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Different Diacetyl Perception Detected through MOX Sensors in Real-Time Analysis of Beer Samples

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Abstract: Beer is the most consumed alcoholic beverage; with 177.5 million kiloliters produced every year, it is one of the most relevant food products. Diacetyl is a typical byproduct of yeast metabolism that is formed during the fermentation inside breweries. The perception of this high volatile and butter-like flavor molecule varies according to the kind of beer, from a positive and highly sought characteristic to a characteristic that is avoided. Furthermore, its toxicity when inhaled has been proven. Typical diacetyl analysis includes voltametric detection and chromatographic analysis techniques. Using metal oxide sensors (MOS), this analysis can become fast and cost-effective, evaluating the differences in diacetyl concentrations through resistance variation. The S3+ (Nano Sensor Systems s.r.l.; Reggio Emilia, Italy; device can recognize volatile compounds through a tailormade array of different materials. The results can be shown on a PCA that is directly generated by the instruments and can be used to manage the productive process through an IoT integrated system. Testing different beer typology through electrochemical sensors allows for the validation of this new approach for diacetyl evaluation. The results have shown an excellent ability to detect diacetyl in different beer samples, perfectly discriminating among different concentrations.

Keywords: diacetyl; MOX sensors; beer; real time analysis; IoT device

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1. Introduction

Beer is produced worldwide and consumed in over 150 different styles, each one being characterized by a peculiar attribute [1]. It is the most produced and consumed alcoholic product in the world, with 177.5 million kiloliters being produced every year [2]. The alcoholics market is continuously growing, and it is expected to globally increase its value by 19% from 2018 to 2024 [3]. Through alcoholic fermentation, many different volatile compounds are produced, which starts from the interaction between yeast and the matrix; together with the compounds that characterize raw materials, they have a direct impact on final product's sensory perception. These chemicals belong to different classes, e.g., inorganic compounds, alcohols, organic acids, ester, aldehydes, vicinal diketones including diacetyl, and many oth ers [4]. The production process and ingredients create significant differences in the flavors, which is an important driver for food acceptability. Molecules such as diacetyl or 2,3-Butanedione have a great impact on the flavor of many foods, from dairy products to fermented matrixes including beer, thanks to its small and highly volatile characteristics. Because of its butter-like aroma, it is commonly used as a flavoring agent, and it is considered as GRAS by the FDA [5–7].

Diacetyl is a vicine diketone produced by yeast action on the fermentation process as byproducts of valine and isoleucine amino acid synthesis [8]. Diacetyl is converted into 2,3-butanediol thanks to various reductase enzymes [9,10], and its presence in beer can vary according to the yeast and beer typology [11]. Like many other molecules, it can be an appreciated characteristic of some food products or become a problem if its presence is detected in others [6]. This can be noticed in beer samples, where the lager type usually has a high diacetyl content, with a 0.15 ppm threshold [11,12]; meanwhile, bock beer should not have it in its formulation because its sensory perception is influenced by different volatile compounds. Pilsner and English-style ale usually have a higher concentration [13]. Indeed, lighter beers are usually characterized by higher diacetyl perception because in these samples, the hop and malt do not have a preponderant importance on the flavor. When its concentration exceeds the cited thresholds, non-compliance is produced [4,8]. This difference in choosing typology characterized by different diacetyl concentrations was considered for sample selection. Lager beer is a low-temperature fermented and matured beer, and nowadays, it is the most consumed beer in the world. It is characterized by a sweet smell and taste with important fresh and malty notes [14]. Ale is a high fermented beer with fruitier and sweeter notes than lager, and it is referred to a vast amount of subclasses. The diacetyl flavor threshold on these products are normally 0.10–0.40 ppm [8]. Indian pale ale (IPA) generally has a 5–8% alcohol volume, and it is characterized by a pronounced hop aroma and high bitterness. In this typology, diacetyl's presence can easily generate non-compliance, and the thresholds are really low [4,15].

Implementing a detection system that is able to recognize diacetyl's presence is primarily important. Because of its volatility, quantitative analyses are difficult to pursue; nevertheless, it represents one of the most important analyses in the brewing industries. Its evaluation is an important tool for investigating the presence of problems related to pitching and fermentation, for studying the yeast vitality, and as a marker for beer aging [16,17]. Chromatographic analyses are the most often used techniques to detect diacetyl's presence in foods because of its good results; meanwhile, other analytical procedures include colorimetric assays and voltametric detection [5,8], which can guarantee excellent results for miniaturizing samples [18]. Implementing electronic noses for beer evaluation is nowadays a well-known field, as this topic has been investigated in the last 30 years [19,20]. Nowadays, many studies are currently undergoing the creation and validation of IoT integrated devices that are able to detect different target molecules in fermented products [21]; however, only a few have already been implemented in real production processes. This study follows this research field with the aim of scaling up and implementing the preliminary results shown in this paper to a real production process. For this reason, the sample selection was not only based for different levels of diacetyl presence, but also for the production processes where this device will be implemented.

