

Canister Sampling of MVOC's for Rapid Mold Screening

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Abstract

A new canister based method is presented for detecting Microbial Volatile Organic Compounds (MVOC's) in air. MVOC's have been determined to be an indicator of mold growth because their presence is associated with actively growing mold. MVOC's have been sampled using sorbent tubes but limited sample flow rates require the tube samples to be collected over one or more hours. Canisters can be filled in just a few seconds, providing a faster means of screening an indoor environment for mold.

Canisters have not previously been shown to allow recovery of the entire list of approximately 20 MVOC's that have been determined to be important as mold growth indicators. New developments in Silonite coated (fused silica) canisters and automated heated inlet systems has extended the molecular weight range of canisters to include these heavier compounds. By heating the canister prior to concentrating the sample, compounds that have condensed on the canister wall will go back into the vapor phase as they were when originally sampled. Sampling procedures will be covered, and data will be presented showing reproducibility of the analysis, as well as calibration and detectability. Instrumentation will be discussed outlining the parameters needed to perform the analysis of 20 common MVOC's in heated, fused silica lined canisters.

Introduction

Actively growing mold produces toxic enzymes and mycotoxins that are a concern to human health, so there needs to be a way of detecting actively growing mold. When mold grows it gives off chemicals called Microbial Volatile Organic Compounds (MVOC's). These MVOC's are what produce the characteristic musty odor of mold. MVOC's are small molecules that don't tend to settle out on carpet and other surfaces as do mold spores. They can pass through walls, allowing them to spread throughout the inside of buildings. However, like mycotoxins and enzymes, they can't be transmitted very far outside when exposed to sunlight. Therefore, their presence inside of buildings is direct evidence of active or recently active mold growth.

Discussion

MVOCs can be measured using an evacuated silonite canister to collect a "whole air" sample. The inert Silonite coating on the interior walls of the canister will allow the chemical composition of that air to remain intact until the time of analysis. Some of the MVOC's, however, are relatively high molecular weight compounds and will not remain in the vapor phase. To accommodate these heavier compounds a robotics based autosampler is used which can heat the canister prior to analysis to transfer those heavier

compounds back into the vapor phase as they were when initially collected. An aliquot of the vapor sample is then concentrated using a multi-stage preconcentrator and then injected into a GCMS for analysis.

Other techniques have been used to detect mold but they have limitations. Mold spore counting can be used for mold investigations but the presence of mold spores does not indicate actively growing mold. Furthermore, the concentration of mold spores can vary depending on how much mold spores are kicked up in the air from recent activity, even just walking across a carpeted room. MVOC's have been sampled in the past by sorbent tubes but that technique requires sampling pumps to be field calibrated which can lead to errors and can take one or more hours, adding to the cost of the investigation. Canister sampling for MVOC's takes only a few seconds and does not require a highly trained professional. Convenient sampling kits can be used by the virtually anyone following procedures outlined by the testing laboratory. Laboratory analysis is performed using a heated canister autosampler that samples the canister while it is being heated, and transfers the desired volume into the preconcentration system that separates the major air components from the MVOC's so that they can be injected into a Gas Chromatograph/Mass Spectrometer for identification.

Experimental

Neat chemicals for MVOC calibration were obtained from Aldrich except for 2-Methylisoborneol and Geosmin which were obtained from Dalton and 3-Methylfuran which was obtained from Oakwood Products. A cocktail mixture of all of the chemicals was prepared using Entech Standards Preparation software. This software calculates the amount of each chemical to blend together so that equal part per billion by volume (ppbv) concentrations can be made. The cocktail is then diluted into methanol at a 1:10,000 fold dilution so that 1.8 ul of this diluted cocktail can be injected into a 0.4 liter canister followed by pressurization to 15 psig resulting in a 2 ppbv concentration.

Standards were analyzed by vapor concentration and injection into a GCMS. Due to the polar nature of these chemicals and the boiling point of Geosmin being 270 C, canisters were heated to keep all of the chemicals in the vapor phase. This was performed using the model 7500 Robotic Canister Autosampler (Entech Instruments, Inc.) The autosampler placed the canister into an oven at 80 C and held it there for 10 minutes. After the equilibration time the robotic arm goes down onto the sample while it is still in the oven and connects to the canister to withdraw the desired volume. The inlet of the robotic arm is kept at 100 C and the transfer line going to the concentrator is at 150 C. The desired sample volume is then collected using model 7100A sample preconcentrator (Entech Instruments, Inc.). The 7100A is a three stage trapping system that can remove the major air components as well as managing the water and CO₂ while collecting the chemicals of interest. The sample first flows through a glass bead/tenax trap at 40 C, at this temperature MVOC's will trap out while everything else passes through. An additional 200 cc's of helium is purged through the trap to remove any residual water. That trap is then thermally desorbed with 100cc's of helium at 180 C to the second stage trap which is also glass bead/tenax, at -30C. The heavier compounds will trap out on the

