could be as large as $\pm 50\%$. However, the use of the duplicate samplers should minimize the errors to some extent.
- f. At the end of the sampling period, the sampler should be removed and the sampling time recorded. The sealed samples should be send to the laboratory for analysis.

4.3.2 Handling and shipping - the chemical species collected on passive samplers may be exposed to a variety of handling, shipping, and storage conditions. Certain precautions should be taken to minimize the losses and extraneous contamination.

- a. Samples should be sealed securely and identified clearly.
- b. Samples collected should be kept at room temperature or below and not exposed to direct sunlight (especially for VOCs and ozone samplers).
- c. If samplers are to be shipped in aircraft cargo holds, the preferred procedure is to carry the samples on board. The individual carrying the samples should be cognizant of federal regulations limiting or prohibiting the transport of certain materials aboard aircraft and take the appropriate action to ensure compliance.
- d. Samplers should be shipped as soon after sampling as possible, and analyzed as soon as possible (not to exceed five working days).
- e. Bulk solvent samples should never be shipped or stored directly with the collected air samples.

4.3.3 Applications - For indoor air sampling, the passive sampling technique is ideal for large scale field studies since the use of active samplers may be out of the question due to the potentially high variability of contaminant concentrations. It is also ideal for use to investigate the effect of contaminant exposure on chronic health effect, since it would require a sampler with much longer exposure duration than the typical 8-12 hours in active sampling.

For GPAFE testing, the passive sampling technique is recommended to be used as a routine test method used by building operation & maintenance personnel to monitor the removal efficiency and service life of installed GPAFE. Essentially, there is no training required except that the proper procedures shall be followed regarding sampling locations, sampling time, storage (if necessary), and packaging (for shipping the samplers back to manufacturers and analytical laboratories). In most cases, the shipping can be done by mail, since the samplers are small enough to fit inside an envelope.

5.0 Test methods from GPAFE manufacturers

Several air filter manufacturers provide test methods for determining the remaining life of GPAFE. Instead of measuring the contaminants in the air, the methods determine what is in the filter. These methods are outlined as follows:

5.1 Remaining carbon tetrachloride activity - this method is intended for assessing the remaining life of activated carbon for VOCs removal. In summary, the method includes the following steps:

- a. The in-service carbon sample is taken out of the installed GPAFE and sent back to the manufacturer for analysis.
- b. The carbon tetrachloride (CCl_4) activity test (ref. 10) is used to measure the remaining CCl_4 activity of the in-service carbon sample.
- c. The manufacturer reports the remaining life (%) of activated carbon based on the difference of CCl_4 activities between the new and in-service carbon. Some manufacturers use this test method only as an indicator for carbon changeout.

Obviously, this is an over-simplified method for estimating the remaining life of activated carbon for VOCs. If the remaining life is to be reported, the conclusion should be as conservative as possible. Nevertheless, it is still a useful method for determining the saturation life of carbon if the test is conducted on a regular basis. It can be stated with caution that the in-service carbon is saturated with respect to VOCs when the remaining CCl_4 activity decreases to a constant level. However, the effect of relative humidity has to be considered in the interpretation of test data.

5.2 TVOC loading analysis - this is an improved method for determining the saturation life of activated carbon for TVOC. Instead of using a surrogate compound, this method directly measures the TVOC loading from the field conditions. The TVOC loading of in-service carbon sample is measured from the difference of two ASTM test methods. The total volatile test (ref. 48) determines TVOC plus moisture contents, and the xylene extraction test (ref. 49) determines the moisture content. A reliable decision on carbon changeout can be made by monitoring of TVOC loadings on a regular basis.

Furthermore, with a database it is possible from a single TVOC loading test to predict the remaining adsorption capacity for TVOC. Unfortunately, such database does not exist at this time.

5.3 KMNO_4 content analysis - this method is intended for use as a routine test method for determining the remaining activity (e.g., impregnate content) of KMNO_4 -based material. The test method is available from various manufacturers. For the purpose of

adsorbent changeout, many manufacturers provide useful commentary recommendations (e.g., safe, borderline, change, change immediately) based on the range of the KMNO_4 content.

