CHEMICAL COMPOSITION OF DRY CURED HAMS FUMIGATED WITH PHOSPHINE

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Dry cured hams can become infested with ham mites (*Tyrophagus putrescentiae*), ham beetles (*Necrobia rufipes)*, cheese skippers and dermestid beetles during aging. Hams are fumigated with methyl bromide to prevent and eradicate infestations due to these pests (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 on dry cured ham. 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.

Phosphine (PH_3) is a fumigant that is used worldwide to protect stored commodities against pest insects and rodents. Its prominence as a fumigant is due to its low cost, ease of application, lack of residues, and potency (Zuryn *et* al., 2008). PH_3 is extremely volatile, diffuses rapidly, and leaves almost no residues in food commodities following fumigation (Longobardi and Pascale, 2008). The legal limit of phosphine in processed food products is 0.01 ppm (EPA, 1999). Phosphine is highly toxic to organisms undergoing oxidative respiration. Phosphine can eliminate all stages of insect life namely, egg, larvae and adults (Bell, 1976). The most widely used phosphides are aluminum phosphide or magnesium phosphide (Longobardi and Pascale, 2008). Degesch Magtoxin Prepac spot fumigant (with Magnesium Phosphide as the active ingredient; trade name for phosphine) is specially designed for protection from insect damage that occurs in stored commodities (Degesch America Inc., 2007).

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 PH_3 at levels of 0 ppm (control), 200 ppm (low PH_3) and 1000 ppm (high PH_3) for 48 h. The fumigated hams were then evaluated in triplicate (within each replication) for volatile 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 and phosphine residues. 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. Sensory testing (a triangle test) was performed to verify that consumers could not detect sensory differences between phosphine and non-phosphine treated samples.

As phosphine fumigation concentration increased, the amount of phosphine in the hams increased, but all hams contained less than 0.01 ppm, the legal limit of phosphine in hams. The aroma active compounds that were present in the ham samples included carbon disulfide, 2-propanethiol, 3-methylbutanal, heptanal, methional, 2,5- dimethyl pyrazine, unknown, 2-octanone, limonene, benzeneacetaldehyde, 2-methoxy phenol, 2-nonen-1-ol, 4-methyl-2-methoxy phenol, benzothiazole, 4-ethyl-2-methoxy phenol, 2,6-dimethoxy phenol and alpha farnesene. Results revealed that samples had similar odors but that the control sample had slightly more floral, rose like, fresh, clean, cocoa, sweet and smoky ham odors, and the fumigated sample had slightly more unpleasant, putrid, cheesy, green, woody, sweet and fruity 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 alpha farnesene in the high PH_3 fumigated samples when compared to control and low fumigation treatments. For the lean muscle fraction, orthogonal contrasts revealed that the both PH_3 fumigation treatments had higher concentrations of heptanal and benzothiazole when compared to the non-fumigated control. There were also higher concentrations ($p<0.05$) of heptanal, methional and benzothiazole in higher PH_3 fumigation ham treatments as compared to low PH_3 fumigation treatments. In addition, there were elevated concentrations ($p<0.05$) of volatile compounds in high fumigation treatment samples when compared to other treatments.

Consumers were unable to detect a difference ($p>0.75$) between high PH_3 fumigated samples and non-fumigated samples. Only 19 out of 56 people, chose the correct ham, which is a probability of 33.9 %, roughly the probability of randomly guessing which ham is different. Since the p-value was so high ($p>0.75$) and three replications of hams were evaluated, there was sufficient evidence to demonstrate that panelists were unable to perceive sensory differences between non-fumigated hams and hams that were fumigated at 1000 ppm PH_3. These results reveal that the slight differences in aroma quality perceived by GCO are not an indicator of changes in sensory perception. Therefore, 1000 ppm PH_3 could be used to fumigate dry cured hams without negatively impacting sensory quality and without leaving more than 0.01 ppm residue in the ham.

REFERENCES

Bell, C.H. 1976. The tolerances of developmental stages of four stored products moths to phosphine. *Journal of Stored Product Residues*. 12:77-86.

Degesch America Inc. 2007. Use of phosphine to combat *Necrobia rufipes* infestations. http://degeschamerica.com/pests.html.

Environmental Protection Agency. 2007. U.S. Nomination for Methyl Bromide Critical Use Exemptions from the 2007 Phaseout of Methyl Bromide. October 4th . http://www.epa.gov/ozone/science/ods/index.html.

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/.

Environmental Protection Agency. 1999. Aggregate Risk Assessment and Determination of Safety. June 9th. http://www.epa.gov/EPA-PEST/1999/June/Day-09/p14069.htm

Longobardi, F. and Pascale, M. 2008. Rapid method for determination of phosphine residues in wheat. *Food Anal. Methods*. 1:220-225.

Marriot, N.G. and 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.

Rentfrow, G., Hanson, D.J., Schilling, M.W. and Mikel, W.B. 2008. The use of methyl bromide to control insects in country hams in the Southeastern United States. Extension Publication. University of Kentucky Extension/National Country Ham Association. Publication # ASC-171. Pages 1-2.

Zuryn, S., Kuang, J. and Ebert, P. 2008. Mitochondrial Modulation of Phosphine Toxicity and Resistance in *Caenorhabditis elegans*. Toxicological Sciences. 102 (1): 179-186.