# SULFURYL FLUORIDE FUMIGATION EFFECT ON THE COMPOSITION OF DRY CURED HAM SLICES

**M.W. Schilling[1*], R.K. Sekhon[1], T.W. Phillips[2], W.B. Mikel[1]**

**[1] Department of Food Science, Nutrition and Health Promotion; Mississippi State University, Mississippi State, MS**
**[2] Department of Entomology; Kansas State University, Manhattan, KS**

Methyl bromide is commonly utilized as a fumigant in the dry curing of hams to prevent the infestation of ham beetles (*Necrobia rufipes*), cheese skippers, dermestid beetles, and ham mites(*Tyrophagus putrescentiae*) (EPA 2006). Although methyl bromide is the only known fumigant that is effective at preventing these arthropod infestations, it depletes the stratospheric ozone layer (Marriott and Schilling 2004). From audits and surveys performed by our research group, it was determined that there is somewhere between 60 and 100 dry cured ham processors, with 20-25 of these processors producing the majority of the product (Rentfrow et al. 2006). The request for the use of methyl bromide has been granted at 18,000 - 20,000 kg since the lack of availability of methyl bromide in dry cured ham processing would result in significant market disruption and this amount of methyl bromide currently meets the needs of the industry (EPA 2006).

Very little research has been reported on the use of methyl bromide alternatives in the fumigation of dry cured pork, but one of the most promising alternatives to methyl bromide appears to be sulfuryl fluoride, a chemical that was developed in the 1950s (Meikle and Stewart, 1962) and is now produced by DOW Agrosciences under the trade name ProFume. This product was registered for use in processing facilities that produce dry cured ham in the summer of 2005 (EPA 2005). This rule states that there can be no more than 20 ppm fluoride and 0.2 ppm sulfuryl fluoride in the final ham product. This product had not previously been registered for use as a fumigant for dry cured ham because it is absorbed by proteins, so it is anticipated that residues may be likely (EPA 2004). Scheffrahn et al. (1987, 1989) studied the effect of using sufuryl fluoride on unprotected foodstuffs. The level that was utilized was extremely high, approximately $360 g/m^3$, 100 times the dosage used to eradicate termites, but these researchers found between 500-2000 ppm of sulfur and fluoride residues in beef and cheese. Both of these products have high protein contents, similar to country cured ham so it is expected that these levels could be similar in ham if fumigated at such high concentrations.

Non-fumigated dry cured ham slices (3/8 cm thick, 9 cm long) were placed into 3.8 l glass fumigation jars and suspended in air with a paper clip hook. This hook was attached to the sample port that was covered with an injection septum. A battery powered fan was placed inside each jar to circulate gas. Three replications of hams were fumigated with sulfuryl fluoride (ProFume, DOW Agrosciences) for 48 h at levels of 0, 12, 24, or 36 mg/L, respectively. After fumigation treatments were performed, ham samples were evaluated in triplicate (within each replication) for sulfuryl fluoride, fluoride ion, sulfate ion, and volatile compounds. A randomized complete block design was utilized to evaluate the effects ($p<0.05$) of fumigation concentration on the concentration of the compounds listed above. When significant differences occurred among treatments ($p<0.05$), Tukey's Honestly Significant Differences Test was utilized to separate treatment means.

Sulfuryl fluoride standards of 0.1 and 9.6 ppm were utilized to verify the detection and retention time of sulfuryl fluoride using a gas chromatograph-flame photometric detector (GC-pFPD). Sulfuryl fluoride standards were detected, but sulfuryl fluoride was not detected in any samples treated at 0, 12, and 24 mg/L. Two out of nine samples fumigated at 36 mg/L had residual SF concentrations of less than 0.3 ppm relative abundance and average values were below 0.1 ppm for all ham slices. A linear relationship existed ($p<0.05$) between fumigation concentration and fluoride residue concentration in the ham. Significant differences existed ($p<0.05$) among all treatments with mean values of 0.1, 12.4, 24.9, and 35.4 ppm fluoride for 0, 12, 24, and 36 g/L of sulfuryl fluoride, respectively. This signifies that the 24 g/L and 36 g/L treatments may not be commercially viable options since 20 ppm is the legal limit for fluoride in hams. However, the surface area relative to volume would be much smaller in commercial applications since whole hams would be fumigated and not ham slices. Therefore, further trials need to be performed to determine the exact levels that could be utilized under real-world conditions. However, it is evident that the dry cured hams will absorb fluoride from sulfuryl fluoride fumigation. No differences ($p>0.05$) existed in volatile sulfur compounds among treatments when analyzed on the GC-pFPD, but use of 36 mg/L caused elevated ($p<0.05$) levels of carbon disulfide and methional when compared to the control treatment using a gas chromatograph mass-spectrometer. It appears from these data that fumigation of sulfuryl fluoride would not cause inherent aroma/flavor differences in ham as determined from our instrumental analyses. However, human sensory testing needs to be performed on samples that are fumigated and contain below the legal limit of fluoride to verify the lack of flavor differences between fumigated and non-fumigated samples. It appears that sulfuryl fluoride has potential as a fumigant for dry cured ham. However, testing also needs to be performed to determine the ability of the fumigant to control *Tyrophagus putrescentiae* and *Necrobia rufipes*. Research is also needed to examine the fumigant's effect on sensory quality and fluoride concentrations when whole dry cured hams are fumigated.

## REFERENCES


Marriott, N.G., Schilling, M.W. 2004. Dry Cured Pork Research Review. White Paper. National Country Ham Association, Inc. National Country Ham Association Annual Meeting. April 2-4, 2004. Morehead City, NC. pp. 1-62.

Meikle, R.W., Stewart, D. 1962. The residue potential of sulfuryl fluoride, methyl bromide, and methane-sulfonyl fluoride in structural fumigations. J. Agric. Food Chem. 10:393-397.

Rentfrow, G., Hanson, D.J., Schilling, M.W., Mikel, W.B. 2006. Methyl bromide use to combat mite infestation in dry-cured ham during production. 2006 Annual International Research Conference on Methyl Bromide Alternatives and Emission Reduction, Orlando, FL, November 5-9, 108.

Scheffrahn, R., Osbrink, W.L., Hsu, R., Y-Su., N. 1987. Desorbtion of residual sulfuryl fluoride from structural and household commodities by headspace analysis using gas chromatography. Bull. Environ. Contam. Toxicol. 39:769-775.

Scheffrahn, R., Hsu, R.C., Osbrink, W.L., Y-Su, N. 1989. Fluoride and sulfate residues in foods fumigated with sulfuryl fluoride. J. Agric. Food Chem. 37(1):203-206.

United States Environmental Protection Agency. 2006. Final Rulemaking: The 2006 Critical Use Exemption from the Phase-out of Methyl Bromide. January 30th. http://www.epa.gov/spdpublc/mbr/.

United States Environmental Protection Agency. 2005. Sulfuryl fluoride; Pesticide Tolerance. Federal Register Environmental Documents. July 15th. 70:135 http://www.epa.gov/EPA-PEST/2005/July/Day-15/p13982.htm.

United States Environmental Protection Agency. 2004. Methyl Bromide Critical Use Nominations for Post Harvest Use on Dry Cured Pork Products. http://www.epa.gov/ozone/mbr/2004_USHam.pdf.