Metal oxide sensors (MOS) have been widely studied for their ability to produce an electrical signal, which starts from chemicals present on sample [22]. An S3+ (Nano Sensor Systems s.r.l.; Reggio Emilia, Italy; www.nasys.it (accessed on 15 December 2022) device is an innovative tool that has been already used with success in other previous studies concerning quality control and food technology [23–25]. Thanks to its electrochemical and nano oxide metal sensors, its ability to interconnect, and possibility to be remotely controlled, this device can be efficiently used for many applications, including quality control in production processes. For this reason, its implementation in diacetyl analysis is based on solid scientific knowledge, starting from its instrumental composition. Before the sensor's application in inline devices, they must be calibrated to establish the functional relationship between the measured values and specific analytical quantities [26]. This expensive and time-consuming procedure plays a key role in providing reliable sensor performances [27].

The S3+ device can contribute important information to different stages of the production process, starting from the arrival of raw materials to process monitoring, as well as the analysis of results. Furthermore, implementing data analysis through the PCA technique

makes it possible to have a fast and easy-to-read data visualization. This process control can be a great innovation because it can drastically reduce power consumption and food waste. Indeed, the usually performed traditional analyses are destructive, slow, and expensive. Implementing a continuous way to control a system can recognize undesired chemicals when they are present in traces. In this scenario, corrective actions can be very effective and do not require long and complex treatments. Vice versa, when chemical concentrations are too high, corrective actions cannot be as effective, requiring expensive treatment that have important consequences on the product's final quality or even the possibility of having to trash the products. Nowadays, the current limitation of electronic noses is the incapability of performing quantitative analyses [28].

This work aims to analyze the volatilome of different craft beers, specifically investigating how the presence of diacetyl affects final products according to their typology and aromatic profile. Because the beer market is extremely important and it will grow in the future, implementing new and developed technology can bring an important impact on many fields, from reducing resource waste to improving the final quality. An S3+ device equipped with advanced nanosensors was therefore implemented with the aim of looking for new emerging applications fields for this technology, thanks to its capability of ensuring fast, precise, and cost-effective analyses. This study sought to understand sensor response patterns for this spe cific application. Finally, a post-run analysis was conducted using the principal component analysis (PCA). Furthermore, creating a robust database allows for the implementation and design of pattern recognition algorithms in order to provide fast responses and artificial intelligence algorithms that can predict the situation of interest in order to assure a higher level of quality in the standards and safety in the food/feed production chain. These tailormade, noncommercial devices can be implemented for a selected target molecule on a different matrix, which helps to achieve the digitalization and automation of entire production lines.

2. Materials and Methods

2.1. Sample Preparation

The analysis was conducted in two different steps. First, a 5% hydroalcoholic solution was prepared to emulate the principal beer characteristic in a flavor-free matrix. Later, the analysis was performed on beer samples. Two different 5% hydroalcoholic solutions with different diacetyl concentrations were created at 100 mg/L (S1: Standard 1) and 1 g/L (S2: Standard 2), respectively. In 500 mL of hydroalcoholic solution, three different diacetyl concentrations were tested (0.01 mg/L, 0.06 mg/L, and 1 mg/L) to determine the six best-performing sensors. These concentrations were chosen according to the oral threshold found in the literature [29]. Later, analyses on three different types of beers were conducted: IPA, ale, and lager. Beers were chosen according to their aromatic profile, and we searched for samples with characteristics that were representative of the typology. For each sample, 500 mL were taken, put in a three-hole Pyrex flask, and allowed to rest at 20 °C for 30 min in order to reduce the foam impact. Next, we added a specific quantity of S1 or S2 to each sample to reach the desired diacetyl concentration. To reach 0.01 mg/L of the contaminant, 80 µL of S1 was added. From this concentration, 250 µL of S1 was added to reach 0.06 mg/L; then, 470 µL of S2 was added to reach 1 mg/L. Also considering the analysis in the beer without added contaminant, four different concentrations were tested.

2.2. Calibration of MOX Sensor Array and S3+ Setup

The sensor calibration followed important strict steps in order to obtain the most reproducible production.

At first, the sensor underwent a process of annealing in order to promote the stabilization of the sensing layer on the substrate. This process can change according to the final application of the sensor. The changeable parameters were:

- Temperature between 500 °C and 800 °C;
- Time between 1 h and 10 h.

