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Fluoride Residues in Frozen Foods Fumigated with Sulfuryl Fluoride

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Sulfuryl fluoride, SO_2F_2, is used extensively as a fumigant for structural pest control. A recent study (Scheffrahn et al. 1988) demonstrated that exposure of non-perishable, unprotected food commodities to sulfuryl fluoride (SF) results in permanent residue formation of stable, water-soluble fluorides, detected as anionic F^-. The permanent residue potential from exposure of perishable commodities to SF is a concern during the fumigation of structures such as food establishments and homes which may contain large stores of frozen foods. Removing frozen foods from the structure may not be practical or even feasible. Therefore, a need exists to determine if representative foods, exposed to SF while stored in a freezer, amass detectable increases in extractable fluoride (F^-). This study was conducted to determine residual F^- levels in unprotected and polyethylene bag-protected frozen foodstuffs fumigated with SF.

MATERIALS AND METHODS

The following frozen commodities were fumigated and evaluated for F^- residues: ground beef (Publix Supermarket, meat product), shoestring french-fried potatoes (Ore-Ida, starch product), sweet peas (Green Giant, vegetable product), vanilla ice cream (Borden Homestyle, dairy product), and unbleached wheat flour (Pillsbury, comparative non-perishable). For each fumigation, four 5-gram samples of each of the five commodities were placed in open 89-mL Sweetheart brand paper cups. Peas, potatoes, and ice cream were weighed while frozen. Ground beef and flour were frozen after weighing. Two samples of each commodity were individually sealed with ambient air inside two 1.75-mil quart-size Ziploc (Dow Chemical) storage bags using the existing Ziploc closures. The twenty samples were randomly distributed on shelves inside a 368-liter capacity upright freezer (General Electric) held at -20°C. The freezer was

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housed inside a 4.217-m^3 fumigation chamber maintained at +23°C. Ten additional unbagged samples, two of each food item as prepared above, were simultaneously stored as controls in a separate freezer at -20°C.

The 30-sample preparation above was repeated for six separate fumigations; three at a target concentration of 36 mg/L and three at 360 mg/L of SF in chamber atmosphere. SF was introduced into the chamber and sampled in triplicate from an external sampling port at 0.25, 2, and 19.75 hours (h) with gas sampling tubes by the methods of Scheffrahn et al. (1987a). Freezer air samples were obtained in triplicate from two Tygon sampling lines (intake and return) which circulated air inside the freezer compartment through a second external chamber sampling port. The sampling lines were coupled to the freezer on two 1/4" (6.35 mm) OD copper tubes propped between the magnetic door seal and door seat. To insure SF entry under worst-case assumptions and still maintain an internal temperature of -20°C, two additional 3-cm pieces of 3/8" (9.53 mm) OD copper tubing were placed between the seal and seat on the opposite side of the door from where sample lines entered.

Atmosphere samples (0.5 mL) from the tubes were analyzed for SF concentration by GC following the method of Scheffrahn et al. (1987b). At 20 h, the chamber was aerated for 5 min, the freezer was opened, and food samples were removed from bags and thawed. The samples were placed in 125-mL stoppered flasks containing 50 mL of deionized water. The potatoes and peas were mashed inside the flasks. The flasks were mechanically shaken at 60 cycles/min for 1 h at room temperature. Ten mL of each resultant suspension was centrifuged at 2000 rpm for 30 min. Five mL of supernatant formed by the centrifugation was stored at -20°C in polyethylene vials until F^- electrode analysis.

Crude extract supernatants (5 mL) were diluted with 5 mL of water plus 10 mL of F^- analysis diluent (FAD, Corning). A fluoride-selective combination electrode (F^- and reference electrode in one probe; Orion 96-09) connected to a pH/ion analyzer (Fisher Accumet 950) were used for F^- determinations. The analyzer was calibrated from 0.05 to 10 ppm with 10 mL aqueous standard solutions of NaF in 10 mL FAD. Readings (ppm) were multiplied by a factor of 20 to equal F^- residues in food prior to their dilution for purposes of extraction and analysis. The probe provided a level of detection of 0.04 ppm (= 0.8 ppm w/w F^- equiv. in food). Recovery experiments were carried out in triplicate for each commodity with NaF fortifications of 1, 5, 20, and 100 ppm (w/w F^-) added to aqueous media prior to the extraction process.

Two additional non-food fumigations (36 and 360 mg/L) were carried out to determine the level of protection from SF exposure afforded by the two 1.75-mil Ziploc bags. For each fumigation, six empty cups were double-bagged and fumigated in a manner identical to foodstuff samples. Immediately after fumigation, both bags were pierced simultaneously by syringe, a 0.5 mL air sample removed from the inner bags, and analyzed for SF concentration using GC methods above, but with electron-capture detection. Two unfumigated control bag units were prepared for each fumigation to verify the absence of SF in bag atmospheres.

