chemosensors

MDPI

Article

Development and Preliminary Analytical Evaluation of a Portable Electronic-Nose Method for Discriminating *Cassia grandis*-Enriched Rice Beverages Using Chemometrics and HS-SPME-GC-MS

Víctor Manrique Fernández [1], Daniel Martín Vertedor [2,3], Francisco Pérez-Nevado [1,3], Jesús Lozano Rogado [4] and Ismael Montero Fernández [3,5,*]

[1] School of Agricultural Engineering, Universidad de Extremadura, 06007 Badajoz, Spain; vimanriqu@alumnos.unex.es (V.M.F.); fpen@unex.es (F.P.-N.)
[2] Plant Health Service, Junta de Extremadura, N-5, km 391.7, Villafranco del Guadiana, 06195 Badajoz, Spain; daniel.martin@juntaex.es
[3] Research Institute of Agricultural Resources (INURA), Avda de la Investigación, s/n, Campus Universitario, 06006 Badajoz, Spain
[4] Department of Electrical, Electronic, and Automatic Control Engineering Systems and Automatic Control Engineering Area, School of Industrial Engineering, Universidad de Extremadura, 06006 Badajoz, Spain; jesuslozano@unex.es
[5] Department of Analytical Chemistry, Faculty of Science, Universidad de Extremadura, 06006 Badajoz, Spain
* Correspondence: ismonterof@unex.es

Abstract

This study presents the development and preliminary analytical evaluation of a portable electronic nose (E-nose) for differentiating rice-based beverages containing 0, 5, 10, and 20% (*w*/*v*) *Cassia grandis* pulp. The system was evaluated through optimization of the operating conditions, assessment of short-term repeatability and robustness, exploratory chemometric analysis, and complementary volatile characterization by headspace solid-phase microextraction coupled with gas chromatography–mass spectrometry (HS-SPME-GC-MS). The optimized conditions comprised a sample volume of 20 mL, a headspace equilibration time of 10 min, an adsorption period of 60 s, and a desorption period of 30 s. Under these conditions, the sensor responses exhibited relative standard deviations (RSDs) ranging from 1.88 to 3.67% during ten consecutive measurements. Robustness experiments involving deliberate variations in the operating parameters yielded RSDs between 0.87 and 2.48%, although reducing the desorption time to 20 s decreased the mean sensor response by 5.29%. Three independent beverage preparations were produced for each formulation, and ten E-nose measurements were obtained per formulation, resulting in 40 instrumental measurements. Principal component analysis (PCA) accounted for 96.18% of the total variance in the first two components (PC1: 87.04%; PC2: 9.14%) and revealed differences in sensor-response patterns among formulations. The control (A0) and the formulation containing 20% *C. grandis* pulp (A20) occupied distinct regions of the PCA space, whereas A5 and A10 exhibited greater similarity. Complementary HS-SPME-GC-MS analysis revealed formulation-dependent differences in chromatographic peak areas, particularly for terpene-related compounds. For example, the linalool peak area increased from 18.34×10^6 in A0 to 535.50×10^6 arbitrary units in A20. Nevertheless, preparation-grouped cross-validation and independent predictive validation could not be established from the available experimental records.

Check for updates

Received: 20 September 2026
Revised: 27 October 2026
Accepted: 5 November 2026
Published: 10 November 2026

Copyright: © 2026 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license.

Keywords: *Cassia grandis*; electronic nose; MOS sensors; HS-SPME-GC-MS; volatile organic compounds; PLS-DA; PLSR; food authentication

1. Introduction

In recent decades, functional beverages have gained prominence in the global market, driven by increasing demand for the health benefits and functional properties they offer such as antioxidant, anti-inflammatory, and prebiotic effects, or general health promoting qualities [1–3]. Furthermore, the growing diversity of formulations and raw materials used has created a significant need to develop new analytical methods capable of ensuring authenticity, quality, and food safety [4].

The regulatory compliance of functional beverages currently poses one of the major challenges for the food industry. The inherent variability of natural ingredients, differences associated with manufacturing processes, and the potential for adulteration or partial substitution of raw materials can significantly affect both the sensory properties and the chemical composition of the final products. Traditionally, the characterization of these matrices has been carried out using advanced instrumental techniques such as gas chromatography–mass spectrometry (GC-MS), high-performance liquid chromatography (HPLC), and various spectroscopic methods. Although these methodologies offer high levels of sensitivity and selectivity, they often require relatively complex sample preparation procedures, long analysis times, and expensive equipment, thereby limiting their use as rapid control tools in industrial settings [5,6].

Among emerging plant-based raw materials with potential application in the development of functional foods, *Cassia grandis* L. f. stands out; it is a tree species belonging to the Fabaceae family that is widely distributed across the tropical regions of Latin America. Traditionally, its fruit pulp has been used in both the diet and folk medicine due to its nutritional and functional properties. The pulp is a significant source of bioactive molecules, including phenolic compounds, flavonoids, carotenoids, and minerals, thereby sparking interest in incorporating this fruit into new food formulations [7,8]. Furthermore, 'carao' pulp in fermented matrices can enhance various functional properties, such as antioxidant activity, hypoglycemic activity, intestinal functionality, and the growth of probiotic microorganisms [9,10]. The pulp has also been used to create innovative food products; for instance, studies by Montero-Fernández et al. (2025) [11] demonstrated that incorporating carao pulp into California-style olives not only adds value to the product through the inclusion of phenolic compounds and minerals but also helps mitigate the formation of acrylamide, a toxic compound produced during thermal processing.

Among the quality attributes of functional beverages, aroma is one of the most important parameters due to its indirect influence on consumer acceptance. Volatile organic compounds (VOCs) are responsible for the aroma profile and can provide valuable information regarding product authenticity and quality. Headspace solid-phase microextraction coupled with gas chromatography–mass spectrometry (HS-SPME-GC-MS) has established itself as one of the most effective techniques for analyzing VOCs in food matrices; this methodology combines high sensitivity with minimal sample preparation, enabling the identification of aroma compounds present even at low concentrations [12–14], and is considered a reference technique for characterizing volatile compound profiles in complex food matrices. In this context, electronic noses have emerged as complementary analytical tools for the rapid assessment of volatile fingerprints in complex food matrices.

Inspired by the human olfactory system, these devices utilize chemical sensors capable of responding collectively to complex mixtures of volatile organic compounds, Inspired by

the human olfactory system, these devices utilize chemical sensors capable of responding collectively to complex mixtures of volatile organic compounds, generating characteristic response patterns that can be analyzed using multivariate statistical techniques [6,15,16]. Electronic noses (E-noses) are developed using an array of semiconducting metal oxide (MOS) sensors; their operation relies primarily on changes in electrical conductivity resulting from interactions between gases in the sample's headspace and the active surface of the semiconductor material. Consequently, each sensor exhibits a differential response to various chemical groups, enabling a combination of multiple sensors to discriminate between samples with different aromatic compositions [16,17].

E-noses have been used for purposes such as varietal classification, determination of geographical origin, adulteration detection, and quality control of products including wines, coffee, olive oil, honey, fruit, dairy products, and fermented beverages [15,18] while also enabling in situ analysis and facilitating their integration into routine control systems within the food industry. The information generated by sensor arrays is often highly complex due to the multivariate nature of the signals obtained. Consequently, the application of chemometric tools is essential for extracting information and enhancing the discriminative capability of sensor systems. Notable methodologies include Principal Component Analysis (PCA); Linear Discriminant Analysis (LDA), which maximizes separation between predefined groups; and Partial Least Squares Discriminant Analysis (PLS-DA). These techniques have proven highly effective for classifying complex food matrices based on data obtained from electronic noses [15,17]. The selection of the beverage matrix was based on traditional horchata-type preparations consumed in Central and South America, which commonly incorporate ingredients such as rice, cinnamon, black pepper, and other complementary components. In this context, *Cassia grandis* L. f., commonly known as carao, is a tropical fruit of particular interest due to its content of bioactive compounds and its potential application in functional food formulations. However, incorporating carao pulp into beverages presents an important technological and sensory challenge, since high concentrations may impart undesirable metallic, iron-like, and earthy taste characteristics, potentially reducing consumer acceptability. Therefore, controlling the proportion of carao pulp is relevant for developing formulations that balance the incorporation of bioactive ingredients with acceptable sensory properties. In the present study, four horchata-type beverage formulations containing 0, 5, 10, and 20% (w/v) of *C. grandis* pulp were investigated while maintaining the remaining ingredients constant. This experimental design allowed us to evaluate whether differences in carao incorporation could be distinguished through the volatile fingerprints recorded by a portable electronic nose. Such an approach could provide a rapid analytical screening tool for formulation verification and quality control during the development of carao-enriched functional beverages, without requiring chromatographic analysis for every routine measurement.

Although electronic noses combined with chemometric techniques have been widely investigated for food quality assessment and discrimination, their application to specific beverage formulations requires careful optimization and evaluation of analytical performance. The contribution of the present study lies in the integrated assessment of a portable electronic-nose system for rice-based beverages containing different proportions of *Cassia grandis* pulp. Unlike approaches focused primarily on pattern recognition, this work combines systematic optimization of headspace sampling and sensor operating conditions, evaluation of short-term repeatability and robustness, supervised and unsupervised chemometric discrimination, and complementary HS-SPME-GC-MS characterization to explore the chemical changes underlying the sensor responses. Therefore, this study aimed to develop and evaluate a portable electronic-nose methodology for discriminating rice-based beverages containing different proportions of *Cassia grandis* pulp (0, 5, 10, and 20%, w/v).

The analytical approach combined optimization of measurement conditions, assessment of short-term repeatability and robustness, and chemometric analysis, supported by HS-SPME-GC-MS characterization of volatile profiles.

2. Materials and Methods

2.1. Reagents and Chemicals

Fresh mature fruits of *Cassia grandis* L. f. were collected in Honduras during the harvesting season. The pulp was manually separated from the seeds and pods, homogenized using a laboratory blender, packed in airtight polyethylene bags, protected from light, and stored at −20 °C until beverage preparation. Commercial rice (*Oryza sativa* L.), ground cinnamon (Cinnamomum verum J. Presl), and black pepper (*Piper nigrum* L.) were purchased from a local supermarket in Badajoz (Spain). Food-grade citric acid (≥99.5% purity) was used as an acidifying agent during beverage formulation.

Ultrapure water (18.2 MΩ·cm) obtained from a Milli-Q water purification system (Millipore, Bedford, MA, USA) was used throughout the study. Sodium chloride (NaCl, ≥99.5%, Sigma-Aldrich, St. Louis, MO, USA) employed for headspace solid-phase microextraction (HS-SPME), sodium hydroxide (NaOH, ≥98.0%, PanReac AppliChem, Barcelona, Spain) used for titratable acidity determination, and calibration buffer solutions (pH 4.00 and pH 7.00, Crison Instruments, Barcelona, Spain) used for pH meter calibration were of analytical grade. All solvents and reagents used throughout the analytical procedures were of analytical or chromatographic grade.

For volatile compound characterization, a StableFlex™ DVB/PDMS fibre (65 µm; Supelco, Bellefonte, PA, USA) was employed for HS-SPME extraction. Helium (99.999% purity, Air Liquide, Paris, France) was used as the carrier gas for all gas chromatographic analyses.

2.2. Preparation of Cassia grandis Beverages

Four beverage formulations containing increasing concentrations of *Cassia grandis* pulp were prepared to evaluate the capability of the portable electronic nose to discriminate different aroma profiles. A control formulation without *Cassia grandis* (A0) and three beverages containing 5% (A5), 10% (A10), and 20% (A20, *w*/*v*) of *Cassia grandis* pulp were produced under identical processing conditions.

Initially, 50 g of commercial rice were mixed with 200 mL of ultrapure water and homogenized for 30 min at room temperature using a magnetic stirrer. Subsequently, food-grade citric acid (0.5%, *w*/*v*), ground cinnamon (5 g), and ground black pepper (2 g) were added to obtain a standardized beverage matrix and to improve flavour stability. Finally, the corresponding amount of *Cassia grandis* pulp was incorporated into each formulation according to the experimental design, and the mixtures were homogenized until complete dispersion of all ingredients. The prepared beverages were filtered through a fine stainless-steel sieve to remove coarse particles and transferred into sterile amber glass bottles. All samples were stored at 4 °C and analysed within 24 h of preparation to minimize physicochemical and aromatic changes.

Each beverage formulation was prepared independently in triplicate following the same protocol. Before physicochemical characterization, HS-SPME-GC-MS analysis and electronic nose measurements, samples were equilibrated to room temperature (25 ± 1 °C). The analytical sequence was randomized to avoid possible systematic errors associated with instrumental drift or sample ageing. The overall workflow used for the preparation of the *Cassia grandis* beverages and the subsequent analytical characterization is summarized in Figure 1.