Once the annealing was finished, each sensor was subjected to a period of ageing in air to reduce and standardize the sensing layers electrical resistance (Ω). This period can change the sensitivity to VOCs, which future applications will demand. Overall, the sensor was proven in a tried-and-tested system. This one was equipped by the following:

- A chamber test with a standardized dimension, which promote a smooth flow in and out of the chamber;
- A mass flow program that absorbs and controls the flow from the air and ethanol pressure cylinders;
- An electronic board that controls the conditioning and monitoring of the sensor at the working temperature, transduces the chemical signal in an electrical signal, and sends all the data to the cloud.

The S3+ device was composed of a sensor chamber, fluid dynamic circuit for the distribution of volatile compounds, and electronics control system. In the sensor steel chamber, six inhouse-developed MOX sensors were contained. These sensors were differently doped: two of them were created using SnO_2, two were SnO_2 with Pd, and two were SnO_2 with Au. The working temperature was 500 °C (Table 1). It allowed for the separation between sensors and the environment. The dimensions of the chamber were 11 × 6.5 × 1.3 cm. The sensors were previously selected for the best performance during the preliminary tests. The volatile compounds were forced to only pass through an inlet and an outlet into the sensor chamber. The sensor response is based on the change of its resistance (ΔR) over time, which is caused by its interaction with different kinds of volatile compounds. The reactions between the oxygen species adsorbed on the surface of the sensor and the target molecules lead to the variation in the concentration of charge carriers in the sensing material, affecting its electrical conductance [30]. The environmental parameters inside the chamber such as temperature, humidity, and flow were constantly monitored. The dynamic fluid circuit was composed of a pump (Knf, model: NMP05B), polyurethane tubes, an electro valve (Camozzi Group s.p.a., model: K000-303-K11M), and a metal cylinder with activated carbon. This was used to filter air, avoiding the passage of environmental odors that may alter the final response. The solenoid valve was positioned at the inlet of the chamber to control the flow of the pump, with a maximum of 250 sccm. The electronic board processed all sensor responses by detecting the outgoing electrical resistance; it also controlled the operating sensor's temperature, which is an important parameter for the detection of volatile compounds. Finally, the system was able to send data to the web app dedicated to the S3 device via an internet connection [31], being an IoT device.

Table 1. Schematic description of the setup for different sensing elements.

Type of Sensor	Doping	Working Temperature (°C)
MOX sensor MOX sensor MOX sensor	SnO_2	500 °C
	SnO_2 + Pd	500 °C
	SnO_2 + Au	500 °C

The sample order was randomized, with two analyses performed each day. In total, 22 different analysis were performed during the study, vacuuming the air on the headspace through a polypropylene (PP) tube, which was held by Parafilm®. Two different carbon filters were used, with one being attached to the sample in order to filter the air substitution on headspace and one being attached to the S3+ device. This setup is shown in a schematic way in Figure 1A, whereas Figure 1B shows the actual setup used. For each analysis, 10 different measurement were taken, for a final total of 220 different measurements. Each measurement was carried out according to the following parameters: 100 s for the creation of the baseline by the suction of filtered air, 300 s of sampling from the sample headspace, and 600 s for signal recovery through the fresh intake of filtered air.

