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Experimental design and chemometric techniques applied in electronic nose analysis of wood-aged sugar cane spirit (*cachaça*)

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ABSTRACT

Wood barrel aging distilled beverages corresponds to a process capable of aggregate flavor compounds that may change sensory profiles and improve distillates quality. The analysis of the flavor compounds to determine degree of maturation of distillate relies most on costly techniques such as chromatography, so that more affordable and less laborious technologies may be suitable for wood-derived flavor determination in beverages, such as digital olfactometry. An electronic nose system reliability may take into consideration appropriate sample preparation method in order to obtain optimal performance over detection of odor compounds. An optimized pre-injection method was established for cachaça analysis in an electronic nose system after an experimental Rotational Central Composite Design, considering the sample preparation factors: incubation temperature, samples ethanol content, stirring period and equilibrium period. Raw data underwent the chemometric technique Multiple Co-inertia Analysis for feature extraction in prior to optimization design. The chemometric approach for data pre-treatment and analysis demonstrated favorable performance for electronic nose application. The optimal sample preparation included dilution of the aged distillate to lower ethanol content (10% v/v), sample incubation at 49 °C and excluded stirring and equilibrium stages, leading to a simpler and less time-consuming protocol.

1. Introduction

Wood aging distilled beverages has been used along centuries in order to improve distillates' flavor, being imperative for high quality beverages such as brandy, whisky, wine spirits [1], and eventually rum. The aging process is one of the most important factors that define distilled spirits quality, and although it is not mandatory in Brazilian sugar cane spirit (*cachaça*) production [2], it is becoming recurrent among appreciated brands focused on product innovation and highest added value.

According to IBRAC [3], exportation of cachaça reached more than 60 countries in 2017, adding up to US$ 15.8 million in revenues. This amount corresponds to an increase of 13.4% in relation to the past year, while in the same period, it was reported an increase of only 4.3% in exported volume, indicating a proportionally greater increase in revenue compared to the exported volume growth, reflecting a scenario of more added value and better quality cachaças gaining international visibility.

Cachaça production may pursue the Good Manufacturing Practices (GMP) to achieve higher quality production. Besides aging process being a critical control point [1], considering factors such as endogenous variations (e.g. wood species, cachaça composition in prior to aging) and exogenous (e.g. cellar environment, time-length), it has also a difficulty to qualitatively analyze the distillate along the aging process, involving subjective decisions and complex cognitive process performed by expert tasters or panel that might be in constant sensory training to execute the task of characterize the distillate and meet the quality standards.

Recent studies investigated the changes in composition of distilled beverages during aging process in wood barrels, remarking aging congeners formation pathways through lignin degradation along time [4,5]. Those reactions and compounds concentrations in final beverage correspond to actual quality parameters, being even applicable for fraud detection [6]. The kinetics of lignin degradation rely on numerous factors besides aging time-length, such as barrel number of previous uses, warehouse temperature, and initial ethanol content of the spirit [7]. Moreover, Driver [8] remarks a new tendency in the whisky market

Abbreviations: DHS, Dynamic Headspace; GC-MS, Gas Chromatography-Mass Spectrometry; GMP, Good Manufacturing Practices; HPLC, High-Performance Liquid Chromatography; LDP, Lignin Derived Products; MCOA, Multiple Co-inertia Analysis; MOS, Metal Oxide Semiconductor; RCCD, Rotational Central Composite Design; SHS, Static Headspace; VOC, volatile odor compound.

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quality parameters, indicating that age will be lesser weighted as determinant of quality as other means of differentiation, innovation and premiumization may rise.

Quality assessment of aged spirits is currently based on chromatographic techniques, namely HPLC and GC [4,9–13,14,15]. Those techniques generally require consumables, including solvents and pure substances, and intensively-trained work force, which may be financially unfavorable for smaller industries considering the number of samples involved in product development. The small cachaça producers may be strict with compliance of GMP, even though they still have scarce access to online analysis to help with instant decision making. In order to appease this situation, a suitable monitoring system for aged cachaça encompassing reliability, easy-to-use and affordable would fulfill the current scenario and complement quality assessment procedures in industry.

