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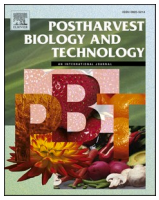

Quality monitoring of table grapes stored in controlled atmosphere using an S3 + MOS nanosensor device

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ABSTRACT

This study explores the use and the effectiveness of advanced sensor technology to monitor and maintain the quality of table grapes, cv. Italia, stored at 2 °C in controlled atmospheres (CA) over different storage times. Two CA conditions were evaluated: CA-1 with suitable conditions (3 % O_2, 10 % CO_2) and CA-2 harsh conditions (3 % O_2, 30 % CO_2), in comparison to conventional air storage. Using the Metal Oxide Gas sensors (S3 + electronic nose) and the classical approach of Solid Phase Microextraction-Gas Chromatography-Mass Spectrometry (SPME-GC-MS) to validate sensor data, the research analyzed the grapes' volatilome, identifying total volatile organic compounds (VOCs) and markers of freshness and quality degradation. Results indicate that gaseous mixtures significantly influence the volatile composition of grapes, affecting sensory attributes and shelf life. While both CA treatments improved visual quality by reducing oxidation, browning, and mould development, they also increased respiration rates, leading to the production of volatiles that negatively impacted aroma over time. The S3 + electronic nose findings are closely aligned with GC-MS results, demonstrating that grapes stored in CA-2 deviated significantly from both fresh samples and those stored in CA-1 or conventional air. CA-2, with its higher CO_2 concentration, was the least favorable for maintaining grape quality. The study highlights the potential of S3 + IoT nanosensors for real-time VOC monitoring, providing an effective tool for agri-food quality management. Integrating S3 + sensors into storage systems could optimize conditions, minimize waste, and enhance supply chain efficiency and sustainability.

1. Introduction

Table grapes (Vitis vinifera L.) are among the most widely consumed and appreciated fruit worldwide due to their versatility, health benefits, and wide variety of types and flavors (Zhou et al., 2022). Traditional sulfur dioxide fumigation, used in combination with cold storage to preserve their quality, poses risks to both food safety and the environment (Suh and Kim., 2020). This has prompted research into finding safer alternatives (Soldateli et al., 2023a).

A common and effective approach to extend the postharvest life of table grapes involves modifying the atmosphere surrounding the fruit. This is typically achieved through the application of modified (MA) or controlled atmospheres (CA), which adjust the levels of oxygen (O_2) and carbon dioxide (CO_2) by reducing O_2 and/or elevating CO_2 concentrations. These methods, which do not rely on synthetic chemicals, do not leave toxic residues on the fruit. Furthermore, because they are cost-effective and simple, they have gained widespread public acceptance and are now widely used commercially (Palacios et al., 2011).

Maintaining a proper equilibrium between CO_2 and O_2 concentrations reduces the respiration rate and slows metabolic reactions, which

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inhibits the growth of many microorganisms by interfering with their cellular metabolism (Palacios et al., 2011). High CO_2 concentration (15 Kpa or above) is known to effectively delay softening and senescence, and to control fungal growth during the storage of table grapes (Maoz et al., 2019; Shahkoomahally et al., 2021; Sanchez-Ballesta et al., 2020; Artés-Hernández et al., 2004; Crisosto et al., 2002a; Soldateli et al., 2023b).

However, when CO_2 levels rise to 20 kPa or higher, off-flavors and fermentative metabolism may develop, leading to increased concentrations of ethanol and acetaldehyde, which negatively affect sensory quality (Cefola and Pace, 2016). In addition, non-optimal CO_2 storage conditions can trigger or exacerbate the activity of key enzymes involved in the browning reaction in grapes, namely polyphenol oxidase (PPO) and peroxidase (PDO). This process depends on the grape variety. Some varieties may show resilience to CO_2-induced browning, while others may be more prone to enzymatic activation, leading to accelerated degradation. Therefore, it is crucial to understand how different grape cultivars respond to high CO_2 conditions in order to optimize storage strategies and maintain fruit quality over time (Sangeetha and Sarada., 2015).

The aroma of table grapes is one of the key factors that attract consumers. Therefore, it is important to identify the volatile organic compounds (VOCs) emitted during the postharvest storage of table grapes in modified atmospheres (MA). Table grape VOCs release is closely associated with either the maintenance of freshness or the onset of deterioration. Many authors describe as the changes in VOCs profile in terms of their increase or decrease, in fresh fruit during storage, are suitable indicators to determine the quality changes in the product and check the shelf life (Tiwari et al., 2020; Mohapatra et al., 2020; Taiti et al., 2015).

Over the past decade, the traditional chemical method for analyzing volatile organic compounds (VOCs) in fresh fruits has relied on solid-phase microextraction (SPME) coupled with gas chromatography and mass spectrometry (SPME-GC-MS). While this technique provides detailed and comprehensive results, it is also time-consuming, destructive, complex, and costly. Recent technological advancements have led to the development of more sensitive, miniaturized, and cost-effective sensors, such as metal oxide (MOS) sensors, which are revolutionizing food quality monitoring. In particular, the electronic nose, based on MOS sensor arrays, leverages these innovations to rapidly, portably, and economically detect VOC emissions, offering valuable insights into product freshness and deterioration (Galstyan et al., 2018; Di Stefano et al., 2012).

The SPME-GC-MS technique enables detailed and quantitative analysis of volatile compounds, specifically identifying the molecules present in the table grapes stored under different CA. In contrast, an electronic nose (S3 + device), equipped with MOS sensors, provides a global comparative analysis of the volatile profile of the same samples. This approach allows for the differentiation between samples without the need to identify each individual compound. Furthermore, the S3 + MOS sensors can detect variations in VOC emissions compared to a reference sample, signalling potential changes in storage conditions.

The S3 + MOS sensors, sensitive to a wide range of VOCs, are already used in various agri-food sectors, such as dairy products (Sberveglieri et al., 2016), beverages (Núñez-Carmona et al., 2021; Greco et al., 2021), and many other applications (Genzardi et al., 2024; Núñez-Carmona et al., 2022). Numerous studies have also demonstrated the use of sensor array systems integrated with machine learning techniques for monitoring the quality and freshness of fruits (Thakur and Khan., 2023; Ghasemi-Varnamkhasti et al., 2019; Gancarz et al., 2017; Xu et al., 2017; Konduru et al., 2015). MOS-based electronic noses have been applied to fruits such as apples, pears, peaches, apricots, blueberries, melons, and mandarins, to predict the optimal harvest day and monitor shelf life (Berna, 2010). Additionally, these sensors have been used to assess the development or loss of aroma during transportation to markets (Wang et al., 2021; Baietto and Wilson, 2015). In the case of grapes, a MOS-based electronic nose has been applied to estimate the ripening time and predict the geographical origin of wine grape samples (Sayago et al., 2003).

