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Desorption of Residual Sulfuryl Fluoride from Structural and Household Commodities by Headspace Analysis Using Gas Chromatography

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Sulfuryl fluoride, SO_2F_2, is a widely used fumigant for structural pest control (Monroe 1969, Ebeling 1975). Structural fumigation requires that the entire building be sealed or enclosed in tarpaulins to confine the gas for a predetermined concentration and time depending on the target organism, weather, and physical nature of the building. Because structural materials, furnishings, and household effects are also exposed to the fumigant, these act as sorptive matrices. Desorption of sulfuryl fluoride (SF) from some commodities may continue after the building has been reoccupied. The limited air exchange in modern, environmentally controlled buildings and the greater use of synthetic polymers in structures dictate a need to assess the levels of SF desorption from fumigated materials associated with human dwellings. In this study we analyze SF desorption levels over a 40-day period from 13 structural and household commodities at two exposure concentrations by gas chromatography of headspace.

MATERIALS AND METHODS

Commodities analyzed for SF residues were: concrete block, gypsum/cardboard drywall, wood, fiberglass insulation (Owens-Corning), expanded polystyrene insulation (Perma-R-Foam, Dunnellon, FL), top soil, ridge-and-furrow type carpet padding, polyester cushion fiber, wool fabric, cotton fabric, leather (baseball glove), latex baby bottle nipples (Gerber), and plastic toy soldiers (Taiwan). All commodities were subdivided into pieces <13 mm at their greatest width. Two-gram samples of polyester and fiberglass and 1 g of polystyrene were held in 15 cm OD paper bowls, and 10 g each of the remaining matrices were held in 90 or 150-ml paper cups. A 4,217 liter fumigation chamber was used to fumigate these samples at 25°C and ca. 90% RH following the procedure of Scheffrahn et al. 1987. Samples were fumigated for 20 h at 36 or 360 mg/l; equivalent to 8,640 or 86,400 ppm (vol. SF/vol. air),

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respectively. Two samples of each matrix were included for each of six aging periods at each concentration. Fumigations at each concentration were replicated three times, once per week, to yield a total of 936 samples (six samples/matrix/age/concentration).

After fumigation, samples were moved to an air-conditioned room (23°C, 70% RH) where aeration took place for 2, 8, or 26 h, or 5, 20, or 40 days. At the appropriate sampling time, samples were transferred to 120-ml serum bottles (Fisher Sci. Co., listed as 100-ml) and crimp-sealed with 20 mm Teflon TFE-lined septa (Fisher). After 24 h equilibration, a 0.5 ml volume of headspace was removed by syringe (1-ml Tuberculin, B-D) for gas chromatographic analysis. Analyses were performed on an HP 5890A instrument fitted with two 2.5 m X 2 mm ID glass columns packed with 80-100 mesh Chromosorb 101 (Alltech Assoc., Inc.). Low SF residues were measured with a linearized Ni-63 electron capture detector (ECD) using argon:methane (95:5) as carrier gas. Residue levels above 280 ppm were determined with a thermal conductivity detector using helium as carrier. Constant oven temperature of 50°C and carrier flows of 20 ml/min eluted SF after ca. 2 min and water vapor in ca. 6 min. Detector responses were integrated with a Spectra-Physics 4290 computing integrator.

Standards were prepared from neat SF by serial dilution in empty serum bottles. Linear regressions of ECD response to 5 continuous ranges of SF standards were required because the extremely wide range of residues detected could not be accurately calculated from a single line equation. Peak areas were quantified by comparison with the appropriate standard response curve selected from the integrator memory. Coefficients of variation for all standards were <2%. In recovery studies, commodities were sealed in serum bottles, spiked with 50 ppm SF, and analyzed after 24 h. Recoveries were between 93-100% with the exception of concrete block (<1%), carpet pad (54%), and polystyrene (120%).