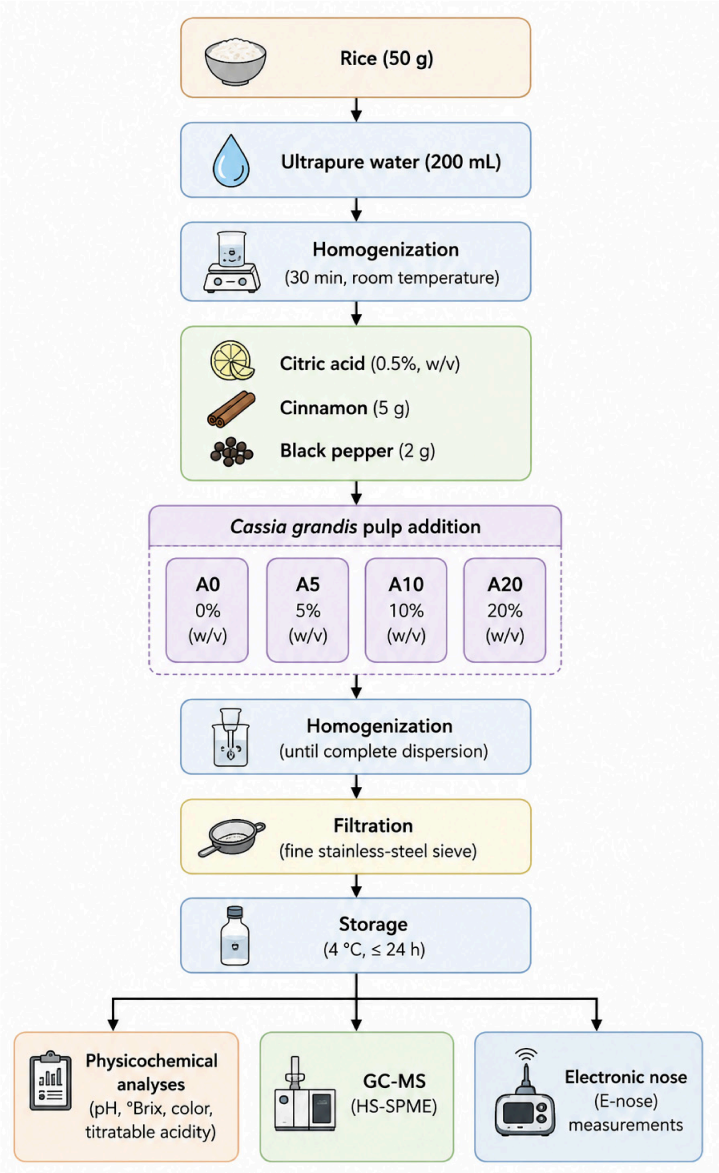


Figure 1. Workflow for the preparation of *Cassia grandis* beverages used for analytical validation of the electronic nose method.

2.3. Experimental Design

The experimental design adopted in this study is summarized in Figure 2. Four beverage formulations containing increasing concentrations of *Cassia grandis* pulp (0, 5, 10 and 20%, *w*/*v*) were prepared independently in triplicate under identical processing conditions. The control formulation without *Cassia grandis* (A0) was included as the reference sample, whereas formulations A5, A10 and A20 were used to evaluate the influence of increasing pulp concentration on the physicochemical properties, volatile profile and electronic nose responses.

The analytical methodology comprised three consecutive stages. First, the physicochemical properties of each formulation, including pH, soluble solids (°Brix), titratable acidity and colour parameters (CIELab), were determined. Secondly, volatile organic compounds (VOCs) were characterized by HS-SPME-GC-MS as the reference analytical technique for aroma profiling. Finally, the same samples were analysed using the portable electronic nose under optimized operating conditions. The electronic nose responses were

subsequently processed using multivariate chemometric techniques to evaluate the discrimination capability of the proposed analytical method.

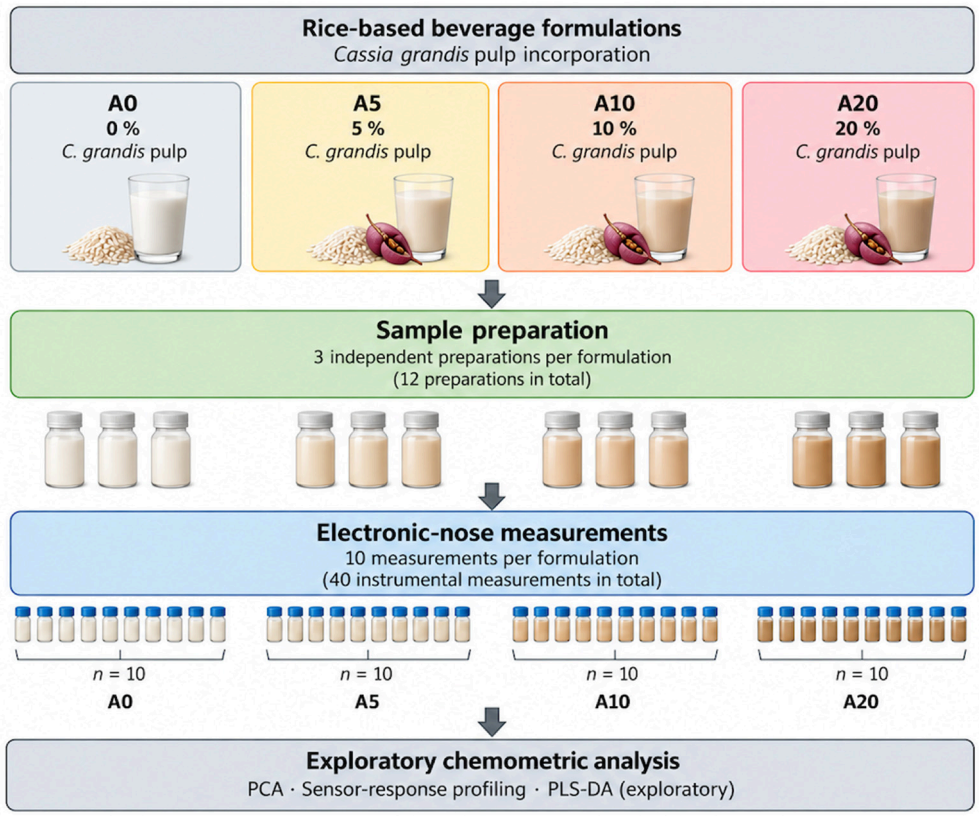


Figure 2. Schematic representation of the experimental design and exploratory chemometric analysis of rice-based beverages containing different concentrations of *Cassia grandis* pulp. Four formulations were investigated: A0 (0%), A5 (5%), A10 (10%), and A20 (20%).

All measurements were performed under controlled laboratory conditions, and the order of sample analysis was randomized to minimize systematic errors associated with instrumental drift or temporal variations. The complete experimental workflow was designed to evaluate the analytical performance of the portable electronic nose and to compare its discrimination capability with the reference chromatographic technique. The complete analytical workflow followed throughout this study is illustrated in Figure 2. The experimental design was developed to evaluate the performance of the proposed portable electronic nose for the discrimination of *Cassia grandis* beverages and its comparison with the reference chromatographic technique.

2.4. Physicochemical Characterization

The physicochemical properties of the beverage formulations were evaluated by determining pH, total soluble solids (°Brix), titratable acidity, and colour coordinates (CIELab system). All analyses were performed in triplicate at room temperature (25 ± 1 °C), and the results were expressed as mean ± standard deviation. The pH of each beverage was measured directly using a calibrated digital pH meter (Crison Instruments, Barcelona, Spain). Prior to each analytical session, the instrument was calibrated using certified buffer solutions at pH 4.00 and 7.00 according to the manufacturer's recommendations. Total soluble solids were determined using a digital refractometer (Atago Co., Ltd., Tokyo, Japan), and the results were expressed as °Brix at 20 °C [19].

Colour measurements were performed using a DigiEye imaging system (VeriVide Ltd., Leicester, UK) operating under standardized D65 illumination conditions. Colour parameters were expressed according to the CIELab colour space as L* (lightness), a* (red–green coordinate), and b* (yellow–blue coordinate), following the recommendations of the Commission Internationale de l'Éclairage [20].

Titratable acidity was determined by acid-base titration following the AOAC Official Method 942.15 [19]. Briefly, 1.0 mL of beverage was diluted with 10.0 mL of ultrapure water, and five drops of phenolphthalein indicator were added. Samples were titrated with standardized 0.01 N sodium hydroxide solution until the appearance of a persistent pale-pink endpoint (approximately pH 8.2). Titratable acidity was expressed as percentage of citric acid equivalents.

2.5. VOC Characterization by HS-SPME-GC-MS

The volatile organic compounds (VOCs) present in the different *Cassia grandis* beverage formulations were characterized by headspace solid-phase microextraction coupled to gas chromatography–mass spectrometry (HS-SPME-GC-MS), following the methodology described by Sánchez et al. (2021) [21] with minor modifications. Briefly, 2.0 mL of each beverage were transferred into 20 mL amber glass headspace vials containing 7.0 mL of sodium chloride solution (30%, w/v) to promote the salting-out effect and enhance VOC extraction. The vials were immediately sealed with PTFE/silicone septa and equilibrated at 40 °C for 30 min under continuous agitation.

Volatile compounds were extracted using a 65 µm StableFlex™ DVB/PDMS fibre (Supelco, Bellefonte, PA, USA). After the extraction step, the fibre was thermally desorbed in the injector port of the gas chromatograph under splitless mode. Chromatographic analyses were performed using a Bruker 456 gas chromatograph coupled to a Scion TQ triple quadrupole mass spectrometer (Bruker Daltonics, Bremen, Germany) equipped with a DB-WAXetr capillary column (60 m × 0.25 mm i.d. × 0.25 µm film thickness; Agilent Technologies, Santa Clara, CA, USA). Helium (99.999% purity, Air Liquide, Paris, France) was used as carrier gas at a constant flow rate of 1.0 mL min^{-1}. The mass spectrometer operated under electron impact ionization at 70 eV. Mass spectra were acquired in full-scan mode over an m/z range of 35–350. Volatile compounds were tentatively identified by comparing their electron-impact mass spectra with reference spectra available in the NIST Mass Spectral Library. Chromatographic retention times (RTs) were recorded for the detected peaks and are reported in Supplementary Table S1. Experimental linear retention indices were not available in the analytical dataset, and compound identities were not confirmed using authentic reference standards. Accordingly, the reported compound assignments should be considered tentative. No enantiomeric assignments were made, as the non-chiral DB-WAXetr stationary phase does not permit enantiomeric discrimination.

HS-SPME-GC-MS analyses were performed in triplicate for each beverage formulation (A0, A5, A10, and A20), resulting in a total of 12 chromatographic analyses. Whenever possible, compound identities were confirmed by comparing their calculated linear retention indices with literature values. For semi-quantitative comparison of volatile compounds among beverage formulations, chromatographic peak areas obtained by HS-SPME-GC-MS were used as instrumental indicators of relative analyte abundance. Peak areas were integrated for the identified compounds and grouped according to their corresponding chemical families. The sum of the integrated peak areas was used to evaluate changes in the overall chromatographic signal among formulations. Since compound-specific calibration curves were not established, the peak areas were not converted into absolute concentrations. Accordingly, the results were interpreted as semi-quantitative indicators of volatile abundance,

taking into account potential differences in extraction efficiency and mass spectrometric response among compounds.

For the semi-quantitative evaluation of the volatile profiles, the integrated GC-MS peak areas of the identified compounds were used as indicators of their relative instrumental abundance. Compounds were grouped according to their chemical families, and the corresponding peak areas were summed for each beverage formulation. The total integrated peak area was also calculated to compare the overall chromatographic signal among formulations. Since compound-specific calibration curves were not established, the resulting peak areas were expressed in arbitrary units and were not interpreted as absolute VOC concentrations. Differences in detector response factors and HS-SPME extraction efficiency were considered when interpreting the results.

2.6. Portable Electronic Nose

The volatile profiles of the different *C. grandis* beverage formulations were analysed using a portable electronic nose (E-nose) developed by the University of Extremadura (Spain) [22,23]. The device was specifically designed for rapid, non-destructive analysis of food aroma through the detection of volatile organic compounds (VOCs using an array of metal oxide semiconductor (MOS) gas sensors. The portable electronic nose incorporates four commercial gas-sensing modules: BME680 (Bosch Sensortec GmbH, Reutlingen, Germany), SGP30 (Sensirion AG, Stäfa, Switzerland), CCS811 (ScioSense B.V., Eindhoven, The Netherlands), and iAQ-Core (ScioSense B.V., Eindhoven, The Netherlands).