Regarding the previous characteristics demanded for a new device, a potential solution to be considered is an electronic nose (or digital olfactometer). As idealized by Jack [16], an instrument capable of reporting flavor real-time data along production stages in spirits production would be a favorable scenario for quality warranty. At the perspective of flavor analysis, a qualitative approach may be more suitable, once high-precision quantification methods are already well established (namely chromatography), and likely achievable. So that, devices able to capture a "smellprint", combined to pattern recognition trained algorithm, correspond to suitable solutions for flavor assessment [17–19], applicable to beverages industry.

The development of such device, dedicated to small producers of cachaça productive control and monitoring, and based in electronic nose technology may encompass metal oxide semi-conductor gas sensors responsible for transform chemical stimuli, coming from samples headspace, into digital signal for interpretation by pattern recognition machine learning techniques. The applicable algorithms demand data from known samples to train over the classification task (supervised learning), which may have high quality and be representative considering the intended task to obtain satisfactory performance results and consolidate a robust system [20].

Thus, flavor online analysis in industries may support considerable improvements in product standardization, monitoring and assisted decision-making to achieve higher quality and strengthen market of aged cachaça. In favor of obtaining representative data in an electronic nose system, it must take into consideration optimized parameter for sample preparation in prior to injection. In this scenario, the most relevant volatile odor compounds from samples may be found in headspace and detrimental factors' influence over sensors operation may be minimized (e.g. high moisture).

Suitable sampling techniques may attend demands such as recovery of compounds of interest, operational speed and simplicity [21]. These characteristics take into account factors such as sample incubation temperature, stirring period, ethanol content of sample and equilibrium time, that may impact on the recuperation of volatile and semi-volatile compounds to be analyzed.

Physical properties of the sample, such as increasing samples' temperature or longer equilibrium period, may interfere on aroma substances volatility and consequently lead to the concentration in headspace [22]. Physicochemical properties such as sample dilution rate or ethanol content may modulate aroma compounds hydrophobicity, providing a selective release from the sample to the headspace [23].

Stirring samples in headspace analysis represent the so-called Dynamic Headspace (DHS) method, which is observed in sample preparation techniques for electronic noses devices analysis [21,24,25], even presenting better performance for samples discrimination when compared to other techniques such as Static Headspace extraction [21]. Static Headspace (SHS) corresponds to the most common technique among electronic noses systems [21,26–28], mainly due to its simplicity [21], and provides favorable control when associated to vapor-flow injection [29,30].

Considering the numerous possible combinations of factors and the necessity to determine optimal conditions for a specific situation, an appropriate experimental design may be appropriate to minimize the necessary number of runs, maximize performance, obtain the best results and turn feasible the optimization task [31,32]. So that, the methodology selected corresponds to rotational central composite design (RCCD), which merges statistical and mathematical procedures to model the relationships among independent variables (factors or parameters tested) and dependent variable (response) [33,34].

RCCD experiment is based on testing combinations of factors in different levels, considering repetition of central points along the experiment, intercalating with factorial points, for process stability verification, and axial runs for second-order model fitting and checking adequacy [35], the last representing an appropriate strategy for eventual saturation-type response displayed by gas sensors [36].

Despite the considerable reduction of necessary tests, RCCD may consider the feasibility of sequential runs, which may be restrictive considering experimental nature and conditions. So that, a desirable solution relies on a design technique named "confounding", that correspond to an arranging in smaller-size blocks containing a determined number of treatment combinations in one replicate. Myers et al. [35] states a consideration over this method based on incomplete blocks design but it is compensated by the special structure of the experimental design construction and analysis.