6.0 Recommendations

As discussed in this report, there are three types of test methods that can be used to determine the effectiveness of installed GPAFE in commercial and public buildings for indoor air quality purposes.

Although real-time instruments are ideal for monitoring the removal efficiency and service life of GPAFE, the cost prevents building engineers from such use.

Active sampling is an accurate, short term test method. It is most suitable for building engineers to validate the removal efficiency of GPAFE shortly after the installation, or at any time when there is an urgent need to check its removal efficiency. Such situations may occur when there is an anticipated increase in pollutant loads (e.g., building renovation or painting activity) or there is reasonable doubt that GPAFE is no longer working (e.g., worker complaints of poor air quality or odors).

Passive sampling, because of its low cost and ease of operation, has the potential to be the most attractive field method for GPAFE testing. Although certain limitations may apply, this technique in general has the capability of sampling air over a very large time span, say from a few hours to a few weeks, without sacrificing its accuracy. This flexibility makes it ideal for both short term and long term monitoring of a wide range of GPAFE. Passive sampling methods are available for a wide range of contaminants including VOCs, ozone, nitrogen dioxide, formaldehyde, and sulfur dioxide. In order to reliably determine when to change GPAFE, it may be necessary for building engineers to set up a GPAFE monitoring program in which passive sampling for targeted contaminants is conducted on a regular basis. This sampling program can be very cost effective, since the cost of each sampling (including analysis) is considerably less than \$100, and the shipping of samplers (for analysis) can be done by mail.

As pointed out in this report, both active and passive sampling methods have been widely used for ambient and indoor air sampling. However, the use of these methods for field testing of GPAFE is still a new application, and this kind of test data is almost non-existent in public domain. Therefore, it would be necessary to conduct a field study to collect actual test data for various contaminants under representative use of GPAFE, particularly in office buildings, and use these data to prepare a complete document on the test protocols that can be implemented by building engineers.

To properly apply these techniques for field testing of GPAFE, several key issues need to be addressed in Phase 2 of this research project as follows:

Sampling time - The sampling time must be long enough to collect adequate amount of sample for subsequent analysis. This would depend upon the sampling rate of a particular method and contaminant concentrations. A guideline must be provided with respect to each method and concentration range.

Sampling location - Ideally, the sampling locations shall be such that they measure the representative upstream and downstream concentrations of GPAFE. We recommend sample locations 5-15 cm in front of GPAFE for upstream sampling and 2.4-3 m for downstream sampling (this distance is a conservative estimate for achieving uniform mixing of air flow). However, in many instances, the air flow may not be well mixed right before entering the GPAFE due to the improper installation, or simply there is no 2.4-3 m duct space for downstream sampling. For these situations, the traverse sampling is required to obtain a good average of concentration. The guideline shall identify such installations and the protocols for traverse sampling.

Effect of flow velocity - The duct velocity in GPAFE installations is typically in the range of 0.19-0.28 m³/s. Currently, there are no test data available to assess the effect of such high velocity on the accuracy of both active or passive sampling. This issue needs to be fully investigated. If such effect does exist, the corrections shall be given to account for duct velocity.

7.0 Scope of phase 2 work

7.1 Objectives - the objectives for phase 2 of this research project will focus on the following:

- a. Conduct a field test program to determine and monitor the effectiveness of GPAFE used in buildings for indoor air quality purposes.
- b. Based on the collected test results, validate and refine the test protocols and application guide outlined in the Phase 1 report.
- c. Prepare documentation that allows building engineers to implement the cost-effective test protocols for determining or monitoring the performance of installed GPAFE for indoor air quality applications.

7.2 Targeted gaseous and vaporous contaminants - for any air sampling, one must first determine what contaminants are to be measured. For general purpose IAQ in office buildings, it has largely been agreed that volatile organic compounds, ozone, formaldehyde, sulfur dioxide, and various forms of oxides of nitrogen (NO₂-NO) are the most common or prevailing contaminants in terms of their abundance in buildings and health effect on occupants.