These modules provide a total of eleven gas-related analytical output channels, rather than eleven physically independent MOS sensors. Specifically, the BME680 provides one gas-resistance channel; the SGP30 provides four gas-related outputs (eCO_2, TVOC, raw H_2, and raw ethanol signals); the CCS811 provides three outputs (eCO_2, TVOC, and sensor resistance); and the iAQ-Core provides three outputs (eCO_2, TVOC, and sensor resistance). Although the BME680 also incorporates temperature, relative humidity, and atmospheric pressure sensing capabilities, these environmental variables were not included in the eleven-variable dataset used for chemometric analysis. The experimental setup was based on direct headspace exposure, without the use of an external pumping or gas injection system. The portable electronic nose was positioned directly above the sample container, allowing the volatile organic compounds released from the beverage to reach the integrated gas sensors. During the exposure stage, the sensing elements interacted with the volatile compounds present in the headspace, generating changes in their electrical responses. These signals were continuously recorded by the device and subsequently used to characterize the volatile fingerprint of each beverage formulation. After each measurement, the E-nose was exposed to clean ambient air to facilitate sensor recovery and re-establish the baseline before analyzing the next sample. A schematic representation of the experimental configuration is provided in Figure 3.

The portable device (39 × 33 mm) incorporates a microcontroller for signal acquisition, Bluetooth communication, and a rechargeable power supply, enabling real-time data transmission to a dedicated smartphone application developed for sensor control and data acquisition. Headspace sampling was performed through direct exposure of the integrated gas-sensing elements to the volatile compounds released from the beverage, without the use of internal or external pumping systems. The electronic nose was positioned directly above the sample container, allowing passive diffusion of volatile compounds towards the sensing elements.

The portable electronic nose provided eleven analytical output signals from the four integrated MOS sensor modules, including gas resistance, total volatile organic compound (TVOC) estimates, equivalent CO_2 (eCO_2) estimates, and gas-sensitive responses associated

with hydrogen and ethanol. Sensor signals were continuously acquired at a sampling frequency of 1 Hz. Following the previously described signal-processing procedure, a response feature was calculated for each analytical channel from the maximum and minimum signal values recorded during the measurement cycle, according to the expression $R = (Xmax - Xmin) \times 100$ where Xmax and Xmin represent the maximum and minimum values of the corresponding signal, respectively.

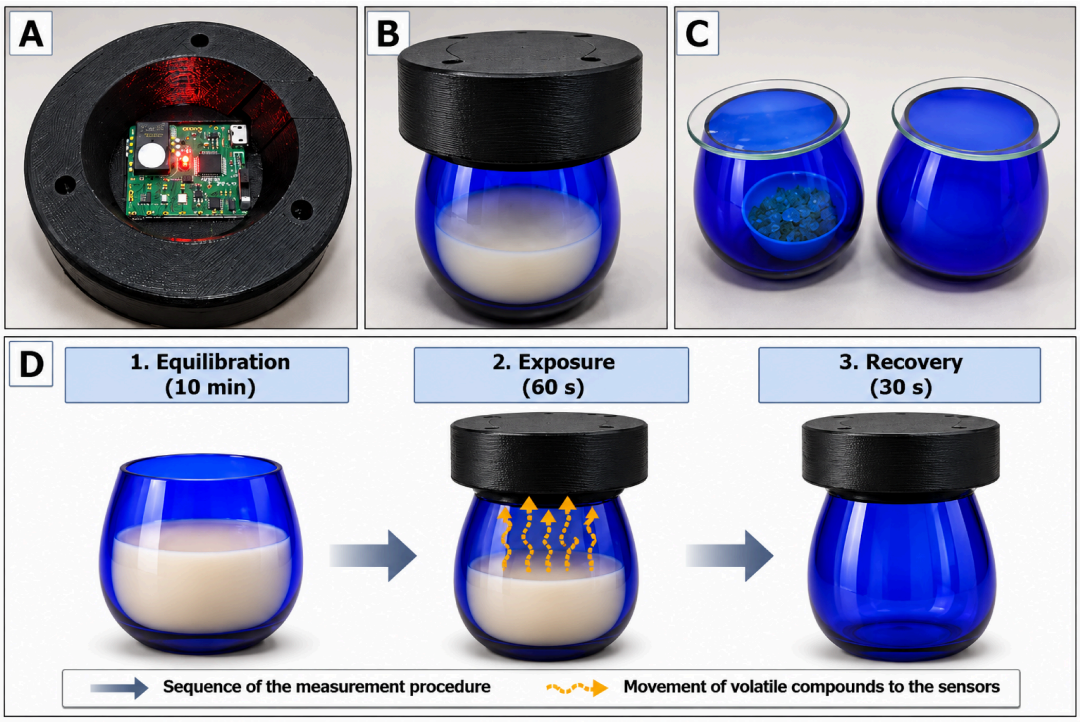


Figure 3. Experimental configuration and measurement procedure of the portable electronic nose. (**A**) Internal view of the electronic nose showing the gas-sensing modules. (**B**) Electronic nose positioned on the sample container. (**C**) Sample containers used for the analysis. (**D**) Schematic representation of the three measurement stages: equilibration (10 min), exposure (60 s), and recovery (30 s). The grey horizontal arrows indicate the sequential progression of the measurement procedure, while the yellow upward arrows represent the movement of volatile compounds from the sample headspace towards the gas-sensing modules during the exposure stage.

For each measurement, 20 mL of beverage was transferred into a standard wine tasting glass and allowed to equilibrate under controlled laboratory conditions before analysis. The measurement cycle consisted of two consecutive stages: (i) an adsorption phase, during which the sensor chamber was exposed to the sample headspace for 60 s, allowing VOC interaction with the sensor surfaces, and (ii) a desorption phase, during which clean ambient air was introduced into the chamber for 30 s to restore the sensor baseline before the next measurement. Sensor signals were recorded at a sampling frequency of 1 Hz, resulting in one measurement per second for each sensor throughout the analytical cycle.

For each beverage formulation, ten electronic nose measurements were performed across three independently prepared batches to account for variability associated with sample preparation.

Between consecutive analyses, the sensor chamber was completely purged to minimize memory effects and reduce carry-over between samples. All electronic nose measurements were conducted under controlled laboratory conditions at 25 °C. The optimization of the analytical procedure was restricted to sample volume, headspace equilibration time, sensor exposure time, and recovery time. Prior to the analytical measurements, the portable

electronic nose was switched on and allowed to warm up for 30 min to promote stabilization of the MOS sensor responses. This initial stabilization period was carried out before sample analysis and was independent of the headspace equilibration time. All measurements were subsequently performed under controlled laboratory conditions at 25 °C.

2.7. Optimization of Analytical Conditions

Prior to analytical validation, the operating conditions of the portable electronic nose were optimized to maximize sensor response, improve repeatability, and minimize the total analysis time. Four experimental parameters were evaluated: sample volume, headspace equilibration time, adsorption time, and desorption time. During the optimization process, one parameter was varied while the remaining experimental conditions were kept constant. Sample volumes of 10, 15, 20 and 25 mL were evaluated using standard wine tasting glasses. Subsequently, headspace equilibration times of 5, 10, 15 and 20 min were investigated to determine the minimum time required to establish a stable equilibrium between the beverage matrix and the volatile compounds present in the headspace.

The adsorption phase was evaluated using exposure times of 30, 45, 60 and 90 s, whereas desorption times of 20, 30, 45 and 60 s were tested to ensure complete recovery of the sensor baseline before subsequent analyses. Each experimental condition was evaluated in ten independent replicates. The optimum analytical conditions were selected considering the magnitude of the sensor response, baseline stability, repeatability expressed as relative standard deviation (RSD), and the total duration of the analytical cycle. Based on these criteria, the optimal operating conditions were established as 20 mL sample volume, 10 min headspace equilibration time, 60 s adsorption time, and 30 s desorption time. These conditions were subsequently applied throughout the analytical validation and chemometric analysis.

2.8. Analytical Validation

The analytical performance of the proposed portable electronic nose was evaluated under the optimized operating conditions following the general recommendations for analytical method validation [24]. The validation study included the assessment of repeatability, robustness, and classification performance for the discrimination of *Cassia grandis* beverage formulations.

The repeatability of the analytical method was evaluated by performing ten consecutive measurements of the same beverage formulation under identical experimental conditions using the same electronic nose and operator. Sensor responses were recorded for each measurement, and repeatability was expressed as the relative standard deviation (RSD,%) of the sensor signals. The robustness of the proposed method was assessed by introducing small deliberate variations in the optimized operating parameters. Sample volume (±2 mL), headspace equilibration time (±2 min), adsorption time (±10 s), and desorption time (±10 s) were individually modified while maintaining the remaining analytical conditions constant. The influence of these variations on sensor response stability and classification performance was subsequently evaluated.

The classification capability of the portable electronic nose was evaluated using supervised chemometric models. Model performance was assessed by cross-validation, which is widely accepted for estimating the predictive ability and generalization performance of classification models [25]. The predictive performance of each model was evaluated using confusion matrices, from which accuracy, sensitivity, specificity, precision and F1-score were calculated. Principal component analysis (PCA) was used to investigate the multivariate distribution of the electronic-nose responses obtained from rice-based beverages containing different concentrations of *Cassia grandis* pulp. Partial least squares discriminant analysis

(PLS-DA) was additionally used to explore the discriminatory information contained in the sensor-response profiles. The measurements were obtained from independently prepared beverage batches; however, the correspondence between individual instrumental measurements and their original preparation batches could not be reconstructed from the available acquisition records. Consequently, preparation-level grouped cross-validation could not be performed. Any classification results obtained through measurement-level resampling were therefore interpreted exclusively as exploratory measures of within-dataset discrimination and not as estimates of predictive performance for independently prepared samples. No independent external validation of the classification model was claimed.

2.9. Chemometric and Statistical Analysis

The multivariate dataset generated by the portable electronic nose was processed using chemometric techniques to evaluate its ability to discriminate the different *Cassia grandis* beverage formulations. Prior to statistical analysis, the sensor responses were organized into a data matrix in which rows corresponded to individual measurements and columns represented the responses of the eleven analytical output channels. Exploratory data analysis was initially performed by Principal Component Analysis (PCA) to visualize sample distribution, identify clustering patterns and detect possible outliers. Linear Discriminant Analysis (LDA) was subsequently applied to maximize class separation among the different beverage formulations.

Partial Least Squares Discriminant Analysis (PLS-DA) was performed to evaluate the predictive classification capability of the proposed analytical method. Model performance was assessed using cross-validation to estimate the predictive ability and generalization performance of the classification model [26]. Five-fold cross-validation was performed by randomly assigning individual measurements to the different folds, without grouping them according to their corresponding sample preparation. Consequently, measurements originating from the same independently prepared batch could be included in both the training and validation subsets. Therefore, the resulting classification metrics should be interpreted as estimates of performance at the measurement level rather than as evidence of predictive performance for entirely independent beverage preparations.

PLS-DA model performance was evaluated using five-fold cross-validation, with individual measurements randomly assigned to the different folds. Ten measurements per formulation were obtained from three independent sample preparations. Since cross-validation was performed at the measurement level rather than by grouping measurements according to their preparation, the resulting performance metrics were considered indicators of discrimination within the investigated experimental dataset. This approach allowed the classification performance of the electronic nose to be assessed under the experimental conditions studied, although independent batch-level predictive validation remains necessary. Classification performance was evaluated by calculating the overall accuracy together with sensitivity, specificity, precision and F1-score obtained from the corresponding confusion matrices. Principal Component Analysis (PCA) and Linear Discriminant Analysis (LDA) were performed using IBM SPSS Statistics version 18.0 (IBM Corp., Armonk, NY, USA), whereas PLS-DA modelling was carried out using MATLAB R2024a (MathWorks Inc., Natick, MA, USA). Statistical significance was established at $p < 0.05$.

2.10. Correlation Between E-Nose Responses and VOC Profile

Partial Least Squares Regression (PLSR) was applied to investigate the relationship between the responses generated by the portable electronic nose and the volatile organic compounds (VOCs) identified by HS-SPME-GC-MS [26]. The PLSR model was developed using the electronic nose sensor responses (X matrix) as predictor variables and the relative

abundances of the VOCs identified by HS-SPME-GC-MS (Y matrix) as response variables. For PLSR modelling, individual electronic-nose measurements were used as observations in the predictor matrix (X), with the eleven analytical channels representing the predictor variables. Each E-nose measurement was paired with the GC-MS volatile profile corresponding to its beverage formulation (A0, A5, A10, or A20). Consequently, individual E-nose measurements belonging to the same formulation shared the same GC-MS reference values in the response matrix (Y). This approach was used to investigate formulation-dependent associations between sensor responses and volatile composition rather than to establish independent sample-level quantitative predictions. The PLSR models were developed using two latent variables (LVs). Model performance was evaluated using grouped cross-validation, in which all E-nose measurements belonging to the same beverage formulation were assigned to the same validation fold. This procedure prevented measurements sharing identical formulation-level GC-MS reference values from being simultaneously included in the calibration and validation subsets. RMSEC and RMSECV were calculated using autoscaled response variables and are therefore dimensionless. The quality of the PLSR model was evaluated using the coefficient of determination (R^2), root mean square error (RMSE), and the corresponding score and loading plots. These parameters were used to assess the predictive performance of the model and to investigate the relationship between the chromatographic volatile profile and the responses generated by the electronic nose. PLSR modelling was performed using MATLAB R2024a (MathWorks Inc., Natick, MA, USA).

