Environmental Chamber Test Protocol for Measuring Chemical Emissions, Including Sulfur Compounds from Drywall with Preliminary Results

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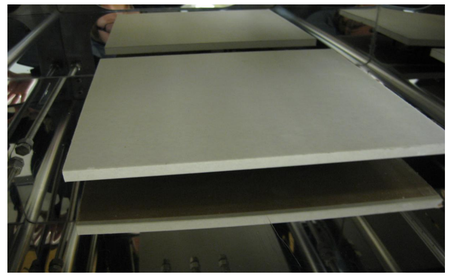
Abstract

Recently, drywall produced in China has been implicated as the cause of health complaints and corrosion of metal components in houses, with sulfur compounds as the potential source. Federal and state agencies are interested in determining if sulfur containing chemicals are being released from this drywall and identifying the compounds. To assist these agencies, as well as product manufacturers and users, an environmental chamber protocol for evaluating chemical emissions from drywall was developed. The protocol follows ASTM testing and analytical procedures for the identification of chemical emissions. The method allows the material to produce emissions as it would in a house, yielding a more accurate assessment of product performance in residential environments and the resultant chemical exposure. Testing is conducted at standard and at elevated environmental conditions (temperature and humidity). Chemical emissions from the product are collected on solid sorbents and analyzed by gas chromatography/mass spectrometry (GC/MS). In addition, emissions are collected in Tedlar® bags and analyzed by chemiluminescence for a target list of reduced sulfur compounds. A series of "suspect" drywall products were studied using these methodologies. More than 50 sulfur containing compounds were observed in the emissions. The primary classes of sulfur compounds observed were thiols, disulfides and thiophenes. The results of these studies showed that elevated heat and humidity exacerbate the release of sulfur compounds. In general, emission levels increased tenfold with a 25 F increase in temperature. Additionally, ~400 non-sulfur VOCs were identified emitting from the products, including alcohols, ketones, alkanes, alkenes, aromatics, carboxylic acids, amines and furans.

Dynamic Environmental Chamber used for emissions testing for building materials such as drywall



Drywall loaded into environmental chamber for testing

Methodology – Environmental Chamber

The drywall samples were tested in small-sized environmental chambers approximately 95 L in volume. The environmental chamber operation and control measures used in the studies followed the guidance of ASTM Standard D 5116 "Standard Guide for Small-Scale Environmental Chamber Determinations of Organic Emissions from Indoor Materials/Products" (1). The chambers are manufactured from stainless steel, with the interiors polished to a mirror-like finish to minimize contaminant adsorption. Air flow through the chambers enters and exits through aerodynamically designed air distribution manifolds also manufactured of stainless steel. Supply air to the chambers is stripped of formaldehyde, VOCs, and other contaminants, so that background levels present in the empty chamber fall below strict levels (<10 µg/m³ TVOC, <10 µg/m³ total particles, <2 µg/m³ formaldehyde, and <2 µg/m³ for any individual VOC). The chambers are process controlled and equipped with a continuous data acquisition system for verification of the operating conditions of air flow, temperature, and humidity. Products evaluated under standard conditions were tested at 73 F and 50% RH. Products evaluated under elevated conditions were tested at 98 F and >50% RH. The samples are loaded into the chambers such that all surface areas are exposed.

Gas chromatograph/mass spectrometer (GC/MS) used to analyze volatile organic compounds (VOCs) emitting from building materials such as drywall

Methodology – Analytical Measurements

Volatile Organic Compounds (VOCs), Including Sulfur Containing VOCs

VOC measurements were made using gas chromatography with mass spectrometric detection (GC/MS). Chamber air was collected onto a solid sorbent, which was then thermally desorbed into the GC/MS. Instrumentation included a sample concentrator and a gas chromatograph with a mass selective detector (GC/MS). The sorbent collection technique, separation and detection analysis methodology is adapted from techniques presented by the USEPA and other researchers. The technique follows USEPA Method IP-1B and ASTM D 6196 and is generally applicable to C_6 - C_{16} organic chemicals with boiling points ranging from 35ºC to 250ºC (2-6). While measurements are typically reported to a quantifiable level of 2 µg/m³, for this study lower levels of detection were applied to identify chemicals with very low odor thresholds in the sub part-per-billion levels, such as sulfur containing VOCs.

The individual VOCs were separated and detected by GC/MS. Individual VOCs were quantified (relative to toluene as a standard) and identified using a specialized indoor air mass spectral database and a general mass spectral library available from the National Institute of Standards and Technology (NIST). This library contains mass spectral characteristics of more than 75,000 compounds as made available from NIST, the USEPA and the National Institutes of Health (NIH). The identification match is based on data which includes the gas chromatographic retention time of the compound in addition to the mass spectrum.

