7. 3 Microbial Volatile Organic Compounds (MVOCs)

7.3.1 *Types and Occurrence*

Microbial volatile organic compounds (MVOCs) are low molecular weight (MW) chemicals present in the indoor environment primarily as the result of the metabolic actions of bacteria and fungi. For almost two decades now there have been suggestions that such volatiles could be partially to blame for IAQ problems caused by fungal growth.[1–9] In addition, the ability of MVOCs to diffuse from enclosed wall cavities, from behind apparently impermeable vinyl wallpaper and vapor barriers, or off HVAC filters free of visible contamination has been of growing interest to investigators seeking to employ MVOCs as non-destructive indicators of latent mold growth.[10–12] This latter application might be characterized as the use of MVOCs with a micro-ecological perspective (e.g., to ascertain ongoing biodeterioration). Regardless of their intended use, however, at this time the practical utility of MVOCs remains to be demonstrated.

MVOCs are produced during active growth of microorganisms, especially molds, and are typically found in the indoor environment at very low concentrations. A description of MVOCs by chemical group was prepared by Wilkins et al.[13], and is presented in Table 7.2. The true diversity of microbial volatiles is greater than implied by Table 7.2, however, with many also occurring in indoor air from sources other than microbes. Therefore, there will always be an underestimate of the total microbial impact on a given space when assessed by MVOCs, since only a few VOCs qualify as originally and uniquely of microbial origin.[14] There is no universally accepted listing of MVOCs—perhaps with good reason, given the current state of knowledge—but there is a select group of compounds most researchers would accept as arising uniquely from microbial production in indoor environments. The initial description of Class A and Class B MVOCs[14] was a necessary first step, but was based on limited observations under limited environmental conditions. Using as the sole criterion MVOCs detected by ≥ 3 authors in field studies, the compounds in Table 7.3 are suggested as a current compilation of MVOCs of unequivocal status.

Several MVOCs are highly distinguishable by their odor, and for this reason their occurrence is easily associated with damp facilities where mold or moisture are at issue.[15] Perhaps the most characteristic of such odors is that produced by geosmin, with an earthy smell often linked to sesquiterpenes or similar compounds.[16] The detection limit of the human olfactory system for geosmin is in the range of 150–200 ng/m^3. The MVOC 2-methyl-iso-borneol is also perceived as earthy. Other easily recognized odorous MVOCs are 1-octen-3-ol (mushroom like at 10 μg/m^3) and 2-octen-1-ol (musty odor at 16 μg/m^3). Chemically related compounds that may contribute to these odor perceptions include 3-octanol, 3-octanone[10], or other 8-carbon organics sometimes referred to as the "C8 complex".[17] In field studies of buildings with visible mold, total concentrations of 18 MVOCs correlated with odor perceptions when odors were categorized into one of three descriptions. "Fungus-like" odors could not be recognized below 0.035 μg/m^3, while a "slight fungal odor"

Table 7.2. MVOCs by Category[a]

Biosynthetic Types	Sub-Category
Hydrocarbons:	Alkanes alkenes, dienes, trienes
Terpenes:	hemi-(C5 hydrocarbons, alcohols, ketones) mono-(C10 hydrocarbons, alcohols, ethers, ketones) sesqui-(C15;C11;C12 hydrocarbons, alcohols, ketones) di-(C20 hydrocarbons)
Alcohols: (saturated, unsaturated, branched)	
Carboxylic acids and esters: (saturated, unsaturated, branched, diols, ketols)	
Ketones and corresponding alcohols: (methyl(2-)ketones (+alcohols)-(saturated, branched) ethyl(3-)ketones and (+alcohols)-(saturated, unsaturated) cyclic	
Sulfur derivatives:	(thiols, mono-, di-, trisulfides) S-methyl thioesters, thioethers)
Aromatic compounds: (hydrocarbons, alcohols, ethers, ketones, phenols)	
Heterocyclics:	N (alkyl and alkoxypyrazines, indoles, pyrroles) O (alkyl furans, c and d-lactones)

[a]Source: Wilkins, Larsen, and Simkus[(13)]

Table 7.3. Fourteen MVOCs as Suggested by Consistent Isolation in ≥ 3 Field Surveys

3-methyl furan
1-butanol
3-methyl-1-butanol
3-methyl-2-butanol
2-pentanol
2-hexanone
2-heptanone
3-octanone
3-octanol
1-octen-3-ol
2-octen-1-ol
2-nonanone
Borneol
Geosmin

described concentrations of 0.05–1.72 μg/m^3, and total concentrations of 0.16–12.3 μg/m^3 were most often labeled as a "strong" fungus-like odor.[18] Table 7.4 identifies the predominant MVOCs reported in this and seven other field surveys conducted in response to IAQ interests.