RESULTS AND DISCUSSION

Sulfuryl fluoride headspace accumulations resulting from 36 mg/l (Table 1) and 360 mg/l (Table 2) exposures varied extensively among the matrices. Polystyrene insulation released the greatest quantities of SF, ca. 50 times more than the next highest desorbing matrix, latex nipples, at 2 h. Residues from polystyrene surpassed all other commodities until the 40-day post-fumigation analysis when greater volumes of SF desorbed from polyester fibers. Initial residues from the six commodities giving off most SF were 10-12 fold greater at the 360 mg/l SF exposure and varied over the next 3

Table 1. Headspace residues of sulfuryl fluoride in ppb ($\bar{X} \pm$ SD) from aged samples after exposure to 36 mg/l for 20 hours[1]

Commodity	Post-exposure time 2h	8h	26h	5d	20d	40d
Cotton	4 ±3	2 ±1	0.5 ±0.3	0.5 ±0.3	0.4 ±0.2	nd
Wool	78 ±86	40 ±31	37 ±45	15 ±20	3 ±4	1 ±0.9
Leather	87 ±37	50 ±11	26 ±7	7 ±3	2 ±3	nd
Carpet Pad	0.5 ±0.3	0.4 ±0.2	<0.1	0.3 ±0.4	0.4 ±1	nd
Polyester	9,174 ±1,587	3,814 ±2,393	2,995 ±244	620 ±90	44 ±5	7 ±0.5
Nipple	20,256 ±749	8,007 ±1,148	856 ±168	2 ±3	0.6 ±0.6	nd
Toy	2,204 ±186	930 ±304	558 ±42	89 ±16	8 ±0.8	1 ±0.5
Topsoil	81 ±24	21 ±6	7 ±4	1 ±1	0.3 ±0.2	nd
Wood	14,496 ±7,140	6,179 ±2,720	2,369 ±443	82 ±40	0.3 ±0.3	nd
Drywall	6 ±4	2 ±1	0.4 ±0.3	0.5 ±0.7	0.4 ±0.7	nd
Polysty.	975,347 ±100,335	531,889 ±28,417	267,237 ±8,997	48,129 ±8,566	390 ±33	5 ±0.9
Concrete	0.4 ±0.3	1 ±2	<0.1	<0.1	<0.1	nd
Fiberglass	10 ±4	4 ±3	1 ±1	0.2 ±0.3	2 ±2	nd

1 Volume SF/vol. headspace per gram commodity (i.e. actual residues divided by no. grams per sample). nd = not detected.

Table 2. Headspace residues of sulfuryl fluoride in ppb ($\bar{X} \pm SD$) from aged samples after exposure to 360 mg/l for 20 hours[1]

Commodity	Post-exposure time 2h	8h	26h	5d	20d	40d
Cotton	45 ±31	10 ±2	8 ±7	1 ±0.7	0.2 ±0.4	<0.1
Wool	1,210 ±459	849 ±392	520 ±212	183 ±46	31 ±16	11 ±4
Leather	755 ±221	573 ±142	247 ±81	83 ±21	4 ±0.5	0.3 ±0.2
Cpt. Pad	12 ±6	3 ±0.8	1 ±0.5	0.3 ±0.3	0.1 ±0.2	<0.1
Polyester	93,350 ±10,324	58,757 ±4,098	34,173 ±2,779	7,302 ±1,035	481 ±31	92 ±9
Nipple	218,829 ±45,544	99,230 ±11,224	15,216 ±2,341	9 ±4	<0.1	<0.1
Toy	23,110 ±2,048	15,717 ±1,334	7,048 ±372	1,124 ±127	85 ±7	14 ±2
Topsoil	1,001 ±251	338 ±175	71 ±9	18 ±6	3 ±1	0.3 ±0.4
Wood	169,790 ±58,749	89,146 ±23,693	32,784 ±13,641	1,897 ±1,246	2 ±2	<0.1
Drywall	60 ±15	20 ±8	6 ±1	0.8 ±0.3	<0.1	<0.1
Polysty.	9,742,060 ±1,142,053	4,936,716 ±265,080	2,216,094 ±200,194	233,329 ±126,118	2,788 ±1,329	15 ±14
Concrete	48 ±59	16 ±14	2 ±0.6	0.9 ±1	<0.1	<0.1
Fibergls.	124 ±30	59 ±39	16 ±3	6 ±4	0.5 ±0.7	0.3 ±0.3