This study aims to explore the innovative use of the S3 + electronic nose and validate its application during the storage of table grapes. The parallel SPME-GC-MS analysis provided a detailed chemical characterization of VOCs, helping to assess the S3 + device's effectiveness as an early warning system. Large-scale application of the S3 + device could enable real-time, non-invasive monitoring of VOCs in table grapes, offering a timely alternative to conventional methods. This technology could improve the management of the table grape supply chain, allowing prompt interventions in atmospheric regulation for long-term storage, optimizing product availability for international trade or off-season periods. Furthermore, it could contribute to the sustainability of food production by reducing waste and the environmental impact (Poeta et al., 2023).

2. Materials and methods

2.1. Plant material and storage conditions

Table grapes (*Vitis vinifera* L., cv Italia) were provided by a farm located in Foggia (South of Italy). All vines were cultivated under identical conditions with standardized horticultural practices and harvested at the full maturity stage (total soluble solid content of about 16° Brix) and immediately transported to the Postharvest laboratory of Institute of Sciences of Food Production of National Research Council of Italy (ISPA-CNR). Harvested bunches were selected based on the absence of defects or diseases, and were randomly distributed into three clusters, each one representative of each storage treatment applied. Two controlled atmosphere (CA) mixtures were applied using different concentrations of CO_2 (10 or 30 KPa) mixed with 3 KPa of O_2 in nitrogen named CA-1 (3.0/10 KPa O_2/CO_2), and CA-2 (3.0/30.0 KPa O_2/CO_2). Table grapes samples stored in air were used as controls (Ctrl); all samples were stored at 2 (± 1.0) °C. The CA-1 and CA-2 treatments were realized using Milano 2 equipped with independent cabinets (Fruit Control Equipment srl, Locate di Triulzi, Italy). For each CA treatment and Ctrl, 16 samples (4 replicates × 4 storage times) were prepared, by placing ≈ 1 kg of table grape (3 bunches of about 350–400 g) inside each PET trays (model CL1/135 Carton Pack, Rutigliano, Italy).

All samples were analysed at harvest (0 d) and after 10, 20, 30, and 40 d of the cold storage for the quality factors, sensory descriptors, volatile organic compounds (VOCs) using SPME-GC-MS and S3 + device the innovative Custom IoT Nanosensors (Fig. 1).

2.2. Chemicals and reagents

As regards enzymatic activity, polyvinylpyrrolidone and sodium phosphate monobasic monohydrate were purchased from Sigma Aldrich (Milan, Italy), sodium phosphate dibasic hepta-hydrate and hydrogen peroxide were obtained from Honeywell Fluka (New Jersey, USA). Chlorogenic acid was purchased from Alfa Aesar Co. Inc. and 2-Mercaptoethanol 99 % purity was obtained from Alfa Aesar (New Jersey, USA). Finally, helium, carbon dioxide and nitrogen at a purity of 99.99 % was obtained by Sapio s.r.l. (Bari, Italy).

2.3. Quality and sensory attributes of table grape assessed at harvest and during storage

2.3.1. Respiration rate, sensory analysis, relative water content, mould incidence and image analysis

The respiration rate of table grape bunches was measured at harvest day and each sampling time using a closed system as reported by Cefola et al. (2018). For each treatment and replicate (n = 4) about 400 g of fruit were removed from CA cabinets and stored up to 24 h at 2 °C. After that the samples were put into 3.6 L sealed plastic jars (one jar for each replicate), and CO_2 was allowed to accumulate up to 0.1 KPa

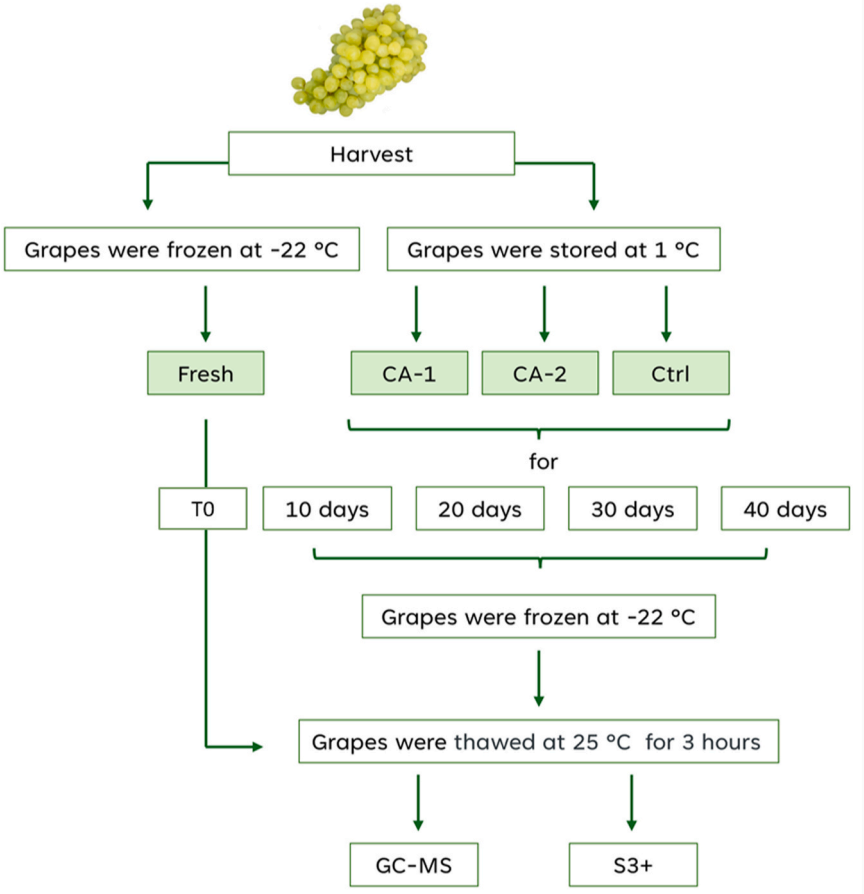

Fig. 1. Schematic representation of the experimental plan for Volatile Organic Compounds analysis.

(concentration of the CO_2 standard). The time taken to reach this value was calculated, by taking CO_2 measurements at regular time intervals using a gas chromatograph (p200 microGC, Agilent, Santa Clara, CA, USA) equipped with dual columns and a thermal conductivity detector (Kader, 2002). Respiration rate was expressed as mg CO2 kg^{-1} h^{-1}.

The relative water content (RWC) of rachis was measured on fresh samples and during storage on rachis pieces obtained using a knife cutter, of about 1 cm for a total of 2.5 g of rachis for each replicate (Cefola et al., 2018).

The weights of the samples were measured as fresh (Fw), after 24 h of rehydration (Rw) in distilled water at room temperature, and after drying (Dw) at 65 °C in the oven until a constant weight was achieved. The RWC was calculated as a percentage using the following formula (Sanchez-Ballesta et al., 2006):

$$RWC\ (\%) = (Fw\text{-}Dw)/(Rw\text{-}Dw) \times 100 \quad (1)$$

The sensory analysis of table grapes was performed by a selected group of 7 panelists (made up of 4 females and 3 males), according to descriptors reported by Cefola et al. (2018). On fresh and stored bunches, visual quality (VQ) was evaluated using a ranging scale from 5 to 1 (5 = excellent; 4 = good; 3 = fair, limit of sensory acceptability; 2 = poor; 1 = very poor).

