Sulfuryl Fluoride Residues of Fumigated Foods Protected by Polyethylene Film

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Gas chromatographic headspace analysis was used to determine the postfumigation levels of residual sulfuryl fluoride (SF) in eight food items sealed in polyethylene plastic film or exposed directly to SF. Two layers of 2-mil polyethylene film reduced residual SF levels in food more than 96%. A single 4-mil layer reduced SF levels by at least 79% at 2 h postfumigation. Vegetable oil desorbed the greatest quantity of residual SF of all commodities tested. Half-loss times and partitioning of SF between the headspace and food depended on the nature of the food matrix. Less SF penetrated the inner, doubled, 2-mil polyethylene bags than single 4-mil bags.

Sulfuryl fluoride (SF) is widely used as a fumigant to control termites and other structural pests (Ebeling, 1978). Label directions for structural fumigation with SF specify that food, feed, drugs, and medicinals (including those items in the refrigerators and freezers) must be sealed in containers such as polyethylene plastic bags of at least 4-mil thickness or an equivalent such as two, 2-mil bags (Dow, 1982). The purpose of this investigation was to determine, by headspace analysis, amounts of residual SF present in fumigated food and medicinal items with and without the protection provided by one 4-mil- or two 2-mil-thick barriers of polyethylene plastic film. Penetration of SF through 2- and 4-mil polyethylene film was also quantified.

MATERIALS AND METHODS

Procedure. Note: Sulfuryl fluoride is a toxic, colorless, and odorless gas that must be handled with extreme caution by certified personnel. The following eight food items were fumigated with SF at 36 mg/L (ca. 10 times the drywood termite rate): unbleached enriched flour (Pillsbury), Kibbles 'n Bits dog food (Ken-L Ration), powdered nonfat milk (Carnation), vegetable cooking oil (Crisco), dried beef, acetaminophen (Extra-Strength Tylenol, McNeilab), Red Delicious Washington apples, and Twinkies snack cakes (Hostess, individually wrapped). Four of these commodities were fumigated with SF at 360 mg/L: flour, oil, acetaminophen, and apples. Commodities, except for whole apples and wrapped snack cakes, were weighed (10 g) into cups and all commodities placed in wire cages (45 × 32 × 8 cm). Apples and snack cakes were subdivided and weighed (10 g) after the specified aeration times. Enough of each commodity was fumigated so each headspace evaluation utilized a unique food sample. All commodities were fumigated simultaneously under three conditions: uncovered, sealed in one 4-mil- and sealed in two 2-mil-thick polyethylene film layers. The plastic was sealed around cages by tightly rolling ca. 20 cm of the overlapped film along three sides and clamping the roll every 5 cm.

Commodities were fumigated for 20 h at 27 ± 1 °C in a 4.2-m^3 fumigation chamber as described by Scheffrahn et al. (1987). After fumigation, the chamber was aerated ca. 8 min with forced ventilation to reduce SF concentration below 5 ppm. The chamber door was then opened, polyethylene barriers were removed from cages, and commodity aeration was continued in the laboratory at room temperature. Residual SF was evaluated by headspace (the volume above a liquid or solid in a closed container) analysis at postfumigation aeration periods of 2, 8, 26, 120, 480, and 960 h. After each specified aeration time, duplicate samples were placed in glass vials (120 mL) and crimp-sealed with Teflon TFE-lined septa (Fisher), and residual SF was allowed to equilibrate with vial headspace for 24 h. A 0.5-mL volume of headspace was withdrawn by a 1-mL tuberculin syringe and manually injected into a gas chromatograph to quantify residual SF. The entire procedure was replicated three times for each of the two fumigant exposure concentrations.

