

## CHEMICAL COMPOSITION OF DRY CURED HAMS FUMIGATED WITH SULFURYL FLUORIDE

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Dry cured hams are fumigated with methyl bromide to prevent the infestation of ham mites (*Tyrophagus putrescentiae*), ham beetles (*Necrobia rufipes*), cheese skippers and dermestid beetles (EPA 2006). Currently, there are at least 22 dry cured ham processing facilities in Kentucky, Missouri, North Carolina, Virginia, Tennessee, and Georgia that fumigate dry cured pork with methyl bromide (Rentfrow et al. 2008). Methyl bromide is a broad spectrum pesticide that is the only known fumigant that is effective at eradicating ham mite infestations. However, this fumigant also depletes the stratospheric ozone layer (Marriott and Schilling, 2004) and is classified as a Class 1 ozone depleting substance (EPA 2007). Minimal research has been reported on the use of methyl bromide alternatives. Alternative fumigants must be evaluated for their efficacy against pests, their economic viability and their effects on the sensory quality and safety of the ham product.

Sulfuryl fluoride (SF) is an alternative to methyl bromide that was registered for use in dry cured ham processing facilities in the summer of 2005 (EPA 2005). Sulfuryl fluoride is as effective as methyl bromide at controlling grain weevils, flour beetles, and other pests associated with some food products (NPMA, 1998), but no research has been reported on its effectiveness against the pests commonly associated with dry cured pork. The registration of SF states that there can be no more than 20 ppm fluoride and 0.01 ppm sulfuryl fluoride in the final ham product. It has been reported that when SF is used to fumigate food products, it can be absorbed by oils and sulfate and fluoride ions may bind to proteins, resulting in the possibility of unsafe residues in the product (EPA 2004) as well as cause variability in volatile compound composition that could affect product quality.

Dry cured hams that had not previously been exposed to fumigants were obtained and cut into sections (28 cm x 11 cm x 11 cm) that were approximately half the size of a whole ham so that they would fit into commercially available fumigation jars. Three replications of hams were fumigated with SF (ProFume, DOW Agro sciences) at levels of 0, 12, 24, 36, and 72 mg/L for 48 h. The fumigated hams were then evaluated in triplicate (within each replication) for sulfuryl fluoride, fluoride, volatile compounds and volatile sulfur compounds within each replication. A randomized complete block design was utilized to evaluate the effects ( $p < 0.05$ ) of fumigation concentration on the concentration of volatile compounds, sulfuryl fluoride, and fluoride. When significant differences occurred among treatments ( $p < 0.05$ ), Tukey's mean separation test was utilized to separate treatment means. In addition, orthogonal contrasts were used to determine if differences existed between fumigation treatments and control samples for GC-MS data.

For fluoride determinations, hams were cut and separated into fat and muscle fractions prior to grinding. An Accumet Fluoride Ion Combination Glass Electrode was used to determine fluoride ion concentration. Differences existed ( $p < 0.05$ ) among fat fractions for all treatments with mean values of 1.1, 3.4, 6.2, 7.5 and 14.0 ppm for 0, 12, 24, 36 and 72 mg/L of sulfur dioxide, respectively. In addition, differences existed ( $p < 0.05$ ) among muscle fractions of all treatments with mean values of 1.1, 3.1, 5.5, 7.1 and 13.2 ppm for 0, 12, 24, 36 and 72 mg/L of sulfur dioxide. It appears that both protein and lipid absorbed fluoride during SF fumigation, and concentration of fluoride was directly related to fumigation concentration. The data also show that the fluoride concentrations in all treatments were lower than the legal limit of fluoride which is 20 ppm (EPA 2004). Sulfur dioxide standards of 9.76 and 515 ppm were utilized to verify the detection and retention time of sulfur dioxide using a gas chromatograph-pulsed flame photometric detector (GC-pFPD). SF was not detected in 0 and 12 mg/L fumigation treatments but was tentatively detected at low concentrations in hams that were fumigated at concentrations of 24, 36 and 72 mg/L.

Volatile compounds were tentatively identified using the library search algorithm, NIST02 Mass Spectral Database on the GC-MS and were further substantiated by obtaining odor descriptors from the gas chromatograph-olfactometer/flame ionization detector (GCO-FID). In addition, retention indices (RIs) were calculated and compared to RIs that are reported in literature. The aroma active compounds that were present in the ham samples included carbon disulfide, 2-butanone, 3-methylthiopropional, 3-methylbutanal, 2-methyl-2-undecanethiol, hexanal, heptanal, methional, 2-octanone, limonene, 2-nonen-1-ol, benzothiazol and cubenol. Results show that samples had similar odors but the 0 mg/L sample had more floral, mushroom like, fresh and clean odors, and the 72mg/L sample had more fishy, unpleasant, putrid, cheesy, green and smoky odors associated with the volatile aroma impact compounds in the ham.

There were minimal differences in the concentration of volatile compounds among the different fumigation treatments. In the lipid fraction, there were higher concentrations ( $p < 0.05$ ) of 3-methylbutanal and hexanal in the 72 mg/L samples when compared to other treatments. These compounds are indicators of lipid oxidation and may have been induced by fumigation with SF at 72 mg/L. For the lean muscle fraction, orthogonal contrasts revealed that the 72 mg/L treatment had higher concentrations of carbon disulfide and 2-methyl-2-undecanethiol when compared to the non-fumigated control. In addition, there were elevated concentrations of volatile compounds in 72 mg/L samples when compared to other treatments. This study revealed that there were minimal aroma/flavor differences in the different ham treatments based on instrumental analysis. If SF is proven effective at eradicating ham mites and beetles, sensory testing will need to be performed to verify that minimal flavor differences exist between fumigated and non-fumigated hams.

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