For VOCs, there is a long list of compounds of measurable concentrations in indoor air. Even with passive sampling, this may significantly increase the analysis cost and create difficulty and confusion in data interpretation and management if all the individual compounds are to be measured. As discussed in this report, the adsorption capacity of activated carbon is primarily determined by the boiling point of compounds. Therefore, the breakthrough behavior of a VOC mixture on a carbon bed is such that low boiling point compounds will break through first, followed by compounds with medium boiling points. The carbon bed is near complete saturation when high boiling point compounds start to break through. Compounds with similar boiling points will break through at about the same time period. This predictable behavior makes it possible to select three compounds with distinctly different boiling points to represent the breakthrough of a whole VOC mixture. In this regard, three compounds, heptane, toluene, and ethyl benzene are recommended. The service life can be based on heptane removal efficiency if one elects to use complete removal of all VOCs as a criterion for GPAFE changeout, toluene efficiency if the criterion is based on TVOC, or ethylbenzene if one elects to change GPAFE when it is completely saturated and no longer can remove any VOCs. We recommend the use of toluene as most indoor air guidelines for VOCs are based on the concentration of TVOC.

7.3 Type of building - this program will select office buildings as the main test sites. However, other building environments such as airports, hospitals, museums, archives, and schools should also be included. Indoor air quality in these environments is an important issue as well. Furthermore, these environments are more motivated to maintain acceptable indoor air quality and are likely to have gas-phase air filtration equipment in the HVAC systems. A good mixture of building selection will be three office buildings with different pollutant loads (new, renovated, and existing) and HVAC systems (VAV and CAV), and three buildings selected from airports, hospitals, museums, archives, and one school.

7.4 Type of GPAFE - the program will include various types of GPAFE that have representative use in buildings for indoor air quality purposes. Although this may have no significant impact on the test method itself, the data obtained may help engineers to evaluate and select GPAFE for their applications. Furthermore, these data may serve as a baseline or frame work for engineers to estimate removal efficiency and service life of various GPAFE in field conditions.

The GPAFE selection can be based on type (panel or pleated type), type of adsorbent, amount of adsorbent, and particle size of adsorbent.

7.5 Sampling methods and programs - the objective of this research project is to come up with a cost-effective and reliable field test method for GPAFE testing. In this regard, the program shall include both active and passive sampling methods for GPAFE testing, with particular emphasis on passive sampling techniques. Several specific programs are suggested as follows:

- a. Establish test protocols for using passive sampling methods to determine the service life of GPAFE (long term). All the test sites will be monitored with passive sampling methods for at least twelve months or until GPAFE shows no remaining capacity left to remove these contaminants. The sampling should be conducted on a regular basis. Four to six samplings and analysis for each selected contaminant should be carried out at different time intervals during this program.
- b. Establish test protocols for using active sampling methods to determine the removal efficiency of GPAFE (short term). Active sampling should be conducted at several selected sites to determine the removal efficiency of GPAFE for various contaminants. The timing for conducting such tests would be, for instance, to determine the removal efficiency of GPAFE shortly after the installation, when there is an anticipated increase of pollutant load, or simply at different time intervals.
- c. Determine the representative sampling locations for large GPAFE installation.
- d. Based on the collected VOC data, recommend a few compounds that can be used to determine the service life of GPAFE.
- e. Monitor TVOC loading analysis and correlate the results with those obtained from passive VOC sampling.

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TABLE 1. GAS-PHASE AIR FILTRATION EQUIPMENT USED IN HAVAC SYSTEMS

Type of adsorber	Residence time	Amount of adsorbent	Particle size of adsorbent	Depth
Panel type	0.035-0.1 seconds	20-90 lbs	4x6 or 4.8 mesh	12"-31"
Pleated type	0.001-0.03 seconds	a few ounces to 15 lbs	-20 mesh	1"-12"

Adsorbents: Activated carbons, impregnated activated carbons, potassium permanagnate-based sorbent, and zeolites