For each treatment and sampling day, decays occurred on stored table grapes, and it was visually assessed. Decay was sensorially scored on 1–5 scale where 1 =no decay; 2 =slight decay, but product saleable, < 2 % affected; 3 =moderate decay, product useable but not saleable, < 5 % affected; 4 =moderately severe, < 15 % affected; and 5 =severe, unusable (Cefola et al., 2011).

The moulds incidence was calculated using the formula reported by Youssef and Roberto (2014): Moulds incidence (%) = (Number of decayed bunches/Total number of bunches)× 100.

Colour parameters of table grape bunches were measured using the image analysis. The vision system adopted was equipped with an AP3200TPGE RGB digital camera (JAI Ltd., Yokohama, Japan), providing a spatial resolution of 3.2 MP at 2 fps and a colour depth of 24 bit/pixel with a lens of 12 mm focal length and F1.8 (KOWA Lens mod. LM12NC3 1/2) allowing a field of view of 35 × 30 cm. The digital camera was placed inside a HPB60D photo studio box (HAVOX, Vendôme, France), equipped with two LEDs, composed of 60 diodes in each one that supplied the lighting used to capture images of bunches. A colorimetric reference target was positioned within the camera's field of view inside the box (X-Rite ColorChecker Passport 24 patches). Images were processed using Matlab® R2021b (MathWorks Inc., Natick, MA, USA). The method reported by Gonzalez et al. (2004) were applied to isolate the raw images of table grape bunches from the background to create a binary image. This algorithm removed unnecessary image borders and extracted the RGB colour components (red, green, and blue) from raw images. The RGB data was converted into *L*, a*,* and *b** colour space and used to calculate the deltaE using the equation reported by Pathare et al. (2013).

2.3.2. Polyphenol oxidases (PPO) and peroxidases (POD)

PPO and POD activity was determined according to the method reported by Palumbo et al. (2024). In detail, table grapes berries were cut in small pieces and 10 g for each replicate was homogenised for 1 min in ice with 20 mL of chilled phosphate buffer (0.05 M, pH 6.2) and 30 g L^{-1} of polyvinylpyrrolidone (PVPP). The mixture was filtered through two layers of Miracloth and centrifuged at 15,000 × g for 15 min at 4 °C. The supernatant was recovered and kept in ice until being assayed (within 5 h). For the PPO assay, the enzyme activity was

determined by using 15 mM chlorogenic acid in 0.05 M potassium phosphate buffer, pH 6.2, following the oxidation of 15 mM chlorogenic acid at 410 nm for 2 min by a spectrophotometer (UV-1800, Shimadzu, Kyoto, Japan). One unit of PPO activity was defined as a 0.001 absorbance (Abs) change per minute per gram of fresh weight under the above assay conditions. POD activity in the supernatant fractions was determined with 15 mM chlorogenic acid as a reducing substrate in a reaction mixture containing 0.1 M potassium phosphate buffer, pH 5.0, and 30 mM H_2O_2. The oxidation of chlorogenic acid was assessed by observing the absorbance increase at 470 nm for 2 min. One unit of PPO activity was defined as a 0.001 Abs change per minute per gram of fresh weight under the above assay conditions.

2.4. Volatile organic compounds (VOCs)

The samples were retrieved from the freezer (-22 °C), and three destemmed grape berries (5 g each) were placed in sterile containers at room temperature (25 °C) for 3 h. This allowed the release of volatiles and equilibrium between the headspace and solid phase. Duplicate values were obtained for each sample in separate containers for statistical validity. For the analysis, a DVB/CAR/PDMS 50/30 µm SPME fiber (Supelco Co., Bellefonte, PA, USA) was utilized and exposed to the sample headspace at 25 °C for 10 min to capture volatile organic compounds (VOCs). Separation of the extracted compounds was performed using a GC 2020 gas chromatograph (Shimadzu, Kyoto, Japan) connected to an MS-QP2020 mass spectrometer (Shimadzu, Kyoto, Japan). The SPME fiber was thermally desorbed in the inlet of the gas chromatograph for 6 min in direct mode at 240 °C. A MEGA-5MS column (25 m × 0.25 mm × 0.25 µm film thickness) from Agilent Technologies (Santa Clara, CA, USA) was used for the separation. The mass spectrometer operated in electron ionization (EI) mode at 70 eV, with the ion source maintained at a temperature of 240 °C. It scanned a range from 35 to 500 *m/z* in total ion current (TIC) mode at intervals of 0.3 s. Hydrogen gas with 99.99 % purity, supplied by the GENius PF500 system (FullTech Instruments Srl, Rome, Italy), was employed as the carrier gas, at 35.7 kPa, 2.2 mL/min flow, 87.4 cm/sec linear velocity, and 4.0 mL/min purge flow. Detector temperature was 240 °C. The GC oven program started at 40 °C for 3 min, then increased by 4 °C/min to 120 °C, and from 7 °C/min to 220 °C, with a total run of 40 min. Peaks were integrated automatically by area, considering at least 70 peaks with areas not below 500 AMU. Additional parameters for peak integration involved a slope of 100/min, a peak width of 2 s, a drift rate of 0/min, and a doubling time of 1000 min, without applying any smoothing. Peak identification used the Nist11, Nist 11b, and FFNSC2 libraries, and name attribution was using semiquantitative analysis selecting as a main criteria a similarity index with a value over 90 %. The quantification of volatile compounds was represented as relative abundance (percentage of GC area) and reported as mean values accompanied by their standard deviations (SD).

2.5. MOX sensor analysis

Following the same procedure used for GC-MS analysis, 5 g of table grapes were thawed at 25 °C for 3 h prior to analysis with the S3 + device. The samples were placed inside a polypropylene (PP) container, designed with two openings in the lid to allow for the insertion of aspiration tubes.

2.5.1. Calibration of MOX sensor arrays

The S3 + system and its sensor arrays, employed in this study, were designed and refined in collaboration with NANO SENSOR SYSTEMS Srl, a spin-off company from the University of Brescia, Italy. This device features an array of metal-oxide sensors, constructed from specialized materials tailored to detect specific target compounds (Shunping et al., 2009). The calibration of the S3 + MOX sensor array followed a structured procedure to ensure stability, reproducibility, and accurate detection of volatile organic compounds (VOCs). Initially, each sensor underwent a high-temperature annealing process, ranging between 500 and 800 °C for 1–10 h, to stabilize the sensing layer and eliminate potential contaminants that could interfere with sensor responses. Following this step, the sensors were aged in a continuous flow of filtered air for a defined period (Cai et al., 2014). This clean air aging process was essential to reduce baseline resistance variability and ensure that all sensors reached a steady-state operating condition before experimental use. The calibration process was conducted in a controlled chamber equipped with a precise gas flow regulation system, allowing the sensors to be exposed to defined VOC mixtures at known concentrations. A mass flow controller ensured uniform distribution of the gaseous compounds across all sensors. The electronic board played a crucial role in the calibration process by regulating the operating conditions of the sensors, monitoring real-time variations in electrical resistance, and controlling temperature settings. The board collected resistance signals and transmitted the data to a cloud-based processing platform, enabling continuous validation of sensor responses (Genzardi et al., 2024). The S3 + device includes a dedicated sensor chamber, a fluid dynamic system for the uniform distribution of volatile compounds, and an electronic control unit. The setup housed six custom-designed MOX sensors, doped with SnO_2, SnO_2/Pd, and SnO_2/Au, in a steel chamber maintained at 500 °C (Table 1), ensuring precise environmental differentiation (Poeta et al., 2023).