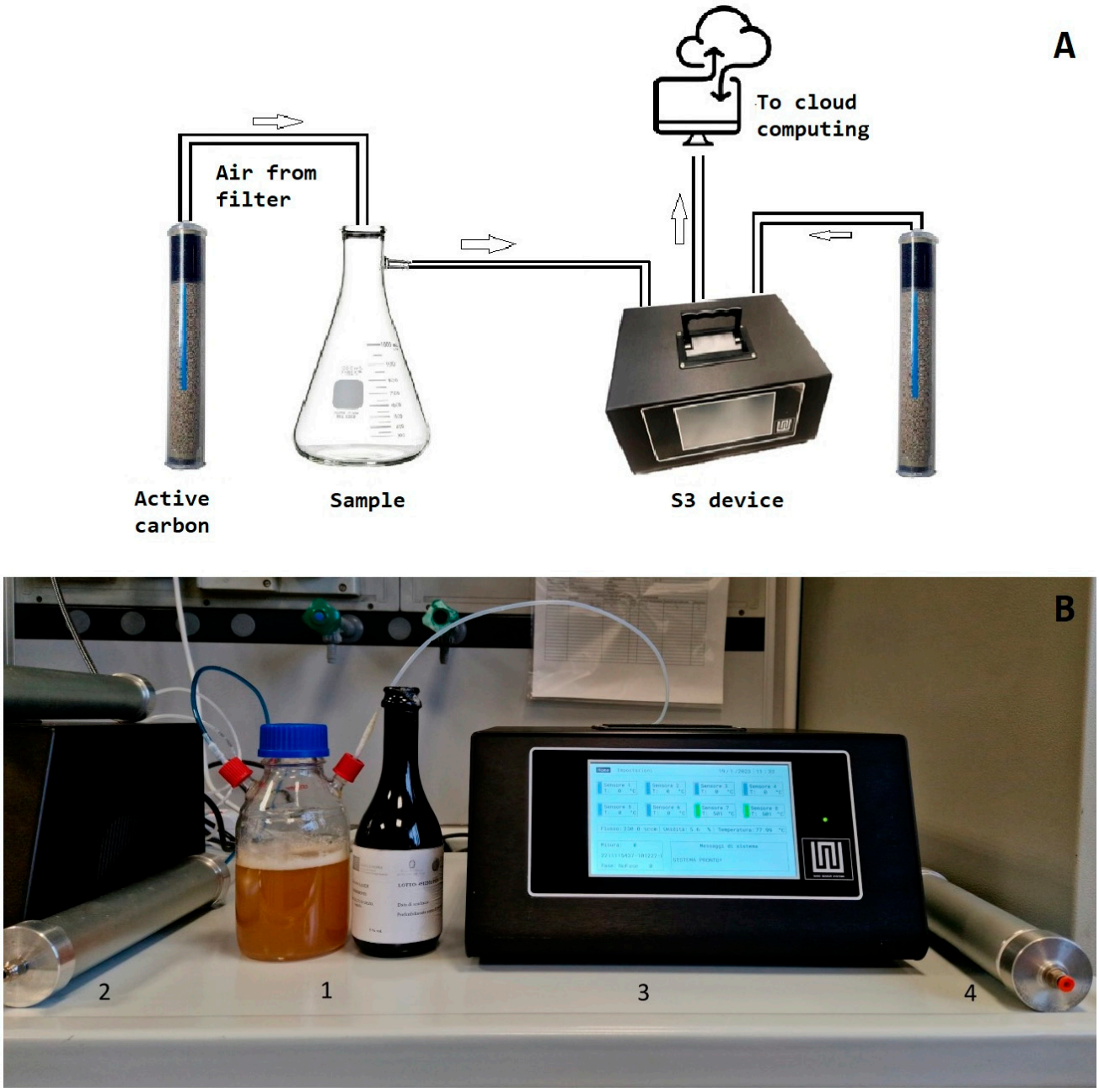

Figure 1. (**A**) Schematic representation of the instrumental analysis setup. (**B**) Analysis conducted on a lager beer sample. Beer is stored inside a three-hole Pyrex flask (1). One hole is closed, while the others two are connected with an active carbon filter (2) on the left exit and the S3+ device (3) on the right exit. Filtered lab air was used as the carrier gas. Furthermore, the S3+ device was connected to a second active carbon filter (4) to reduce the environmental contribution during the signal recovery.

2.3. Data Analysis

The outcome results, expressed as the difference in the resistance value, were sent to the cloud and managed on the Microsoft Azure platform, where they were traduced by the PCA technique, which emphasized variation and brought out strong patterns in the dataset. These data were then traduced by a multivariate statistical analysis using MATLAB, R2019b (MathWorks, Natick, MA, USA). Sensor outputs such as resistance were normalized at the first acquisition value (R0). For each sensor, the difference between the first value and the minimum value during the analysis was calculated. Therefore, the R/R0 parameter and standard deviation was calculated for every sensor during all 10 measurements and before performing the PCA analysis with 10% maximum uncertainty. Thanks to the PCA, it was possible to emphasize the variation and bring out strong patterns in the dataset. In order to do so, all of the outcome PCA were analyzed through specific features selection, which were specifically defined for each sensor. Features were previously extracted for each sensor from its recorded track. This decision is thanks to the implementation of a random forest, which is a tree-based classifier. The selected features (supervised selection) for all of the outcome PCA were: mean last 60 (mean of the latest 60 samples measurements); mean (mean of the obtained values); minimum (minimum value of the curve); integral (signal's integral, calculated by "Simpson's Rule"); difference (differences between mean of last 5 samples minus the mean of the firsts samples); maximum (maximum value of the curve); and delta-R (difference between higher and lower resistance value). Thanks to the feature selection, it is possible to maximize the margin among two different classes according to their importance on the features in the defined dataset [32]. To determine what can be defined as an outlier, three times the standard deviation (99.7%) was set as the reaction threshold.

3. Results and Discussion

Data collected by the chosen six sensing elements were recorded and stored into the web app in order to be easily managed by employers to quickly monitor the production process on any device. An example of the recorded tracks is visible in Figure 2, where differences among sensing elements are due to the dissimilar interaction with the sample, the non-identical dopant used, and structural characteristics. From the track, it is possible to see how the system is able to make measurements with a good replicability over time. During the withdrawal phase, a drop can be noticed, with a ΔR value always being greater or equal to 75%. Furthermore, the recovery phase takes place correctly, returning the baseline to the starting resistance value.