The present study intended primarily to define the optimal parameters for preparation of sugar cane aged spirits samples for injection in electronic nose prototype, considering incubation temperature, sample dilution, stirring and equilibrium periods. Likewise, it was planned to evaluate the sensors array susceptibility to different sample preparation parameters. The objective of obtaining optimized procedure from surface responses and a fitting model considered suitable implementation of signal data pre-treatment based on chemometric approach.

2. Material and methods

2.1. Samples

Samples of Brazilian sugar cane spirit aged in different oak barrels (Table 1) were selected to perform the optimization method based on RCCD. The sugar cane spirit was produced in 2011 in the distillery of the Agri-Food Department of the College of Agriculture, University of São Paulo. Sugar cane juice was extracted, fermented and further distilled following double distillation, based on the method used in the production of whisky [37]. The barrels were acquired from a French cooperage. The oak woods underwent identical production process. The barrels were constructed with an average volume of 225 L. Aging process started with sugar cane spirit standardized at 55% ABV and was conducted at room temperature (22 ± 5 °C), relative humidity of 55 ± 10%.

The characterization of the aged spirits was based on aging-marker compounds, namely products of ligning degradation, analyzed by HPLC methodology [5,10,11]. This method of classification of distillates includes characteristics beyond the period of barrel aging in years (e.g. 12 or 18-year-old whisky). The maturation parameter was selected as class variable [20] for further training of algorithms to be implemented in electronic nose data analysis.

Considering that maturation parameter is based on LDPs, which present low volatility, and that electronic nose systems are intrinsically based on volatile composition analysis, the proposed e-nose system intends to correlate both responses and generate a classification model to estimate the samples' level of maturation based on the headspace composition. A similar association considering HPLC data and volatile profile from electronic nose for wheat contamination analysis was successfully implemented by Lippolis et al. [38].

Table 1
Composition of LDP (mg/L) of samples employed for RCCD test session.

Wood	Toast level	Use condition	Aging period (months)	Sample Code	LDP parameter			Maturation level [5]
					Sum S	Sum C	Sum Acs	
French Oak	Medium	Extensive	120	A	17.2	12.4	11.3	Moderate-aged (5–10 yrs)
French Oak	Medium	First fill	36	B	15.2	6.3	9.4	Young (<5 yrs)

LDP – Lignin Derived Products, Sum S – Sum of sinapaldehyde, syringaldehyde and syringic acid, Sum C – Sum of coniferaldehyde, vanillin and vanilic acid, Sum Acs – Sum of vanilic acid and syringic acid.

Table 2
HPLC method gradient elution and wavelengths specifications [2].

Time (min.)	Solvent A (%)	Solvent B (%)	Wavelenght (nm)
0	100	0	271
6	100	0	280
25	60	40	276
34	60	40	320
37	60	40	320
40	100	0	271
45	100	0	271

Solvent A - water: acetic acid, 98:2 (v/v); Solvent B - methanol–water–acetic acid, 70:28:2 (v/v/v).

2.2. High performance liquid chromatography analysis (HPLC)

In order to obtain the maturation degree [5] for samples A and B, the quantification of aging congeners was performed over the samples analyzed using high-performance liquid chromatography (HPLC; Shimadzu, model LC-10AD), equipped with two Shimadzu LC-20AD pumps, a UV–vis detector Shimadzu SPD-20A, a system controller CBM-20A and an autosampler. The standard compounds used in this study were vanillin, vanillic acid, syringaldehyde, sinapaldehyde, syringic acid and coniferaldehyde, all produced by Sigma-Aldrich (St Louis, MO, USA), purity >99%. The HPLC method employed in this study had two mobile phases composed of water: acetic acid, 98:2 (v/v) (Solvent A), and methanol–water–acetic acid, 70:28:2 (v/v/v) (Solvent B) with gradient elution (Table 2), total flow of 1.25 mL/•min and volume of injection 20 μL. A pre-column Shimadzu VP-ODS (1 cm × 4.6 μm) and a C18 reversed-phase column model, Shim-pack VP-ODS (4.6 mm × 25 cm × 5 μm), both thermostatized at 40 °C, were used. The UV detector was programmed at variable wavelengths (Table 2). The sample preparation involved previous filtering samples using Millex-HV filter with PVDF membrane (diameter 13 mm, pore size 0.45 μm). The quantification of the compounds was performed based on external calibration curves of six standard concentration points [2].