glass beads while the lighter compounds will trap on the tenax. This multibed trap allows easy desorption of all of the analytes, which is necessary because the trap is desorbed with the GC carrier gas flow rate of 1.5 cc/min. The sample is then cryofocused and injected into a GCMS (Hewlett Packard 5890II/5971A). Table 1 shows the parameter of the 7100A. Table 2 shows the conditions of the GCMS.

Table 1

7100A Trapping Conditions

Sample Temp	80 C
Trap Temp 1	40 C
Dry Purge Volume	200 cc
Desorb Temp 1	180 C
Desorb Volume	100 cc
Trap Temp 2	-30 C
Desorb Temp 2	180 C
Cryofocus Temp	-60 C

Table 2

5890II/5971A Conditions

Column	DB-5 30m, 0.32mm ID, 1.0u film, flow at 1.5 cc/min
Oven	37 C (1min) 6C/min to 100 C, 25C/min to 240C (hold 2 min)
MS Scan	35 amu to 155 amu

Different volumes of the standard were analyzed in order to construct a calibration curve. Samples are analyzed using 200 cc, so with 200 cc being the nominal volume of the 2 ppbv standard, 400 cc equals 4 ppbv, 160 cc equals 1.6 ppbv, 120 cc equals 1.2 ppbv, 80 cc equals 0.8 ppbv, and 40 cc equals 0.4 ppbv; yielding a 6 point calibration curve. The percent Relative Standard Deviation (%RSD) of the calibration curve is shown in appendix A. A method blank was analyzed to show background levels, no MVOC's were detected except 2-Methylisoborneol did persist at 0.2 ppbv. Some chromatograms are displayed in Appendix 2, including a total ion chromatogram of a 2 ppbv standard.

The next set of analyses was to determine the Method Detection Limit (MDL). A series of standards at 0.1 ppbv were analyzed, seven replicate analyses were used to determine the standard deviation; the student T value of 3.14 was multiplied by the standard deviation to determine the MDL. That data is listed in table 3.

To complete this data set, the presence of mold was evaluated in a typical household. A 0.4 liter minican grab sample was taken from a kitchen sink garbage disposal and was analyzed to find several MVOC's including 2-Butanone at 0.3 ppbv, 2-Pentyl furan at 0.1 ppbv, 2-Ethyl-1-hexanol at 0.6 ppbv, and 1-Octanol at 0.8 ppbv. Data correlating the concentration of MVOC's to hazardous mold levels has been shown that below 8 ng/L of

total MVOC's most people will not have any allergic reaction, between 8 and 30 ng/L some people may have moderate allergic reactions, and at levels above 30 ng/L there will be very probable allergic reactions. In the above sample the ppbv concentrations would total about 8 ng/L but this was from a garbage disposal and not the ambient indoor air, so this level should not pose a serious health threat.

Conclusion

An effective means of analyzing indoor air for MVOC's has been demonstrated. Quality control measurements show the reproducibility of the analytical technique employed to be consistent with other methodologies used in air analysis, such as EPA method TO15. The sampling technique is simplified when compared to other mold investigations and mold was detected in a home thought to be free of contamination. There have been many cases of mold problems reported throughout our country but often times economics does not allow for average homeowners to test their environment. Now there is a more cost effective and potentially more accurate approach to mold investigations.