TABLE 2. REAL-TIME INSTRUMENTS FOR COMMON GAS-PHASE CONTAMINANTS IN INDOOR AIR

Gases and vapors	Method of detection	Sensitivity
O ₃	UV photmetric	1 ppb
NO ₂ , NO _x , and NO	chemiluminescence	0.1-0.5 ppb
SO ₂	pulsed fluorescence	1 ppb
Corrosive gases film	thickness of copper and silver	NA
VOCs	catalytic oxidation (TVOC)	high ppb-low ppb
Specific VOCs	infrared spectroscopy	5-11 ppb

TABLE 3. ACTIVE SAMPLING FOR COMMON GAS-PHASE CONTAMINANTS IN INDOOR AIR

Gases and vapors	Sampling method	Analysis	Sensitivity
VOCs	adsorption tube with porous solids (tenax, charcoals, or multisorbents)	GC/MS	ppb-ppt
NO ₂	wet impinger with absorbing agent (sulfanilic acid)	colorimetric	2ppb
SO ₂	wet impinger with absorbing agent (TCM)	colorimetric	10 ppb
HCHO	wet impinger with absorbing agent (DNPH)	HPLC with UV detector	low ppb

TABLE 4. PASSIVE SAMPLING METHODS FOR COMMON GAS-PHASE CONTAMINANTS IN INDOOR AIR

Gases and vapors	Collection method	Analysis	Sensitivity
VOCs	diffusion and adsorption	solvent extraction GC/MS analysis	ppb-ppt
NO ₂	diffusion and adsorption	colorimetry	low ppb
HCHO	diffusion and adsorption	colorimetry	low ppb
SO ₂	diffusion and adsorption	ion chromatography	low ppb
O ₃	oxidation of nitrite	ion chromatography	low ppb

TABLE 5. FIELD METHODS FOR GPAFE TESTING-APPLICATION GUIDE

Methods	Capability	Operation	Availability	Cost
Real-time	Continuous data	Unattended operation	Ozone, sulfur dioxide	>\$10,000
Instruments	Accuracy: $\pm 1\%$ or less Detection limit: ≤ 1 ppb Response time: ≤ 100 sec	Power source required	Nitrogen dioxide	
Active sampling	1-24 hr time-averaged data Sampling time: 1-24 hr Accuracy: $\pm 5-10\%$ Detection limit: <sub-ppb Lead time: 1-3 weeks	Attended operation Power source required Sampling device required (active sampling is normally conducted by trained personnel)	VOCs, formaldehyde, sulfur dioxide, nitrogen dioxide	\$200-500 per analysis
Passive sampling	1-24 hr time-averaged data (1-4 weeks for VOCs) Sampling time: 1-24 hr (1-4 weeks for VOCs) Accuracy: $\pm 10-15\%$ ($\pm 20-25\%$ for VOCs) Detection limit: sub-ppb Lead time: 1-3 weeks (2-7 weeks for VOCs)	Unattended operation No other devices required Easy to install Small sampler size Power source is not required	VOCs, ozone, nitrogen dioxide, sulfur dioxide, formaldehyde	<\$100/each (including analysis)

TABLE 6. PERFORMANCE SPECIFICATION FOR REAL-TIME INSTRUMENT

	Ozone	Nitrogen dioxide	Sulfur dioxide
Range:	0-1 ppm	0-1 ppm	0-1 ppm
Noise	0.5 ppb	0.2 ppb	0.5 ppb
Lower detection limit	1 ppb	0.4 ppb	1 ppb
Zero drift	<1 ppb/24 hour	<0.4 ppb/24 hour	<1 ppb/24 hour <2 ppb/week
Span drift	± 1%/month	± 1%/24 hour	± 0.5%/week
Response time	20 seconds	80 seconds	110 seconds
Precision	1 ppb	1 ppb	1 ppb
Operating temperature	15-35 °C	15-35 °C	15-35 °C

TABLE 7. STANDARD TEST METHODS FOR ACTIVE SAMPLING-VOCs

	ASTM D 5466-93	ASTM D 3686/3687
Sampling method	evacuated canister	charcoal tube
Analysis method	GC/MS	GC/MS
Sampling time	10-30 sec (subatmospheric) 1-24 hours (pressurized)	1-24 hours
VOCs	Works well for a wide range of stable compounds (-30-180 °C boiling point)	Does not work well with low boiling point compounds, but this can improve with the use of multisorbent tube
Low detection limit	<1 ppb	1 <ppb
High detection limit	300 ppb	NA
Accuracy	±5-10%	±5-10%