The chamber dimensions were 11 × 6.5 × 1.3 cm, and sensors were selected based on performance. MOX sensors responded to volatile compounds via changes in electrical resistance, affecting conductance (Genzardi et al., 2022). The fluid circuit included a pump, tubes, electro valve, and activated carbon cylinder for air filtration. The solenoid valve regulated pump flow, maxing at 250 standard cm^3 /min. The electronic board detected resistance changes and controlled sensor temperature, critical for detecting volatiles, and transmitted data to the S3 + web app, underscoring its IoT functionality (Masson et al., 2015).

2.5.2. S3 + setup

The sample was connected to two carbon filters: one to purify the air in the headspace and the other linked to the S3 + device. Each analysis had a total duration of 13 min, divided into three phases: 100 s for sensor stabilization, 200 s for sample measurement, and 500 s for sensor recovery. Ten replicates were performed for each sample, analyzing the sensor output, such as resistance, which was normalized relative to the initial acquisition value (R0). For each sensor, the difference between the initial resistance value and the minimum resistance value observed during analysis was calculated. Following this, the R/R0 parameter and its standard deviation were computed for all sensors across the 10 replicates. Data from the sensors were transmitted to the Microsoft Azure platform, which hosts two web-based tools: a management portal and a mixture classification service. The output data from the sensors were processed and interpreted using multivariate statistical analysis.

2.5.3. Post-run analysis

Linear Discriminant Analysis (LDA) is a statistical method commonly employed in pattern recognition and machine learning to determine a linear combination of features that optimally distinguishes between two or more event classes (Xanthopoulos et al., 2013). In this study, LDA was applied using data from MOX sensors as predictor variables and various gas classes as target variables.

Table 1
Description of the setup for different sensing elements.

SENSOR	DOPING	WORKING TEMPERATURE (°C)
MOX sensor	SnO_2	500 °C
MOX sensor	SnO_2 + Pd	500 °C
MOX sensor	SnO_2 + Au	500 °C

2.6. Statistical analysis

To evaluate the effect of storage atmosphere (CA-1; CA-2; and control) and storage time on the measured parameters, all the data were subjected to a two-way analysis of variance (ANOVA), and means were separated by Tukey's test at $P < 0.05$ (5 % significance level) using StatGraphics Centurion XVI.I (Stat Point Technologies, Inc., Warrenton, VA, USA) software. For each time of storage, a one-way ANOVA was performed to determine the effect of storage conditions on the qualitative characteristic considered. A selection of VOCs of stored table grapes over storage time, including the respiration rate, visual quality score, and decay incidence were modelled by using a multivariate principal component analysis (PCA) to establish a relationship between the studied parameters.

3. Results and discussion

3.1. Quality and sensory attributes of table grape stored in controlled atmosphere

To better understand the effects of CA storage on table grapes, we evaluated various parameters related to their quality, including visual quality, enzymatic activity, and respiration rates. The visual quality of grapes is crucial for determining their freshness and commercial appeal, as an attractive appearance directly influences consumer choice. Enzymatic activity and respiration rate play a key role in indicating ripening and decay, affecting color and reflecting metabolic activity.

Controlled atmosphere based on low oxygen and high CO_2 (CA-1 or CA-2) improved the VQ of table grapes, limiting oxidation and browning of berries and deleting mould occurrence as reported in Fig. 2. In detail, VQ decreased during storage in all samples, with higher scores in CA-1, followed by CA-2 and Ctrl samples (Fig. 2A). The VQ was assigned by the panellist on the basis of the appearance of bunches and rachis. A