2.3. Electronic nose prototype

The electronic nose device developed for this research included metal oxide semiconductor (MOS) sensors listed in Table 3, a microcontroller, an air pump, internal ventilation unit in sensor chamber, sample flask and software required for data acquisition, processing and statistical analysis (Fig. 1). The choice of MOS sensors was considered due to their considerable chemical stability, long life, low humidity interference, affordable cost, high sensitivity and applicability for a wide range of chemicals and foods [39–42].

2.4. Experimental design

The experiment investigated four factors: sample incubation temperature during established time (8 min), the ethanol content in samples (dilution), stirring period and equilibrium period length. In order to obtain a model that considers quadratic behavior of factors in the response (Table 4), a combination of factors comprising a central point (0), its upper (+1) and lower (−1) proportional variations, and axial points (+α and -α) were tested. The ranges proposed for coded levels of each factor were based on previous researches which optimized headspace extraction [43]. According to previous studies [44–46] sample preparation for electronic nose analysis considered as levels the following factors: incubation temperature (greater than 40 °C) and ethanol content (lower than 12% $v \cdot v^{-1}$). Lower temperature considered in experimental design was defined as room temperature (25 °C). Higher ethanol content at 40% ($v \cdot v^{-1}$) was considered because it represents the level found in commercial distillates. Parameters such as stirring period and equilibrium period length were also proposed due to their influence on headspace extraction according to Henry's constant [47].

Table 3
Description of sensors employed in electronic nose prototype and their application according to manufacturer (Hanwei Electronics Co.).

Sensor	Main application
MQ2	LPG (Liquid Petroleum Gas), Methane, Propane, Butane, Hydrogen (H_2), Alcohol, Natural Gas, flammable
MQ3	Alcohol, Ethanol, Benzene, hexane
MQ4	LPG, Methane, H_2, Carbon monoxide (CO), Ethanol
MQ5	H_2, LPG, Methane, Propane, Butane, Ethanol, CO, iso-butane, Propane
MQ6	LPG H_2, Methane, Propane, Butane, Ethanol, CO, iso-butane, Propane
MQ7	CO, H_2, LPG, Methane, Ethanol
MQ8	H_2, LPG, Methane, CO, Ethanol
MQ9	CO, Methane, LPG, Flammable gas
MQ135	Ammonia, Benzene, Ethanol, CO_2, CO, NH_4

2.5. Data treatment procedure

The response variable corresponds to the pair-wised distance between the two distinct samples evaluated according to each pre-injection procedure. Sensor signals were transformed in prior to data analysis. The steady-state characteristic considered [40] was calculated as follows: signals from each sensor were corrected in relation to baseline readings ($R_t = (r_t - r_b)/r_b$), where R_t is the standardized signal, r_t represents the raw signal for sample at the steady-state of injection, and r_b is the baseline signal. Finally, signals were filtered by Weighted Median (WM) method [48], considering a calculation window correspondent to ten previous samples, and weight ratio between current read and median ($\alpha/(1-\alpha)$) with $\alpha = 0.1$, in order to obtain a smoother signal [49].

The pre-treated sensor signals obtained were further pretreated employing a Standard Normal Variate (SNV), in order to eliminate additive effects [50–52], then feature extraction performed by Principal Component Analysis (PCA), which is a technique of transformation of original data, extracting most of the information into uncorrelated variables called principal components, containing most of existing variance among the data points [42].