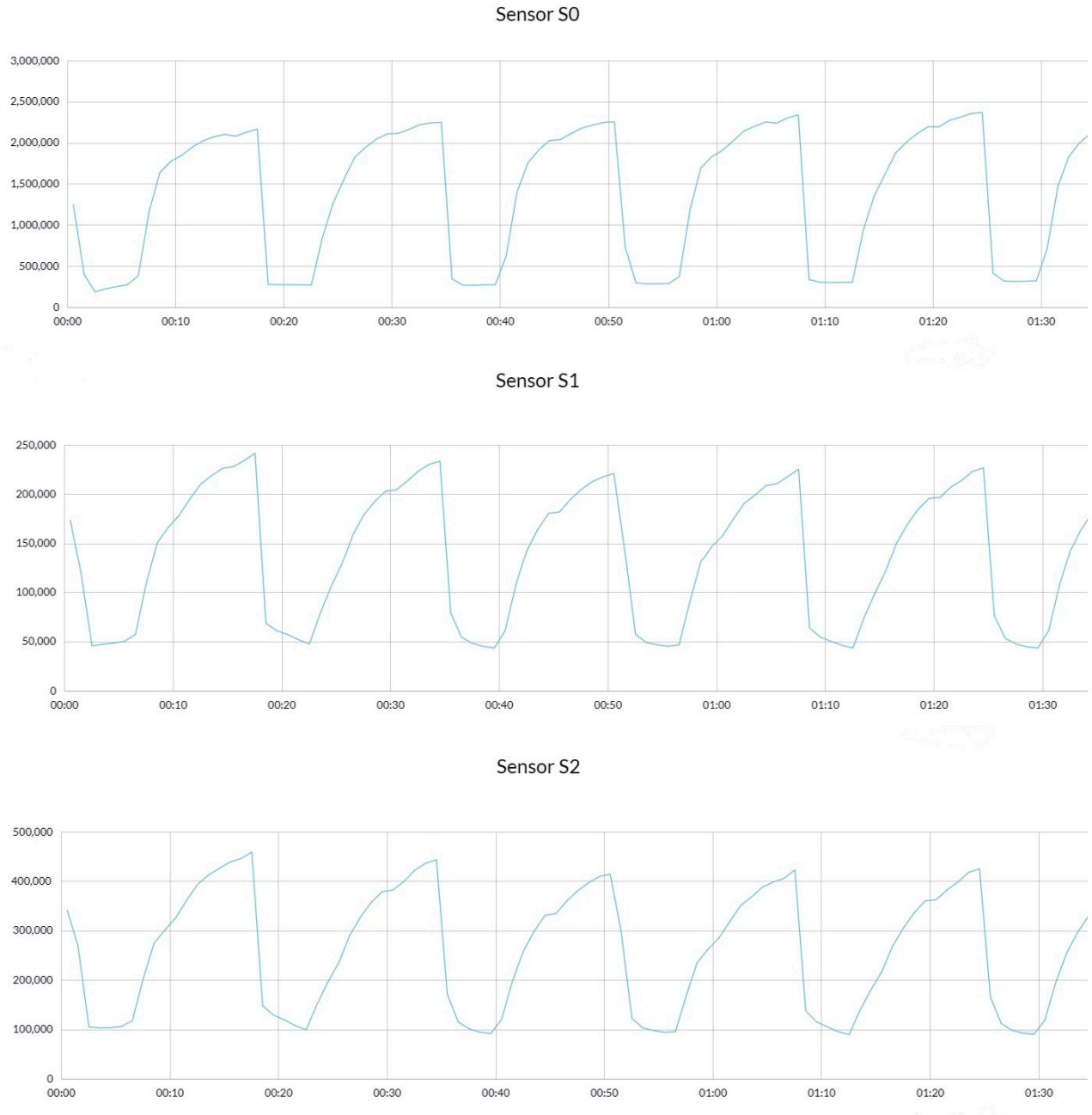

Figure 2. Three different recorded tracks made by differently doped sensing elements on the same sample: Sensor S0: SnO_2 + Pd; Sensor S1: SnO_2; Sensor S2: SnO_2 + Au. The *y*-axis shows the resistance value (Ω) while the *x* axis shows time (s). Once the tracks have been recorded, this project firstly has the aim of correctly selecting the best-performing sensor array for this specific application. As shown in Figure 3, the selected sensing elements are able to detect and discriminate 5% hydroalcoholic solution samples with different diacetyl concentrations. The selected features were mean last 60, mean, minimum, integral, difference, maximum, and delta-R. All three different concentrations (0.01 mg/L, 0.06 mg/L, and 1 mg/L) are recognized as different among themselves and, for that reason, this specific sensor's array was implemented for next steps.