3. Results and Discussion

3.1. Physicochemical Characterization of Cassia grandis Beverages

The physicochemical characteristics of the four beverage formulations were evaluated to determine the influence of increasing *Cassia grandis* pulp concentration on the beverage matrix. As shown in Table 1, the incorporation of *C. grandis* produced marked changes in pH, soluble solids, titratable acidity and colour parameters. The pH progressively increased from 5.87 in the control beverage (A0) to 6.45, 6.87 and 6.93 in A5, A10 and A20, respectively. A similar concentration-dependent trend was observed for total soluble solids, which increased from 0.9 °Brix in A0 to 6.1 °Brix in A20. Titratable acidity also increased with the proportion of *C. grandis*, ranging from 0.097% in the control formulation to 0.241% in A20.

Table 1. Physicochemical characterization of the different beverage formulations (pH, °Brix, titratable acidity, and CIELab colour parameters).

Sample	pH	°Brix	Titratable Acidity (%)	L*	a*	b*
A0	5.87 ± 0.10 ^{a}	0.9 ± 0.2 ^{a}	0.097 ± 0.012 ^{a}	81.24 ± 0.24 ^{a}	0.56 ± 0.17 ^{a}	15.21 ± 0.11 ^{a}
A5	6.45 ± 0.09 ^{b}	3.8 ± 0.2 ^{b}	0.124 ± 0.010 ^{a}	45.12 ± 2.43 ^{b}	21.45 ± 1.18 ^{bc}	31.34 ± 3.56 ^{bd}
A10	6.87 ± 0.08 ^{c}	5.2 ± 0.2 ^{c}	0.187 ± 0.012 ^{b}	34.67 ± 1.56 ^{c}	27.45 ± 1.89 ^{bc}	27.45 ± 2.45 ^{c}
A20	6.93 ± 0.07 ^{c}	6.1 ± 0.2 ^{d}	0.241 ± 0.013 ^{c}	39.56 ± 1.34 ^{c}	27.45 ± 1.23 ^{bc}	22.45 ± 1.34 ^{c}

Note: Values are expressed as mean ± standard deviation. L* denotes lightness, a* the green–red axis, and b* the blue–yellow axis. Different superscript letters within the same column indicate statistically significant differences ($p < 0.05$); values sharing at least one letter are not significantly different. Values for colour parameters are expressed as mean ± standard deviation. Different superscript letters within the same column indicate statistically significant differences ($p < 0.05$).

The increase in soluble solids can be directly associated with the progressive incorporation of *C. grandis* pulp into the rice-based beverage and consequently with the contribution of soluble constituents from the fruit. The simultaneous modification of pH, soluble solids

and titratable acidity indicates that *C. grandis* incorporation substantially altered the composition of the beverage matrix rather than simply introducing additional aroma compounds. This aspect is analytically relevant because the non-volatile composition of liquid food matrices can significantly affect the partitioning and release of aroma compounds into the headspace. López et al. (2024) [27] demonstrated that changes in the non-volatile matrix can markedly modify the headspace concentration of volatile compounds even when the total volatile composition is maintained constant. Similarly, matrix effects have been shown to influence HS-SPME determination of VOCs, making matrix composition an important consideration when comparing volatile profiles among chemically different samples [28].

The addition of *C. grandis* also caused substantial modifications in the visual characteristics of the beverages. Lightness (L*) decreased markedly from 81.24 in A0 to 45.12 and 34.67 in A5 and A10, respectively, indicating pronounced darkening following incorporation of the fruit pulp. In parallel, the a* coordinate increased considerably, reflecting a displacement towards reddish tonalities, while the b* coordinate also increased compared with the control formulation. These variations confirm a concentration-dependent modification of the visual properties of the rice-based matrix caused by incorporation of *C. grandis*. From an analytical perspective, these physicochemical differences are particularly important for interpreting the subsequent HS-SPME-GC-MS and electronic-nose results. HS-SPME is an equilibrium-based extraction technique, and therefore differences in sample composition can modify analyte partitioning between the liquid matrix, headspace and extraction phase [29]. The differences subsequently detected in the volatile fingerprints is also relevant to MOS-based electronic noses because sensor responses depend on the nature and concentration of VOCs reaching the sensor array, with different chemical classes producing characteristic response patterns [30].

3.2. Volatile Profile Characterization by HS-SPME-GC-MS

HS-SPME-GC-MS analysis revealed substantial differences in the volatile fingerprints of the rice-based beverages following the incorporation of *C. grandis* pulp. A total of 38 volatile compounds were identified across the four formulations and classified into different chemical families, including monoterpenes and their derivatives, aromatic aldehydes, carboxylic acids and their derivatives, phenylpropanoids, sesquiterpenes, and other volatile compounds. As shown in Figure 4, the sum of the integrated chromatographic peak areas varied considerably among formulations, increasing from 5.62×10^8 a.u. in A0 to 1.45×10^9 a.u. in A5, decreasing to 9.02×10^8 a.u. in A10, and reaching 2.98×10^9 a.u. in A20. Thus, the overall chromatographic signal did not increase monotonically with the percentage of *C. grandis* pulp. The differences were also associated with changes in the contributions of individual chemical families, particularly aromatic aldehydes, monoterpenes, and carboxylic acid derivatives. These results indicate that pulp incorporation modified both the overall chromatographic signal and the volatile fingerprint of the beverages. Nevertheless, the summed peak areas should be regarded as semi-quantitative instrumental indicators rather than direct measurements of total VOC concentration [31,32].

The stacked bars represent the summed chromatographic peak areas of the compounds assigned to each chemical family, expressed in arbitrary units (a.u.). Peak areas were used as semi-quantitative indicators of volatile abundance and do not represent absolute VOC concentrations.

Among the different chemical families, monoterpenes and their derivatives exhibited marked variations following the incorporation of *C. grandis* pulp. In particular, the integrated chromatographic peak area of linalool increased from 1.83×10^7 a.u. in the control formulation (A0) to 5.36×10^8 a.u. in A20, corresponding to an approximately 29-fold increase in instrumental signal. Similarly, the peak area assigned to α-terpineol increased

from 2.84×10^6 to 3.48×10^7 a.u., representing an approximately 12-fold increase, subject to confirmation of the compound assignment across formulations. In contrast, eugenol exhibited a smaller variation, with its peak area decreasing from 5.26×10^7 a.u. in A0 to 4.65×10^7 a.u. in A20. These findings demonstrate that the incorporation of *C. grandis* was associated with compound-specific changes in chromatographic responses rather than a uniform increase in all volatile constituents. Nevertheless, these variations should be interpreted as semi-quantitative changes in instrumental signal rather than absolute differences in analyte concentrations. The relevance of terpenes and terpenoids as discriminant volatile markers has also been demonstrated in other plant-derived matrices. For example, previous studies using HS-SPME-GC-MS-based volatile profiling have shown that monoterpenes and sesquiterpenes can contribute substantially to the variability among botanical samples and support their discrimination using chemometric techniques [31].

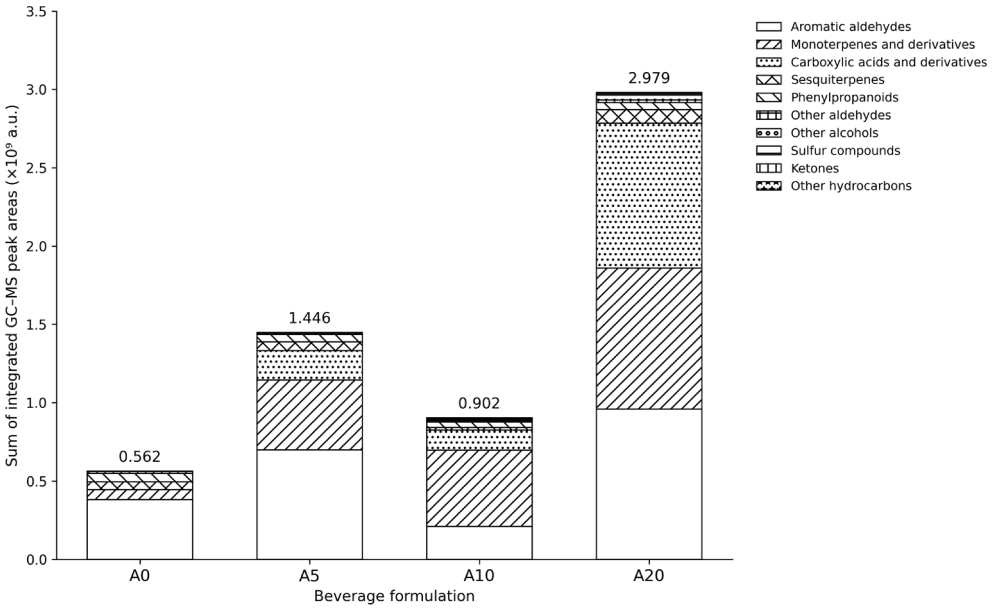


Figure 4. Distribution of integrated HS-SPME-GC-MS peak areas among volatile organic compound (VOC) families identified in rice-based beverages containing different concentrations of *Cassia grandis* pulp. A0, A5, A10, and A20 correspond to formulations containing 0, 5, 10, and 20% (*w*/*v*) of *C. grandis* pulp, respectively.

Linalool, in particular, is widely recognized as a characteristic plant-derived volatile and is frequently reported among the dominant aroma compounds of aromatic plant-based foods and beverages. The complete list of volatile compounds detected by HS-SPME-GC-MS, together with their retention times and integrated chromatographic peak areas for each beverage formulation (A0, A5, A10, and A20), is provided in Supplementary Table S1.

The comparison of integrated chromatographic peak areas provides additional information beyond the relative distribution of volatile compounds. Although the A20 formulation exhibited the highest summed GC-MS peak area, the response was not proportional to the amount of *C. grandis* pulp added, as A10 showed a lower total chromatographic signal than A5. Furthermore, the relative contributions of the different chemical families varied among formulations, indicating changes in the composition of the detected volatile fingerprint. These differences may reflect the contribution of volatile compounds associated with *C. grandis*, interactions among beverage ingredients, and changes in the partitioning of analytes between the liquid matrix, headspace, and SPME fibre. Consequently, the observed chromatographic variations cannot be attributed exclusively to an increase in VOC concentration resulting from pulp addition. Similar behaviour has been observed in

complex plant matrices, where differences in raw material composition, processing and interactions among volatile and non-volatile constituents modify the relative distribution of VOC families rather than affecting all compounds in the same direction. Volatilomic approaches based on GC-MS have therefore increasingly been combined with multivariate analysis to identify chemically meaningful fingerprints instead of relying exclusively on individual compounds [31–33].

The incorporation of *C. grandis* also introduced compounds that were absent or detected at substantially lower levels in the control beverage. Acid derivatives represented an important fraction associated with the fruit containing formulations, particularly compounds derived from butanoic acid. In addition, octanoic and nonanoic acids were detected, with the highest levels being observed in A10. Previous studies have investigated the incorporation of *C. grandis* pulp into food formulations, providing relevant background for the characterization of this ingredient in complex food matrices [11]. Short- and medium-chain organic acids, aldehydes and related derivatives are especially relevant to aroma characterization because even compounds occurring at relatively low abundance may contribute substantially to the final aroma profile when their odor thresholds are low. More generally, current flavoromics studies emphasize that the sensory relevance of a volatile profile depends not only on total concentration but also on the chemical identity and odor potency of the individual constituents.

Changes were also observed among carbonyl compounds. Benzaldehyde and other aldehyde- and ketone-related compounds were predominantly detected in formulations containing *C. grandis*, while acetophenone showed a notable contribution in A20. Aldehydes, ketones and alcohols constitute recurrent groups in GC-MS profiles of beverages and can act as useful markers of differences in raw materials and processing. For example, a recent GC-MS/SPME survey of alcoholic beverages identified extensive diversity among alcohols, aldehydes, ketones, terpenes and aromatic derivatives, demonstrating that the relative distribution of these chemical classes strongly depends on the composition of the starting matrix. In contrast, some compounds associated primarily with the original beverage formulation decreased after addition of *C. grandis*. Trans-cinnamaldehyde, a characteristic volatile compound associated with the cinnamon incorporated into the beverage formulation, exhibited substantial differences in chromatographic response among formulations. Although its relative contribution to the total volatile profile decreased following the incorporation of *C. grandis*, the summed peak area of the chromatographic signals tentatively assigned to this compound increased from 3.76×10^8 a.u. in A0 to 9.59×10^8 a.u. in A20. Both cinnamaldehyde and eugenol are characteristic aromatic plant volatiles and belong to chemical groups commonly detected by GC-MS in spice-derived matrices. The volatile composition of such matrices is generally dominated by terpenoids and phenylpropanoid-type compounds, whose relative abundances can change considerably when aromatic ingredients are combined with other plant materials.