Reduced Sulfur Compounds

Emissions were also collected in specialized Tedlar® bags and analyzed by chemiluminescence for a specific target list of reduced sulfur compounds, including hydrogen sulfide, carbon disulfide and carbonyl sulfide. The analysis is conducted per ASTM D 5504 via gas chromatography with a sulfur chemiluminescence detector.

Drywall Tested at Standard Conditions (73 F and 50% RH)

		Sample ID							
		1	2	3	4	5	6	7	8	9
CAS Number	Chemical Name	Measured Concentration (µg/m³)								
75-33-2	2-Propanethiol			0.1			0.1			
2432-54-4	Butyric acid, thio-, S-hexyl ester								0.2	0.2
110-81-6	Diethyl disulfide				2.5	1.1				
4253-89-8	Disulfide, bis(1-methylethyl)	3.4	1.1	3.1	1.6	0.8	1.8			
5943-30-6	Disulfide, bis(1-methylpropyl)	2.9	1.3	2.4	1.8	1.3	2			
67421-86-7	Disulfide, ethyl hexyl	6.5		6			4.7			
67727-99-5	Disulfide, pentyl propyl	1.7	0.7	1.4	1.1	0.8	1.3			
17374-18-4	Tetrahydro-1,3-oxazine-2-thione									0.2
6028-61-1	Trisulfide, dipropyl	3.9	1.8	2.6	3.2	2.5	3			

Sulfur volatile organic compounds identified emitting from suspect imported drywall tested at standard conditions for temperature (T = 73 F) and relative humidity (RH = 50%). Analysis based on EPA Method IP-1B and ASTM D 6196 for VOCs by thermal desorption followed by gas chromatography/mass spectrometry (TD/GC/MS).

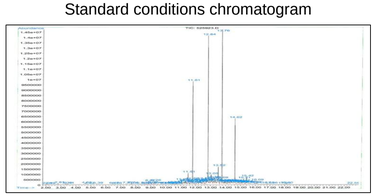
		Sample ID		
		1	6	8
CAS Number	Chemical Name	Measured Concentration (ppbV)		
7783-06-4	Hydrogen Sulfide	nd	nd	nd
463-58-1	Carbonyl Sulfide	nd	nd	nd
74-93-1	Methyl Mercaptan	nd	nd	nd
75-08-1	Ethyl Mercaptan	nd	nd	nd
75-18-3	Dimethyl Sulfide	nd	nd	nd
75-15-0	Carbon Disulfide	nd	nd	nd
75-33-2	Isopropyl Mercaptan	nd	nd	nd
75-66-1	tert-Butyl Mercaptan	nd	nd	nd
107-03-9	n-Propyl Mercaptan	nd	nd	nd
624-89-5	Ethyl Methyl Sulfide	nd	nd	nd
110-02-1	Thiophene	nd	nd	nd
513-44-0	Isobutyl Mercaptan	nd	nd	nd
352-93-2	Diethyl Sulfide	nd	nd	nd
109-79-5	n-Butyl Mercaptan	nd	nd	nd
624-92-0	Dimethyl Disulfide	nd	nd	nd
616-44-4	3-Methylthiophene	nd	nd	nd
110-01-0	Tetrahydrothiophene	nd	nd	nd
638-02-8	2,5-Dimethylthiophene	nd	nd	nd
872-55-9	2-Ethylthiophene	nd	nd	nd
110-81-6	Diethyl Disulfide	nd	nd	nd

Reduced sulfur compounds identified emitting from suspect imported drywall tested at standard conditions for temperature (T = 73 F) and relative humidity (RH = 50%). Analysis conducted per ASTM D5504-01 via gas chromatography with a sulfur chemiluminescence detector, using a 1 ml sample volume. (nd = non-detect)

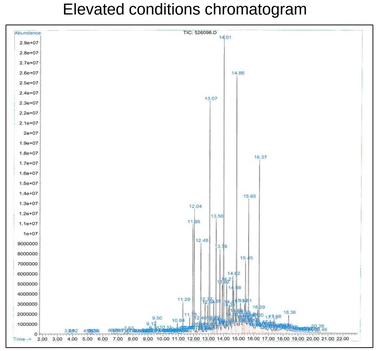
Retention times of selected sulfur containing VOCs identified in the chromatograms

Retention Time	Chemical Name	CAS No.
11.9450	Disulfide, ethyl 1-methylethyl	053986-36-2
12.4821	Disulfide, bis(1-methylethyl)	004253-89-8
13.4997	2-(Isopropyldisulfanyl)butane	067421-86-7
13.9222	Isopropyl isobutyl disulfide	067421-82-3
14.2105	2-Butanethiol, 2-methyl-	001679-09-0
14.4073	Disulfide, bis(1-methylpropyl)	005943-30-6
14.6172	Trisulfide, dipropyl	006028-61-1
15.1213	Disulfide, bis(2-sulfhydrylethyl)-	010008-38-5