TABLE 8. STANDARD TEST METHODS FOR ACTIVE SAMPLING-FORMALDEHYDE
ASTM D 5197-92

Sampling media	silica gel coated with DNPH
Analysis method	HPLC with UV detector
Sampling time	5-60 min. (short term) 1-24 hours (long term)
Low detection limit	low ppb
High detection limit	low ppm
Accuracy	±5-10%

TABLE 9. STANDARD TEST METHODS FOR ACTIVE SAMPLING-NITROGEN DIOXIDE
ASTM D 3608-91

Sampling media	absorption agent (sulfanic acid)
Analysis method	colorimetry
Sampling time	1-24 hours
Low detection limit	2 ppb
High detection limit	5 ppm
Accuracy	< 10%

TABLE 10. STANDARD TEST METHODS FOR ACTIVE SAMPLING-SULFUR DIOXIDE
ASTM D 2419-91

Sampling media	absorption agent (TCM)
Analysis method	colorimetry
Sampling time	1-24 hours
Low detection limit	10 ppb
High detection limit	0.4 ppm
Accuracy	≤ 5%

TABLE 11. TEST METHODS FOR PASSIVE SAMPLING - VOCs

Sampler	personal badge
Sampling media	charcoal pad
Analysis method	GC/MS
Sampling time	1-8 weeks (ppb levels) 1-24 hours (ppm levels)
Low detection limit	0.02 ppb
High detection limit	high ppm
Accuracy	±15-25%
Cost	<\$100 (including analysis)

TABLE 12. STANDARD TEST METHODS FOR PASSIVE SAMPLING - FORMALDEHYDE

ASTM D 5014-94	
Sampler	tube
Sampling media	absorbing agent (MBTH)
Analysis method	colorimetry
Sampling time	15 min. - 24 hours
Low detection limit	9 ppb
High detection limit	14 ppm
Accuracy	±10-15%
Cost	<\$100 (including analysis)

TABLE 13. STANDARD TEST METHODS FOR PASSIVE SAMPLING - NITROGEN DIOXIDE

Sampler	cartridge
Sampling media	TEA coated stainless steel screen
Analysis method	colorimetry
Sampling time	1-24 hours
Low detection limit	2 ppb
High detection limit	low ppm
Accuracy	±10-15%
Cost	<\$100 (including analysis)

TABLE 14. TEST METHODS FOR PASSIVE SAMPLING - SULFUR DIOXIDE

Sampler	cartridge
Sampling media	sodium carbonate treated filter
Analysis method	ion chromatography
Sampling time	1-24 hours
Low detection limit	1-2 ppb
High detection limit	low ppm
Accuracy	±10-15%
Cost	<\$100 (including analysis)

