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Release of copper from embedded solid copper bullets into muscle and fat tissues of fallow deer (*Dama dama*), roe deer (*Capreolus capreolus*), and wild boar (*Sus scrofa*) and effect of copper content on oxidative stability of heat-processed meat

I. Schuhmann-Irschik [a], M. Sager [b], P. Paulsen [a,*], A. Tichy [c], F. Bauer [a]

[a] Institute of Meat Hygiene, Meat Technology and Food Science, Department for Farm Animals and Veterinary Public Health, University of Veterinary Medicine Vienna, 1210 Vienna, Austria
[b] Special Investigations in Element Analysis, Austrian Agency for Health and Food Safety, 1220 Vienna, Austria
[c] Bioinformatics and Biostatistics Platform, University of Veterinary Medicine Vienna, 1210 Vienna, Austria

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ABSTRACT

When venison with embedded copper bullets was subjected to different culinary processing procedures, the amount of copper released from the embedded bullet was affected more by the retention period of the bullet in the meat during cool storage, than by the different heating protocols. The presence of copper fragments had no significant effect on levels of thiobarbituric acid reactive substances (TBARS). Conversely, TBARS in lean meat (fallow deer, wild boar, roe deer) were significantly affected by culinary treatment (higher TBARS in boiled and boiled-stored meat than in meat barbecued or boiled in brine).
In pork–beef patties doped with up to 28 mg/kg Cu, TBARS increased after dry-heating and subsequently storing the meat patties. The amount of copper doping had no effect on TBARS for 0 and 7 days of storage, but a significant effect at day 14 (fat oxidation retarded at higher Cu doses). Evidence is presented that wild boar meat may be more sensitive to fat oxidation than pork–beef.

1. Introduction

The use of lead-containing rifle bullets for hunting large game is under debate because of detrimental environmental effects (Cao, Ma, Chen, Hardison, & Harris, 2003; Evangelou, Hockmann, Pokharel, Jakob, & Schulin, 2012) and food safety issues (Hunt et al., 2009; Knott, Gilbert, Hoccom, & Green, 2010). Consequently, there is increased interest in "lead-free" rifle bullets, either of core-jacket type (i.e. tin core instead of lead) or "monoliths" composed of copper only or a copper-alloy (Irschik, Wanek, Bauer, Sager, & Paulsen, 2014). In a previous work, copper contents in large wild game killed with monolithic copper-bullets were studied. Using a non-fragmenting bullet construction, copper contents around the shot wound were not significantly different from those expected for venison. Copper fragments embedded into meat would release copper to the surrounding meat tissue, but only over a very limited distance. It was estimated that, per portion, copper contents would not exceed the recommended daily intake for this metal (Irschik, Bauer, Sager, & Paulsen, 2013). The effect of culinary processing, was, however, considered only as regards marinating in red wine. A study of Mateo, Rodriguez-de la Cruz, Vidal, Reglero, and Camarero (2007) on the release of lead from fragments embedded in muscle from quails reported substantial increase in lead contents during culinary processing according to a traditional Spanish recipe. Currently, no data exist on the copper contents of meat with embedded copper fragments after culinary treatment. Recently, it has been shown that increased heavy metal contents in inner organs of wild boar are associated with higher levels of thiobarbituric acid reactive substances (TBARS) (Šuran, Prišc, Rašic, Srebočan, & Crnic, 2013).

The aim of this study was, therefore, to determine if culinary processing of meat from different game species with embedded copper particles would be more prone to fat oxidation as compared with meat without embedded particles.

In addition, oxidative stability of copper-doped meat patties was examined. Based on observations in fermented meats from wild boar which indicate that wild boar meat is more susceptible to rancidity than is pork (Paulsen, Vali, & Bauer, 2011), the oxidative stability of wild boar meat patties was compared to that of patties from a pork–beef mix.

* Corresponding author.
E-mail address: peter.paulsen@vetmeduni.ac.at (P. Paulsen).

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2. Materials and methods

2.1. Sample preparation for the determination of TBARS and copper content in meat from wild game, considering copper release from embedded fragments during meat storage and processing (experiment 1)

Lean meat originated from fallow deer (*Dama dama*), roe deer (*Capreolus capreolus*) and wild boar (*Sus scrofa*), which had been shot at regular hunting events, and subsequently had been eviscerated and placed in a chiller within 3 h post-mortem. For each of the three species, the following experiment was conducted separately.

Shoulder and hind leg muscles were excised from one carcass 24–48 h post-mortem. Subsequently, muscles were cut into 72 cubes of 30 g weight, and randomly assigned to 36 different groups (see below and Fig. 1).

The 36 bags (each containing 2 meat cubes, thus forming the experimental unit, or "sample") were randomly assigned to 12 groups in a 2-factorial design. An overview on the sequence of treatments is depicted in Fig. 1.