The differences observed in the relative chromatographic profiles of A0, A5, A10, and A20 indicate changes in the proportional contributions of several volatile compounds, including monoterpenes and compounds associated with the cinnamon-containing beverage matrix. These results suggest that the incorporation of *C. grandis* pulp modifies the overall volatile fingerprint of the formulations. The combined evaluation of multiple volatile signals may therefore provide useful complementary information for distinguishing beverage formulations, although the present results do not establish the superiority of this approach over individual marker compounds [31,34].

3.3. Optimization of the Portable Electronic Nose Operating Conditions

The operating conditions of the portable electronic nose were optimized to achieve a high and stable sensor response while maintaining adequate repeatability and minimizing total analysis time. Optimizing experimental parameters is particularly important for electronic nose measurements, as variations in headspace generation, sampling conditions, and sensor exposure can substantially affect signal intensity, repeatability, and discrimination capability of the sensor array [35]. Consequently, the influence of sample volume, headspace equilibration time, adsorption time, and desorption time on the analytical response was systematically evaluated (Figure 5).

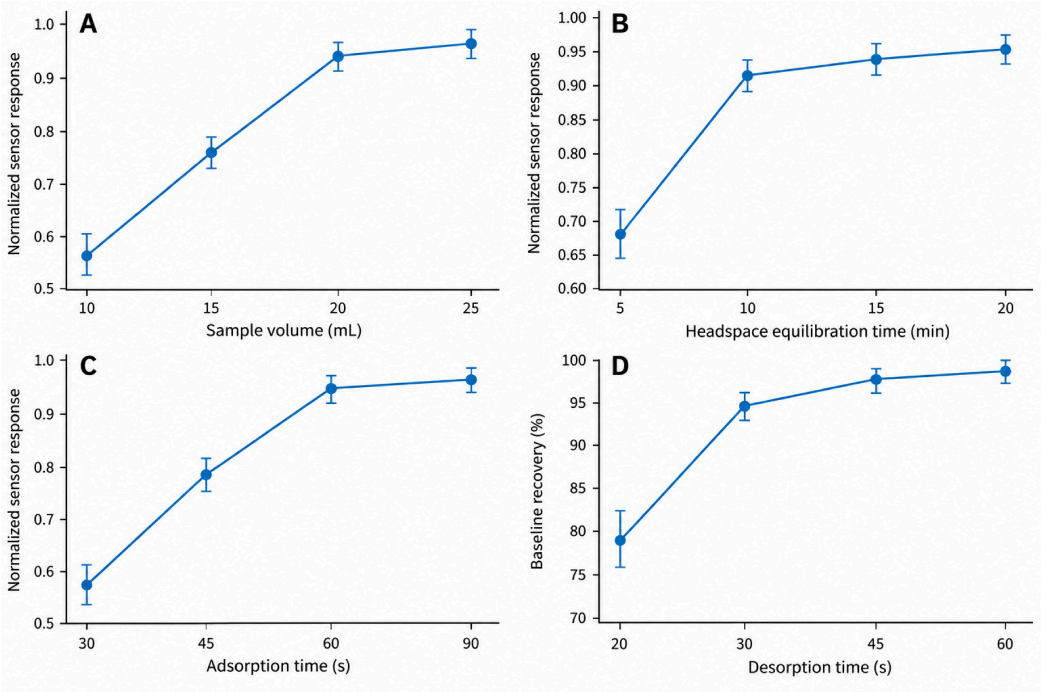


Figure 5. Effect of the operating parameters on the response of the portable electronic nose: (**A**) sample volume, (**B**) headspace equilibration time, (**C**) adsorption time, and (**D**) desorption time. Results are expressed as mean ± standard deviation of ten independent measurements.

Sample volume had a marked influence on the response generated by the sensor array. Increasing the beverage volume from 10 to 20 mL resulted in a progressive increase in the normalized sensor response, from approximately 0.55 at 10 mL to 0.76 and 0.94 at 15 and 20 mL, respectively. However, a further increase to 25 mL produced only a slight improvement in the response (0.96), suggesting that the amount of VOCs available in the headspace was approaching a condition in which further increases in sample volume produced limited additional sensor response. This behaviour is consistent with the dependence of electronic-nose signals on the concentration and composition of volatile compounds reaching the sensing surface; MOS sensors may exhibit concentration-dependent responses over specific concentration ranges [30]. Therefore, 20 mL was selected as the optimum sample volume, since it provided a high sensor response without unnecessarily increasing sample consumption.

A similar behaviour was observed for headspace equilibration time. Increasing the equilibration period from 5 to 10 min markedly enhanced the sensor response, which increased from approximately 0.68 to 0.93. In contrast, extending the equilibration time to 15 and 20 min resulted in only minor additional increases (0.95 and 0.96, respectively). Headspace generation constitutes a critical stage in electronic-nose analysis because the con-

centration of volatile compounds delivered to the sensor array directly influences both the magnitude and reproducibility of the resulting signals. Previous studies have demonstrated that variations in headspace and sampling conditions can produce substantial quantitative changes in electronic-nose responses and consequently affect measurement repeatability and sample discrimination [36,37]. The limited increase observed beyond 10 min therefore indicated that extending the equilibration period provided little additional analytical benefit. Consequently, 10 min was selected as the optimum headspace equilibration time, representing an appropriate compromise between sensor response and analytical throughput.

Adsorption time also affected the response of the electronic nose. Increasing sensor exposure to the sample headspace from 30 to 60 s produced a progressive increase in normalized response from approximately 0.57 to 0.95. Extending the adsorption period to 90 s resulted in only a marginal additional increase (0.97), indicating that the response was approaching a relatively stable region. The response of MOS-based electronic noses originates from the interaction of volatile compounds with the sensing surfaces, involving adsorption/desorption and associated changes in the electrical properties of the sensors. Consequently, both the concentration of the volatile compounds and the duration of sensor exposure can influence the magnitude and dynamics of the recorded signal [30]. Moreover, previous optimization studies have demonstrated that information contained in the adsorption curve, including its maximum and slope, can strongly influence the analytical performance of multisensor systems [36]. Accordingly, 60 s was selected as the optimum adsorption time, since extending exposure to 90 s produced only a limited improvement while increasing the duration of the analytical cycle.

The desorption step was optimized considering the ability of the sensors to recover their initial baseline after exposure to the sample headspace. A desorption time of 20 s resulted in incomplete baseline recovery, with approximately 79% recovery, indicating persistence of the sensor response after removal of the sample atmosphere. Increasing the desorption time to 30 s improved baseline recovery to approximately 95%, whereas only minor improvements were obtained at 45 and 60 s (approximately 98 and 99%, respectively).

3.4. Analytical Validation of the Portable Electronic Nose

Following optimization of the operating parameters, the analytical performance of the portable electronic nose was evaluated in terms of short-term repeatability and robustness. For each of the eleven analytical channels, repeatability was assessed using the extracted sensor response feature calculated from the maximum and minimum signal values, as described in Section 2.6. The relative standard deviation (RSD, %) was calculated from the ten consecutive measurements as the ratio of the standard deviation to the mean response. These parameters were assessed under the optimized conditions established in Section 3.3 (20 mL sample volume, 10 min headspace equilibration, 60 s adsorption and 30 s desorption). Short-term repeatability was evaluated from ten consecutive measurements of the same beverage sample under the optimized operating conditions, using the same electronic nose device and operator. The sensor array showed low variability between consecutive measurements, with RSD values ranging from 1.88 to 3.67% across the eleven sensor responses (Table 2). The lowest variability was observed for S8 (RSD = 1.88%), whereas S4 showed the highest RSD (3.67%). Nevertheless, all sensors exhibited RSD values below 4%, demonstrating a consistent response of the multisensor systems during repeated analysis.

The low dispersion observed among consecutive measurements indicates that the optimized headspace generation and measurement cycle provided reproducible exposure of the sensor array to the volatile fraction of the beverage. Moreover, the relatively homogeneous repeatability obtained across sensors with different response characteristics suggests that

the optimized adsorption and desorption periods were sufficient to minimize variability associated with incomplete sensor recovery between successive measurements. This aspect is particularly relevant for portable MOS-based electronic noses, in which fluctuations in headspace composition, sensor recovery and short-term baseline variation may contribute to analytical variability. The eleven sensor responses showed satisfactory short-term repeatability, with RSD values ranging from 1.88 to 3.67% (Table 2). The lowest variability was observed for S8 (RSD = 1.88%), whereas S4 showed the highest variability (RSD = 3.67%). Nevertheless, RSD values remained below 4% for all sensors, indicating consistent performance of the multisensor array during consecutive measurements. Short-term repeatability was evaluated from ten consecutive measurements of the same beverage sample under the optimized operating conditions. The normalized sensor responses showed stable profiles across consecutive measurements, with no evident systematic drift during the measurement sequence (Figure S1).

Table 2. Short-term repeatability of the portable electronic nose under multisensor conditions.

Sensor	Mean Normalized Response	SD	RSD (%)
S1	0.842	0.019	2.26
S2	0.764	0.023	3.01
S3	0.915	0.018	1.97
S4	0.681	0.025	3.67
S5	0.798	0.021	2.63
S6	0.873	0.020	2.29
S7	0.736	0.026	3.53
S8	0.904	0.017	1.88
S9	0.825	0.024	2.91
S10	0.779	0.022	2.82
S11	0.861	0.019	2.21

SD, standard deviation; RSD, relative standard deviation.

Robustness was subsequently evaluated by introducing small deliberate variations around the optimized operating conditions in order to assess the susceptibility of the portable electronic nose to minor changes in the measurement protocol. This evaluation is particularly relevant in electronic-nose analysis, since variations in headspace generation and sampling conditions may affect sensor response and measurement reproducibility [36]. Sample volume was varied from the nominal value of 20 mL to 18 and 22 mL, headspace equilibration time from 10 min to 8 and 12 min, adsorption time from 60 s to 50 and 70 s, and desorption time from 30 s to 20 and 40 s. The responses obtained under each modified condition were compared with those recorded under the nominal optimized conditions.

As shown in Table 3, the electronic nose response remained relatively stable following the deliberate variations introduced into the analytical procedure. Changes in sample volume resulted in deviations of −1.21% and +2.66% for 18 and 22 mL, respectively, relative to the nominal condition. Similarly, modification of the headspace equilibration time to 8 and 12 min produced response variations of −2.26% and +2.63%, respectively. These relatively small variations indicate that minor deviations in sample volume and equilibration time did not substantially alter the overall response of the sensor array. This behaviour is particularly relevant for headspace-based electronic-nose measurements, where control of sampling conditions is important to ensure consistent exposure of the sensors to the volatile fraction of the sample [33].

Table 3. Robustness assessment of the portable electronic nose under deliberate variations in the optimized operating conditions.

Parameter	Experimental Condition	Mean Normalized Response	SD	RSD (%)	Relative Change (%)
Nominal conditions	20 mL/10 min/60 s/30 s	0.994	0.017	1.69	Reference
Sample volume	18 mL	0.982	0.016	1.62	−1.21
	22 mL	1.020	0.012	1.18	+2.66
Headspace equilibration time	8 min	0.971	0.024	2.48	−2.26
	12 min	1.020	0.009	0.87	+2.63
Adsorption time	50 s	0.956	0.022	2.35	−3.78
	70 s	1.021	0.017	1.69	+2.74
Desorption time	20 s	0.941	0.021	2.25	−5.29
	40 s	1.007	0.012	1.17	+1.27

SD, standard deviation; RSD, relative standard deviation. Relative change was calculated with respect to the response obtained under nominal optimized conditions.

Slightly greater effects were observed when the adsorption time was reduced to 50 s, resulting in a −3.78% change, whereas increasing the adsorption period to 70 s produced a variation of +2.74%. Desorption time showed the greatest influence among the investigated parameters. Reducing the desorption period from 30 to 20 s resulted in a decrease of approximately 5.29% in the mean response relative to the nominal condition, whereas increasing it to 40 s produced only a minor variation (+1.27%). The greater effect observed at the shorter desorption time may be associated with incomplete recovery of the sensing system between consecutive measurements, supporting the selection of 30 s during the optimization study. Adequate sensor recovery and short-term signal stability are particularly important in portable electronic noses, since residual sensor responses and short-term instability may compromise measurement reproducibility. Despite these deliberate modifications, measurement variability remained low, with RSD values ranging from 0.87 to 2.48% for the modified conditions. These results indicate that small variations around the optimized sample volume, equilibration time and adsorption time had a limited influence on the analytical response, while the greater sensitivity observed when shortening the desorption period highlights the importance of maintaining sufficient recovery time between consecutive measurements [37].