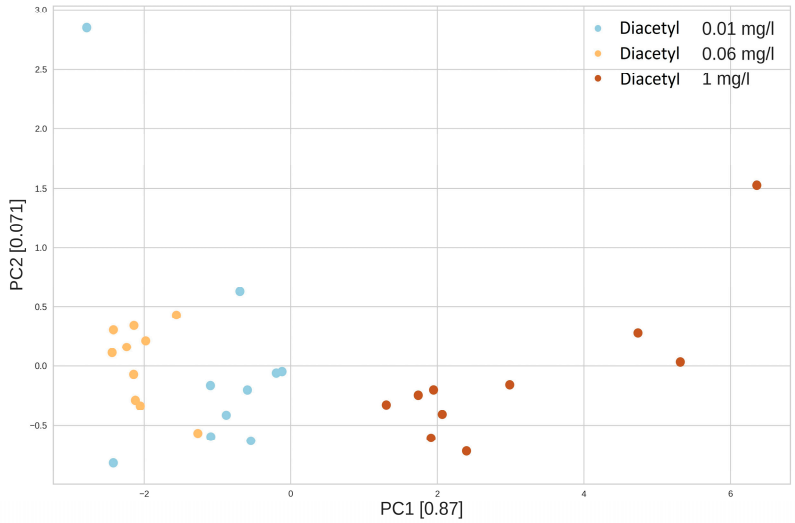

Figure 3. PCA on the 5% hydroalcoholic solution. Blue: 0.01 mg/L; yellow: 0.06 mg/L; brown: 1 mg/L.

Once the ability to discriminate a simplified solution was demonstrated, the capability to detect a difference among the different beers was tested. Figure 4 depicts the outcome PCA of untreated ale, IPA, and lager, which produced three different clusters according to the different beers' aromatic patterns through the difference in the detected resistance by the sensitive elements. The selected features were the integral and delta-R. Through this representation, it is possible to describe all of the collected dataset by both reduced principal components, as the sum of these PCs reached 100% of the variance.

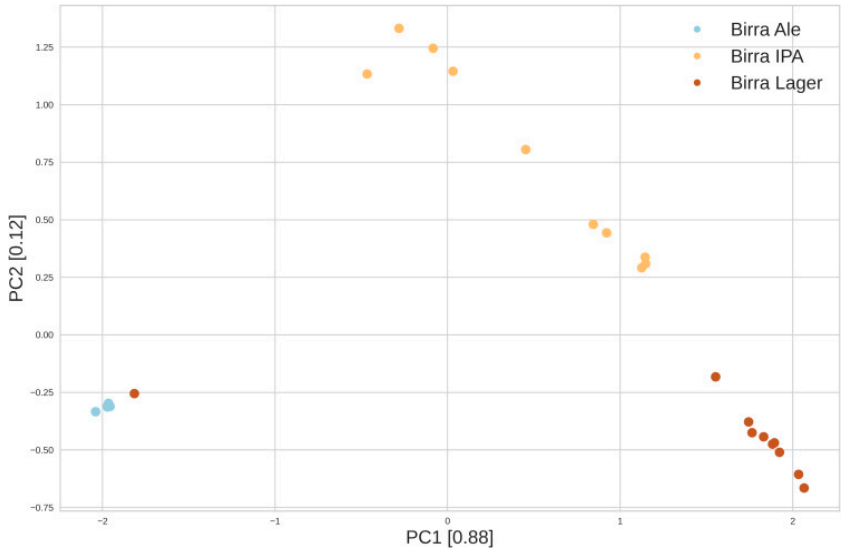

Figure 4. PCA obtained by the different types of beer. Light blue dots: ale; yellow dots: IPA; brown dots: lager. As described, the second part of the analysis was focused on investigating the S3+ device's discriminant capacity in the beer samples. We performed 19 different tests and compared the results of different types of beers and different diacetyl concentrations. The results of the analysis show that the S3+ device is able to detect differences in molecule concentrations at levels that are smaller than the human perception threshold. This ability is demonstrated in Figure 5 with the remarkably high explained variance on the outcome PCA. Indeed, two different clusters are visible in the IPA samples. Nevertheless, two different populations (brown dots and light blue dots) are still visible, showing how the device is able to recognize even very small differences among the samples. The selected features were mean and difference.