Table 3

MVOC MDL Study

0.1 ppbv	ppbv	ppbv	ppbv	ppbv	ppbv	ppbv	ppbv	ppbv	MEAN	SD	MDL(ppbv)	MDL(ng/L)
2-Butanone	0.16	0.16	0.16	0.15	0.17	0.17	0.17	0.16	0.162857	0.007559	0.023736	0.071209
2-Methyl furan	0.16	0.14	0.18	0.16	0.18	0.17	0.14	0.16	0.161429	0.016762	0.052632	0.179824
3-Methyl furan	0.16	0.17	0.17	0.16	0.16	0.16	0.15	0.16	0.161429	0.006901	0.021668	0.074033
2-Methyl -1- propanol	0.17	0.16	0.18	0.16	0.17	0.14	0.14	0.16	0.15275	0.015275	0.047964	0.14789
3-Methyl -2-butanol	0.14	0.15	0.15	0.12	0.14	0.17	0.13	0.14	0.142857	0.016036	0.050352	0.184624
2-Pentanol	0.27	0.27	0.24	0.24	0.28	0.27	0.23	0.25	0.257143	0.01976	0.062048	0.227509
3-Methyl -1-butanol	0.1	0.13	0.12	0.13	0.11	0.12	0.12	0.11	0.118571	0.01069	0.033568	0.123083
2-Methyl-1-butanol	0.13	0.14	0.13	0.13	0.14	0.14	0.11	0.13	0.131429	0.01069	0.033568	0.123083
1-Pentanol	0.16	0.14	0.16	0.15	0.18	0.15	0.15	0.15	0.155714	0.012724	0.039954	0.146498
2-Hexanone	0.13	0.15	0.16	0.13	0.13	0.15	0.13	0.14	0.14291	0.01291	0.040537	0.168905
2-Heptanone	0.14	0.15	0.15	0.14	0.13	0.12	0.15	0.14	0.14547	0.011547	0.036258	0.172224
2-Methylisoborneol	0.14	0.13	0.12	0.16	0.16	0.15	0.13	0.14	0.141429	0.015736	0.049411	0.263524
3-Octanone	0.23	0.26	0.24	0.25	0.24	0.25	0.26	0.24	0.247143	0.011127	0.034939	0.18634
3-Octanol	0.12	0.11	0.11	0.11	0.1	0.11	0.09	0.10	0.107143	0.009512	0.029867	0.161782
2-Pentyl furan	0.12	0.14	0.13	0.11	0.14	0.13	0.12	0.12	0.127143	0.011127	0.034939	0.200897
2-Ethyl-1-hexanol	0.12	0.13	0.14	0.11	0.14	0.12	0.12	0.12	0.125714	0.011339	0.035604	0.192856
1-Octanol	0.13	0.15	0.12	0.12	0.15	0.13	0.12	0.13	0.131429	0.013452	0.042239	0.228794
2-Methoxy-3-pyrazine	0.1	0.1	0.1	0.11	0.13	0.12	0.11	0.11	0.11547	0.011547	0.036258	0.229631
Geosmin	0.09	0.1	0.11	0.1	0.1	0.1	0.09	0.09	0.098571	0.006901	0.021668	0.164316
1-Octen-3-ol	0.09	0.1	0.1	0.11	0.09	0.09	0.1	0.09	0.097143	0.007559	0.023736	0.126593

Appendix A

Response Factor Report GC/MS Ins

Method : C:\HPCHEM\1\METHODS\MVOC0413.M (Chemstation Integrator)
 Title :
 Last Update : Sun Apr 17 13:23:19 2005
 Response via : Initial Calibration