TABLE 15. TEST METHODS FOR PASSIVE SAMPLING - OZONE

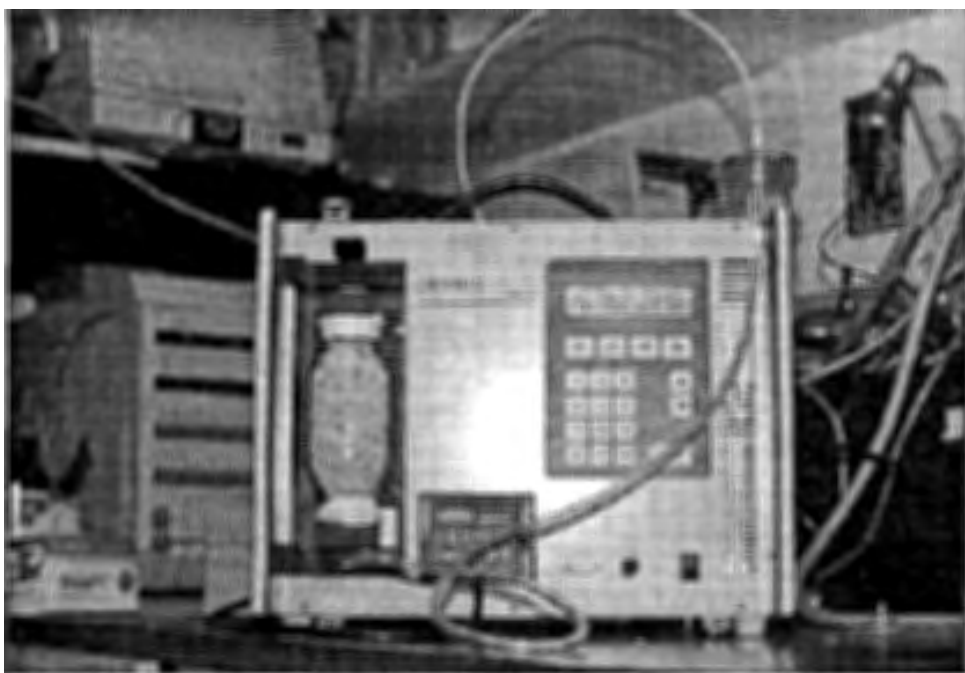
Sampler	cartridge
Sampling media	potassium carbonate and sodium nitrite coated filter
Analysis method	ion chromatography
Sampling time	1-24 hours
Low detection limit	1-2 ppb
High detection limit	low ppm
Accuracy	±10-15%
Cost	<\$100 (including analysis)

TABLE 16. A LIST OF SUPPLIERS FOR PASSIVE SAMPLERS

Supplier	pollutants
GMD 570 Formaldehyde Dosimeter Bacharach, Inc.; 625 Alpha Drive Pittsburgh, PA 15238 Tel: (412) 963-2200	formaldehyde
DGA Passive Monitors 4526 Telegraph Road, Ste. 205 Ventura, CA 93003 Tel: (805) 644-0125	formaldehyde sulfur dioxide ozone
3 M Passive Monitors 3M Center Bldg. 275-6W-01 St. Paul, MN 55144 Tel: 800-666-6477	volatile organic compounds formaldehyde ethylene oxide mercury vapor
SKC 575-001 Passive Sampler SKC West; P.O. Box 4133 Fullerton, CA 92634-4133 Tel: 800-752-9378	volatile organic compounds
Ogawa Passive Samplers Ogawa & Co.; 1230 SE 7th Avenue Pompano Beach, FL 33060 Tel: (305) 781-6233	sulfur dioxide nitrogen oxide nitrogen dioxide ozone
Air Quality Research 2800 7th St. Berkeley, CA 94710 Tel: (415) 644-2097	formaldehyde nitrogen dioxide
Microfiltration Systems 6800 Sierra Ct. Dublin, CA 94568 Tel: (415) 828-6010	nitrogen dioxide