Standard conditions chromatogram



Elevated conditions chromatogram



References

1. ASTM D 5116, "Standard Guide for Small-Scale Environmental Chamber Determinations of Organic Emissions from Indoor Materials/Products." ASTM, West Conshohocken, PA, 2006.
2. Winberry, W. T., et al., "Compendium of Methods for the Determination of Air Pollutants in Indoor Air", Office of Research and Development, USEPA, RTP, NC, April 1990.
3. Bertoni, G., F. Bruner, A. Liberti, and C. Perrino, "Some Critical Parameters in Collection, Recovery, and Gas Chromatographic Analysis of Organic Pollutants in Ambient Air Using Light Adsorbents." J. Chromatogr., 203, 263-270 (1981).
4. Bruner, F., G. Bertoni, and G. Crescentini, "Critical Evaluation of Sampling and Gas Chromatographic Analysis of Halocarbons and Other Organic Air Pollutants." J. Chromatogr., 167, 399-407 (1978).
5. Mangani, F., A. Mastrogiacomo, and O. Marras, "Evaluation of the Working Conditions of Light Adsorbents and Their Use as Sampling Material for the GC Analysis of Organic Air Pollutants in Work Areas." Chromatographia, 15, 712-716 (1982).
6. ASTM D 6196, "Practice for the Selection of Sorbents and Pumped Sampling/ Thermal Desorption Analysis Procedures for Volatile Organic Compounds in Air." ASTM, West Conshohocken, PA, 2003.
7. ASTM D 5504, "Standard Test Method for Determination of Sulfur Compounds in Natural Gas and Gaseous Fuels by Gas Chromatography and Chemiluminescence." ASTM, West Conshohocken, PA, 2008.

Drywall Tested at Elevated Conditions (98 F and >50% RH)

		Sample ID								
		1	2	3	4	5	6	7	8	9
CAS Number	Chemical Name	Measured Concentration (µg/m³)								
505-20-4	1,2-Dithiane					1.4	0.5	2.6		
109-79-5	1-Butanethiol			0.1						
541-31-1	1-Butanethiol, 3-methyl-			0.1				0.6		
111-31-9	1-Hexanethiol							1.1		
110-66-7	1-Pentanethiol			0.1						
52195-40-1	1-Propene, 1-(methylthio)-, (Z)-							0.1		
513-53-1	2-Butanethiol	1.2	0.2	1.3	0.8	0.3	7.6			
1679-09-0	2-Butanethiol, 2-methyl-				24.3	10.8	33.1			
1679-06-7	2-Hexanethiol			0.4						
52326-10-0	2-Methyl-3-(methylthio)-1-propene						0.8			
2084-19-7	2-Pentanethiol	0.5	0.2	0.7	0.2	0.2	4			
75-33-2	2-Propanethiol			0.7			2.9		0.1	
632-15-5	3,4-Dimethylthiophene			0.1						
33959-26-1	3-Methyl-3-hydroxybutane-1-thiol						1.2			
616-31-9	3-Pentanethiol	0.4	0.1	0.4		0.2	2			
108-98-5	Benzenethiol						6.8			
54789-20-7	Benzo[b]thiophene, 2,3-diethyl-				1.1	0.7				
16587-45-4	Benzo[b]thiophene, 2,7-diethyl-						1.3			
16587-51-2	Benzo[b]thiophene, 2-ethyl-5-methyl-					1.2	2.2			
16587-43-2	Benzo[b]thiophene, 2-ethyl-7-methyl-	2.3	1	0.9	4.6	5.4	5.8			
16587-32-9	Benzo[b]thiophene, 2-propyl-						1.8			
16587-46-5	Benzo[b]thiophene, 7-ethyl-2-propyl-				4.4	2.7				
75-15-0	Carbon disulfide								0.2	
1679-07-8	Cyclopentanethiol			0.1			1.1			
132-65-0	Dibenzothiophene					0.3				
110-81-6	Diethyl disulfide		0.7	2.1	15.8	4.8	28			
597-35-3	Diethyl sulfone					0.2	3.6			
72437-50-4	Disulfide, 1-methylethyl isopentyl					1.7	2.1			
4253-89-8	Disulfide, bis(1-methylethyl)	14.6	8.1	13.8	42.8	21.5	57.3			
5943-30-6	Disulfide, bis(1-methylpropyl)	14.5	7.8	10.4	38.3	16	61.1			
10008-38-5	Disulfide, bis(2-sulfhydrylethyl)-	3.1	1.6	2.3	38.8	16.2	60.7			
624-92-0	Disulfide, dimethyl				0.2					
629-19-6	Disulfide, dipropyl	3.9	1.4	3.3	16.2	6.4	29.5			
53966-36-2	Disulfide, ethyl 1-methylethyl	6.1	3.5	6.3	62	22.9	64.3			
67421-86-7	Disulfide, ethyl hexyl	21.4	13.3	16.7	53.9	26.7	52.4			
2179-60-4	Disulfide, methyl propyl						4.7			
67727-99-5	Disulfide, pentyl propyl	7.7	4	5.7	14.1	7.9	24.7			
72437-66-2	Disulfide, propyl isopentyl	1.8	0.7		5.8	1.8				
63986-03-8	Ethyl n-butyl disulphide				8.7	3.2	17			
30453-31-7	Ethyl n-propyl disulfide	0.9			0.6					
67421-82-3	Isopropyl isobutyl disulfide				39.1	53.5	17.1			
20333-39-5	Methyl ethyl disulphide	0.3	0.1	0.4	2.4	0.5	3.9			
40136-65-0	Methyl isopropyl disulphide	2	0.8	1.6	5.2	1.6	9			
67421-87-8	Methyl sec-butyl disulphide	1.3	0.7	1.3	3	1.2	5.4			
5008-73-1	Propane, 1-[(1-methylethyl)thio]	0.2	0.2		0.2	0.2	3.1			
7446-09-5	Sulfur dioxide						1.8			
5955-98-6	Thiirane, 2,3-dimethyl-, trans-						0.4			
1072-43-1	Thiirane, methyl-						0.4		0.1	
632-16-6	Thiophene, 2,3-dimethyl-				0.2	0.1	0.6			
638-00-6	Thiophene, 2,4-dimethyl-	0.8	0.3	0.4						
638-02-8	Thiophene, 2,5-dimethyl-						2.5			
1689-79-8	Thiophene, 3-(1,1-dimethylethyl)-	0.8	0.3	0.6						
35686-14-7	Thiophene, 3,4-diethyl-				1.7	0.6	3.1			
6028-61-1	Trisulfide, dipropyl	11.1	5.7	8.7	36.4	15.8	48.8		1.3	0.3