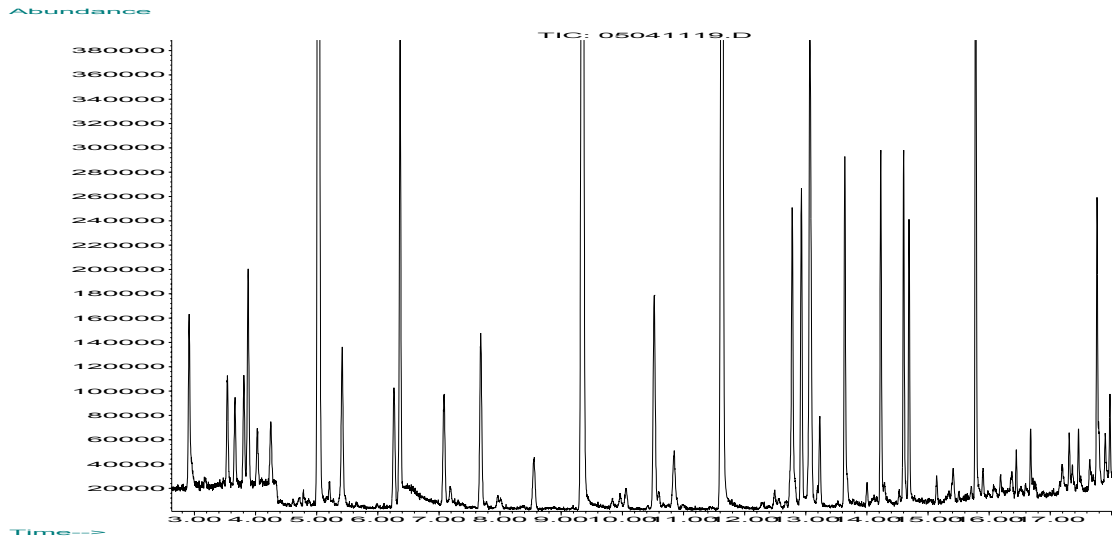
Calibration Files

1 =05041114.D 2 =05041115.D 3 =05041116.D
 4 =05041118.D 5 =05041119.D 6 =05041151.D

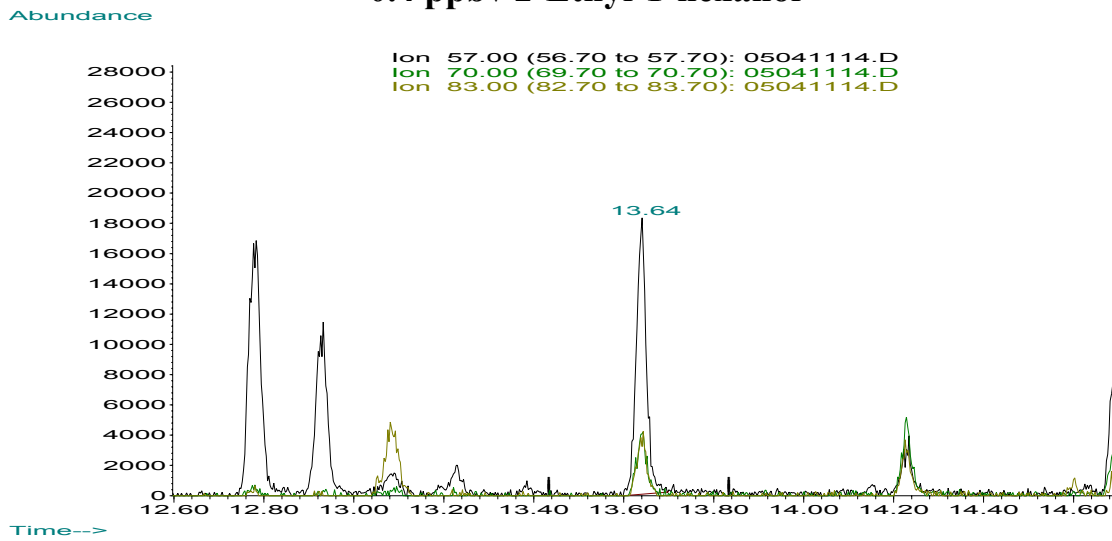
Compound	1	2	3	4	5	6	Avg	%RSD
1) 2-Butanone	1.577	1.714	1.388	1.242	1.190	1.073	1.364	E5 17.9
2) 2-Methyl Furan	3.507	3.142	2.349	2.313	1.995	2.047	2.559	E5 24.2
3) 3-Methyl Furan	3.317	3.220	2.570	2.557	2.172	2.169	2.668	E5 18.8
4) 2-Methyl-1-Propanol	1.884	1.464	1.306	1.392	1.075	1.148	1.378	E5 20.8
5) I 1,4-Difluorobenzene	-----ISTD-----							
6) 3-Methyl-2-Butanol	3.098	2.677	2.818	2.584	2.635	2.517	2.715	7.10
7) 2-Pentanol	3.344	2.678	2.292	2.303	2.098	2.200	2.418	19.03
8) 3-Methyl-1-Butanol	0.781	0.669	0.658	0.625	0.621	0.542	0.640	11.82
9) 2-Methyl-1-Butanol	1.405	1.228	1.080	1.085	1.098	0.754	1.063	21.60
0) 1-Pentanol	1.065	0.900	0.948	0.908	0.888	0.853	0.931	7.36
1) 2-Hexanone	1.515	1.372	1.342	1.290	1.280	1.306	1.364	6.40
2) I Chlorobenzene-d5	-----ISTD-----							
3) 2-Heptanone	5.446	4.870	4.619	4.367	4.371	4.109	4.561	10.35
4) S 4-Bromofluorobenzene	0.742	0.742	0.738	0.733	0.732	0.747	0.739	0.71
5) 2-Methyl-iso-borneo	2.058	1.719	1.533	1.537	1.378		1.557	20.43
6) 3-Octen-1-ol	3.778	3.757	3.654	3.598	3.615		3.647	3.00
7) 3-Octanone	1.062	0.967	0.932	0.926	0.855	0.824	0.916	9.09
8) 3-Octanol	1.855	1.738	1.706	1.625	1.630	1.539	1.671	6.27
9) 2-Pentyl Furan	8.085	7.475	7.139	6.908	6.681	6.425	7.038	8.30
0) 2-Ethyl-1-Hexanol	3.489	3.349	3.099	3.005	2.957	2.704	3.047	9.66
1) 1-Octanol	0.806	0.743	0.713	0.724	0.681	0.621	0.705	8.79
2) 2-Methoxy-3-pyrazin	3.535	3.257	2.944	2.621	2.467	2.352	2.802	16.24
3) Geosmin	2.413	2.057	1.812	1.473	1.618	1.329	1.749	21.55

