Authentication Methodologies of Artisan and Sourdough Breads: State-of-the-Art and Perspectives

Kristian Pastor1,*, Jovana Kojić2, Nataša Nastić1, Dejan Dobrijević3, Mirjana Horvat4, Zoltan Horvat4, and Marijana Ačanski1

1 Faculty of Technology, University of Novi Sad, Bulevar cara Lazara 1, 21000 Novi Sad, Serbia
2 Institute of Food Technology Novi Sad, University of Novi Sad, Bulevar cara Lazara 1, 21000 Novi Sad, Serbia
3 Faculty of Medicine, University of Novi Sad, Hajduk Veljkova 3, 21000 Novi Sad, Serbia
4 Faculty of Civil Engineering Subotica, University of Novi Sad, Kozaracka 2a, 24000 Subotica

* Correspondence: kristian.pastor@uns.ac.rs; herr.pastor.kristian@gmail.com
Received: 11 November 2021; Accepted: 29 January 2022

Abstract: Food authentication has received a lot of attention in the scientific community during the last decade. Various techniques have been applied in order to verify authenticity of cereals, pseudocereals, and flour, such as microscopic, biomolecular, and chemical (chromatographic, spectroscopic and isotopic). However, research on developing methodologies for detecting fraud in the market of bread and other bakery products is still being neglected. This is especially true for specialty products – artisan and sourdough breads, having higher prices on the food market due to specific production methods, high-quality ingredients and health-beneficial effects. Bearing this in mind, there is a strong obligation for the scientific community to develop and validate rapid, accurate, reliable and robust methods for verifying authenticity of specialty breads and other bakery products. These goals could be fulfilled by employing contemporary analytical instrumentation, providing the analyst with complex datasets, which are nowadays most frequently being processed by chemometric tools and machine learning algorithms.

Keywords: artisan bread; sourdough bread; authentication; instrumentation.

1. Introduction

The fraud practices in the food market have been known since the Age of Antiquity [1,2]. During the 19th century limestone, gypsum, and alum were being added to baking flour to increase weight, strychnine was added to beer to increase bitterness, and copper, lead and mercury salts were added to sweets to provide nice color and shine [3-5].

Consumer interest in authenticity, quality, and safety of food products is constantly growing [6]. Authenticity is associated with truthfulness, thus, a food product is said to be authentic if it has not been the subject of any fraud [7]. European and global food policies require an authentic product on the food market. This actually means that the product label must match its actual composition, origin (geographic, botanic, and genetic), and production method (conventional, organic, and traditional) [2,8,9].

Globalization, market development, rapid distribution systems, and diversification of food products, are leading to increasing adulteration and contamination practices, that are becoming more international with far-reaching consequences [2,4,9,10,11]. The most common type of food adulteration—economically motivated adulteration—is defined as a misleading and deliberate substitution or addition of certain ingredients to a food product, in order to increase the apparent value of the product, or reduce the cost of its production, with the consequence of a certain economic gain [4,5]. Depending on the nature of an added substituent, the obtained adulterated product might
pose a potential risk to the health of the consumer. Besides economic, this adds a health and safety component to the aspect of food authentication [6,8,12]. Bearing this in mind, global policies require strict monitoring and control of food authenticity, quality and safety. Therefore, a clear trend to apply novel techniques and methodologies with this aim does exist. Traditional methodologies are sometimes still being used. However, novel authentication methodologies, that would complement or even replace standard ones, are definitely needed, being environmentally friendly, cost-effective and rapid [8,9]. This trend is stimulated by consumers, regulatory bodies, and the food industry [2,9].

The top ten countries in the world that are most actively engaged in developing food authentication methodologies are members of the European Union, in addition to the United States and China [2]. European Commission legislations highlight the consumers' rights to have an insight into the true information about the food they buy [13,14,15]. These aim to prevent food adulteration and consumer fraud. A very common example of food fraud is the substitution of a certain high-quality ingredient with a similar one, but cheaper. Thus, the consumer is, in most cases, not able to recognize this procedure [1,6,8,16].