To further investigate the dynamics of SF penetration through polyethylene film, plastic bags were purged of air and sealed at one end with a Seal-a-Meal (Dazey Corp.) heat sealer. After the air-tight seal was made, the 2- and 4-mil-thick bags were measured as 30.5 × 33.0 and 24.8 × 40.6 cm, respectively. Dry air was introduced at a known flow rate into the bags with a hypodermic needle. The 2- and 4-mil single bags and the internal bag of a double 2-mil bag were filled with 3000 mL of air, and the hole created by the needle was sealed with cellophane tape. All single bags had a surface area to volume ratio of 0.67 cm^2/cm^3. In the double-bag system, 300 mL of air was injected between bags to yield a 6.7 cm^2/cm^3 ratio of outer bag surface area to between bag volume. Four replicates of each bag type were fumigated with SF at 3.6 or 36 mg/L for 20 h. Immediately after fumigation, a 0.5-mL sample of air was withdrawn from within and between bags and analyzed for SF concentration by gas chromatography.

Gas Chromatography. SF analyses were performed on a Hewlett-Packard 5890A instrument fitted with two 2.5 m × 2 mm (i.d.) glass columns packed with 80–100-mesh Chromosorb 101 (Alltech Associates Inc.). SF residues were measured with a linearized ^{63}Ni electron capture detector (ECD) using argon–methane (95:5) as carrier gas. Residue levels in plastic bags were determined with a thermal conductivity detector using helium as carrier when SF levels were over 280 ppm (v/v). Constant oven temperature of 50 °C and carrier flow 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 Model 4290 computing integrator.

Quantitation. External standards were prepared from neat SF by serial dilution in empty sealed glass vials. Linear regression of the area of ECD response to SF concentration required five continuous ranges of SF standards because detector response was not linear in the wide range of residues encountered. SF residues were quantified as ppb weight of SF to the weight food (w/w). Actual par-

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Table I. Sulfuryl Fluoride Residues (Mean ± SD, ppb) in Foods Fumigated at 36 mg/L for 20 h by Direct Exposure or Protected with One 4-mil- or Two 2-mil-Thick Layers of Polyethylene Film

sample	aeration time, h	no. layers protective polyethylene film		
		0	1 × 4-mil	2 × 2-mil
flour	2	174 ± 8.3	13 ± 17	1.0 ± 2.4
	8	115 ± 6.8	7.7 ± 10	0.6 ± 1.5
	26	46 ± 2.1	2.4 ± 4.2	0.1 ± 0.4
	120	3.9 ± 0.1	0	0
	480	0	0	0
dog food	2	750 ± 176	134 ± 90	28 ± 44
	8	135 ± 56	28 ± 30	2.7 ± 4.7
	26	7.1 ± 1.6	0.8 ± 1.3	0.1 ± 0.2
	120	0	0	0
powdered milk	2	5.4 ± 2.4	0.4 ± 0.4	0.1 ± 0.2
	8	0.6 ± 0.5	0	0
	26	0	0	0
oil	2	23720 ± 910	4619 ± 3902	746 ± 1084
	8	16319 ± 493	3027 ± 2630	499 ± 723
	26	6428 ± 308	933 ± 711	155 ± 227
	120	105 ± 16	15 ± 15	1.9 ± 3.8
	480	0.6 ± 1.0	0	0
	960	0	0	0
beef	2	134 ± 28	10 ± 8.5	0.9 ± 1.1
	8	64 ± 19	1.5 ± 1.1	0
	26	26 ± 7.7	0.4 ± 0.6	0
	120	2.6 ± 1.3	0	0
	480	0	0	0
acetaminophen	2	17 ± 8.5	3.5 ± 2.7	0.3 ± 0.1
	8	6.4 ± 2.7	1.0 ± 2.0	0
	26	3.4 ± 2.1	0.7 ± 0.6	0
	120	0.2 ± 0.2	0	0
	480	0	0	0
apple	2	4092 ± 2213	70 ± 90	2.0 ± 1.5
	8	286 ± 158	1.5 ± 2.9	0
	26	5.5 ± 1.8	0	0
	120	1.1 ± 0.4	0	0
	480	0	0	0
cake	2	218 ± 140	25 ± 40	0.5 ± 0.8
	8	180 ± 115	4.3 ± 4.7	0.7 ± 1.1
	26	7.9 ± 9.4	2.3 ± 3.7	0
	120	0.1 ± 0.1	0	0
	480	0	0	0