As with bioaerosol data, the comparison of MVOC concentrations in complaint buildings to background levels may be of some use to IAQ investigators. Generally, levels of MVOCs found indoors are typically orders of magnitude lower than VOCs in industrial settings and on par with typical VOCs emanated from anthropogenic sources. For example, Ryan et al.[19], reported average benzene, toluene, and xylene concentrations of only 2.3, 41, and 3.3 μg/m^3, respectively, in a building free of any IAQ complaints. These values are in the same order of magnitude as some common MVOCs detected in pure culture, where average values range from 1.1 μg/m^3 (2-pentylfuran) to 31.8 μg/m^3 (1-octen-3-ol).[20] MVOCs determined under field conditions yield similar results. Based on data from 30 reference buildings generally free of mold or other microbial growth issues, background MVOC concentrations in the range of only 2.2–8.8 μg/m^3 are to be expected. These concentrations are essentially similar to outdoor air, where MVOC values ranged from 1.1–9.5 μg/m^3, with an average in 27 samples of 4.5 μg/m^3.[10] While professional interpretation concerning acceptable MVOC levels is of paramount importance in all sampling scenarios, levels significantly higher than these background ranges may indicate active microbial proliferation.

Many studies of MVOCs generated under pure culture conditions have been completed on standard enriched media (e.g., rice agar, MEA, DG-18, and yeast extract sucrose), and a similar volume of pure-culture work exists on media developed from building materials such as gypsum board, cardboard, wallpaper paste, and wood. Because of its notoriety, a number of authors have examined MVOCs produced from strains of *Stachybotrys chartarum* in pure culture on both of these groups of media. One such study[21] reported culturing this agent (using *S. chartarum* strains isolated from Cleveland, Ohio) on gypsum board and rice media. Only a single MVOC (1-butanol) was detected from the less-nutritive gypsum board cultures, whereas thujopsene, 1-butanol, 3-methyl-1-butanol, and 3-methyl-2-butanol were all detected on rice media. In agreement with other authors' pure culture work, volatile profiles were very similar among the three *S. chartarum* strains studied. Most of the MVOCs detected peaked early in the study (Weeks 1–3), then tapered off to very low or non-detectable concentrations by Weeks 4–6. Although the utility of studies such as this to field investigators are obviously quite limited, they do warrant monitoring for possibly important future findings.

7.3.2 Health Effects

Research shows that while mold volatiles may contribute to health effects, particularly in residential housing[1,3,9,14,22,23], exposure to MVOCs has not been conclusively linked to health effects. For example, Mendell[24] found in a review of 33 studies on environmental factors related to SBS only sparse or inconsistent associations between

Table 7.4. MVOCs Designated as Such and Identified by Authors in Field Surveys

Name	Miller et al.,[25]a	McJilton et al.,[26]b	Ström et. al.,[10]	Wessen & Schoeps,[14]	Morey et al.,[27]	Fischer et al.,[28]	Elke et al.,[11]	Pedersen et al.,[29]c
3-methyl furan			x	x	x	x		
2-pentyl furan				x		x		
2-methyl-1-propanol			x	x				
1-butoxy-2-propanol		x						
2-methyl-1-proprionic acid		x						
1-butanol			x	x				x
2-methyl-1-butanol						x		
3-methyl-1-butanol	x		x	x	x	x	x	
3-methyl-2-butanol			x	x	x		x	
fenchone				x			x	
2-pentanol			x	x	x		x	
2-methylpropan-1-ol				x		x		
2-hexanone	x		x	x	x		x	
3-hexanone						x		
2-heptanone	x		x	x	x		x	x
4-methylheptan-3-one				x				
3-octanone			x	x	x	x	x	
3-octanol			x	x	x	x		
1-octen-3-ol			x	x	x	x	x	

Table 7.4. MVOCs Designated as Such and Identified by Authors in Field Surveys (continued)

Name	Miller et al.,[25]a	McJilton et al.,[26]b	Ström et. al.,[10]	Wessen & Schoeps,[14]	Morey et al.,[27]	Fischer et al.,[28]	Elke et al.,[11]	Pedersen et al.,[29]c
2-octen-1-ol			x	x	x			
2-nonanone				x			x	x
2-isopropyl-3-methoxy-pyrazine			x		x			
karveol				x				
borneol			x	x	x	x		
geosmin			x	x	x	x		
dimethyl disulfide				x				x
b-farnesene						x		
terpineol				x			x	
thujopsene				x			x	
ethyl isobutyrate				x		x		
ethyl-2-methylbutyrate						x		

[a] A total of 17 VOCs were detected, but the authors only list these 3 as representative of fungal activity.
[b] Determined VOCs as a result of bacterial growth, not otherwise identified by genus or species.
[c] Determined VOC emissions from heated dusts collected from chairs in conference rooms, auditoriums, and a cafeteria of a single, non-problematic facility.