RESULTS AND DISCUSSION

The exposure rate terms for SF were calculated as accumulated concentrations or CT (concentration X time) values in mg·h/L (Tables 1 and 2). Mean freezer atmosphere CT values for the 36 and 360 mg/L food fumigations were 727.5 and 6802.7 mg·h/L, respectively (Table 1). Similar freezer CT values were obtained for the two empty bag fumigations (Table 2). SF concentrations equilibrated between chamber and freezer atmospheres within 2 h with some reduction of SF concentrations at 19.75 h due to sorption and/or chamber leakage (Tables 1 and 2). Final mean SF concentrations of 0.36 and 7.43 mg/L inside the inner Ziploc bags resulting from 587.9 and 6265.4 mg·h/L freezer exposures yielded respective inner bag CTs of 3.6 and 74.3 mg·h/L. Therefore, the inner bag CT values were a reduction of ca. 99.6 and 98.8% of the exposure rates experienced by the unprotected frozen samples. For comparison, Osbrink et al. (1988) observed a >96% reduction in transient SF residues in foods protected by two 2-mil layers of polyethylene film.

No residues above the minimum level of detectability (0.8 ppm w/w) were observed in any of the bagged or control samples. For the unprotected commodities, flour had the highest residues (5.9 and 89.7 ppm) at both exposure levels followed in order by ground beef, ice cream, peas, and french fries (Table 3). Flour fumigated at +27^{o}C under otherwise similar conditions was found to contain 70 and 475 ppm of F^{-} at 36 and 360 mg/L of SF, respectively (Scheffrahn et al. 1988), indicating that the degradation reactions of SF may be temperature dependent. Recoveries at the 1 ppm fortifications, near the level of detectability, were ca. 200% but approached 100% at the higher fortification levels (Table 3).

The results of this study indicate that at more conventional SF exposures (ca. 100 mg·h/L), F^{-} residues in typical frozen foods would probably not exceed 1 ppm. These foods would likely have lower surface-to-volume ratios than the small quantities of foods fumigated in

this study, thus resulting in even lower residues. F^- residues (i.e. SF exposure) can be drastically reduced when foods are protected by securely sealed polyethylene film.

Table 1. Sulfuryl fluoride CT values in chamber and freezer atmospheres during food fumigations

Sample Source	Target SF Conc (mg/L)	Mean mg/L SF at Hours[1] 0.25	2	19.75	CT[2] (mg·h/L)
Chamber	36	38.9	37.7	35.1	731.9
	360	381.6	350.8	347.0	7012.8
Freezer	36	34.1	37.8	35.1	727.5
	360	219.8	351.6	340.8	6802.7

1 Means of 9 samples.
2 Equals $0.25h\ \bar{X} + 2h\ \bar{X} + 9(2h\ \bar{X} + 19.75h\ \bar{X})$ when assuming a linear SF diffusion rate.

Table 2. Sulfuryl fluoride CT values in chamber, freezer, and inner bag atmospheres during empty bag fumigations

Sample Source	Target SF Conc (mg/L)	Mean mg/L SF at Hours[1] 0.25	2	19.75	20	CT[2] (mg·h/L)
Chamber	36	40.9	-[3]	33.6	-	745.3
	360	353.6	317.4	300.4	-	6231.2
Freezer	36	24.8	-	34.0	-	587.9
	360	276.5	329.4	299.5	-	6265.4
In Bag	36	-	-	-	0.36	3.6
	360	-	-	-	7.43	74.3

1 Means of 3 samples/fumigation for chamber and freezer; In bag means for six bags/fumigation.
2 See Table 1 for calculating CT values for chamber and freezer. For inner bag atmosphere, CT equals $10(20h\ \bar{X})$ assuming linear SF diffusion rate through polyethylene film.
3 Not sampled.

Table 3. Mean fluoride residues (w/w) in unprotected frozen foods fumigated with sulfuryl fluoride at 727 and 6803 mg·h/L and percent recovery of fortified foods

Food	CT (mg·h/L)	F^- ppm[1] ± SD	$\bar{X}$ % recovery at ppm[2] 1	5	20	100
Beef	727	2.5 ± 1.1	162	124	106	97
	6803	66.1 ± 24.4				
Fr. Fries	727	trace	215	122	109	101
	6803	17.8 ± 7.2				
Peas	727	trace	184	121	104	100
	6803	19.2 ± 2.6				
Ice Cream	727	0.9 ± 0.6	195	116	106	96
	6803	25.7 ± 17.9				
Flour	727	5.9 ± 3.6	196	106	105	98
	6803	89.7 ± 9.9				

1 Means of 6 samples, level of detectability = 0.8 ppm.
2 Means of 3 samples, maximum SD 19.6% of mean.

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