Appendix B

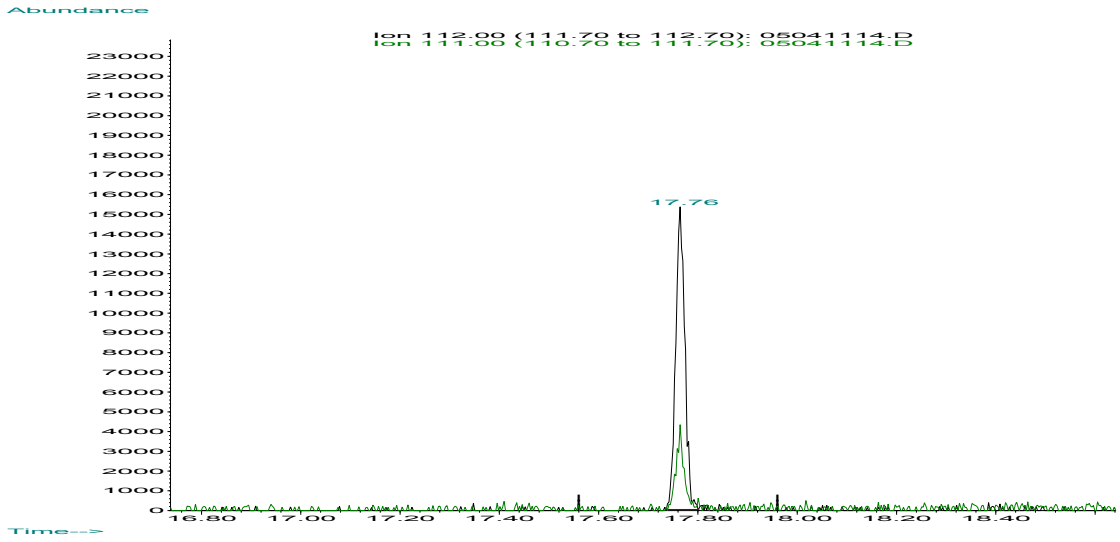
Full Scan Total Ion Chromatogram of MVOC's



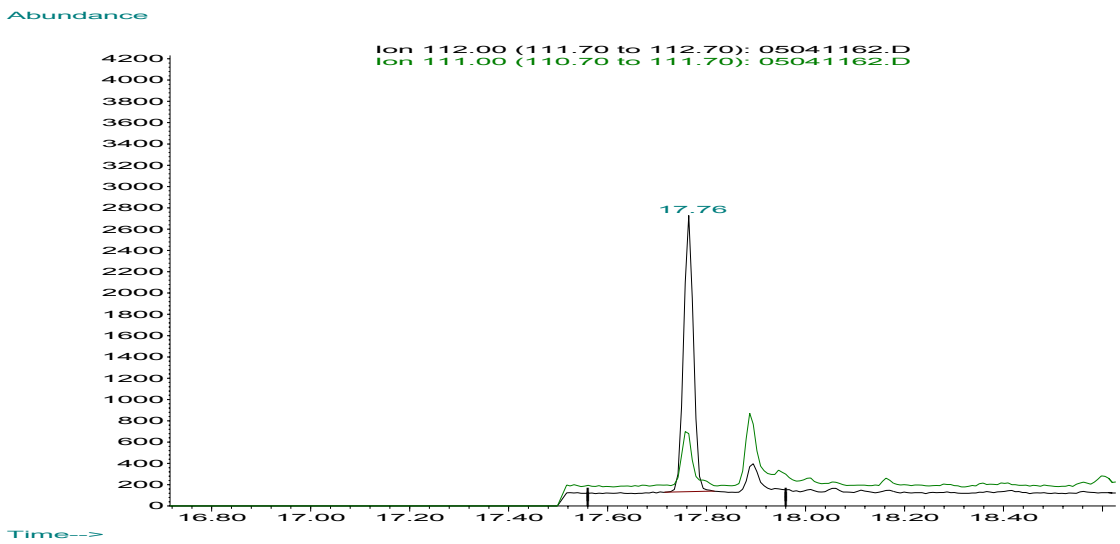
0.4 ppbv 2-Ethyl-1-hexanol



0.4 ppbv Geosmin in Full Scan



0.1 ppbv Geosmin SIM



Selected Ion Chromatogram for Garbage Disposal sample 2-Ethyl-1-hexanol