There are various analytical approaches applied to verify food authenticity and detect fraud, such as: chemical - by determining the profile and content of food chemical compounds; biomolecular - by analyzing DNA; isotopic - by measuring ratios of certain stable isotopes; and others [7]. Some authors believe that the future of this scientific field is framed by the synergistic fusion of complementary techniques, and the processing of obtained complex datasets by novel statistical approaches [6]. Since 2001, many publications have appeared, which suggest the application of both novel and/or traditional methods, all coupled with chemometric tools and machine learning algorithms, for output processing. It must, however, be noted that fraud practices are constantly being developed, often surpassing the power of established analytical protocols for their detection [15].

2. Authentication of Bread and Bakery

Food commodities most susceptible to adulteration include cereal products, edible oils, milk and dairy, fish and meat, fruit and juices, coffee and tea, nuts, spices, honey, wine, and many more, Figure 1 [9,11]. Being produced in vast amounts annually (with more than 2 billion tons), cereals definitely represent the most important food crop in the world [17]. Verifying authenticity of cereal products is necessary in order to determine the accuracy of the product label. This would prevent unfair economic gain of some producers. European Union and Codex Alimentarius regulations require mandatory declaration of ingredients that may cause intolerance and allergic reactions. This applies in particular to gluten-containing cereals, such as wheat (including common bread wheat, durum wheat and spelt), rye, barley, oats and their hybrids, as well as products derived from these plant species [14,18,19]. According to [9], the focus of the scientific community on researching authentication methodologies of bread and bakery products is the lowest in percentage, with only 1% of scientific articles being published in the overall analysis of all food commodities, Figure 1. This issue gained scientific focus relatively late, between 2011 and 2014, Figure 2 [9].
A detailed overview of the application of various techniques: microscopy (light and scanning electron microscopy), biomolecular (polymerase chain reaction - PCR and enzyme-linked immunosorbent assay - ELISA), spectroscopy (infrared, fluorescence, imaging, nuclear magnetic resonance), separation techniques (liquid and gas chromatography), and even traditional methods, such as titration, in verifying authenticity of cereal (wheat, spelt, rye, oat, barely, corn, and rice) and pseudocereal flour (buckwheat and amaranth), and bread products is given in [20]. This review reveals that studies were mostly dealing with determining the geographical origin of cereal/pseudocereal cultivation. The possibility of determining botanical origin was mainly
investigated using biomolecular techniques and gas chromatography. Furthermore, the authentication botanical origin of cereals and flour was far more explored compared to final bakery products, such as bread.

3. Authentication of Artisan and Sourdough Breads

Nowadays, sourdough bread and other sourdough-based baking goods (e.g. biscuits, crackers, pastry, pizza, and pasta) are enjoying an increasing popularity as convenient, nutritious, stable, natural, low processed, and healthy food. In fact, the use of sourdough in bakery industry has received a great attention worldwide in recent years, as evidenced by the advent of a diversified (but limited) number of products in the market, and research and development activities dedicated to this topic by companies [21]. It needs to be pointed out that no national legislation anywhere in the world regulates and protects traditional sourdough and artisan breads. However, the use of sourdough has to be guaranteed to meet both bakery and consumer expectations, and to fulfil legal requirements [22]. An overview of artisan and sourdough bread authentication procedures, available in the literature, is given in table 1.

Table 1. A literature overview of artisan and sourdough bread authentication procedures.

<table>
<thead>
<tr>
<th>Aim</th>
<th>Technique</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sourdough bread</td>
<td>PCR</td>
<td>[22]</td>
</tr>
<tr>
<td>Italian PDO sourdough bread</td>
<td>NMR</td>
<td>[23]</td>
</tr>
<tr>
<td>Italian PGI sourdough bread</td>
<td>IR-MS</td>
<td>[24]</td>
</tr>
<tr>
<td>PDO Italian durum sourdough <em>Altamura</em> bread</td>
<td>GC/MS</td>
<td>[25]</td>
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<tr>
<td>Rye bread</td>
<td>GC</td>
<td>[26]</td>
</tr>
<tr>
<td>Whole wheat bread</td>
<td>GC</td>
<td>[27]</td>
</tr>
<tr>
<td>Emmer and eincorn flour</td>
<td>qNMR</td>
<td>[28]</td>
</tr>
<tr>
<td>Buckwheat bread</td>
<td>GC/MS</td>
<td>[29]</td>
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<tr>
<td><em>Pane Nero di Castelvetrano</em> bread</td>
<td>HPLC-SNP</td>
<td>[30]</td>
</tr>
<tr>
<td>Spelt and rye bread</td>
<td>LC/MS-MS</td>
<td>[32]</td>
</tr>
<tr>
<td>Chia, sesame and flax seeds</td>
<td>LC/MS-MS</td>
<td>[33]</td>
</tr>
<tr>
<td>Corn, rye, oat bread</td>
<td>PCR</td>
<td>[34]</td>
</tr>
<tr>
<td>Durum wheat bread</td>
<td>PCR</td>
<td>[35]</td>
</tr>
<tr>
<td>PDO sourdough <em>Altamura</em> bread</td>
<td>PCR</td>
<td>[36]</td>
</tr>
<tr>
<td>Emmer and eincorn flour</td>
<td>DNA-TBP</td>
<td>[37]</td>
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</tbody>
</table>