VOC levels and work-related symptoms.[30] There is no compelling evidence concerning the irritation potency of MVOCs at the concentrations published to date, and the toxicological relevance of these exposures is similarly unclear.[31] MVOCs have been suggested as the cause of lethargy, headache, and irritation of the eyes and mucous membranes of the nose and throat.[32] Additional sensory effects may include upper respiratory tract symptoms (nasal congestion, nasal secretion, rhinitis, sore throat and hoarseness) as well as lower respiratory tract symptoms (cough, phlegm production, and wheezing).[33] MVOC concentrations were shown to be significantly elevated ($p < 0.05$) in homes reporting a higher prevalence of asthma, hay fever, wheezing and eye irritation, although none of the reported associations with health effects was statistically significant.[11]

7.3.3 *Sampling and Analysis*

There are no standard methods for the sampling and analysis of MVOCs, and there is no unambiguous description of standard MVOCs. Nevertheless, sampling can be effectively accomplished, and might be targeted at those compounds listed in Tables 7.2 or 7.3. MVOCs can be collected in a variety of ways, with retention onto an adsorbent in a stainless steel tube being perhaps the most prevalent technique. Other devices readily commercially available include the **SUMMA canisters** (popular with laboratories processing volatiles via EPA methods), mini canisters (e.g., Entech 0.4 L stainless steel container), and-in at least one instance for MVOCs-passive diffusion devices. Figure 7.2 depicts representative media types available for the collection of MVOCs.

As a rule of thumb, sampling for MVOCs should always be performed in such a way as to maximize the amount of **analyte** collected. Samples can be collected at a variety of flow rates, typically ranging from 20-200 mL/min depending primarily on the amount of sampling time available to the hygienist. Because the expected concentrations for MVOCs are low, breakthrough of the targeted analyte is rarely a concern.

Thermal desorption (TD) of analytes from one or a series of synthetic adsorbents directly onto a capillary gas chromatograph (GC) column, followed by quadrapole mass spectral (MS) analysis of the eluting peaks (i.e., TD/GC/MS) is the most commonly employed analytical method for the detection, identification, and quantitation of MVOCs. According to Keller et al.[34], thermodesorption is 100 times more sensitive than the solvent extraction technique.

There has been insufficient research to propose a comprehensive method specifically for MVOCs. However, NIOSH Method 2549 for VOC screening via TD/GC/MS does exist. That method stipulates a minimum volume of 1 L and a maximum of 6 L, to give a limit of detection of 100 ng per tube "or less."[35] When passive dosimeters have been utilized, they have typically been exposed for a period of 4 weeks.[11]

Sampling strategies for MVOCs are similar to those for most other contaminants: area, personal, and "clean air" samples can be collected as desired. Generally, samples should be collected in the indoor area of concern, outdoors near air intakes, and (where possible) in indoor reference locations in a problem-free building for compar-