1 See footnote in Table 1.

Table 3. Ratios of sulfuryl fluoride residues in wood versus other high-residue commodities and percents of original (2h) residue remaining to 5 days

Commodity	SF Exp. Conc.	2h x:wood	8h x:wood	8h %2h	26h x:wood	26h %2h	5d x:wood	5d %2h
Polyester	36	0.63	0.62	42	1.3	33	7.6	7
	360	0.55	0.66	63	1.0	36	3.8	8
Nipple	36	1.4	1.3	40	0.36	4	0.02	<0.01
	360	1.3	1.1	45	0.46	7	0.005	<0.01
Toy	36	0.15	0.15	42	0.24	25	1.1	4
	360	0.14	0.18	68	0.21	30	0.59	5
Wood	36	1	1	43	1	16	1	0.6
	360	1	1	53	1	19	1	1
Polysty.	36	67	86	55	113	27	587	5
	360	57	55	51	68	23	123	2

sampling periods between 8-23 times the amounts detected in the 36 mg/l samples. Although initially low, residues from wool were the most persistent in proportion to initial levels, and wool was the only commodity with residues greater than 1% of the initial 2-h value after 20 days of aeration.

The low residues observed for concrete block and carpet pad coupled with low recoveries of SF in spiked samples suggested formation of unknown non-volatile reactants, possibly by alkaline hydrolysis or chemisorption, in these porous commodities. SF loss due to concrete block exposure was extreme as recovery from samples spiked with 8,640 ppm was <10 ppb within 18 h. High recovery of SF from polystyrene was due to the displacement of headspace volume by this high-volume commodity.

Using wood as a standard matrix for comparison, desorption of SF proceeded more slowly after both exposure concentrations for polystyrene, polyester, and the plastic toy, and more rapidly for the latex nipple matrices (Table 3). Of these high-residue commodities, residence time of SF in polyester was proportionally the greatest at 26 h (33-36% of initial), however, at this sampling period, gross residues from polystyrene still exceeded those desorbed from polyester by more than 60 fold. Correlation coefficients for the plot of natural logarithms of SF residues (ppb) with time (h) indicate good negative first-order linearity for high-residue commodities (Table 4). The slopes of these desorption curves are commodity specific but of similar magnitude for both exposure levels.

Table 4. Desorption dynamics[1] of sulfuryl fluoride for high-residue commodities up to 5 days post-exposure.

Commodity	SF Exp. Conc.	Correl. Coef. (r)	Slope (m)	Half life[2] (hours)
Polyester	36	-0.954	-0.0195	36
	360	-0.980	-0.0198	35
Nipple	36	-0.990	-0.0747	9.3
	360	-0.998	-0.0838	8.3
Toy	36	-0.963	-0.0238	29
	360	-0.982	-0.0239	29
Wood	36	-0.988	-0.0407	17
	360	-0.986	-0.0356	19
Polystyrene	36	-0.971	-0.0230	30
	360	-0.979	-0.0289	24

1 Correponding to first order equation, $\ln C = -kt + b$; where C = SF residue conc., rate constant $k = -m$, t = time in hours, and b = y intercept (constant for each commodity at $t = 0$).
2 Half life = $(\ln 2)/k$.

Therefore, in this range, SF residues are proportional to initial fumigant concentrations. Desorption rates, represented by half-life times (Table 3), are similar at both exposure levels, and are dictated by matrix type.

An exposure of 36 mg/l for 20 h, the lower rate in this study, represents a high field rate for SF as recommended for the control of wood-boring beetles. Current label instructions for SF specify that after fumigation, a structure be suitably aerated and then reoccupation permitted when airborne concentrations fall below 5,000 ppb. Although this study does not attempt to simulate a field situation, the data suggest that caution be exercised under some circumstances. If a fumigated structure contains large amounts of one or more highly sorptive commodities such as wood, polystyrene, or polyester; and if the structure is poorly ventilated when reoccupied, additional aeration or subsequent air monitoring may be advisible to insure that accumulations of desorbing SF do not exceed established levels.

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