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Chromatographic fingerprints supported by artificial neural network for differentiation of fresh and frozen pork

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ABSTRACT

The sale of defrosted meat without reporting the use of frozen storage is a method of food adulteration. The aim of this study was to determine the possibility of differentiating fresh pork neck, loin and ham from frozen pork neck, loin, ham and also from spoiled pork with an electronic nose (E-nose) based on ultra-fast gas chromatography (UFGC) supported by supervised artificial neural network (ANN). The performance of the Principal Components Analysis (PCA) models was applied in this research to check the possibility to classify pork samples in the respective freshness group. The applied ANN was a three-layer (excluding input layer) non-linear perceptron consisting of more than 200 cells and using sigmoidal function and no bias. The ANN was implemented as a C program with automated (batch) learning capability. Tests were carried out on pork meat from pigs obtained from a breeding farm. The chromatographic fingerprint of samples of fresh meat, frozen-thawed meat and spoiled meat were analyzed by the ANN. The study has shown that use of E-nose with the ANN allows to effectively recognize fresh (80%), frozen-then-thawed (85%) and spoiled meat (90%). In practice this technique may be applied to quick, cheap and reliable introduction and rapid recognition of chopped pork and for the differentiation of fresh and frozen pork.

1. Introduction

Pork and pork products are a popular food group for many consumers (Delgado, 2003). This comes from feeding habits and from the fact that meat is an important source of proteins and some micronutrients like iron and group B vitamins (Biesalski, 2005). Meat quality and proper meat labeling is of concern to consumers and control authorities, as well as meat processing industry and retailers. According to a report from the Commission for European Parliament and European Council 83% of customers eat meat at least 2–3 times a week. Consumption of pork equals 49% of total consumption of meat. In turn, 70% of total production of manufactured meat in the EU is pork (European Commission, 2013). In the case of the majority of manufacturing plants, raw material such as meat is delivered chopped, mixed or fragmented, the meat was obtained from different suppliers. In this process the key problem is the ability to identify meat that serves to determine a source of meat and its state – fresh or thawed.

According to European Commission current identification systems are ineffective and are not valid for tracing and transferring information about the meat sources on certain stages of food chain, despite executive regulation of EU Commission 931/2011 from September 19th, 2011 on requirements of tracing possibilities stated with regulation 178/2002 of European Parliament and Council regarding food of animal origin being in force since July 1st, 2012 (EU, 2011a).

Recognition of cut meat is usually done visually. It is difficult to find an analytic method for verification of authenticity of cut meat. Potentially one of those methods could be a method based on measurement of contents of collagen in different muscles (Ballin, 2010). NIR hyperspectral imaging together with chemometrics appears to be a promising method (Kamruzzaman, ElMasry, Sun, &

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Sun, 2011), however there is no data concerning its application for identification of small cut meat pieces of one meat species. Electronic nose was used for identification of different meat species, but not for different muscles of the same species (Mirmohseni & Hassanzadeh, 2001; Tian, Wang, & Cui, 2013).

Regulation No 1169/2011 2014 of the European Parliament and of the Council on the provision of food information to consumers introduced mandatory indication of the country of origin or place of provenance for unprocessed meat of pig and expiration date, date of freezing (for frozen products) and presence of information if product is thawed (EU, 2011b). These regulations are in force since December 13th, 2014.

Information indicating that meat is fresh or frozen-thawed is very important for quality as well as for consumer safety. Sale of frozen-then-thawed meat without proper information about fact of freezing removes the possibility of choice for the consumers and it is a method of food adulteration (Ballin & Lametsch, 2008; Ballin, 2010). Food authenticity becomes more and more important feature in the trade, thus recipients and manufacturers are concerned with reliable labeling (Sentandreu & Sentandreu, 2014).

There are many described analytic methods that allow to recognize whether meat is fresh or was frozen (Ballin, & Lametsch, 2008; Sentandreu &Sentandreu, 2014). Most of the known methods such as enzymatic, DNA based, bio-imaging, spectroscopy, NIR-spectroscopy with chemometrics as well as gas chromatography with mass detector (GC-MS) or flame-ionization detector (FID) are based on comparative analysis between fresh and frozen-then-thawed samples. One of the non-destructive, fast and promising methods is a spectroscopic technique in different configurations used recently by many researchers (Douglas, Barbin, Sun, & Su, 2013; Ma et al., 2015).

Sensory tests evaluating odor of fresh and frozen-then-thawed meat samples allow to distinguish evaluated pork samples as well (Elsbernd, Patience, & Prusa, 2016). Odor is an important factor in determining the meat quality (Khan, Jo, & Tariq, 2015). Microbiological processes causing meat spoilage are the source of specific volatile organic compounds (Casaburi, Piombino, Nychas, Villani, & Ercolini, 2015). Nowadays a profile of volatile compounds is used as a specific fingerprint for food quality analysis more and more often (Cuadros-Rodríguez, Ruiz-Samblas, Valverde-Som, Perez-Castano, & Gonzalez-Casado, 2016; Vestner et al., 2016; Zhang, Zhang, Dediu, & Victor, 2011).