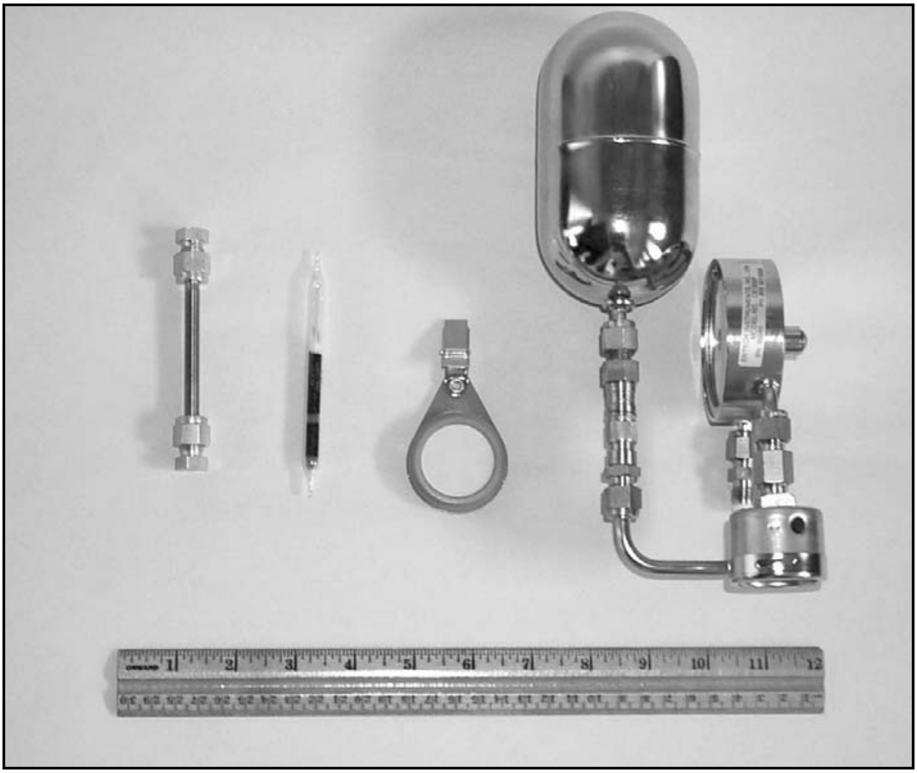

Figure 7.2. Typical MVOC samplers. From left: 9-cm adsorbent filled stainless steel tube, shown with brass end plugs; charcoal-filled glass tube; passive dosimeter; mini-canister with flow regulator assembly. ©Timothy J. Ryan, PhD, CIH. Used with permission.

ison. Care should be exercised to avoid any obvious organic vapor sources (i.e., non-MVOC organics), as they may overload the sampling media and thereby mask certain co-eluting compounds of interest.

A variety of adsorbents are available for the heterogonous compounds considered MVOCs, but for practical purposes, selection can reasonably be limited to only a few. Sunesson et al.[(36)], tested eight readily available commercial sorbents (Tenax TA, Tenax GR, Chromosorb 102, Carbotrap C, Carbotrap B, Anasorb 727, Anasorb 747, and Porasil) under varying conditions of humidity and analyte concentration. Using 10 probable MVOCs of differing polarity and volatility, at concentrations like those in problem buildings (i.e., 1–50 μg/m^3), the sorbents were evaluated for water effects, high background compounds, relative recovery of analyte, adsorptivity, and stability during thermal desorption.

Results indicated that both Anasorb varieties and Chromosorb 102 suffered from excessive water uptake problems. This is an important point, in that excessive moisture can be a typical issue in microbially contaminated buildings. Accordingly, it is recommended that those adsorbents be avoided in MVOC field studies. Porasil eluted excessive background peaks, while both Carbotraps absorbed the common MVOC 2-propanol only poorly (as did all sorbents at the lowest of levels tested). Despite a somewhat low breakthrough volume for < C_6 compounds, the Tenax adsorbents were ultimately recommended for the largest variety of MVOC sampling scenarios. Tenax is the most frequently used sorbent for low concentrations of organics in air by thermal desorption, is chemically inert, thermally stable, has low water effects, low backgrounds (except for toluene and benzene, neither of which are MVOCs), and good storage stability. While neither Tenax TA nor Tenax GR was the optimal adsorbent for 2-propanol, Tenax GR had additional failings when tested in 2-methylisoborneol, geosmin, and 1-octen-3-ol concentrations. For these reasons, Tenax TA was judged to have the best overall properties for MVOC field sampling. In their concluding remarks, the authors noted that in fact none of the adsorbents was suitable for all mixtures under all conditions. Based on their findings, the ultimate recommendation for complete MVOC sampling was to employ multisorbent tubes packed for the analytes most anticipated. For example, Tenax TA followed by Chromosorb 102 or charcoal might be an appropriate series for a majority of MVOCs.

7.3.4 *Summary*

When presented with MVOC sampling data, the hygienist must be guarded in his or her interpretation of results. Very often the laboratory report from an MVOC scan will show a large number of non-detects (i.e., below the lower detection limit), and the prevalence or patterns of the MVOCs seen will be quite variable. Certainly, average MVOC concentrations ranging from the high nanogram to low microgram per cubic meter of air might be considered as normal or typical in non-problematic buildings. However, notable (and consistent) elevation of even a single presumptive MVOC in Table 7.3 is reason for further investigation for possible microbial growth or amplification sites.

In summary, the promise of MVOCs as a powerful tool for the IAQ field investigator remains somewhat elusive. Given the lack of any unambiguous health effects directly and conclusively linked to MVOC exposures, the very low concentrations of these compounds even in ostensibly contaminated environments, and the absence of any consensus as to acceptable versus levels of concern of even a single MVOC, sampling for MVOCs in most IAQ investigations is of indeterminate value. Research on quantitative and qualitative patterns of MVOC occurrence (i.e., “profiles”) is being actively pursued. Ultimately the potential of MVOCs to act as broad indicators of the ecological state of a building may be realized. For these reasons the industrial hygienist should remain current with professional literature on the topic.

7.3.5 *References*

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