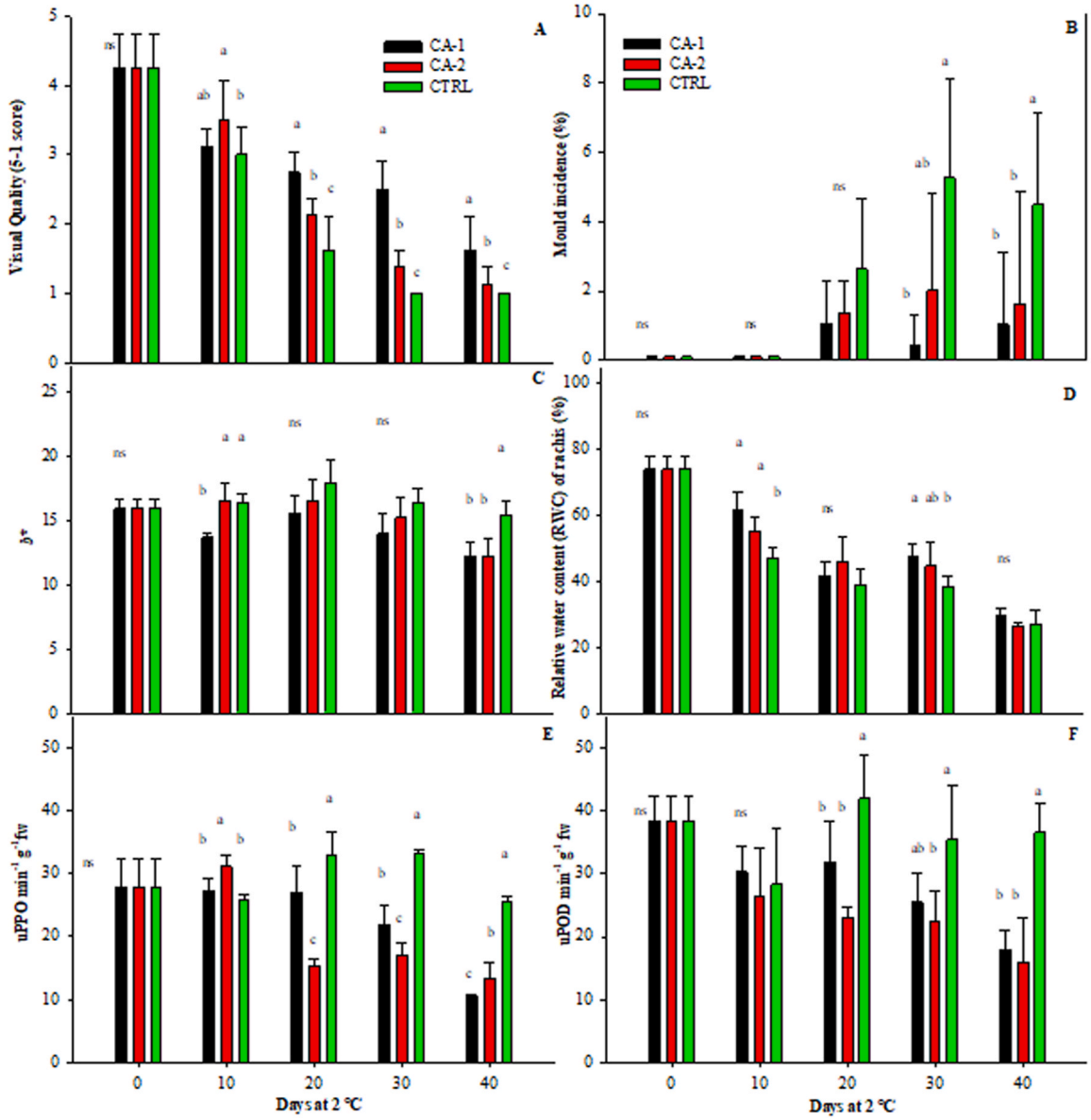

Fig. 2. Effects of controlled atmosphere (CA-1: 3/10 O_2/CO_2%, CA-2: 3/30 O_2/CO_2%; CTRL air-storage) on: A) visual quality, B) Decay, C) b* value, D) relative water content of rachis, E) PPO activity and F) POD activity of table grapes cv. Italia during storage time. Bars represent standard deviations. Means with different letters at the same time of storage are significantly different according to Tukey's test (*P* value ≤0.05).

comparative objective evaluation was also carried out measuring the berry browning (by b* color parameter) and RWC (Fig. 2C and D).

Regarding, b* parameter, significantly higher values were measured in ctrl than CA samples, at the end of the storage (Fig. 2C), meaning a browning development in control berries also confirmed by the behaviour of PPO and PDO, the two key enzymes involved in the oxidation process (Fig. 2E-F). Indeed, these enzymes showed higher activity during the entire storage in Ctrl samples than in CA samples. During storage, both CA conditions preserved the RWC of rachis at values like those of fresh table grapes (Fig. 2D). In contrast, in Ctrl the RWC value showed a marked decrease, as previously reported by other authors (Cefola et al., 2018; Rosales et al., 2013).

Moreover, the high level of CO_2 in the CA delayed the mould development with respect to the Ctrl table grape samples (Fig. 2B). These results suggested an effect of high CO_2 on decay control as previously reported by different authors (Cefola and Pace, 2016; Valero et al., 2006; Teles et al., 2014; Soldateli et. al., 2023a; Liu, 2013; Soldateli et al., 2023b). Similarly to our results, Crisosto et al. (2002b) reported that a treatment with 10 KPa CO_2 combined with 3, 6 or 12 KPa O_2 on 'Red Globe' cultivar limits *Botrytis* decay development during 12 weeks of cold storage.

On the other hand, if CA with low oxygen and high CO_2 concentrations caused an improvement of the visual appearance of table grapes, a negative effect on respiration rate and the volatile profile was shown. Regarding the respiration rate, while Ctrl samples did not show any change during storage, samples stored in CA-1 and in CA-2 showed a severe increase in respiration rate, reaching a peak of about 6- and 12-mL CO_2 kg^{-1} h^{-1} respectively, after 20 d. Then a decrease was measured in both CA stored samples (Fig. 3).

A similar behaviour was reported by Cefola et al. (2018) on "Italia" table grape stored in modified atmosphere of high CO_2 (20–30 %), confirmed a stressful condition due to high CO_2, that in our trail, when the gas concentrations were almost constant, was already measured applying 10 % of CO_2 in low Oxygen. The increase in respiration rate is the physiological response of injured table grapes, that means the development of fermentative metabolism, with negative influences on sensory quality and the loss of the overall quality (Cefola and Pace, 2016).

These results confirm that the application of high CO_2 ($\geq$ 10 %) in low oxygen on table grapes (cv Italia) might cause physiological injury, due to the inhibition (by high CO_2) of several enzymes of Krebs cycle (including succinate dehydrogenase). This could cause anaerobic respiration or the accumulation of succinic acid, which is potentially toxic to cells (Kader, 2002; Kays, 1991). The deeper investigation of volatile organic compounds confirmed this hypothesis, as detailed below. Finally, regarding the weight loss (Fig. 3B), a significantly higher increase was measured in Ctrl samples, than CA table grapes, due to the development of senescence in the air-stored samples (Kader, 2002).

3.2. VOCs detected in table grape stored in controlled atmosphere

By regulating and optimizing the levels of oxygen and carbon dioxide, controlled atmosphere storage can help to preserve the aromatic profiles of table grapes, keeping them fresher for longer without relying on chemical preservatives. In particular, VOCs had a key role in determining aroma quality of table grapes. In our samples subjected to various storage conditions, 113 volatile compounds were identified using GC-MS analysis, with 33 metabolites consistently detected across samples. These compounds belong to diverse chemical classes, including aldehydes, alcohols, alkanes, alkenes, carboxylic acids, ketones, terpenes, and ethers, all of which contribute to the grapes' aroma and perceived flavor profile (Garrido and Borges, 2013). Alkanes were the most abundant group, followed by alcohols, reflecting the typical volatile composition in grapes (González-Barreiro et al., 2015). Notably, the neutral aromatic nature of the cv. Italia variety limited terpene presence, a distinction often seen in neutral grape varieties compared to non-Muscat aromatic or Muscat grapes (Wu et al., 2020).

In line with our findings on the VOCs in table grapes over time, some of the same molecules were also identified and quantified by Yang et al. (2011) and Kaya et al. (2022), who used chemical standards for their analysis. The most prominent compounds were analyzed using a two-way ANOVA, showing significant effects from factors such as storage conditions (CA-1, CA-2, or control) and time, along with their interactions, on the majority of compounds (Ethanol; Hexanal; 1-Hexanol; 2,4-dimethyl-1-decene; D-Limonene; Anethole; 4-methyl-benzaldehyde; 2,6,6-trimethyl-octane; 2-butyl-1-octanol; 2-Isopropyl-5-methyl-1-heptanol; 3,8-dimethyl-undecane; Pentadecane). Despite statistically significant effects from these factors, most compound values showed no significant differences after 40 d of storage, indicating some instability in volatile profiles over time.