Real-time instruments for ozone, nitrogen dioxide, and sulfur dioxide



Active sampling method

Figure 1 - Test methods for measuring gaseous contaminants in indoor air

Composite Sorbent Cartridges

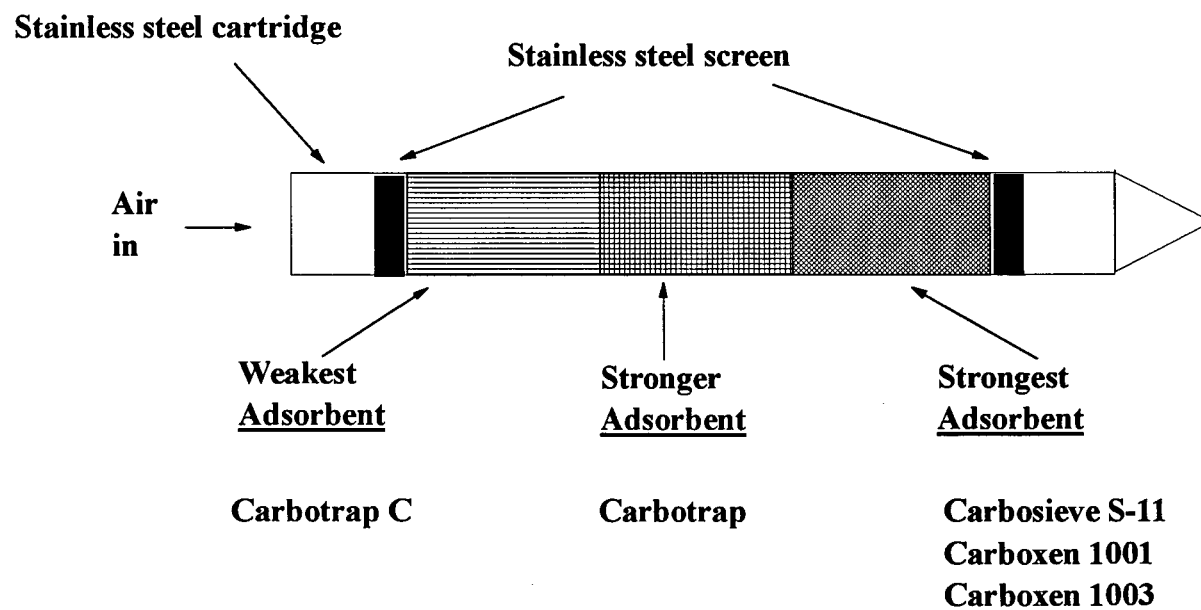


Figure 2. A multisorbent tube for sampling VOCs in indoor air (active method)

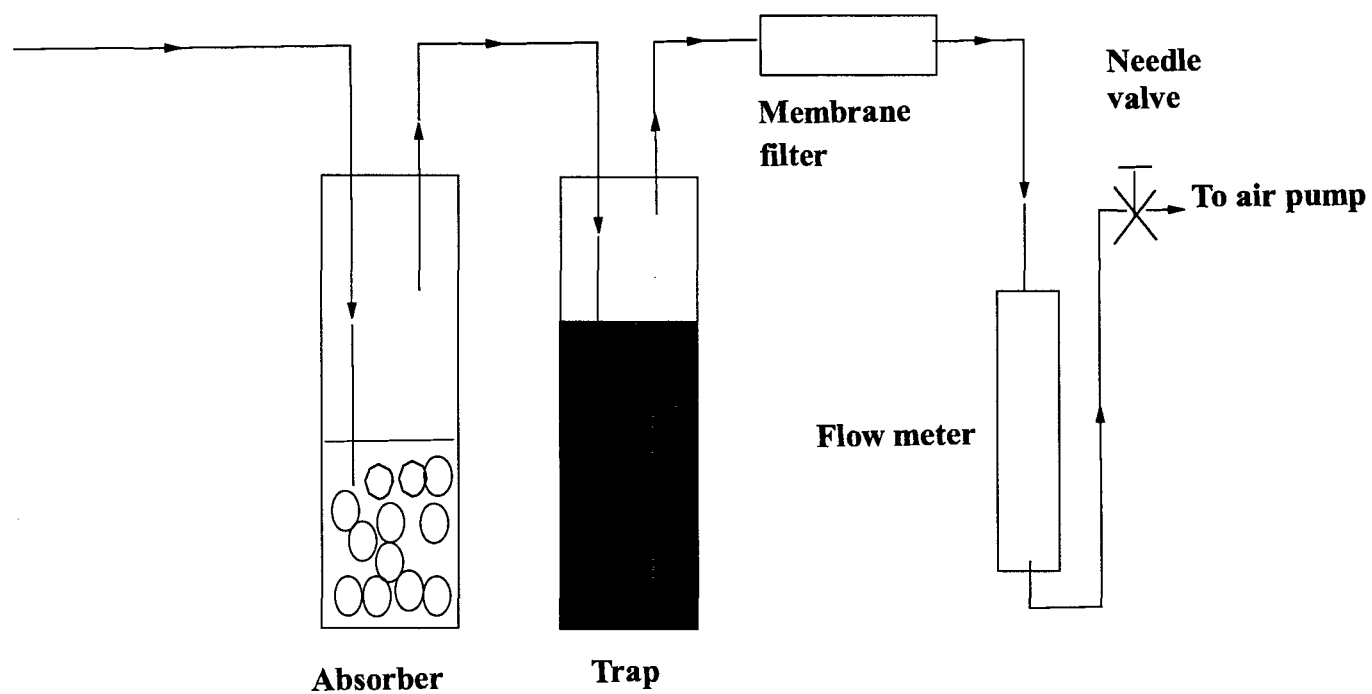


Figure 3. An active sampling apparatus for sulfur dioxide (ASTM D-2914)