titioning of SF between the headspace and the food matrices was tested by sealing food items (10 g) in headspace vials in duplicate, spiking with 5 ppb SF (limit of sensitivity 0.05 ppb w/w), and analyzing headspace after 24 h as described above. We assume the concentration of SF in the gaseous phase is proportional to the total SF present (Henry's law) when applied to a constant-volume system at a specified time. Linear regression was used to determine the desorption pattern of the residual SF from fumigated food. The data were fit to the first-order equation $\ln C = -kt + b$, where C = SF concentration (headspace divided by the appropriate partition coefficient) at time t, rate constant $k = -m$ with m being the slope, and b = y intercept. Half-loss time ($t_{1/2}$) in hours was calculated from $t_{1/2} = (\ln 2)/k$. Calculations obtained from the first-order equation do not reflect the extremely rapid decline in residual sulfuryl fluoride that occurs during the first 2 h of aeration and will inflate SF half-loss times calculated from portions of this protracted desorption curve.

RESULTS AND DISCUSSION

Results indicate that two 2-mil layers of polyethylene film provide greater protection of food from SF exposure as compared to the single 4-mil layer of film (Tables I and II). The double 2-mil film reduced SF residues by more than 96% over unprotected commodities at the 2-h aeration period for both SF exposures. The single 4-mil treatment reduced SF residues by at least 79% in foods exposed to 36 mg/L and >91% for 360 mg/L exposures sampled at 2 h. Except for vegetable oil, which contained the most residual SF of all commodities tested, none of the foods fumigated at 36 mg/L in 4-mil or two 2-mil films had detectable residues at 5 days postexposure. Half-loss

Table II. Sulfuryl Fluoride Residues (Mean ± SD, ppb) in Foods Fumigated at 360 mg/L for 20 h by Direct Exposure or Protected with One 4-mil- or Two 2-mil-Thick Layers of Polyethylene Film

sample	aeration time, h	no. layers protective polyethylene film		
		0	1 × 4-mil	2 × 2-mil
flour	2	6672 ± 1976	59 ± 27	10 ± 17
	8	2367 ± 903	33 ± 17	5.4 ± 8.6
	26	512 ± 289	15 ± 6.5	3.1 ± 4.1
	120	77 ± 49	6.2 ± 6.4	0.8 ± 1.4
	480	8.5 ± 5.9	1.2 ± 1.0	0
	960	0	0	0
oil	2	256446 ± 15608	22431 ± 9020	4371 ± 6283
	8	172468 ± 11854	16000 ± 6390	3086 ± 4538
	26	82454 ± 4173	7445 ± 3790	1284 ± 2094
	120	1791 ± 206	96 ± 66	15 ± 22
	480	31 ± 5.7	2.1 ± 1.0	0.6 ± 0.6
	960	1.5 ± 0.5	1.0 ± 0.6	0
acetaminophen	2	682 ± 347	29 ± 12	8.7 ± 12
	8	208 ± 131	9.2 ± 3.8	2.8 ± 3.8
	26	57 ± 47	4.6 ± 1.9	1.8 ± 1.4
	120	6.0 ± 5.5	1.7 ± 1.8	0.3 ± 0.4
	480	0.3 ± 0.2	0	0
	960	0	0	0
apple	2	69629 ± 22950	4176 ± 3552	402 ± 789
	8	20820 ± 10666	79 ± 90	24 ± 55
	26	382 ± 512	6.6 ± 3.5	1.1 ± 0.4
	120	29 ± 14	1.1 ± 0.7	0
	480	0	0	0