If two samples – fresh and frozen-then-thawed ones – are taken from the same source and analyzed at the same time in the same conditions, recognition of them is now possible by most known methods. However, a problem in meat authenticity tests is that often a sample of fresh meat is not available for comparison with the tested one.

The goal of this research was to develop universal and practical solutions allowing for cheap and quick classification of chopped pork meat. The main objective was to recognize and differentiate fresh and frozen-thawed meat – neck, loin and ham – and spoiled pork. Proposed application consolidates analytical technique such as electronic nose based on ultrafast gas chromatography and chemometrics with artificial neural network. In this research the authors tried to create a research station for identification of chopped pork meat. For this purpose an artificial neural network was used to analyze chromatographic fingerprints, omitting the identification of specific volatile compounds.

2. Materials and methods

2.1. Sample preparation

Tests were carried out on necks, loins and hams of 6 pigs from Pork Quality System (PQS) production (Guzek, Głąbska, Wojtasik-Kalinowska & Wierzbicka, 2013) and of 18 pigs from an experiment with supplementation (Brodowska et al., 2016). 18 pigs were divided into three feeding groups and were given standard control diet (C group – 6 pigs), supplemented with 3% linseed oil diet (L1 group – 6 pigs) and supplemented with 3% linseed oil with 1 mg kg^{-1} of Se and 100 mg kg^{-1} of vitamine E (L2 group – 6 pigs). The feeds were prepared under Nutrient Requirements of Swine (National Research Council, 1998). In the first part of the tests meat from 6 pigs from PQS was delivered to the laboratory. From every element – necks, loins and hams – 14 slices 1 cm thick were cut out – total 42 slices. All samples were vacuum packed, each slice separately. Next, the slices were divided into three groups – two consisting of 18 samples each (6 samples of necks, loins and hams respectively). Samples from the first group were used for immediate tests and marked as fresh meat (F). The second group was frozen and kept at a temperature of −20 °C for 3 months and then was thawed and tested as frozen-thawed (FT) necks, loins and hams. The samples of the third group were stored in refrigerator at 5 °C for 30 days and were tested as non-fresh meat (NF).

In the second part of the tests 18 necks, loins and hams of pigs from experiment with supplementation were delivered to the laboratory (6 from each group: C, L1 and L2). Similarly to the first part of the experiment, every part of meat was divided into 14 slices 1 cm thick each. All samples were vacuum packed and divided into 3 groups: F, FT and NF. Samples were treated analogically as samples from meat from PQS system. For tests of chromatographic fingerprints 6 samples from each slice were prepared. Scheme of selection of three groups F, FT and NF as well as number of all samples is shown in Table 1. Thus, a total number of 1008 samples was prepared for testing, 144 samples from each of 7 tested category (F neck, F loin, F ham, FT neck, FT loin, FT ham and NF meat).

2.2. Electronic nose

Chromatographic fingerprint was obtained by the electronic nose Heracles II Analyzer (Alpha M.O.S., Toulouse, France) based on the UFGC. Heracles II was equipped with two 10 m parallel metal columns of different polarities (MXT-5 and MXT-1701), two Flame Ionization Detectors (FID), headspace (HS), autosampler HS 100 and computer with Alpha Soft software. The pork samples were cut into 5 mm cubic shape pieces (each 2.5 g), closed in 20 ml HS-vials with silicon/teflon septum. The incubation temperature was 55 °C, the time of incubation was 15 min. Autosampler injected 3500 μl of headspace to GC. Work parameters and methodology was described by Wojtasik-Kalinowska (Wojtasik-Kalinowska et al., 2016). The results of the analysis of every sample were chromatographic fingerprints in the form of two chromatograms with analysis time of 70 s (from non- and semi-polar columns) obtained simultaneously.

Table 1
Number and species of pork meat samples.

Species	Number of samples											
	PQS			C			L1			L2		
	F	FT	NF	F	FT	NF	F	FT	NF	F	FT	NF
Neck	36	36	12	36	36	12	36	36	12	36	36	12
Loin	36	36	12	36	36	12	36	36	12	36	36	12
Ham	36	36	12	36	36	12	36	36	12	36	36	12

Abbreviations: PQS-Pork Quality System, C-control group, L1-supplemented with 3% linseed oil group. L2-supplemented with 3% linseed oil with 1 mg kg^{-1} of Se and 100 mg kg^{-1} of vit. E group, F-fresh. FT-frozen-thawed. NF-not fresh.