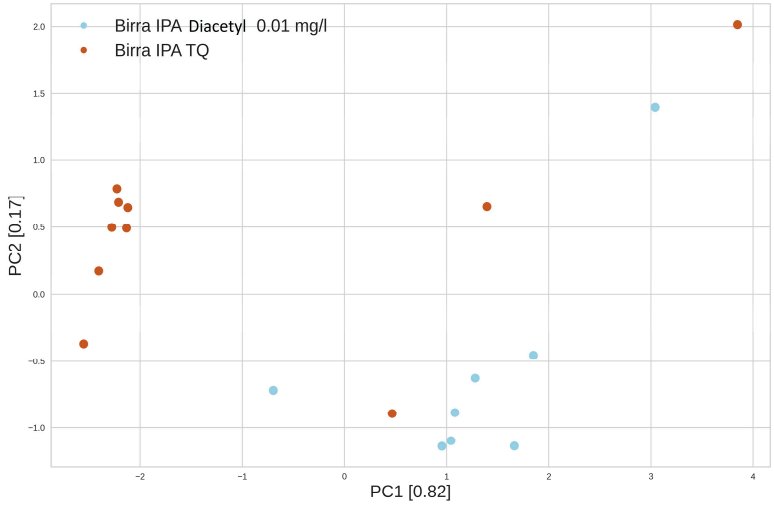

Figure 5. Comparison between two different IPA samples. Brown dots: IPA beer in an unaltered state (US); light blue dots: IPA with 0.01 mg/L of diacetyl. All outliers, as shown in Figure 6, were measured in the first moments of the withdrawals. This can be explained because in the first moments of the analysis, ethanol, CO_2, and other volatile compounds such as diacetyl are accumulated in the headspace. This could mean that the first data analyzed are affected by this quiet moment and, as a consequence, abnormal data are collected that affect the outcome PCA. This specific pattern is recognizable in all of the shown PCA, because no data were considered.

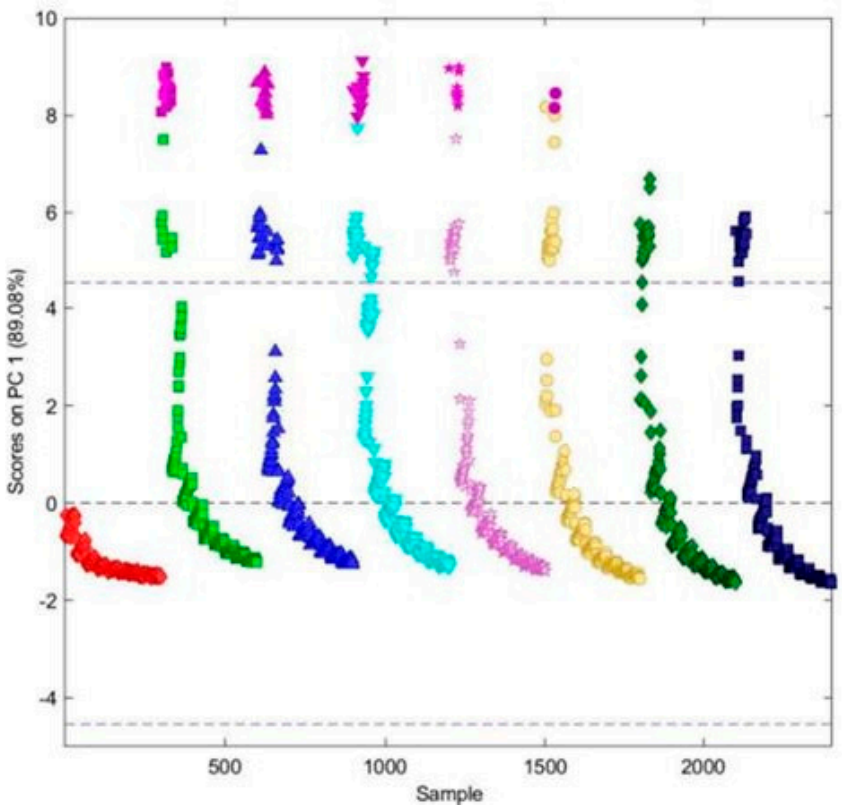

Figure 6. Collected data during 8 replicas of IPA samples with 0.01 mg/L of diacetyl. Purple samples are the reported outliers each color correspond to a single one measurement replicate.

Diacetyl's concentration effectively affects the samples' volatilome, as shown in Figure 7. The selected features were the delta-R and integral. Here, the device's capability to recognize differences between different beer samples and diacetyl concentrations

has been tested. The central cluster composed by light blue and purple dots represents both IPA and lager beers with 1 mg/L of diacetyl. The overlap of these two typologies is due to the preponderant importance of diacetyl in the collected data. In fact, with 1 mg/L of the contaminant inserted, the results are extremely affected by these molecules, and other sensorial differences become less important. This has been observed in every sample, and for this reason, beers with important aromatic differences are recognized as a single central cluster.