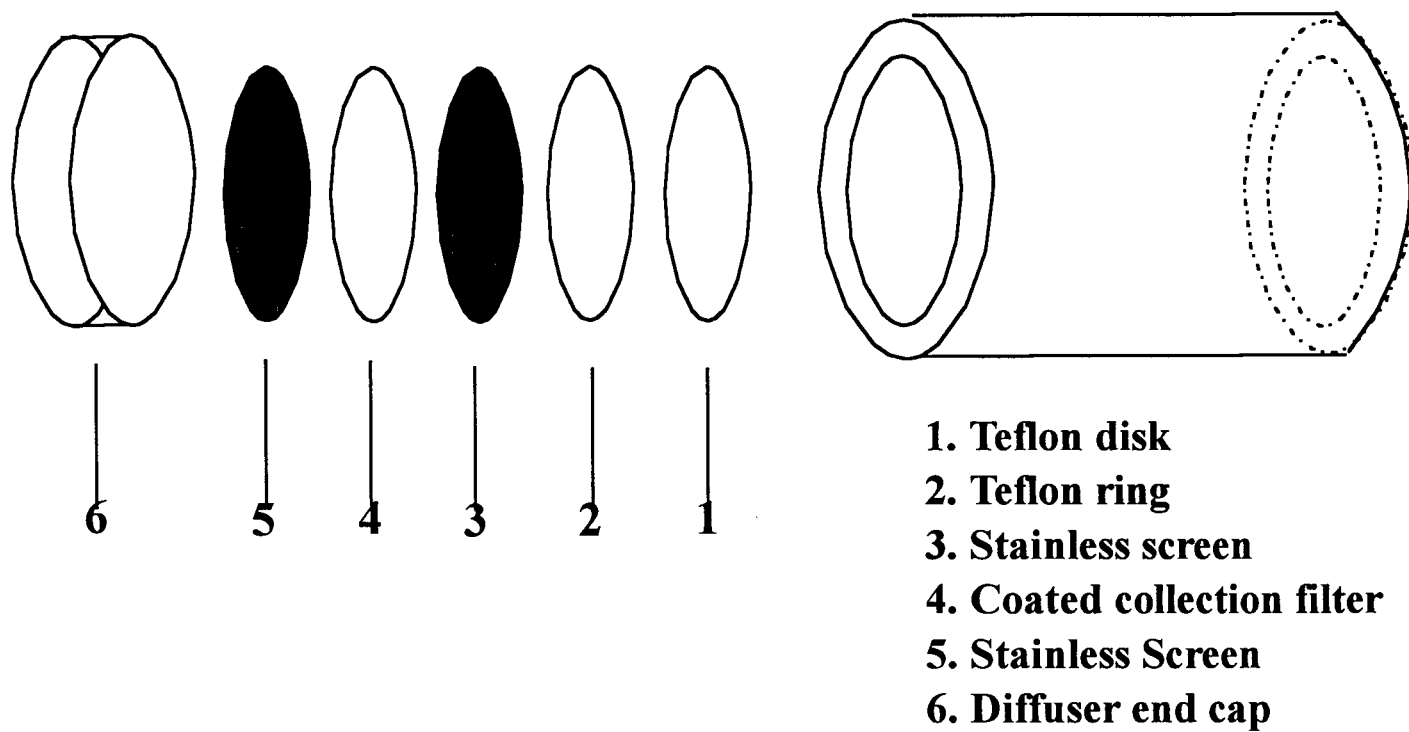


Figure 4. A cartridge for passive sampling of nitrogen dioxide in indoor air