The PCA scores generated for each sensor were analyzed by Multiple Co-inertia Analysis (MCOA) [53], which effectively enables the simultaneous comparison of numerous tables through variance optimization among individuals and correlation increase among scores of those individual tables [54]. This method provides synthetic final global coordinates (scores) and percentage of variance explained (loadings) that were employed in Euclidian weighted distance calculation [55]. Those resulting values obtained from ChemFlow [56] were computed in Statistica 13.5.0 [57] software for ANOVA and Fitted Surface Response modeling analysis.

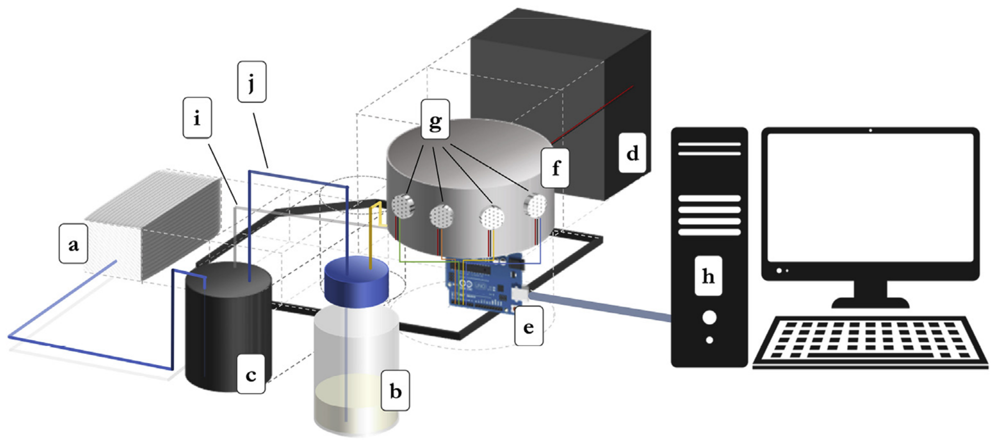

Fig. 1. Scheme of the assembled electronic nose. a – air pump; b – sample flask; c – air drier pre filter; d – power supply; e – microcontroller for data conversion; f – gas sensors' chamber; g – MOS gas sensors; h – computer for data acquisition; i – purge pipeline; j – injection air pipeline.

Table 4
Levels of factors analyzed in two sessions of RCCD experiments for sample preparation optimization.

Situation	Variables			
	Incubation Temperature (°C)	Ethanol Content (% $v \cdot v^{-1}$)	Stirring Period (min.)	Equilibrium Period (min.)
1	48,9 (+1)	33,9 (+1)	4,8 (+1)	2 (−1)
2	48,9 (+1)	33,9 (+1)	1,2 (−1)	2 (−1)
3	48,9 (+1)	16,1 (−1)	4,8 (+1)	8 (+1)
4	31,1 (−1)	33,9 (+1)	1,2 (−1)	8 (+1)
5	48,9 (+1)	16,1 (−1)	1,2 (−1)	8 (+1)
6	31,1 (−1)	16,1 (−1)	4,8 (+1)	2 (−1)
7	31,1 (−1)	33,9 (+1)	4,8 (+1)	8 (+1)
8	31,1 (−1)	16,1 (−1)	1,2 (−1)	2 (−1)
9	40 (0)	25 (0)	3 (0)	5 (0)
10	40 (0)	25 (0)	3 (0)	5 (0)
11	25 (-α)	25 (0)	3 (0)	5 (0)
12	55 (+α)	25 (0)	3 (0)	5 (0)
13	40 (0)	10 (-α)	3 (0)	5 (0)
14	40 (0)	40 (+α)	3 (0)	5 (0)
15	40 (0)	25 (0)	0 (-α)	5 (0)
16	40 (0)	25 (0)	6 (+α)	5 (0)
17	40 (0)	25 (0)	3 (0)	0 (-α)
18	40 (0)	25 (0)	3 (0)	10 (+α)
19	40 (0)	25 (0)	3 (0)	5 (0)
20	40 (0)	25 (0)	3 (0)	5 (0)

3. Results

3.1. Chemometric approach

After MCOA performed over data originated from signals from all sensor array, coming from both samples A and B that underwent the twenty distinct design conditions, a multidimensional plan was obtained presenting presented over 95% of total variance (Fig. 2). Samples A and B pairwise comparison was done taking into consideration the variance weighted coordinates (scores), which was approached as an intra-situation variation metric.