There are a few papers published in 2000s, dealing with the topic of developing procedures for sourdough bread authentication. Further research reports the application of nuclear-magnetic resonance (NMR) and isotope-ratio mass-spectrometry (IR-MS) to differentiate between Italian Protected Designation of Origin (PDO), and Protected Geographical Indication (PGI) sourdough breads, obtained from tender and durum wheat flours, and to determine geographical origin of specialty breads from southern Italy [23,24]. A gas chromatography – mass spectrometry (GC/MS) method for the authentication of PDO Italian durum sourdough *Altamura* bread, using volatile compounds as characteristic fingerprints, is reported in [25].

Some studies demonstrated the potential of Alkylresorcinol levels as relevant biomarkers for determining whole grain wheat and/or rye flour content in bread, using gas chromatography (GC) [26], and for differentiating between breads made from whole wheat flour and refined wheat flour [27]. A quantitative NMR method was developed for verifying authenticity of old wheat varieties - emmer (*Triticum dicoccum*) and einkorn (*Triticum monococcum*), in whole grain flours and breads [28]. These showed to contain high contents of alkylresorcinols, while the same compounds were completely absent from white flour and the corresponding bread.

Other investigations report the employment of: gas chromatography – mass spectrometry technique, with the aim to determine the content of buckwheat and wheat flour in bread [29]; a
denaturing high-performance liquid chromatography combined with single nucleotide polymorphism (HPLC-SNP) to trace durum wheat cultivar *Timilia* in the bread claimed to be *Pane Nero di Castelvetrano* (Castelvetrano Black Bread) [30]; a short-wave near-infrared hyperspectral imaging to detect adulterations in wheat flour and bread with cheap grains, such as sorghum, oats and corn [31]; and a liquid chromatography – tandem mass spectrometry (LC-MS/MS) as a strategy for authentication of wheat, spelt and rye flour addition to bread products, using peptide markers [32]. Furthermore, targeted metabolomics to assess the authenticity of bakery products containing chia, sesame and flax seeds, by analyzing polyphenols using liquid chromatography (HPLC-DAD-ESI-qTOF MS/MS), was studied in [33].

In the frame of bread authentication, most published research articles report the application of a polymerase chain reaction (PCR) to: verify common wheat flour supplementation with corn, rye and oat flours [34]; detect the presence of common soft wheat in durum wheat bread [35]; quantify the presence of demanded durum wheat cultivars in PDO *Altamura* bread [36]; and to quantify emmer and eincorn wheat flour in durum wheat flour, using DNA fingerprinting through tubulin-based polymorphism (TBP) [37]. The research article most tightly related to the topic of authentication of sourdough breads describes the application of a quantitative PCR method to detect the lactic acid bacterial microbiota in bread, and, therefore, discriminate between breads produced with sourdough from those without sourdough fermentation [22].

4. Conclusions

After analyzing the research reported in this overview a conclusion can be drawn that there is a serious lack in analytical methods focusing on developing modern solutions for authentication of breads, especially artisan and sourdough breads, which are lately being promoted as novel and healthier alternatives to common breads. With this in mind, there is a strong obligation for the scientific community to develop and validate methods for verifying authenticity of special breads and other bakery products, using sophisticated or fused instrumentation linked with modern statistical processing of vast amounts of data.

**Funding:** The presented research was funded by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Program no. 451-03-68/2022-14/200134, 451-03-68/2022-14/200222, and 451-03-68/2022-14/200093).

**Acknowledgments:** Dr. Kristian Pastor acknowledges the support from COST Actions CA18101 – *Sourdomics* and CA19145 - *SensorFINT*.

**Conflicts of Interest:** The authors declare no conflict of interest.

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