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Effects of phosphine and methyl bromide fumigation on the volatile flavor profile and sensory quality of dry cured ham

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ABSTRACT

In separate experiments, randomized complete block designs with three replications were utilized to evaluate the effects of phosphine (PH_3) (0, 200 and 1000 ppm for 48 h) and methyl bromide (MB) (0, 4, 8, 16, and 32 mg/L for 48 h) fumigation concentration on the volatile flavor compound concentrations in dry cured ham. Minimal differences existed ($P>0.05$) in the presence and concentration of aroma active compounds in both PH_3 and MB fumigated hams but sulfur and oxidation compounds were more prevalent ($P<0.05$) in the fumigated treatments when compared to the control. As phosphine fumigation concentration increased, the residual concentration of phosphine also increased in the hams ($P<0.05$), but all samples contained levels that are lower than the legal limit of phosphine allowed in stored food products (0.01 ppm) in the United States. A triangle test ($n=56$) indicated that consumers could not discriminate ($P>0.75$) between the control hams and those that were fumigated with PH_3. Minimal aroma/flavor differences existed among MB, PH3 and control hams, and dry cured ham that was fumigated with PH_3 was safe for consumption based on residual phosphine concentrations in the meat tissue.

1. Introduction

Methyl bromide fumigation is conducted in the dry cured ham industry to prevent the infestation of dry cured hams with ham mites (*Tyrophagus putrescentiae* Schrank), ham beetles (*Necrobia rufipes* DeGeer), cheese skippers (*Piophila casei*) and dermestid beetles (*Dermestes lardarius*) (EPA, 2007). Currently, there are at least 22 dry cured ham processing facilities, approximately 65% of plants, in Kentucky, Missouri, North Carolina, Virginia, Tennessee, and Georgia that fumigates dry cured pork products with methyl bromide since it is the only known fumigant that is effective at eradicating ham mite infestations (Rentfrow, Hanson, Schilling, & Mikel, 2008).

Since methyl bromide depletes the stratospheric ozone layer, (Marriott & Schilling, 2004), an international agreement (The Montreal Protocol) was ratified by more than 180 countries to phase methyl bromide out of all industries by 2015 (EPA, 2007). Therefore, alternatives to methyl bromide must be evaluated for their ability to eradicate *Tyrophagus putrescentiae* and *Necrobia rufipes* infestations in dry cured ham. These alternative methods and fumigants must also be evaluated for their effects on the economic viability of processors and their effects on sensory quality and product safety. Both the Environmental Protection Agency (EPA) and the United States Department of Agriculture (USDA) are working with scientists to determine if economically viable and environmentally sound alternatives to methyl bromide exist for the fumigation of dry cured hams (EPA, 2006). Sulfuryl fluoride, carbon dioxide, ozone, and phosphine are currently being evaluated for their effectiveness at eradicating ham mites and red-legged beetles as well as their effects on product quality and safety.

Phosphine (PH_3) is commonly used on a worldwide basis as a grain fumigant and as an alternative fumigant to methyl bromide in order to disinfest stored products and processed foods, which have a maximum allowable phosphine concentration of 0.01 ppm (EPA, 1999). Its prominence as a fumigant is due to its low cost, ease of application, lack of residues, and potency (Zuryn, Kuang, & Ebert, 2008). Phosphine is highly toxic to organisms that undergo oxidative respiration, but is non toxic to organisms that can survive in low oxygen environments (<1%) or that can anaerobically respire. Phosphine can eliminate all stages of insect life (egg, larvae and adults) (Bell, 1976).

The objectives of this research were to evaluate the effects of phosphine and methyl bromide fumigation on the quality and safety of dry cured hams. Quality and safety were evaluated through the determination of volatile compound composition, sensory differences, and residual phosphine concentrations in PH3 fumigated hams.

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2. Materials and methods

2.1. Ham preparation and fumigation

Commercial hams (aged for 70–90 days and smoked with hickory chips) that were cured with salt, sugar, sodium nitrate and sodium nitrite were obtained from a single dry cured ham processor that does not fumigate with methyl bromide or any other fumigant. Three replications ($n=3$ replications, $t=3$ treatments, 3 hams/per replication $N=9$ total hams) were performed on three commercial hams for each treatment in the phosphine experiment. Three replications ($n=3$ replications, $t=5$ treatments, 3 hams/per replication, $N=15$ total hams) were performed on five commercial hams for each treatment in the methyl bromide experiment. The hams (8 kg) were cut in to halves using a band saw so that there were hams sections (28 cm × 11 cm × 11 cm) that were approximately half the size and weight (4 kg) of a whole ham and the ham section would fit into 10.3 L fumigation jars. Hams were cut so that each experimental unit was as similar as possible (size, amount of skin, amount of lean meat tissue).

Experiment I. Three replications of hams were fumigated with PH_3 (Matheson Tri-Gas Inc., Newark, CA) for 48 h at 23 °C at the following target concentrations: 0 ppm (untreated control), 200 ppm and 1000 ppm. Hams were aerated for 12 h to help remove residual fumigant from the ham as well as to mimic industry practice.

Experiment II. Three replications of hams were fumigated with MB for 48 h at 23 °C at following target concentrations: 0 (untreated control), 4, 8, 16, and 32 mg/L.

The fumigated hams were then evaluated in triplicate (within each replication) for volatile compounds within each replication. The different ham samples were cut into ham slices (5–6 mm) that consisted of *Biceps femoris*, *Semitendinosus* and *Semimembranosus* muscles and the intermuscular fat (lipid) and lean muscle fractions were separated. Three ham slices were removed from similar positions within each treatment ham from three different locations within the ham and utilized as the triplicate samples. The ham and lipid tissue from each slice was then weighed and homogenized for 20 s (HC 306, Black & Decker, Towson, MD) with deodorized water to make a ham:water (1:1) mixture that was used for the determination of phosphine and volatile compound peak areas.