3.2. Sensor array performance

In order to verify which sensors displayed more responsiveness for paired distinction between samples, weighted mean and standard deviation of distances between samples A and B were calculated from individual (by-sensor) MCOA scores, considering all twenty situations tested (Fig. 3). These metrics may relate a higher variation to a greater sensibility of each sensors to variations in experimental conditions tested.

The sensors that resulted on greater variation on weighted distance values obtained for the experimental conditions tested were MQ 4, 6, 7 and 135, which were respectively developed for quantification of hydrocarbons (methane, propane and butane), LPG (isobutane and propane), carbon monoxide, and aromatic compounds plus alcohol. The observed range existing for each of the sensors may be related to sample properties [23] that directly affect sensors responses, such as favoring volatilization of molecules with properties analogous to those presented by compounds for which the sensors were developed.

Considering the observed behavior of sensors, it is possible to state that there are sensors more sensible to variations on sample treatment. So that, optimum conditions choice may take into consideration their responses. Lower values of weighted distance (lower distinction power of the sensor array) may be associated to differentiation on concentration of compounds of interest in the headspace inject into sensors' chamber.

Among the four sensors with greater variation, MQ 135 behavior may represent an important role in electronic nose assemble for cachaça analysis. Voss et al. [39] reported that, for the ethanol quantification in beer, MQ 135 response was redundant for performance improvement of the mentioned task, possibly due to a lower affinity or specificity to ethanol detection. Regarding other volatile odor compounds (VOCs) present in aged cachaça, its contribution may be relevant for classificatory task and increase discriminant ability after optimized method for sample preparation.

3.3. Experiment design approach

Concerning the optimization design, significant ($\alpha = 0.05$) modeling results were observed for linear effect of stirring period, linear and quadratic effects for ethanol content, and significant linear interactions for incubation temperature versus stirring and equilibrium period, and ethanol content versus stirring period. Incubation temperature isolated was not a significant factor at $\alpha = 0.05$ for model fitting analysis. Although, this factor's higher and lower levels displayed an important increase over multivariate distance when combined to the other inspected factors (Fig. 4).

Among the factors explored, ethanol content displayed unanimously better conditions for multivariate differentiation between samples at lower concentrations (Fig. 5). This behavior may be related to sensors construction and to already reported ethanol and interferences on MQ sensors [21]. Besides, major water content may benefit the volatility of non-polar compounds [58] that may interact more specifically with sensors that presented greater variability in different conditions tested (MQ 4, 6, 7 and 135). Concerning the ethanol content relation to stirring and equilibrium periods, both presented more important sample differentiation when ethanol content was at the lower and the other factors at