3.5. Chemometric Discrimination of Cassia grandis Beverage Formulations

Following optimization and analytical validation of the portable E-nose, principal component analysis (PCA) was applied to the responses of the eleven analytical output channel to explore the multivariate distribution of the beverage formulations according to *C. grandis* concentration. PCA is commonly applied to electronic-nose datasets as an unsupervised exploratory tool to reduce the dimensionality of multisensor responses and visualize similarities and differences among samples according to their volatile fingerprints [21,38,39].

The PCA score plot obtained for the four beverage formulations is shown in Figure 5. The first two principal components accounted for 96.18% of the total variance, with PC1 explaining 87.04% and PC2 accounting for an additional 9.14%. The high cumulative variance explained by these two components indicates that most of the information contained in the multisensor response matrix could be represented in a two-dimensional space. Similar applications of PCA to electronic-nose data have demonstrated its usefulness for representing complex sensor-response patterns and identifying differences in the volatile fingerprints of food matrices [21,38].

As shown in Figure 6, the PCA score plot revealed a clear distribution of the samples according to beverage formulation. A5 and A10 samples were positioned relatively close to each other, indicating greater similarity in their volatile fingerprints as perceived by the electronic-nose sensor array. In contrast, the control samples (A0) occupied a distinct region of the PCA space, clearly separated from the formulations containing *C. grandis*. The A20 samples also formed a differentiated cluster and showed the greatest separation from the other *C. grandis* containing formulations. The ability of MOS-based electronic noses combined with PCA to reveal differences associated with modifications in food aroma profiles has also been reported in previous studies [37,38]. The proximity between A5 and A10 suggests that the changes in volatile composition occurring between these two concentrations produced comparatively smaller modifications in the global sensor response than those observed between the control and the *C. grandis* containing beverages or between A10 and A20. This interpretation is consistent with the HS-SPME-GC-MS results, which showed substantial changes in the relative distribution of several volatile families following *C. grandis* incorporation, particularly monoterpenes and cinnamic derivatives.

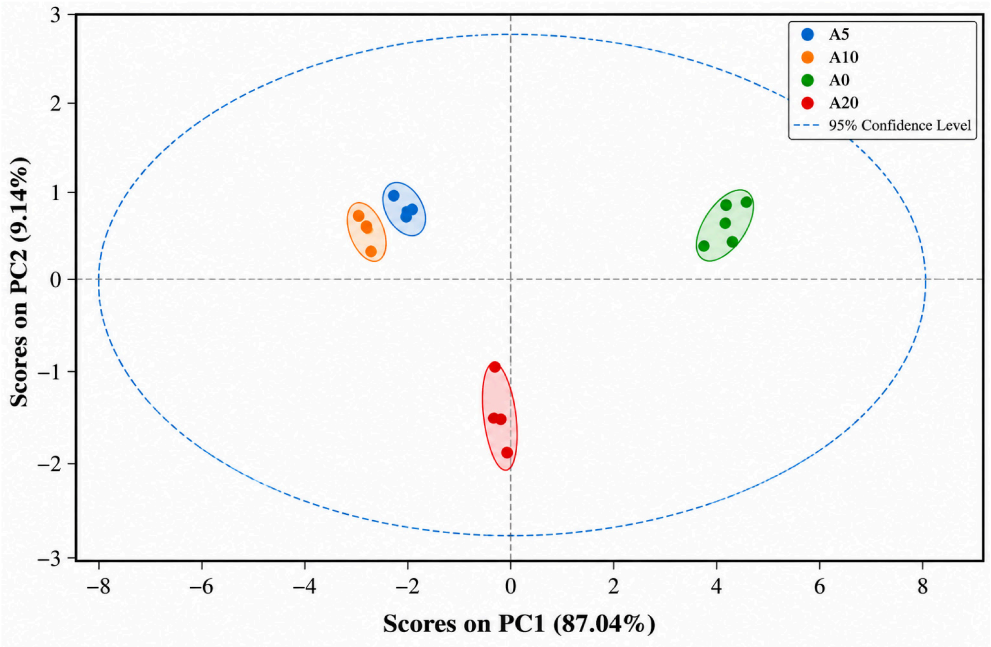


Figure 6. Principal component analysis (PCA) score plot of the portable electronic-nose responses obtained for four beverage formulations containing increasing concentrations of *Cassia grandis* pulp: A0 (0%), A5 (5%), A10 (10%), and A20 (20%). The analysis included 40 individual measurements (10 per formulation), with no averaging or exclusion of observations. Some data points overlap due to their similar PCA scores, resulting in fewer visually distinguishable points. PC1 and PC2 explained 87.04% and 9.14% of the total variance, respectively, accounting for 96.18% of the cumulative variance.

To further assess the discrimination among beverage formulations, linear discriminant analysis (LDA) was applied to the E-nose response matrix using the formulation (A0, A5, A10 and A20) as the predefined grouping variable. Unlike PCA, which provides an unsupervised representation of the main sources of variance, LDA is a supervised approach that maximizes the separation among predefined classes based on linear combinations of the original sensor variables. This approach has been successfully applied to electronic-nose data for the discrimination of food products according to differences in their volatile fingerprints [11].

As shown in Figure 7, the LDA score plot showed a clear discrimination among the four beverage formulations. A0 and A20 occupied markedly differentiated regions of the

discriminant space, whereas A5 and A10 were located comparatively closer to each other, although they formed distinguishable clusters. This distribution was generally consistent with the pattern previously observed by PCA, where the intermediate *C. grandis* concentrations showed greater similarity than the control and the formulation containing the highest pulp concentration.

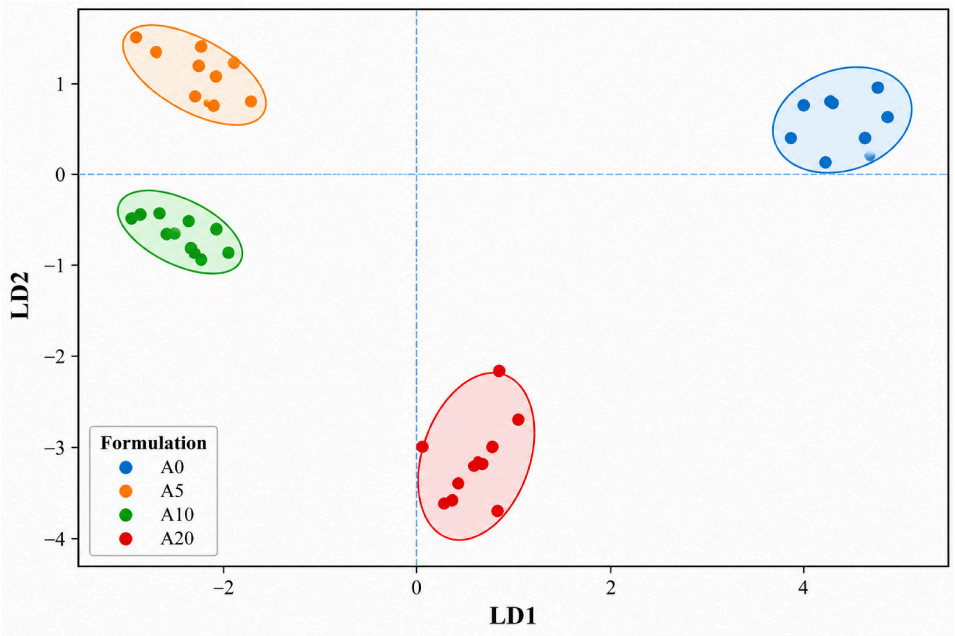


Figure 7. Linear discriminant analysis (LDA) score plot based on the portable electronic-nose responses obtained for beverage formulations containing increasing concentrations of *C. grandis* pulp: A0 (0%), A5 (5%), A10 (10%), and A20 (20%).

The separation observed after applying the supervised model indicates that the combined responses of the eleven analytical output channels contained sufficient discriminatory information to distinguish the beverage formulations according to *C. grandis* concentration. The progressive modification of the sensor fingerprint may be associated with the changes in volatile composition observed by HS-SPME-GC-MS, particularly the variation in monoterpenes, cinnamic derivatives and other volatile compounds following *C. grandis* incorporation. Similar applications have demonstrated the usefulness of combining E-nose responses with supervised chemometric approaches for the discrimination of food samples presenting different volatile profiles [23,39–41].

PLS-DA was applied as a complementary exploratory approach to examine the discriminatory structure of the electronic-nose response matrix. Although measurement-level classification can provide information about differences among the four beverage formulations, these results should not be interpreted as evidence of predictive performance for independently prepared batches. The original preparation identifiers were unavailable in the acquisition records, preventing the implementation of preparation-grouped cross-validation. Accordingly, the classification results are considered descriptive of the dataset under investigation, and no independent predictive performance estimates are reported.

To clarify the experimental structure underlying the chemometric analysis, Table 4 summarizes the rice-based beverage formulations, the number of independent preparations, and the instrumental measurements considered for each formulation. Three independent batches were prepared for each formulation, and ten electronic-nose measurements were obtained per formulation. Although these measurements were distributed among the independent preparations, the original acquisition records did not retain the correspondence

between individual measurements and their respective batches. Consequently, preparation-grouped cross-validation could not be implemented, and the PLS-DA results were interpreted as exploratory evidence of discrimination among the investigated formulations rather than as independently validated estimates of predictive classification performance.

Table 4. Experimental structure of the electronic-nose dataset used for exploratory chemometric discrimination of rice-based beverages.

Formulation	*C. grandis* Pulp (%)	Independent Preparations	E-Nose Measurements
A0	0	3	10
A5	5	3	10
A10	10	3	10
A20	20	3	10

Note. Ten instrumental measurements per formulation were distributed among three independently prepared batches. The original batch identifiers associated with individual measurements were not retained in the acquisition records. Consequently, preparation-grouped cross-validation could not be performed, and the chemometric results were interpreted as exploratory rather than as independently validated predictive estimates.

The exploratory multivariate analysis was intended to characterize differences in electronic-nose response patterns associated with the incorporation of *Cassia grandis* pulp into rice-based beverages. The observed discrimination should therefore be interpreted within the experimental dataset examined. Although the results suggest that the sensor array is responsive to compositional differences among formulations, further validation using independently identified preparation batches would be required to establish the robustness and generalizability of the classification model.

The exploratory sensor-response profiles revealed formulation-dependent differences across the electronic-nose output channels (Figure 8). The standardized responses exhibited distinct multivariate patterns among the four rice-based beverages, indicating that the sensor array was responsive to differences in sample composition. Nevertheless, these differences should be interpreted descriptively, since the absence of preparation-level identifiers prevented an independent assessment of classification performance (Figure 8).

3.6. Relationship Between E-Nose Responses and VOC Profiles

To investigate the chemical basis underlying the discrimination achieved by the portable electronic nose, partial least squares regression (PLSR) was used to explore the relationship between the multisensory responses and the volatile profiles determined by HS-SPME-GC-MS. The electronic-nose responses from the eleven analytical output channels were used as the predictor matrix (X), whereas the relative abundances of the volatile compounds identified by HS-SPME-GC-MS constituted the response matrix (Y). This multivariate approach provides complementary information to the classification models by allowing the sensor fingerprints to be interpreted in relation to changes in the chemical composition of the beverage headspace. The PLSR analysis revealed a structured relationship between the electronic-nose responses and the volatile composition of the four beverage formulations. The distribution of samples in the PLSR multivariate space followed the concentration-dependent pattern previously observed by PCA and supervised classification, with the control (A0) and the formulation containing the highest concentration of *C. grandis* pulp (A20) showing the greatest differentiation, whereas the intermediate formulations A5 and A10 exhibited comparatively greater similarity.