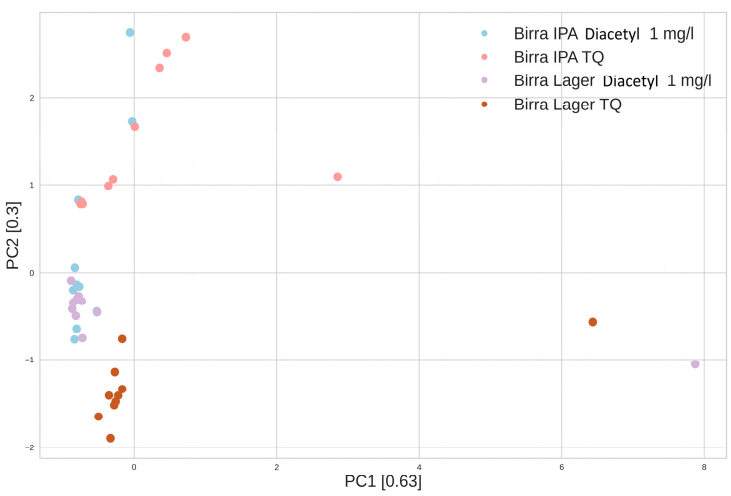

Figure 7. PCA between IPA and lager beers, unaltered and with 1 mg/L of diacetyl. Pink dots: IPA (US); brown dots: lager (US); light blue dots: IPA with 1 mg/L of diacetyl; purple dots: lager with 1 mg/L of diacetyl.

Diacetyl, as can be observed in Figure 8, has a direct impact on the sensors' recorded tracks. Indeed, a small distance between the clusters confirm that all of the used matrix belong to the same typology, and the dissimilarity is attributable to differences in diacetyl increasing the concentration in the lager samples. According to these results, it is possible to implement this device for a real production process to effectively control diacetyl developments. The implemented features were the integral e minimum.

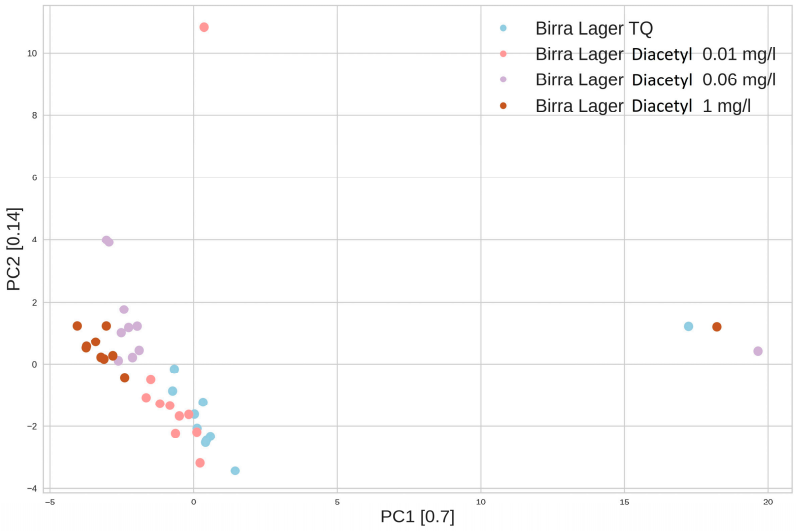

Figure 8. PCA test on different lager samples with growing diacetyl concentration. Light blue dots: lager (US); pink dots: lager 0.01 mg/L; purple dots: lager 0.06 mg/L; brown dots: lager 1 mg/L.

4. Conclusions

Nowadays, there is a limitation mainly with respect to the necessity of using finished products instead of semi-finished products. Because corrective procedures should be implemented on semi-finished products during the production process, a study of how sensors can recognize this non-compliance should be produced in a real matrix. This will be considered during the next step, where the S3+ device will be implemented in a real productive process.

The capability of recognize the difference among different beer types was confirmed by this study. Indeed, all three different beer typologies produced different clusters. This is evidence of the device's capability to recognize different products that start from its volatilome. Furthermore, this device is able to recognize different diacetyl concentrations, also giving as a result a PCA test with a high value of variance explained. Exceeding a specific concentration determines the formation of non-compliances. This is motivated by the fact that regardless of the selected typology, the presence of a specific concentration turns out to be preponderant and mainly affects the outcome PCA.

Through this device, it is possible to perform and implement a control alongside all of the production process. This can improve not only the final quality, ensuring compliance with the imposed standards, but also reduce food and resource waste. Indeed, by applying a constant and non-destructive control on the process, data can be continuously achieved and used to create an IoT integrated system that is able to manage all of the production process. Finally, an analysis through the S3+ device can be performed on other aspects of beer's off-flavors such as dimethyl sulfide in order to investigate the MOX sensor's detection capability for different chemicals. Implementing knowledge on beer's contaminants can improve the capability of quickly recognizing all of the non-compliances. For this reason, MOX sensors can become an active support and can become a highly functional tool for beer production lines and more.

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