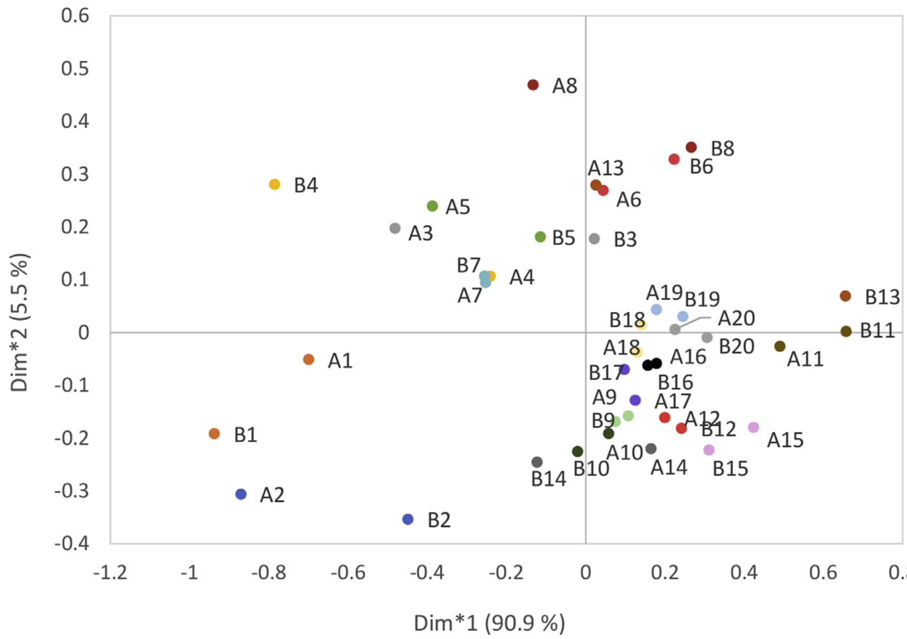

Fig. 2. Representation of multivariate coordinates (scores from MCOA performed over total sensor array signals) between samples A and B analyzed after different experimental pre-injection situations (1–20).

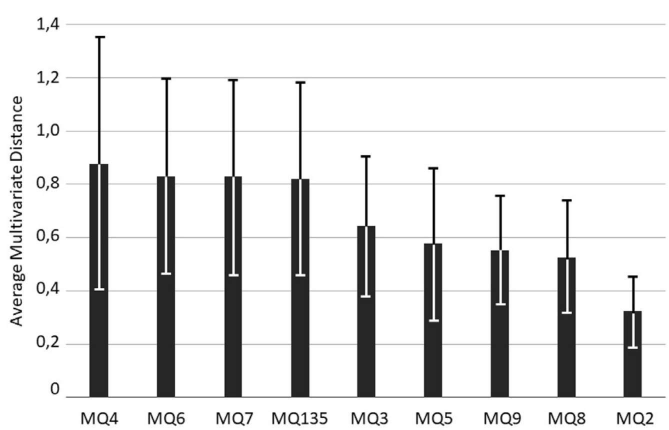

Fig. 3. Centrality and variation metrics, by sensor, of multivariate distance obtained for each injection condition tested.

higher levels.

4. Discussion

The model determined from coded variables (Equation (1)) in RCCD experiment presented R^2 and adjusted R^2 respectively equal to 0.9344 and 0.8962, which corresponds to a favorable ratio of total variance explained by the model over experimental data.

$$Z = -0.85645 \times E + 0.07993 \times E^2 - 0.025945 \times S + 0.055023 \times I \times E - 0.087221 \times I \times Eq - 0.053161 \times E \times S \tag{1}$$

In order to obtain the optimum conditions for each factor to enhance electronic nose differentiation capacity for aged sugar cane spirit samples, a desirability profile was performed considering the predicting interval (-α to +α) of proposed model for coded variables (Fig. 6).

According to desirability results, it was possible to obtain optimum values for each factor tested during sample preparation before injection in electronic nose. The optimum un-coded values for factor correspond to incubation temperature of 49.2 °C, and zero for magnetic plate stirring period and equilibrium time. Those levels represent a maximum