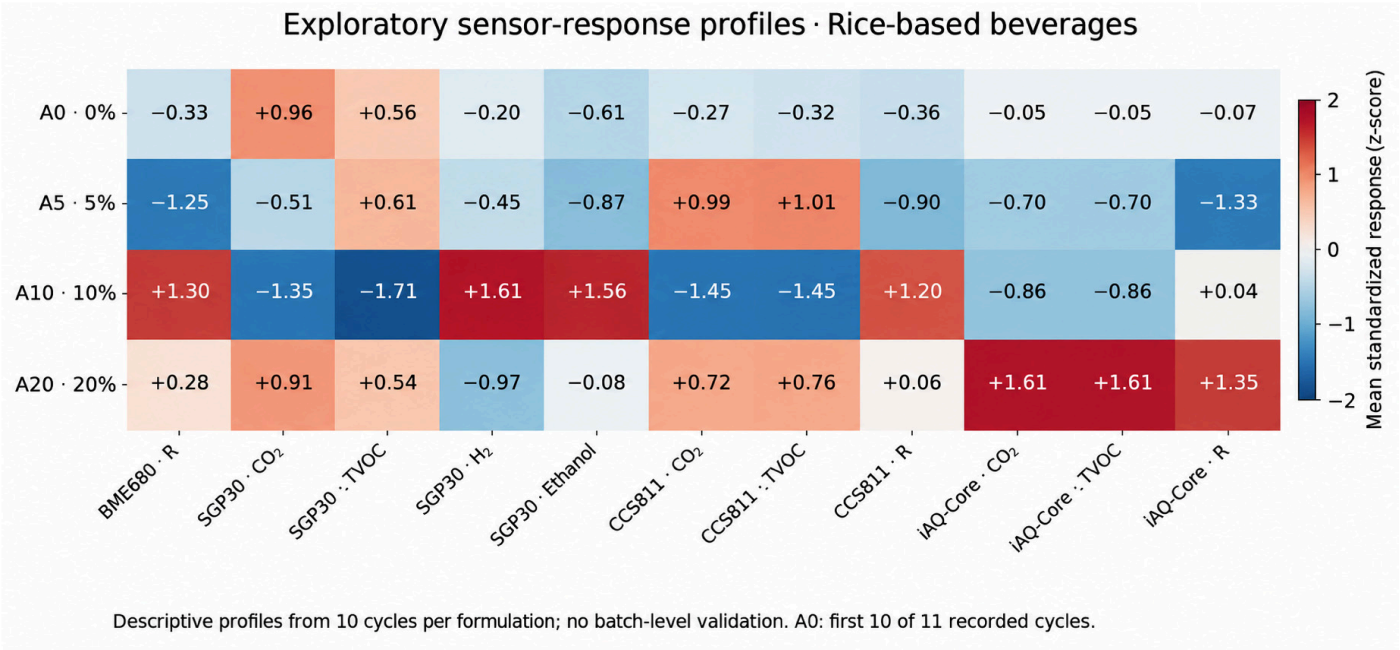


Figure 8. Exploratory sensor-response profiles of rice-based beverages containing 0% (A0), 5% (A5), 10% (A10), and 20% (A20) *Cassia grandis* pulp. The heatmap represents the mean standardized response of 11 electronic-nose output channels, calculated from ten measurement cycles per formulation. Standardization was performed independently for each channel to facilitate comparison of response patterns across formulations.

The relationships between sensor responses and volatile compounds are shown in Figure 9. The multivariate distribution suggested that the discrimination achieved by the electronic nose was associated with the changes in volatile composition produced by the incorporation of *C. grandis*. In particular, the HS-SPME-GC-MS results showed marked changes in monoterpenes and cinnamic derivatives across the formulations. Compounds such as linalool and α-terpineol increased markedly at the highest *C. grandis* concentration, whereas trans-cinnamaldehyde progressively decreased following pulp incorporation. These compositional changes therefore provide a plausible chemical basis for the concentration-dependent modification of the multisensory fingerprint.

A clear association was observed between the positive region of the first PLS component and volatile compounds whose abundance increased with the incorporation of *C. grandis*. In particular, linalool and α-terpineol were projected in the same region as sensors S1 and S2, suggesting that the response of these sensors contributed to capturing the changes in the volatile fingerprint associated with increasing pulp concentration. Hexanal and butanoic acid derivatives were located in the positive region of PLS component 1 but showed negative loadings on PLS component 2, in closer proximity to S3 and S4. These results suggest that different subsets of the MOS array contributed to the overall response to the chemically complex headspace rather than the discrimination being driven by a single sensor.

Conversely, trans-cinnamaldehyde and eugenol were located on the negative side of PLS component 1 and were associated with sensors S5 and S6. This opposite projection with respect to linalool and α-terpineol is consistent with the different concentration-dependent trends observed by HS-SPME-GC-MS. While the relative abundance of monoterpenic alcohols such as linalool and α-terpineol increased markedly with *C. grandis* incorporation, trans-cinnamaldehyde, which was particularly abundant in the control beverage, progressively decreased as the pulp concentration increased. Eugenol followed a similar decreasing tendency. Therefore, the opposite location of these compounds in the PLS space provides a chemically plausible explanation for the differentiation between the control and *Cassia gran-*

dis-containing formulations. The remaining monoterpenes, including α-pinene, β-pinene, camphene and β-myrcene, were predominantly distributed in the negative region of the PLS space and showed closer relationships with sensors S7 and S8.

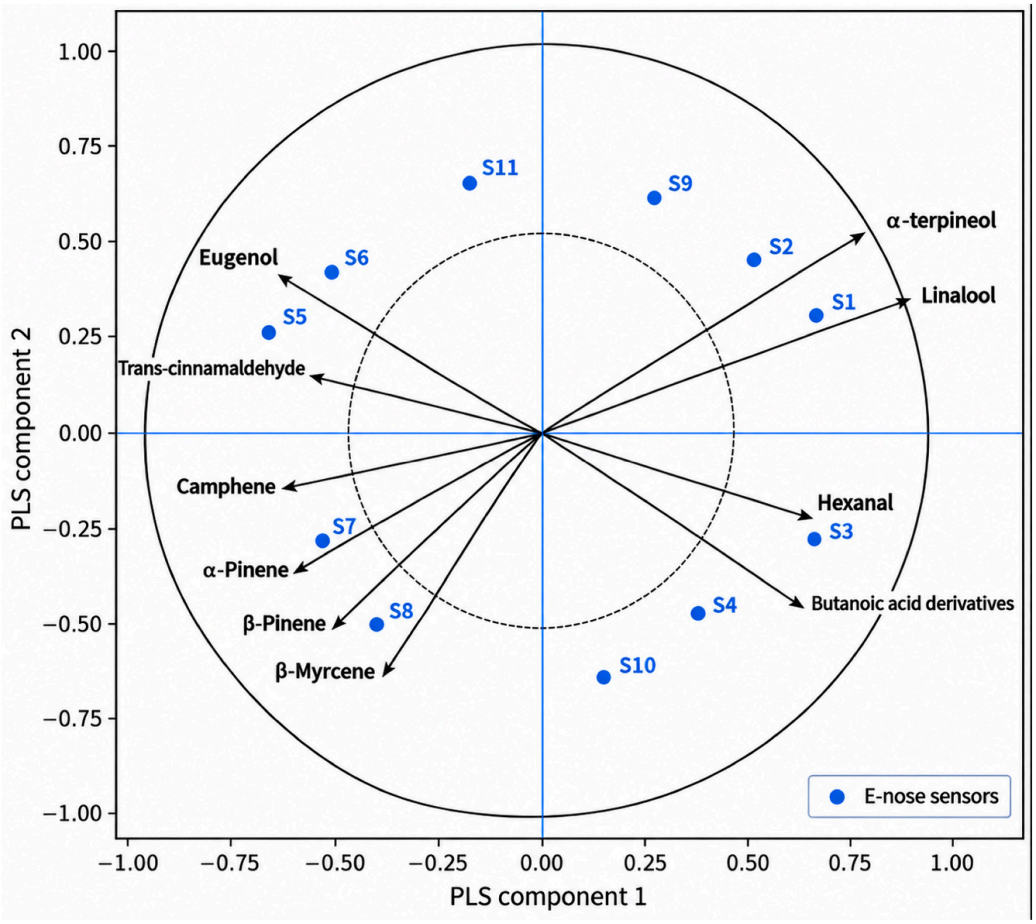


Figure 9. PLS correlation plot showing the relationships between electronic nose (E-nose) responses and selected volatile compounds identified by HS-SPME-GC-MS in *Cassia grandis* beverage formulations. Blue dots represent the eleven E-nose analytical channels (S1–S11), whereas black arrows represent the volatile compounds. Sensor identification: S1, BME680 (gas resistance); S2, SGP30 (eCO_2); S3, SGP30 (TVOC); S4, SGP30 (H_2 raw signal); S5, SGP30 (ethanol raw signal); S6, CCS811 (eCO_2); S7, CCS811 (TVOC); S8, CCS811 (sensor resistance); S9, iAQ-Core (eCO_2); S10, iAQ-Core (TVOC); and S11, iAQ-Core (sensor resistance).

The selected HS-SPME-GC-MS peak areas in rice beverages its presented in Table 5.

Table 5. Selected HS-SPME-GC-MS peak areas in rice-based beverages containing different proportions of *Cassia grandis* pulp.

Compound (as Reported)	A0 (0%)	A5 (5%)	A10 (10%)	A20 (20%)
Linalool	18.34	275.90	420.90	535.50
α-Terpineol	—	13.29	20.04	34.77
Eugenol	52.62	48.62	34.41	46.49
Hexanal	—	2.159	2.045	2.732
2-Propenal, 3-phenyl-(peak 1)	38.83	2.703	211.00	959.10
2-Propenal, 3-phenyl-(peak 2)	337.30	695.00	—	—

4. Conclusions

This study demonstrates the feasibility of a portable electronic nose combined with chemometric analysis for the rapid discrimination of rice-based beverages formulated with different concentrations of *C. grandis* pulp. Optimization of the analytical procedure established 20 mL of sample, 10 min of headspace equilibration, 60 s of adsorption, and 30 s of desorption as suitable operating conditions, providing a stable sensor response while maintaining a short measurement cycle. Under these conditions, theultisensoryr system showed satisfactory short-term repeatability, with RSD values below 4%, and adequate robustness against small deliberate variations in the experimental parameters.

HS-SPME-GC-MS confirmed that the incorporation of *C. grandis* substantially modified the volatile fingerprint of the beverages, particularly through changes in monoterpenes and cinnamic derivatives. These compositional differences were consistently reflected in the electronic-nose responses. PCA explained 96.18% of the total variance in the first two principal components and revealed a concentration-dependent distribution of the formulations, while LDA further confirmed their discrimination. The cross-validated PLS-DA model achieved an overall sensitivity of 90.0%, specificity of 96.7%, precision of 90.0%, and an F1-score of 0.900, with complete discrimination of the control (A0) and highest *C. grandis* concentration (A20) and limited misclassification between the intermediate formulations A5 and A10.

Furthermore, PLSR demonstrated a close relationship between the multisensor responses and selected VOCs determined by HS-SPME-GC-MS, particularly trans-cinnamaldehyde, linalool, and α-terpineol, supporting the chemical interpretation of the sensor fingerprints. Overall, the proposed portable electronic-nose methodology demonstrated promising potential for the rapid screening and discrimination of *Cassia grandis* beverage formulations under controlled experimental conditions. Nevertheless, the present evaluation was limited to short-term repeatability, robustness against minor experimental variations, and the differentiation of four predefined formulations. These findings do not establish a fully validated authentication method. Further investigations involving a broader range of independently prepared samples, inter-day reproducibility, sensor stability, matrix variability, and external validation are necessary before the method can be considered suitable for routine authentication and quality-control applications.

From a practical perspective, the proposed methodology is particularly relevant for the development and quality control of traditional horchata-type beverages enriched with *Cassia grandis* pulp. Although carao represents a promising source of bioactive compounds, its incorporation at high concentrations may introduce undesirable metallic, iron-like, and earthy sensory characteristics, potentially limiting consumer acceptability. In this context, the ability of the portable electronic nose to discriminate beverages containing different proportions of carao pulp (0, 5, 10, and 20%, w/v) provides a potential analytical approach for monitoring formulation consistency and verifying ingredient incorporation. The use of gas-sensor measurements offers the possibility of rapid, non-destructive screening without requiring routine chromatographic analysis. Nevertheless, the electronic nose does not directly assess taste or sensory acceptability, and further studies combining sensor responses with sensory evaluation and independent sample validation are required to establish its usefulness for formulation optimization.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/chemosensors14110253/s1, Figure S1: Short-term repeatability of the portable electronic nose under the optimized operating conditions. Normalized responses of the eleven sensors obtained during ten consecutive measurements of the same beverage sample using the same device and operator. Measurements were performed using 20 mL of sample, 10 min of headspace equilibration, 60 s of adsorption and 30 s of desorption; Table S1: HS-SPME-GC-MS

chromatographic peaks detected in rice-based beverages containing 0% (A0), 5% (A5), 10% (A10), and 20% (A20) *Cassia grandis* pulp.

Author Contributions: Conceptualization, D.M.V. and I.M.F.; Data curation, D.M.V., I.M.F. and V.M.F.; Formal analysis, D.M.V., V.M.F. and I.M.F.; Funding acquisition, I.M.F., F.P.-N. and D.M.V.; Investigation, D.M.V., I.M.F., V.M.F. and J.L.R. Methodology, D.M.V., F.P.-N. and I.M.F.; Project administration, I.M.F. and D.M.V.; Resources, I.M.F., V.M.F. and D.M.V.; Supervision, D.M.V.; Validation, D.M.V. and I.M.F. Visualization, I.M.F. and D.M.V.; Writing—original draft, I.M.F., D.M.V., V.M.F. and D.M.V.; Writing—review and editing, D.M.V. and F.P.-N. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the local government of Extremadura (ref. GR21121—AGA008) and the European Regional Development Fund (FEDER).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The authors confirm that the data supporting the findings of this study are available within the article and the raw data that support the findings are available from the corresponding author, upon reasonable request.