Table III. Desorption Dynamics[a] of Sulfuryl Fluoride from Fumigated Food Items Unprotected and Protected with One 4-mil or Two 2-mil Layers of Polyethylene Films

sample	layers film	fumign, mg/L	correln coeff (r)	intercept (b)	slope (m)	half-loss, h
flour	0	36	−0.989	4.973	−0.031	22.36
	1	36	−0.998	2.643	−0.068	10.19
	2	36	−0.999	0.308	−0.091	7.62
	0	360	−0.892	7.355	−0.012	57.77
	1	360	−0.931	3.358	−0.007	99.03
	2	360	−0.957	1.973	−0.019	36.48
dog food	0	36	−0.992	6.742	−0.187	3.71
	1	36	−0.999	5.198	−0.213	3.26
	2	36	−0.982	3.329	−0.220	3.15
powdered milk	0	36	NA[b]	NA	NA	NA
	1	36	NA	NA	NA	NA
	2	36	NA	NA	NA	NA
oil	0	36	−0.966	9.259	−0.022	31.51
	1	36	−0.997	8.352	−0.048	14.44
	2	36	−0.999	6.572	−0.050	13.86
	0	360	−0.950	11.154	−0.012	57.77
	1	360	−0.889	8.439	−0.011	63.02
	2	360	−0.927	7.422	−0.018	38.51
beef	0	36	−0.975	4.497	−0.031	22.36
	1	36	−0.921	2.023	−0.117	5.93
	2	36	NA	NA	NA	NA
acetaminophen	0	36	−0.980	2.392	−0.034	20.39
	1	36	−0.794	0.928	−0.053	13.08
	2	36	NA	NA	NA	NA
	0	360	−0.922	5.070	−0.014	49.51
	1	360	−0.867	2.654	−0.019	36.48
	2	360	−0.939	1.577	−0.024	28.88
apple	0	36	−0.808	6.084	−0.055	12.60
	1	36	NA	NA	NA	NA
	2	36	NA	NA	NA	NA
	0	360	−0.887	9.865	−0.058	11.95
	1	360	−0.613	5.656	−0.051	13.59
	2	360	−0.968	5.838	−0.229	3.03
cake	0	36	−0.963	5.025	−0.061	11.36
	1	36	−0.853	2.861	−0.086	8.06
	2	36	NA	NA	NA	NA

[a] $\ln C = -kt + b$; C = sulfuryl fluoride concentration (w/w), rate constant $k = -m$ (slope), t = time in hours, b = the y intercept, and half-loss ($t_{1/2}$) = $(\ln 2)/k$. [b] NA = not enough data points to calculate.

Table IV. Penetration of Sulfuryl Fluoride through 2-mil, 4-mil, and Double 2-mil Polyethylene Bags

bag type	fumign rate, mg/L	SF in bag, mg/L ± SD[a]	penetrn rate, μg/cm² per 20 h
4-mil	3.6	0.19 ± 0.02	0.28
	36.0	1.44 ± 0.04	2.15
2-mil	3.6	0.25	0.37
	36.0	2.43 ± 0.14	3.62
2 × 2-mil			
inside bag	3.6	0.06 ± 0.03	0.09
	36.0	0.31	0.46
interspace	3.6	0.93 ± 0.03	0.14
	36.0	5.35 ± 0.86	0.80

[a] Surface area to volume ratio of bags was 0.67 cm^2/cm^3 except the interbag space, which was 6.7 cm^2/cm^3.

of residual SF tended to be consistent within matrices and dependent on the nature of the food matrix (Table III).

