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**AUTHENTICATION OF SIBIU SALAMI BASED ON CHEMOMETRIC  
ANALYSIS OF SPECTRAL DATA**

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## LIST OF ABBRFVIATION

<sup>1</sup>H-NMR: hydrogen nuclear magnetic resonance spectroscopy

AHC Agglomerative hierarchical clustering

EFA: Essential fatty acids

FA: fatty acid

FAME: fatty acid methyl ester

FT-IR: fourier transform infrared spectroscopy

GC-MS: gas chromatography-mass spectrometry

NIT: near infrared transmittance spectroscopy

NMR: nuclear magnetic resonance spectroscopy

PCA: Principal component analysis

PGI: Protected geographical indication

SFA: Saturated fatty acids

TE: Trolox equivalent

UFA: Unsaturated fatty acids

## INTRODUCTION

The sausage products are present in many countries throughout the years has become an indispensable dish for many families. There are some countries in Europe such as Germany, France, Italy, Romanian, Spain, Denmark and some countries in Asia such as Korea, China with long tradition of salami production.

In general, salami can be defined as products made by selecting, chopping, and mixing meat and fat, mixed with seasoning, spices, and authorized additives, that are then ripened and dried (cured) and, sometimes, smoked. However, regional traditions, environmental variations, family recipes, and other factors have rise to a wide range of fermented salami, and it can be said that there are almost as many types of salami as there are geographical regions. This is also attested in the report where they compare fatty acid composition of salami from different countries and their nutritional implications [19].

In some studies, reveal that, in the processing of sausage they have added additional ingredients such as olive oil, lard, spices. This change affects the amount and type of fatty acids found in salami. The studies determined the amount of fatty acids in the product enables us to test and refine new methods to improve the quality of products.

Today, along with the development of science and technical capabilities, we could use a variety of methods and different analysis system for fatty acid content analysing in salami. The main analysis system known as a gas chromatography-mass spectrometry (GC-MS) technique, near infrared spectroscopy technology (NIR), near infrared transmittance (NIT) spectroscopy, nuclear magnetic resonance spectroscopy ( $^1\text{H-NMR}$ ).

Itself every method of analysis have its own advantages and disadvantages. Some method has dominant time benefits others have lower costs of analysis. Hence, researchers continue to drive improvements in analytical methods for fatty acid, to provide accurate process analysis, saving time and chemicals, as well as lower the cost of analysis for each sample.

Fermented salami is products that before consumption passes through a more or less prolonged process of drying and ripening. Sibiu Salami is a famous Romanian

fermented dry salami, produced mainly from pork meat and pork back-fat. The mix is stuffed into natural casings and then smoked, dried and ripened. There is a wide variety of dry-cured salami produced in Romania, the most appreciated is Sibiu Salami, because of the special taste. A similar production procedure is applied for obtaining Dacia, Banatean and Sinaia Salamis. They different mainly is the taste and some of them in the production receipt. Romania has a tradition of over 100 years in producing “Sibiu Salami”, known as “Salam de Sibiu” which has been registered as a “protected geographical indication” (PGI) labelled product in the European Union. The Sibiu salami’s producers have already made export to promote this product outside the country.

The aim of this thesis was to develop a method for authentication of Sibiu Salami against other meat products of its class, using spectral data combined with chemometrical analysis. The GC-MS and NMR spectral data have been used as data base for chemometric analysis.

## **1 LITERATURE REVIEW**

The issue of product quality is one of the top concern in salami products now. There were many countries were different quality problems of dry-cured salami were noticed. The studies about the ingredients and the analysis methods were conducted. Each study has its advantages and significance of its own, overall analysis of the composition and content of fatty acids in the salami is now improved and very interesting.

### **1.1 Studies on different sausage products**

Salami is a type of cured sausage consisting of fermented and air-dried meat, typically beef or pork. Historically, salami was popular among southern and central European peasants because it stores at room temperature for up to 40 days once cut, supplementing a potentially meager or inconsistent supply of fresh meat. Countries and regions across Europe make their own traditional varieties of salami.

### 1.1.1 Studies on Sibiu Salami

Sibiu Salami, in Romania known as “Salam de Sibiu” is a Romanian deli made with pork's meat, pork's fat, salt and condiments. Sibiu Salami are considered as a luxury food.

Traditional sausages-dried salami is meat products that are part of the traditional daily diet, and also highly valued in modern life with an increasing demand. Sausage recipes were developed that took advantage of what people had.

The differences between the various types of dry-cured salami are due to the kind of meat they contain the proportion of lean to fat, spices, and the fineness or coarseness of the grind is what distinguishes one regional Salami from another. Fermented salami are products that before consumption passes through a more or less prolonged process of dry and ripening. Dry salami is made from different types of meat which are mainly made from pork. In Romania, there are some studies related to salami composition but not much. The results showed that GC-MS is a suitable method for quantitative determination of fatty acid in different meat products [1, 2,].