2.2. Determination of phosphine (PH_3) gas

PH_3 gas was purchased from Scott Specialty Gases, Inc. Pasadena, TX. A gastight syringe (Hamilton Inc. Reno, NV) was used to extract the gas from the cylinder by using a regulator, 4-way Luer stopcock (World Precision Instruments, Inc., Sarasota, FL), and a small diameter thin rubber hose pipe. The gas was injected into the injector port of the gas chromatography/pulsed flame photometric detector (GC–pFPD) in phosphorous mode to determine the retention time (peak) of the PH_3 gas. These standards were used to verify the presence of PH_3 when it was detected in hams that were fumigated with phosphine as well as to verify that the syringe was effective at extracting PH_3. Sodium phosphate was used as both an internal and external standard to quantify PH_3 concentration in the ham samples. The molecular weight and percentage of phosphorous in both PH_3 and sodium phosphate were calculated to obtain final values. Sodium phosphate was injected into the GC–pFPD at concentrations of 0.001, 0.005, 0.01, 0.05, 0.1 ppm to make a standard curve. This standard curve was used to quantify the amount of PH_3 in the hams based on ppm phosphate.

2.3. Extraction of volatile compounds by SPME for GC–pFPD, GC–MS and GCO–FID

The solid phase micro-extraction (SPME) method that was used for the extraction of headspace volatile compounds was similar to those that were used in previous studies (Huan, Zhou, Zhao, Xu, & Peng, 2005; Pham et al., 2008). Prior to sampling, new SPME fibers were conditioned under helium flow into a split/splitless GC injection port for 1 h at 270 °C to remove any possible contaminants from the fiber coating. The fiber was then desorbed in the GC injector for 5 min, to determine the presence of extraneous peaks. Homogenized ham samples (10 g) were transferred to pre-cleaned 40 mL amber glass vials (O.D. 28 × 98 mm height, Supelco, Bellefonte, PA) with propylene screw caps and Teflon faced silicone septa (O.D. 22 mm diameter × 31.75 mm thickness, Supelco, Bellefonte, PA). Sodium chloride (0.5 g) was added to the sample in the amber glass vial and was equilibrated at 50 °C for 30 min. The StableFlex 1 cm–50/30 μm three phase (DVB/CAR/PDMS) SPME fiber (1 cm–50/30 μm StableFlex Divinylbenzene (DVB)/Carboxen™ (Car)/Polydimethylsiloxane (PDMS),Supelco, Bellefonte, PA) was inserted into the vial to extract the volatile compounds that were present in the headspace. The three phase SPME fiber was selected since it previously exhibited the best extraction performance for medium and high molecular weight analytes in dry cured hams (Gianelli, Flores, & Toldrá, 2002). The SPME fiber was exposed to the generated sample headspace for 1 h at 50 °C in a thermostatic heating block (Reacti-therm Heating/Stirring Module, Pierce Biotechnology Inc., Rockford, IL) with constant stirring using a magnetic octagonal stirring bar (8 mm diameter × 13 mm length, Fisher, Pittsburgh, PA). The volatiles were thermally desorbed from the SPME fiber into the injection port of a Varian 3900 gas chromatograph (Varian Inc., Walnut Creek, CA), or the injection ports of either a Varian 3800 flame ionization detector with a sniff port or a Varian 3800 with a flame photometric detector.

2.4. Gas chromatography–pulsed flame photometric detector (GC–pFPD)

The GC–pFPD analysis was carried out using a Varian CP-3800 (Varian Inc., Walnut Creek, CA) gas chromatograph that was equipped with a DB-5 column (30 m long × 0.53 mm i.d., 0.25 μm film thickness, J & W Scientific, Folsom, CA) and a flame photometric detector (phosphorous mode). Operating conditions were as follows: injector temperature of 225 °C, column flow rate of 4 mL/min, initial oven temperature of 35 °C for 4 min hold time with 14 °C/min ramp rate to 250 °C, and a pressure of 10 psi and equilibration time of 0.25 min. The detector temperature was 250 °C, and the total running time was 12.36 min. Ultra high purity helium (Airgas, West Point, MS) was used as the carrier gas for the experiment. Analysis of each sample was repeated in triplicate to ensure reproducibility of the results. The identity of PH_3 was confirmed using an authentic standard.

2.5. Gas chromatography–mass spectrometry (GC–MS)

Analysis of volatile compounds (Ruiz, Ventanas, Cava, & Jensen, 1998) that were adsorbed on the SPME fiber was performed using a Varian 3900 gas chromatograph equipped with a CP-1177 Split/Splitless injector and a DB-5 column (30 m long × 0.25 mm i.d., 0.25 μm film thickness, J & W Scientific, Folsom, CA) that was coupled with a Saturn 2100T ion trap mass selective detector (MSD, Varian Inc., Walnut Creek, CA). The operating conditions for the GC portion of the GC–MS were identical to those for the GC–pFPD. For the MS, the interface temperature was 250 °C with an ionization energy of 70 eV. The mass range, scan rate and flow rate were 33–350 atomic mass units, 2.2 scan/s and 0.96 mL/min. Ultra high purity helium (Airgas, West Point, MS) gas was used as the carrier gas for the experiment. Analysis of each sample was repeated in triplicate to ensure reproducibility of the results. The mass spectral data for volatile compounds