The evolution of the VOCs identified in table grapes as affected by controlled atmosphere is shown in Fig. 1S. Despite statistically significant effects from the interaction of these factors, most compound values showed no significant differences after 40 d of storage, confirming the high variability in volatile profiles over time. The results reveal distinct trends for each compound, without a common tendency. For instance, ethanol exhibited pronounced increases under CA-2 conditions up to 30 d of storage, showing the tendency of this sample to a fermentative

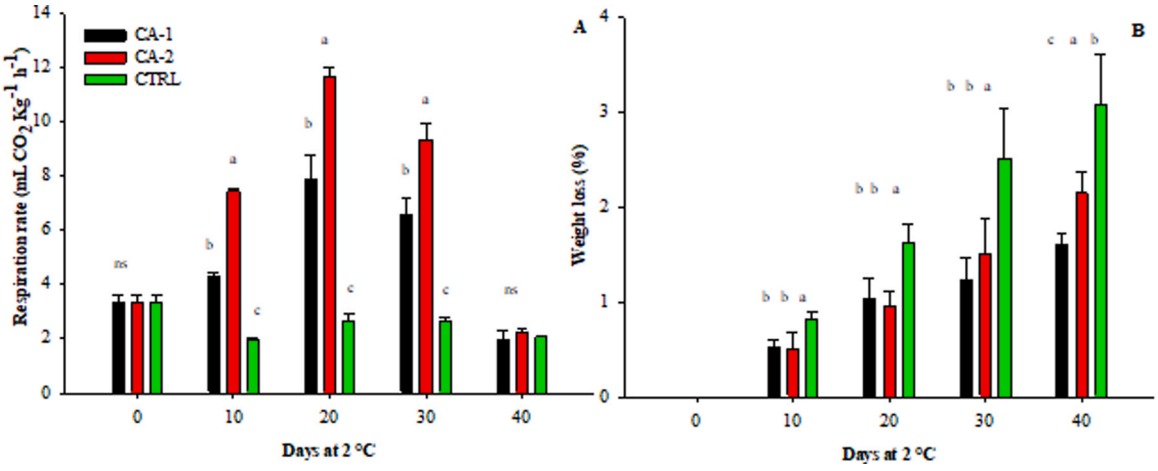

Fig. 3. Effects of controlled atmosphere (CA-1: 3/10 O_2/CO_2%, CA-2: 3/30 O_2/CO_2%; CTRL air-storage) on: A) respiration rate and B) weight loss of table grapes cv. Italia during storage time. Bars represent standard deviations. Means with different letters at the same time of storage are significantly different according to Tukey's test (*P* value $\leq$0.05).

metabolism as described later. Compounds such as 2-butyl-1-octanol; 3,8-dimethyl-undecane; 4-methyl-benzaldehyde, showed relatively stable levels across all the storage conditions. A figure showing the significance ANOVA values between the correlation of volatile compounds and targeted marker VOCs is presented in Table 1S.

Some compounds, like D-limonene and pentadecane, display sharp variations between specific conditions, specifically at the end of storage time for Ctrl and CA-1 samples, respectively, suggesting differential volatilization or metabolic responses, even if no statistically significant differences were observed between samples due to the variability between the replicates. The concentration of hexanal; 1-hexanol; 2,4-dimethyl-1-decene; anethole and 2-Isopropyl-5-methyl-1-heptanol was generally higher for CA-1 samples. For most of them a fluctuating trend was observed, mainly due to the differences between the replications.

A comparison of volatile profiles across storage conditions leads to the supposition that CA-2 was the least favorable, with the highest percentage of senescence and fermentation markers (ethanol among all), followed by the control, and CA-1. The volatile profile under CA-2 indicated heightened spoilage markers, likely due to lower oxygen levels (3/30 kPa O_2), which promoted unfavourable fermentation-related volatiles. These findings suggest that CA-1 provides the best preservation, minimising degradation and maintaining volatile compound stability.

3.3. Relationship among VOCs and quality traits

Data sets containing a representative selection of VOCs, the respiration rate and two sensory parameters (visual quality score and moulds incidence percentage) were collected during the experimental trial, at harvest time and after 10, 20, 30 and 40 d of cold storage in air or the two conditions of controlled atmosphere and subjected to Principal Component Analysis (PCA). The objective was the assessment of the correlation between the variation of quality and sensory parameters and the composition of volatile compounds.

PCA was applied to the final data set accounting for 65.3 % of the total variance, with factors 1, 2 and 3 accounting for 31.4 %, 21 % and 13 %, respectively. The scatter plot of scores of the first three factors (PC) showed the discrimination among the samples related to fresh grapes at harvest and stored in air (Ctrl), CA-1 and CA-2 (Fig. 4). PCA plot provided a visual representation of how various controlled atmosphere conditions influenced the development of volatile compounds in table grape samples over the storage period. It effectively demonstrates the impact of treatment and storage conditions on the quality and composition of berries. Samples distribution indicated a correlation between the gaseous mixture applied during storage and the product quality. Control samples are clustered on the left-hand side of the plot, CA samples are displayed separately for two conditions, CA-1 and CA-2, and time points (e.g., CA-1_10, CA-2_30). Clustering indicates distinct separations between treatment types and durations, with FRESH samples, just harvested, positioned as an outlier. CA-1 and CA-2 samples are more strongly associated with volatile organic compounds (e.g., hexanal; ethanol), while CTRL samples are associated with lower values of these volatiles.

The plot suggests differences in physiological responses and VOCs composition between treatments over time, with CA-treated grapes showing more significant metabolic changes. Air-stored samples (Ctrl) were positively correlated with mould incidence as physical parameters, thus indicating a positive effect of CA in delaying mould occurrence. Consequently, visual quality (VQ) is in an opposite position compared to mould percentage, and is positively correlated with samples stored in CA (both conditions).

Although the cold chain slows down metabolic processes, including respiration rate and enzymatic reactions, grapes still respire and continue to ripe gradually, leading to senescence and deterioration. Specifically, respiration rate, ethanol, pentadecane and 2,4-dimethyl-1-decene are correlated to CA-2-stored samples, demonstrating the fermentative metabolism that develops in these samples due to the stressful storing conditions. Ethanol, produced by the alcoholic fermentation of sugars by yeasts, is a clear indicator of active fermentation or degradation processes in grapes. Ethanol and 1-hexanol are among the characteristic compounds of table grapes stored in the presence of high CO_2 concentrations (Piazzolla et al., 2016). The increase in ethanol concentrations was also reported during the storage of apples and strawberries in high CO_2 due to fermentative metabolism (Cefola et al., 2018).

Phenylpropenes, such as anethole, are compounds found in fresh fruits such as apples, strawberries, and grapes (Atkinson., 2018). Concerning table grape storage, it was observed that anethole is mainly correlated to CA-1-stored samples. This compound is typically present during the fruit ripening, reaching its maximum concentration in ripe