Acknowledgments: We would like to thank the European Union, the European Regional Development Fund (ERDF), and the Regional Government of Extremadura (ref. GR24151) and National Univer-sity of Agriculture (Honduras), for co-financing this work.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Naumovski, N.; Mellor, D.D.; Ranadheera, C.S. Functional beverages, from idea to functionality. *Beverages* **2020**, *6*, 71. [CrossRef]
2. Gupta, A.; Sanwal, N.; Bareen, M.A.; Barua, S.; Sharma, N.; Olatunji, O.J.; Nirmal, N.P.; Sahu, J.K. Trends in functional beverages: Functional ingredients, processing technologies, stability, health benefits, and consumer perspective. *Food Res. Int.* **2023**, *170*, 113046. [CrossRef]
3. Panou, A.; Karabagias, I.K. Composition, properties, and beneficial effects of functional beverages on human health. *Beverages* **2025**, *11*, 40. [CrossRef]
4. Lu, L.; Hu, Z.; Hu, X.; Li, D.; Tian, S. Electronic tongue and electronic nose for food quality and safety. *Food Res. Int.* **2022**, *162*, 112214. [CrossRef]
5. Danezis, G.P.; Tsagkaris, A.S.; Camin, F.; Brusic, V.; Georgiou, C.A. Food authentication: Techniques, trends & emerging approaches. *TrAC Trends Anal. Chem.* **2016**, *85*, 123–132. [CrossRef]
6. Müller-Maatsch, J.; van Ruth, S.M. Handheld devices for food authentication and their applications: A review. *Foods* **2021**, *10*, 2901. [CrossRef]
7. Cordeiro, F.M.M.; Bedoya, S.G.; Santos, D.A.P.; Santos, R.S.; Bacelar, T.V.M.; Buarque, F.S.; Simonelli, G.; Silva, A.C.M.; Lima, Á.S. *Cassia grandis* L.f. Pods as a Source of High-Value-Added Biomolecules: Optimization of Extraction Conditions and Extract Rheology. *Biomass* **2025**, *5*, 24. [CrossRef]
8. Marcía Fuentes, J.A.; Montero Fernández, I.; Zumbado Fernández, H.; Lozano Sánchez, J.; Santos Alemán, R.; Navarro-Alarcon, M.; Borrás-Linares, I.; Saravia Maldonado, S.A. Quantification of Bioactive Molecules, Minerals and Bromatological Analysis in Carao (*Cassia grandis*). *J. Agric. Sci.* **2020**, *12*, 88–94. [CrossRef]
9. Prada, A.L.; Amado, J.R.R.; Keita, H.; Zapata, E.P.; Carvalho, H.; Lima, E.S.; de Sousa, T.P.; Carvalho, J.C.T. Cassia grandis Fruit Extract Reduces the Blood Glucose Level in Alloxan-Induced Diabetic Rats. *Biomed. Pharmacother.* **2018**, *103*, 421–428. [CrossRef]
10. Aleman, R.S.; Marcia, J.; Page, R.; Kazemzadeh Pournaki, S.; Martín-Vertedor, D.; Manrique-Fernández, V.; Montero-Fernández, I.; Aryana, K. Effects of Yogurt with Carao (*Cassia grandis*) on Intestinal Barrier Dysfunction, α-glycosidase Activity, Lipase Activity, Hypoglycemic Effect, and Antioxidant Activity. *Fermentation* **2023**, *9*, 566. [CrossRef]
11. Montero-Fernández, I.; Manrique Fernández, V.; Pérez-Nevado, F.; Saravia-Maldonado, S.A.; Marcía Fuentes, J.A.; Martín-Vertedor, D. Enhancing Nutrient Profile and Reducing Acrylamide in California-Style Table Olives with *Cassia grandis* Fortification. *Foods* **2025**, *14*, 1426. [CrossRef]
12. Bueno, M.; Resconi, V.C.; Campo, M.M.; Ferreira, V.; Escudero, A. Development of a robust HS-SPME-GC-MS method for the analysis of solid food samples. Analysis of volatile compounds in fresh raw beef of differing lipid oxidation degrees. *Food Chem.* **2019**, *281*, 49–56. [CrossRef]

13. Coelho, E.; Lemos, M.; Genisheva, Z.; Domingues, L.; Vilanova, M.; Oliveira, J.M. Validation of a LLME/GC-MS methodology for quantification of volatile compounds in fermented beverages. *Molecules* **2020**, *25*, 621. [CrossRef]
14. Tomaz, I.; Šikuten, I.; Tuščić, V.; Rendulić, N.; Preiner, D.; Buljević, N.; Jagatić Korenika, A.-M.; Jeromel, A. Optimisation of SPME Arrow GC/MS method for determination of wine volatile organic compounds. *OENO One* **2024**, *58*, 1–13. [CrossRef]
15. Karakaya, D.; Ulucan, O.; Turkan, M. Electronic Nose and Its Applications: A Survey. *Int. J. Autom. Comput.* **2020**, *17*, 179–209. [CrossRef]
16. Singh, P.; Habiba, U.; Shafi, Z.; Noor, A.; Pandey, V.K.; Singh, R. Understanding the Concepts of Smart E-Nose Technology in Combination With Machine Learning for New Era of Food Safety: An Advanced Review. *Food Saf. Health* **2025**, *3*, 518–534. [CrossRef]
17. Sanislav, T.; Mois, G.D.; Zeadally, S.; Folea, S.; Radoni, T.C.; Al-Suhaimi, E.A. A Comprehensive Review on Sensor-Based Electronic Nose for Food Quality and Safety. *Sensors* **2025**, *25*, 4437. [CrossRef]
18. Vanaraj, R.; Bincy, I.P.; Mayakrishnan, G.; Kim, I.S.; Kim, S.-C. A Systematic Review of the Applications of Electronic Nose and Electronic Tongue in Food Quality Assessment and Safety. *Chemosensors* **2025**, *13*, 161. [CrossRef]
19. AOAC International. *Official Methods of Analysis of AOAC International*, 22nd ed.; Latimer, G.W., Jr., Ed.; AOAC International: Rockville, MD, USA, 2023.
20. CIE (Commission Internationale de l'Éclairage). *Colorimetry*, 3rd ed.; CIE Publication 15:2004; Commission Internationale de l'Éclairage: Vienna, Austria, 2004; ISBN 978-3-901906-33-6.
21. Sánchez, R.; Martín-Tornero, E.; Lozano, J.; Boselli, E.; Arroyo, P.; Meléndez, F.; Martín-Vertedor, D. E-Nose Discrimination of Abnormal Fermentations in Spanish-Style Green Olives. *Molecules* **2021**, *26*, 5353. [CrossRef]
22. Arroyo, P.; Meléndez, F.; Suárez, J.I.; Herrero, J.L.; Rodríguez, S.; Lozano, J. Electronic Nose with Digital Gas Sensors Connected via Bluetooth to a Smartphone for Air Quality Measurements. *Sensors* **2020**, *20*, 786. [CrossRef]
23. Sánchez-Baltasar, R.; Pérez-Nevado, F.; Martillanes, S.; Montero-Fernández, I.; Lozano, J.; Martín-Vertedor, D. Machine olfaction discrimination of Spanish-style green olives inoculated with spoilage mold species. *Food Control* **2023**, *147*, 109600. [CrossRef]
24. Cantwell, H. (Ed.) *Eurachem Guide: The Fitness for Purpose of Analytical Methods—A Laboratory Guide to Method Validation and Related Topics*, 3rd ed.; Eurachem: Bucharest, Romania, 2025.
25. Brereton, R.G.; Lloyd, G.R. Partial least squares discriminant analysis: Taking the magic away. *J. Chemom.* **2014**, *28*, 213–225. [CrossRef]
26. Geladi, P.; Kowalski, B.R. Partial least-squares regression: A tutorial. *Anal. Chim. Acta* **1986**, *185*, 1–17. [CrossRef]
27. López, R.; Wen, Y.; Ferreira, V. The remarkable effects of the non-volatile matrix of wine on the release of volatile compounds evaluated by analysing their release to the headspaces. *OENO One* **2024**, *58*, 7447. [CrossRef]
28. Liu, Y.; Qian, X.; Xing, J.; Li, N.; Li, J.; Su, Q.; Chen, Y.; Zhang, B.; Zhu, B. Accurate determination of 12 lactones and 11 volatile phenols in nongrape wines through headspace-solid-phase microextraction (HS-SPME) combined with high-resolution gas chromatography-Orbitrap mass spectrometry (GC-Orbitrap-MS). *J. Agric. Food Chem.* **2022**, *70*, 1971–1983. [CrossRef]
29. Williams, M.L.; Olomukoro, A.A.; Emmons, R.V.; Godage, N.H.; Gionfriddo, E. Matrix effects demystified: Strategies for resolving challenges in analytical separations of complex samples. *J. Sep. Sci.* **2023**, *46*, e2300571. [CrossRef]
30. Li, Y.; Zhang, L.; Wang, X.; Liu, H.; Wang, J.; Zhang, Q. Can Electronic Nose Replace Human Nose?—An Investigation of E-Nose Sensor Responses to Volatile Compounds in Alcoholic Beverages. *ACS Omega* **2023**, *8*, 16356–16363. [CrossRef]
31. Janta, P.; Vimolmangkang, S. Chemical profiling and clustering of various dried cannabis flowers revealed by volatilomics and chemometric processing. *J. Cannabis Res.* **2024**, *6*, 41. [CrossRef]
32. Ahamed, Z.; Seo, J.K.; Eom, J.-U.; Yang, H.-S. Volatile compounds for discrimination between beef, pork, and their admixture using solid-phase-microextraction-gas chromatography-mass spectrometry (SPME-GC-MS) and chemometrics analysis. *Food Sci. Anim. Resour.* **2024**, *44*, 934–950. [CrossRef]
33. Fang, X.; Liu, Y.; Xiao, J.; Ma, C.; Huang, Y. GC–MS and LC-MS/MS metabolomics revealed dynamic changes of volatile and non-volatile compounds during withering process of black tea. *Food Chem.* **2023**, *410*, 135396. [CrossRef]
34. Tian, S.; Guo, H.; Zhang, M.; Yan, H.; Wang, X.; Zhao, H. Rapid authentication of *Chaenomeles* species by visual volatile components fingerprints based on headspace gas chromatography-ion mobility spectrometry combined with chemometric analysis. *Phytochem. Anal.* **2022**, *33*, 1198–1204. [CrossRef]
35. Roussel, S.; Forsberg, G.; Grenier, P.; Bellon-Maurel, V. Optimisation of electronic nose measurements. Part II: Influence of experimental parameters. *J. Food Eng.* **1999**, *39*, 9–15. [CrossRef]
36. Knobloch, H.; Turner, C.; Spooner, A.; Chambers, M. Methodological variation in headspace analysis of liquid samples using electronic nose. *Sens. Actuators B Chem.* **2009**, *139*, 353–360. [CrossRef]
37. Fonollosa, J.; Rodríguez-Luján, I.; Trincavelli, M.; Vergara, A.; Huerta, R. Chemical discrimination in turbulent gas mixtures with MOX sensors validated by gas chromatography-mass spectrometry. *Sensors* **2014**, *14*, 19336–19353. [CrossRef]
38. Shi, X.; Li, Y.; Huang, D.; Chen, S.; Zhu, S. Characterization and Discrimination of Volatile Compounds in Roasted Arabica Coffee Beans from Different Origins by Combining GC-TOFMS, GC-IMS, and GC-E-Nose. *Food Chem.* **2025**, *481*, 144079. [CrossRef]

39. Wei, G.; Dan, M.; Zhao, G.; Wang, D. Recent Advances in Chromatography-Mass Spectrometry and Electronic Nose Technology in Food Flavor Analysis and Detection. *Food Chem*. **2023**, *405*, 134814. [CrossRef]
40. Cervellieri, S.; Lippolis, V.; Mancini, E.; Pascale, M.; Logrieco, A.F.; De Girolamo, A. Mass spectrometry-based electronic nose to authenticate 100% Italian durum wheat pasta and characterization of volatile compounds. *Food Chem*. **2022**, *383*, 132548. [CrossRef]
41. Wang, Z.; Zhang, Y.; Yang, X.; Wang, Z.; Xu, T.; Liu, J.; Wang, J. Effect of milling degree on volatile profiles of cooked rice determined by electronic nose and HS-SPME-GC-MS. *Cereal Chem*. **2023**, *100*, 1301–1313. [CrossRef]

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.