Factor 1 was the presence of an embedded copper fragment being able to release copper to the surrounding meat. In particular, three variants were considered:

(1a) no contamination ("blank"),
(1b) contamination by inserting a .223 inch dia. copper bullet (3.5 g weight; Barnes TSX; Barnes Bullets, Mona, USA), in a 30 g meat cube, with the bullet remaining in the meat cube during storage plus subsequent culinary preparation, and
(1c) contamination as under (b), but with the bullet being removed after storage i.e. prior to culinary preparation.

Factor 2 in the experiment was four different procedures of culinary treatment:

(2a) storage in an open plastic bag under aerobic conditions for 7 days at 5 °C, followed by quick roasting ("barbecuing"; 5 min at 170 °C);
(2b) storage with 20 ml of a brine simulant (Table 1, all reagents from Merck, Germany) in an open plastic bag under aerobic conditions for 7 days at 5 °C, followed by boiling in the plastic bag without addition of water (75 °C, 1 h);
(2c) storage in an open plastic bag under aerobic conditions for 7 days at 5 °C, followed by boiling in the plastic bag without addition of water (75 °C, 1 h);
(2d) conditions as under (2c), but with subsequent storage of cooked meat cubes at 5 °C for 7 days.

Table 1
Brine, composed of wine simulant and vinegar (diluted acetic acid), quantities given for a total of 200 g; pH adjusted to 3.55.

Wine simulant (Souci, Fachmann, & Kraut, 2000)	
Ethanol	10.0 g
Lactic acid (1 mol/l)	2.5 ml
Glacial acetic acid	0.07 ml
Malic acid	23 mg
Tartaric acid	150 mg
Water	Ad 100.0
Vinegar	
Glacial acetic acid	5.0 g
Water	Ad 100.0

For the determination of thiobarbituric acid reactive substances (TBARS), the two meat cubes per bag were combined, minced and an aliquot was analyzed at the same day, while the remaining sample material was preserved at −20 °C for copper content determination. In addition, copper content in brine simulant and meat juice released during boiling was determined. All analyses were done in duplicate. Per combination of factors 1 and 2, three samples were studied.

2.2. Sample preparation for assessment of the effect of copper content on TBARS content of meat patties from a pork–beef mix (experiment 2)

For this experiment, 2 kg minced beef and pork (10% fat) were obtained from a local supermarket. Four 500 g-batches were prepared, with 20 g/kg NaCl. To batches 1, 2 and 3, copper powder (particle size < 63 μm; Roth CP21.1, Roth, Karlsruhe, Germany) suspended in 10 ml water, was added to give final contents of 28, 14 and 7 mg/kg, respectively. Meat batter was mixed thoroughly to ensure uniform distribution of copper particles. The fourth batch received 10 ml water, but no copper doping ("blank"). From each batch, 15 meat patties

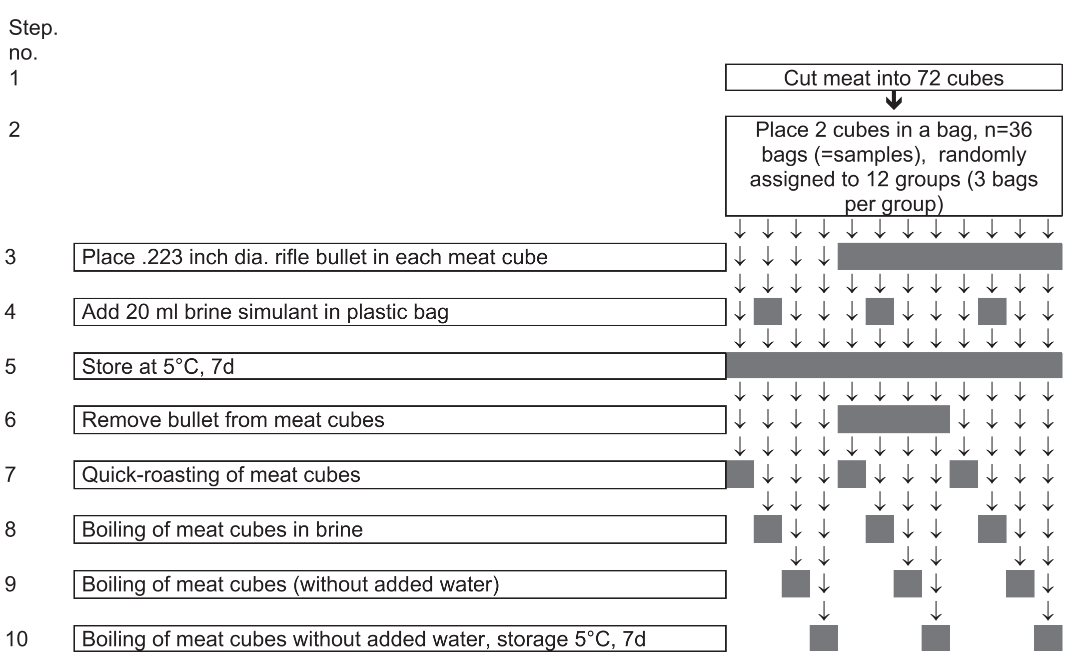

Fig. 1. Storage and processing of muscle cubes with and without embedded copper body (.223 inch dia. rifle bullet).