Sulfur volatile organic compounds identified emitting from suspect imported drywall tested at elevated conditions for temperature (T = 98 F) and relative humidity (RH > 50%). Analysis based on EPA Method IP-1B and ASTM D 6196 for VOCs by thermal desorption followed by gas chromatography/mass spectrometry (TD/GC/MS).

		Sample ID		
		1	6	8
CAS Number	Chemical Name	Measured Concentration (ppbV)		
7783-06-4	Hydrogen Sulfide	38	36	7.4
463-58-1	Carbonyl Sulfide	nd	nd	nd
74-93-1	Methyl Mercaptan	nd	nd	nd
75-08-1	Ethyl Mercaptan	nd	nd	nd
75-18-3	Dimethyl Sulfide	nd	nd	nd
75-15-0	Carbon Disulfide	6.6	6.9	nd
75-33-2	Isopropyl Mercaptan	7.8	nd	nd
75-66-1	tert-Butyl Mercaptan	nd	nd	nd
107-03-9	n-Propyl Mercaptan	nd	nd	nd
624-89-5	Ethyl Methyl Sulfide	nd	nd	nd
110-02-1	Thiophene	6.6	nd	nd
513-44-0	Isobutyl Mercaptan	nd	nd	nd
352-93-2	Diethyl Sulfide	nd	nd	nd
109-79-5	n-Butyl Mercaptan	nd	nd	nd
624-92-0	Dimethyl Disulfide	nd	nd	nd
616-44-4	3-Methylthiophene	nd	nd	nd
110-01-0	Tetrahydrothiophene	nd	nd	nd
638-02-8	2,5-Dimethylthiophene	nd	nd	nd
872-55-9	2-Ethylthiophene	nd	nd	nd
110-81-6	Diethyl Disulfide	nd	3.1	nd

Reduced sulfur compounds identified emitting from suspect imported drywall tested at standard conditions for temperature (T = 98 F) and relative humidity (RH > 50%). Analysis conducted per ASTM D5504-01 via gas chromatography with a sulfur chemiluminescence detector, using a 1 ml sample volume. (nd = non-detect)

Study Results

A series of "suspect" drywall products were studied using these methodologies. The results demonstrated the presence of emissions of organic and inorganic sulfur emissions. The results of these studies also showed that elevated heat and humidity exacerbate the release of sulfur compounds. In general, emission levels increased tenfold with elevated temperature from 73 F to 98 F. In addition, there were approximately 400 other non-sulfur VOCs identified as emitting from the products, all at low levels. These included numerous alcohols, ketones, alkanes, alkenes, aromatics, carboxylic acids, amines and furans. These VOCs coupled with sulfur specific VOCs created complex mixtures, with each individual VOC present at a very low level. The source of these VOCs is unknown since the history, exposure and handling of these products were not controlled or documented.