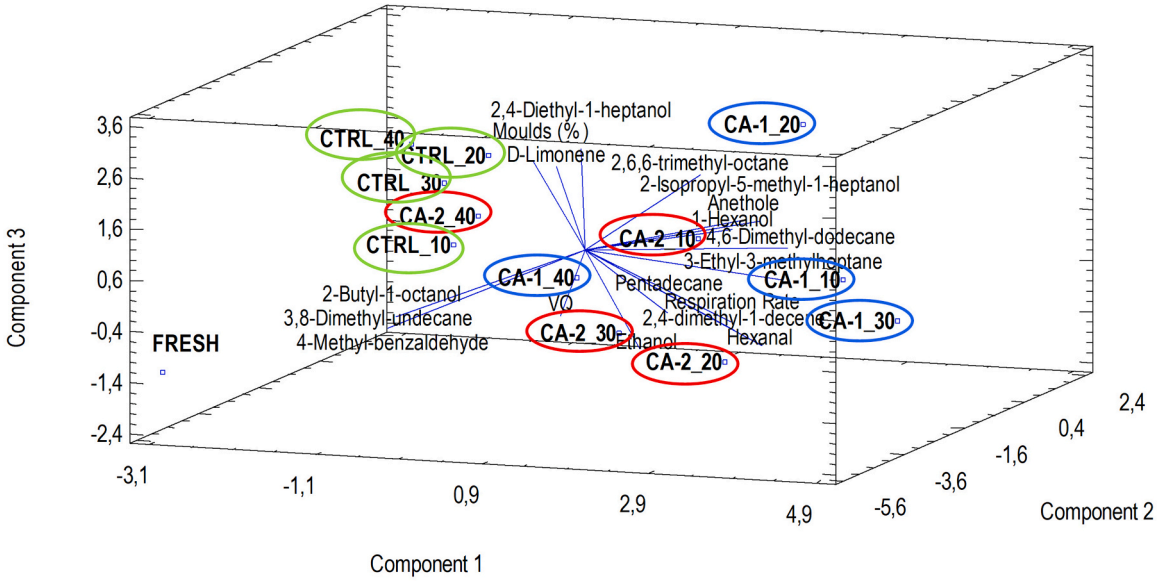

Fig. 4. PCA plots of table grapes analysed at harvest (Fresh, 0d) and after 10, 20, 30 and 40 d of storage in air (control, CTRL_10, CTRL_20, CTRL_30, CTRL_40), 3 %/10 % O_2/CO_2 controlled atmosphere (CA-1_10, CA-1_20, CA-1_30, CA-1_40) and 3 %/30 % O_2/CO_2 controlled atmosphere (CA-2_10, CA-2_20, CA-2_30, CA-2_40) at 5 °C.

fruit.

Accordingly, the volatile compounds selected could be used as alternative indicators to determine table grape quality. Several volatile metabolites might be used as potential markers of non-optimal storage conditions (i.e. high CO_2 concentrations) such as ethanol and 1-hexanol. Alternatively, hexanal and anethole can represent possible freshness markers for 'Italia' table grapes. Hexanal is associated with herbaceous characteristics in many fresh table grape cultivars and might be considered an indicator of freshness for cv. Italia. It is primarily responsible for the characteristic flavor of table grape berries, and its level is influenced by ripening process (Cefola et al. 2018).

3.4. Application of custom IoT nanosensors to estimate table grape quality

To further understand the impact of CA storage conditions on table grape quality, we employed a custom IoT nanosensor system to monitor the volatilome, which provides valuable insights into the chemical changes occurring during storage of table grapes. In Fig. 5, the x-axis corresponds to time measured in minutes, while the y-axis represents the normalized resistance. Employing normalized parameters enables the analysis of a dimensionless dataset, characterized by a mean value of 0 and a variability standardized to 1. This approach is beneficial for comparing samples with different units of measurement or dimensions, which would otherwise hinder accurate analysis (Greco et al., 2022).

The graph clearly shows how the resistance starts at a high value and then decreases. The analysis of the samples is divided into two phases. The first phase involves the analysis of the sample's volatilome, during which chemical substances volatilize and encounter the sensor, causing a decrease in electrical resistance. The second phase, known as recovery, consists of introducing filtered ambient air to restore the sensor to its baseline state, which reflects its electrical resistance under standardized environmental conditions such as humidity, temperature, and oxygen levels (Wei et al., 2011).

In this study, the process included an initial phase of 100 s for sensor stabilization, 200 s dedicated to sample analysis, and 500 s for sensor recovery, resulting in a total analysis duration of 13 min. Each sample underwent 10 replicates, with a total analysis time of 4 h.

The quality of table grapes and consumer acceptance depends on various parameters, including aesthetic and aromatic characteristics. The volatilome encompasses all volatile metabolites, along with other volatile organic and inorganic compounds, derived from an organism, super-organism, or ecosystem. While it is often regarded as a subset of the metabolome, the volatilome also includes external compounds not generated through metabolic processes, such as environmental pollutants, distinguishing it as a unique entity.

In this case, the volatilome consists of several hundred VOCs of varying volatility and polarity. These VOCs can originate from raw materials or form during storage processes. The analysis with the S3 + provided us with useful data to discriminate groups of samples stored differently based on the volatile compounds produced. During table grape storage, chemical processes occurred that led to the release of VOCs, detected by the array of sensors used in this trial. From a practical perspective, this study suggests that the characterization of the grape volatilome requires at least three sensors with complementary sensitivities, in order to provide a reliable and discriminative analysis of VOC profiles. To support the results obtained with GC-MS, an LDA analysis was conducted on the data collected with the S3 + .

The LDA analysis (Fig. 6.) clearly indicates that the red cluster, which represents the fresh samples, distinctly separates from all other clusters. In the hyperplane, the fresh samples are located near the CTRL and CA-1 samples, which are very close to each other. This proximity suggests that the CTRL and CA-1 samples have a similar volatile composition, despite being stored in different atmospheres. Conversely, the samples stored in the CA-2 atmosphere are significantly distant from both the fresh samples and the samples stored under the CA-1 and CTRL atmospheres. This indicates that the CA-2 atmosphere is the least favourable among those analysed, as the samples stored in this atmosphere deviate the most from the fresh samples.

The three MOX sensors in the S3 + device were not analyzed individually or averaged; instead, their combined signals were processed using a multivariate statistical approach to enhance pattern recognition. Each sensor has different sensitivities to specific volatile organic compounds, allowing a more comprehensive characterization of the grape volatilome. Linear Discriminant Analysis (LDA) was applied to classify storage conditions by integrating the unique contributions of each sensor. Sensor responses were normalized to baseline resistance (R/R_o) and incorporated into the LDA model.

This approach captured subtle variations in VOC composition that individual sensors could not detect. The LDA plot (Fig. 6) showed clustering resulting from the combined sensor responses, enabling differentiation between storage conditions and time points. This method improved classification robustness, ensuring no critical information was lost. Results demonstrate that the S3 + device effectively detects changes in volatile profiles over time, distinguishing between samples stored for 10 and 40 days. This ability to track storage duration highlights the sensor array's effectiveness in monitoring postharvest quality and providing real-time insights for controlled atmosphere storage management.

These results align with those obtained from the GC-MS analysis, where the sum of the average percentages of molecules indicative of senescence and fermentation highlights that the worst atmosphere is the CA-2 (3/30 KPa O_2/ CO_2).