The composition and content of fatty acids in dry salami have been reported in many researches nationwide. In a research in Romania, the authors mainly studied in the composition and content of fatty acids in dry salami. The content of different fatty acids in sausage as such as myristic acid (C14:0), palmitoleic acid (C16:1), palmitic acid (C16:0), oleic acid (C18:1), linoleic acid (C18:2), stearic acid, arachidonic acid and saturated fatty acids (SFA); unsaturated fatty acids (UFA); essential fatty acids (EFA). The beef meat and the mixture of a sausage meat were compared. Research results show the content of different fatty acids in beef meat and sausage. Percentage of the fatty acid of beef meat in respective with sausage meat: myristic acid (C14:1) 0.84- 0.09; palmitoleic acid (C16:1) 1.21 - 0.43; palmitic acid (C16:0) 13.46 - 8.47.; oleic acid (C18:1) 22.7 - 28.54; linoleic acid (C18:2) 0.49 - 6.08; stearic acid 11.97 - 8.88 and saturated fatty acids (SFA) 26.28 - 17.44; unsaturated fatty acids (UFA) 24.30 - 35.05; essential fatty acids (EFA). 1.7 - 7.51. It is interesting to observe that unsaturated fatty acids (UFA) in the sausage mixture is higher than in beef meat and also the total saturated fatty acids (SFA) are higher in beef meat then in the sausage mixture.



The changes in fatty acid composition was also mentioned in other studies [1-19]. In another research Dacia sausage (a Romanian fermented dry sausage, produced from raw pork, salt, pepper, garlic, spices, additives and starter culture) was analysed. The meat mix is stuffed into natural casings and then smoked, dried and ripened. During the ripening of fermented sausages, various changes take place, leading to the final characteristics of the sausage. Lipids are abundant in fermented meat products and their changes influence the aroma and the flavor of the final product. One of many indicators that concern the composition, nutritional and content in fatty acids [3, 4]. During the manufacture of Dacia sausage, there was an increase in all of the free fatty acids, with oleic (C18:1) and linoleic (C18:2) being the main fatty acids released. The greatest increase in levels of these fatty acids took place during the drying-ripening stage.

Adding vegetal oil in smoked and boiled salami resulted in increasing both nutritional value and the protection against oxidation [4]. This study has introduced a new meat product, boiled-smoked salami with an addition of sea buckthorn vegetable oil (*Hippophaë rhamnoides* L.) and walnut oil (*Juglans Regia* L) in order to improve PUFAs/SFAs and  $\omega$ -6/ $\omega$ -3 ratios. The vegetable oils have been added for reducing the saturated fatty acids and to increase the poly- and mono - unsaturated fatty acids content. Some chemical characteristics of the salami samples were analyzed by NIR spectrophotometry (FoodScan), the antioxidant capacity by photochemical instrument and fatty acids content by GC-MS. The fatty acids were determined at 4, 11 and 18 days from processing at refrigeration temperature. The lipid profile (g fatty acids/100g fatty acids), the vitamin E content (mg /100g fatty acids) and the antioxidant capacity ( $\mu$ mol TE /g fat) offer information about the nutritive value of the salami with vegetable oils added, respectively, changing in the lipid content and its profile during the storage. The results of this study showed that adding vegetal oil in smoked and boiled salami resulted in increasing both nutritional value and the protection against oxidation. Regarding the nutritional value, the sample prepared with walnut oil had the highest PUFAs content comparing with the sample obtained with sea buckthorn oil that showed higher MUFAs and  $\alpha$ -tocopherol values. The presence of sea buckthorn oil in salami, in relevant ratio, may cause a 10-day delay of the oxidative processes due to moderate PUFAs and higher antioxidant compounds content.

The back-fat sample registered a content of 41.43% of saturated fatty acids, with the palmitic acid as predominant (25.93%). A large percentage of PUFAs was found in walnut oil 73.49g/100g fatty acids, according to the literature values ( $69.55 \pm 0.03$  up to  $75.54 \pm 0.51$ ) (Arimboor & al.). More MUFAs was found in the sea buckthorn oil, 57.25 g/100g fatty acids, higher than the values found in the literature (52.823-54.32%) (Tahira Fatima & al.). Palmitic acid is 36.7% higher in sea buckthorn oil compared to the walnut oil and approximately 50% lower than in meat and back fat. The main MUFA acid, the oleic acid, had the highest value in the sea buckthorn oil (70% compared to the walnut oil and 28% compared to the average value of meat and fat).

From the above findings, in the current situation, research is focusing on the nutritional composition and quality of dried sausage. One of the criteria evaluated are most interested is that the fatty acid composition in dry sausages which are primarily implemented on the system GC-MS analysis. This approach is in tune with the trend of research on dry sausage and countries around the world with the advantages of using modern analytical systems.

### **1.1.2 The studies on other dry-cured salami produced abroad**

In regard to salami, it is thought that the name is derived from Latin words “salsiccia” and “salumen”. In Europe, the main countries that produce salami are Romania, Germany (Tesco German Salami 125G, Salami pepper Germany), Italy (Cremona salami, Nduja, Calabrese salami), Spain (Iberian Salami, Serrano Ham D.O. Teruel) France (Saucisson sec-200g, Garlic cervelat, Chorizo-200g), and Hungary (Bende Teli Hungarian Style Salami). The amount produced is of “several hundred million kg per year.”

Worldwide, there are many different versions of sausages, each with its own cultural and flavour profiles. For example, due to immigration to North America, European settlers brought many traditions, including fermented meats such as bologna or pepperoni. Similar types of sausages are found in the Middle East, where various meats such as beef, lamb, and mutton are used, or in China where “Lap Cheong”, translated as “intestines stuffed in the winter” is usually pork. Likewise, in Eastern