Partitioning ratios of SF between the headspace and food were matrix specific. Greater than 90% recovery was obtained after 24 h from spiked headspace vials containing dog food, acetaminophen, powdered milk, water, and air only, with 93.1, 95.2, 96.2, 100, and 99.7% recoveries, respectively. Appreciable partitioning toward matrices and/or degradation of SF occurred with apple and dried beef, with 45.5 and 47.0% recoveries after 24 h, respectively. Recoveries obtained from oil, flour, and cake were 86.5, 78.0, and 74.9%, respectively. Sulfuryl fluoride is known to undergo hydrolysis in the presence of acids or bases (Cady and Misra, 1974; Jones and Lockhart, 1968). A pH of ca. 3.0 for apples suggests acid-mediated hydrolytic loss of SF in that commodity. Meikle and Stewart (1962) reported 55 ppm SF residues, as halide equivalents, in dried beef fumigated at 28 mg/L for 16 h with ^{35}S-radiolabeled SF. They hypothesized that high sulfur-containing residues from decomposed SF occur in proteinaceous materials where a solvent system, such as the fat in meat, is present. Our study seems to be consistent with this hypothesis, as we obtained a higher recovery (86.5%) from vegetable oil than from either dried beef or flour. Sulfuryl fluoride reacts with the N-terminal amino nitrogen of proteins and free amino acids in the flour (Meikle, 1964) and dried beef. A contradiction to the above-mentioned hypothesis of Meikle and Stewart (1962) appears in the case of dog food, which contains 10% fat and 27% protein but yielded a 93% recovery of headspace SF.

Penetration of SF was greater through single 2-mil bags than single 4-mil bags at both exposure concentrations (Table IV). However, less SF was detected in the inner double 2-mil bags than single 4-mil bags: about 3 times less at 3.6 mg/L and over 4 times less at the 36 mg/L SF exposure rate. This is a result of a reduction in the diffusion rate due to the volume of air between double bags. A lower concentration of SF occurs in the air space between bags compared to the ambient chamber concentration, resulting in a shallower diffusion gradient and slower penetration to the food. Thus, the greater the volume of air space between bags, the slower the predicted penetration rate through the next polyethylene layer. Stewart (1957) reported a penetration rate of 0.62 $\mu g/cm^2$ per h at room temperature through 4-mil polyethylene sheeting from a 35 mg/L SF atmosphere. Assuming a constant penetration rate, this equals 12.4 $\mu g/cm^2$ for a 20-h exposure compared to our value of 2.15 $\mu g/cm^2$ per 20 h. Differences in experimental design or polyethylene polymer probably account for the 6-fold difference in penetration rates. Even small leaks in polyethylene film have a profound effect on SF penetration. We observed a 3-fold increase in SF concentrations recorded from a single 2-mil bag containing a minute leak when compared with a sound bag. This finding should serve warning that only unblemished, tightly sealed, polyethylene film will protect food commodities from greater SF exposures and strengthen the contention that two 2-mil bags are superior protection from SF exposure under field conditions than a single 4-mil bag.

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LITERATURE CITED

Cady, G. H.; Misra, S. "Hydrolysis of Sulfuryl Fluoride". *Inorg. Chem.* **1974**, *13*, 837–841.

Dow *Fumigation Manual for use with Vikane Gas Fumigant*; The Dow Chemical Co.: Midland, MI, 1982; p 1.

Ebeling, W. "Urban Entomology"; Division of Agricultural Sciences, University of California: Berkeley, CA, 1978; pp 54, 55.

Jones, M. M.; Lockhart, W. L. "Kinetics of Decomposition of the Fluorosulphate Ion in Aqueous Solution". *J. Inorg. Nucl. Chem.* **1968**, *30*, 1237–1243.

Meikle, R. W. "The Fate of Sulfuryl Fluoride in Wheat Flour". *J. Agric. Food Chem.* **1964**, *12*, 464–467.

Meikle, R. W.; Stewart, D. "The Residue Potential of Sulfuryl Fluoride, Methyl Bromide, and Methanesulfonyl Fluoride in Structural Fumigations". *J. Agric. Food Chem.* **1962**, *10*, 393–397.

Scheffrahn, R. H.; Su, N.-Y.; Osbrink, W. L. A. "Precise Dosage Delivery Method for Sulfuryl Fluoride in Small-chamber Fumigations". *J. Econ. Entomol.* **1987**, *80*, 705–707.

Stewart, D. "Sulfuryl Fluoride—A New Fumigant for Control of the Drywood Termite *Kalotermes minor* Hagen". *J. Econ. Entomol.* **1957**, *50*, 7–11.

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