4. Conclusions

The study shows that controlled atmospheres with high CO_2 and low O_2 levels improve the visual quality of table grapes and reduce mould growth, thus preventing oxidation. However, these conditions also

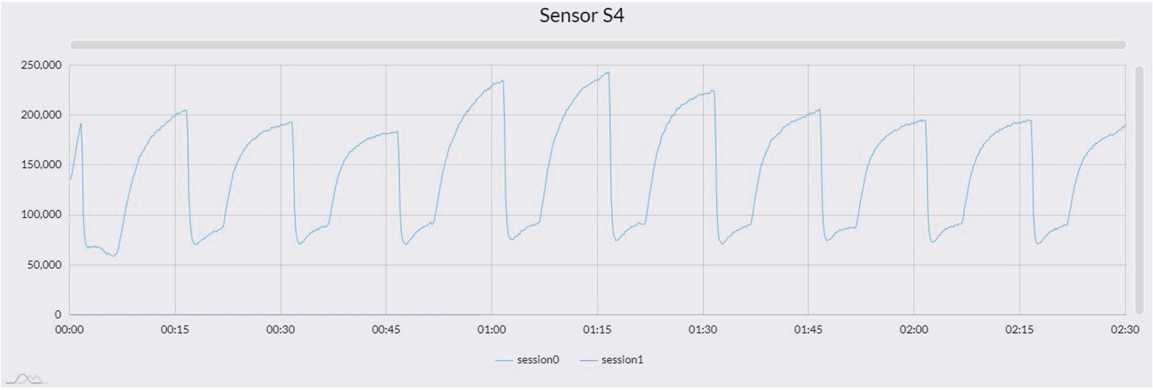

Fig. 5. Graphical representation of the output from a single sensor, where the y-axis represents the resistance value (Ω) and the x-axis represents time (s).

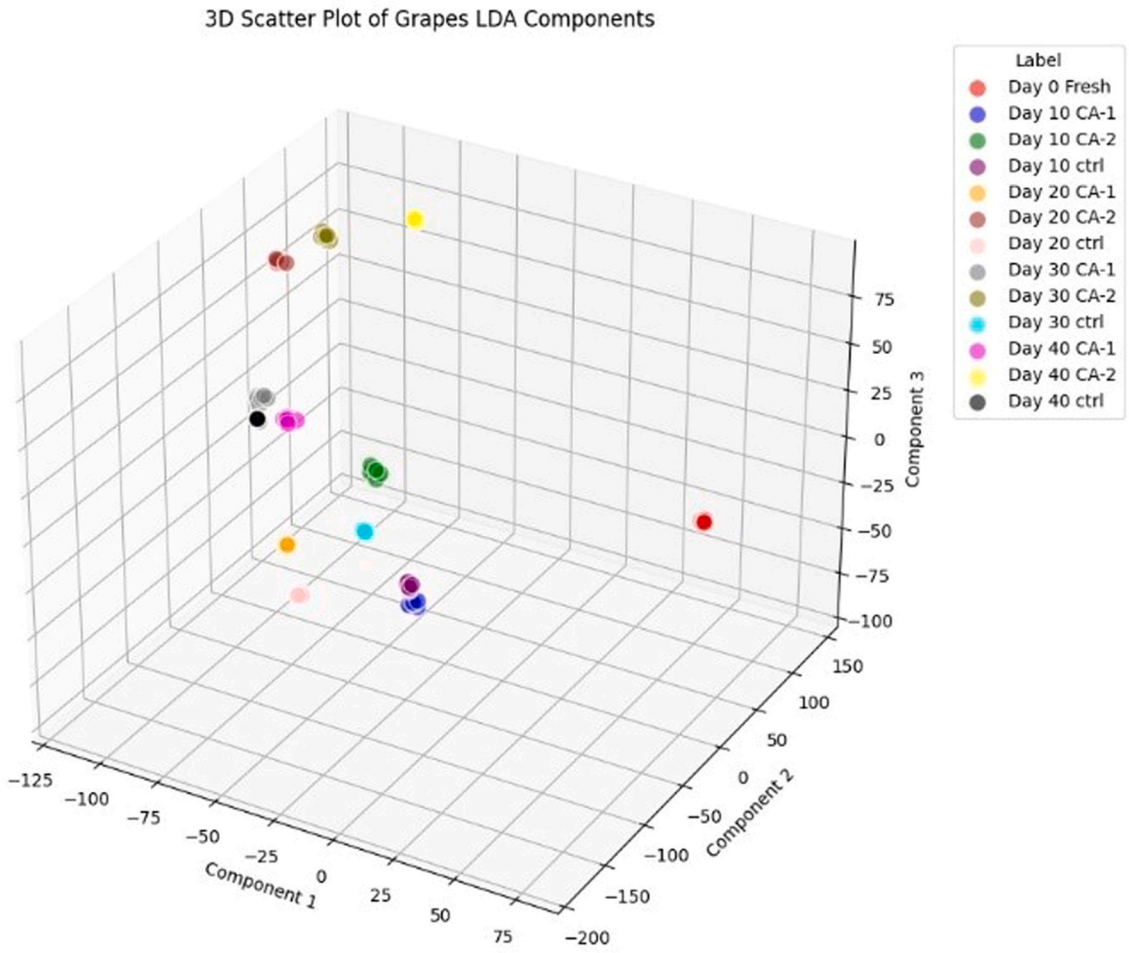

Fig. 6. 3D LDA representing table grape samples stored under different conditions: modified atmospheres (CA-1 and CA-2) and air (CTRL) over various time intervals (10, 20, 30, and 40 days), with fresh samples also included for comparison.

increase respiration rates and produce undesirable volatile compounds, affecting the grapes' freshness and aroma over time. Statistical analysis revealed significant effects of storage conditions and time on volatile compounds, but most compounds showed no significant differences after 40 days, indicating instability. Markers like anethole and hexanal were linked to a 3 % O_2 and 10 % CO_2 atmosphere (CA-1), which can be used as freshness indicators, while ethanol and fermentation-related VOCs were associated with high CO_2 concentration (30 %), the least favorable condition. Further research could optimize CO_2/O_2 balance for better storage. The S3 + electric nose confirmed the findings obtained using the classical GC/MS analysis and proved effective in monitoring grape quality, offering a non-destructive, cost-effective method for extending freshness, reducing waste, and enhancing sustainability. Large-scale application of these sensors throughout the supply chain—from producers to consumers, including transportation, international sales, and long-term storage for off-season demand—could improve final product quality. However, sensor calibration must be customized for different grape varieties and storage conditions, as it is not a one-size-fits-all approach.

CRediT authorship contribution statement

Poeta Elisabetta: Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Caruso Immacolata:** Writing – review & editing, Writing – original draft, Formal analysis, Data curation, Conceptualization. **Genzardi Dario:** Software, Methodology, Investigation, Data curation. **de Chiara Maria Lucia Valeria:** Writing – original draft, Methodology, Investigation, Conceptualization. **Cefola Maria:** Resources, Project administration, Funding acquisition, Conceptualization. **Palumbo Michela:** Methodology, Formal analysis, Data curation. **Sberveglieri Veronica:** Writing – review & editing, Writing – original draft, Validation, Supervision, Resources, Project administration, Methodology, Investigation, Funding acquisition, Conceptualization. **Núñez-Carmona Estefanía:** Writing – review & editing, Writing – original draft, Visualization, Validation, Resources, Conceptualization. **Pace Bernardo:** Writing – review & editing, Conceptualization.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence

the work reported in this paper.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.postharvbio.2025.113587.

Data availability

Data will be made available on request.

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