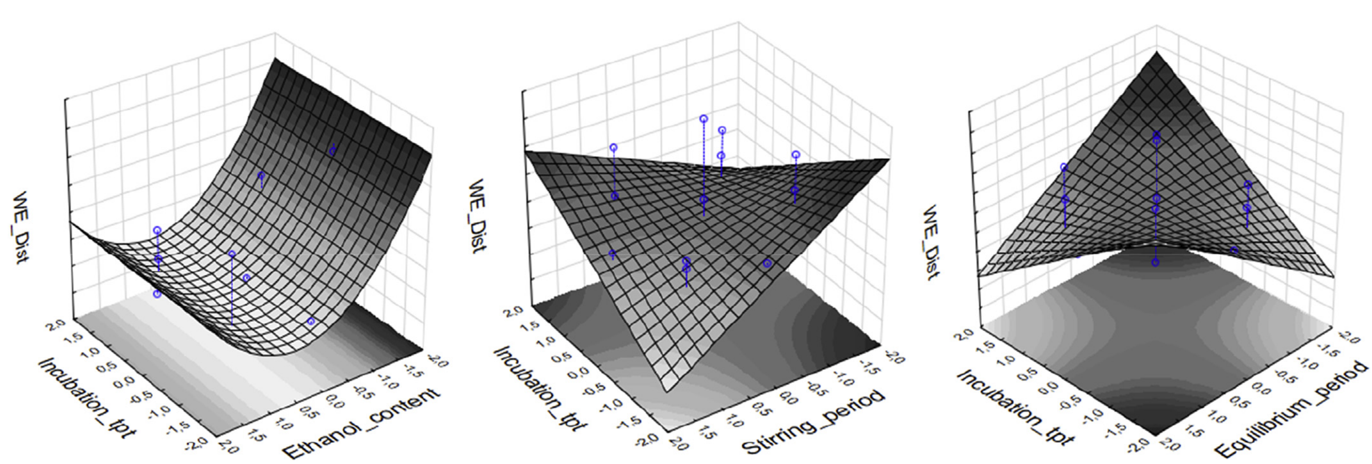

Fig. 4. Incubation temperature response in combination with other factors in sample preparation for electronic nose readings.

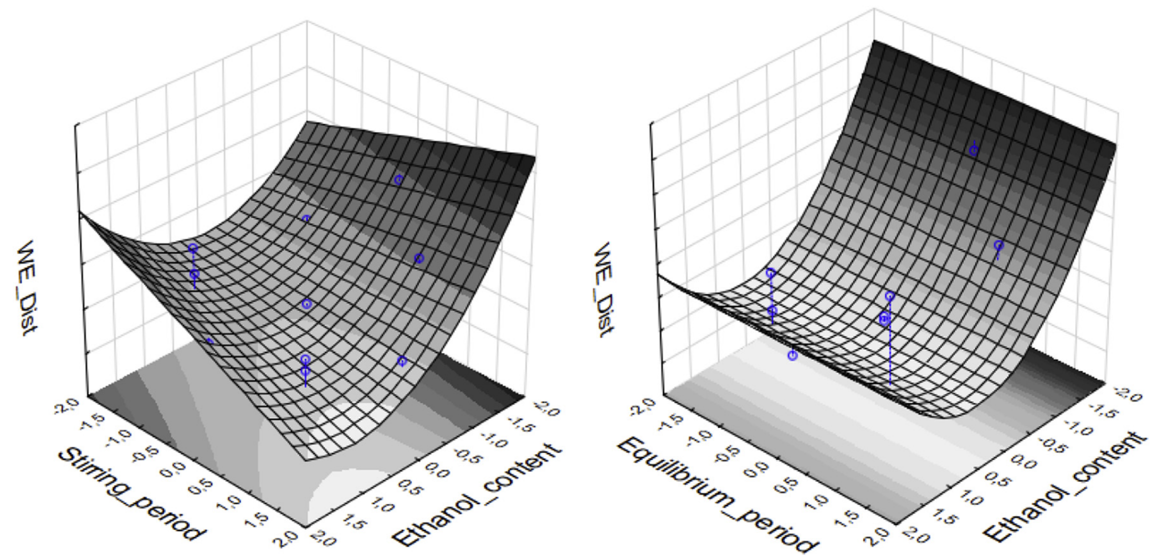

Fig. 5. Response surfaces relating sample preparation factors (ethanol content versus stirring period and equilibrium period) for electronic nose differentiation of samples.

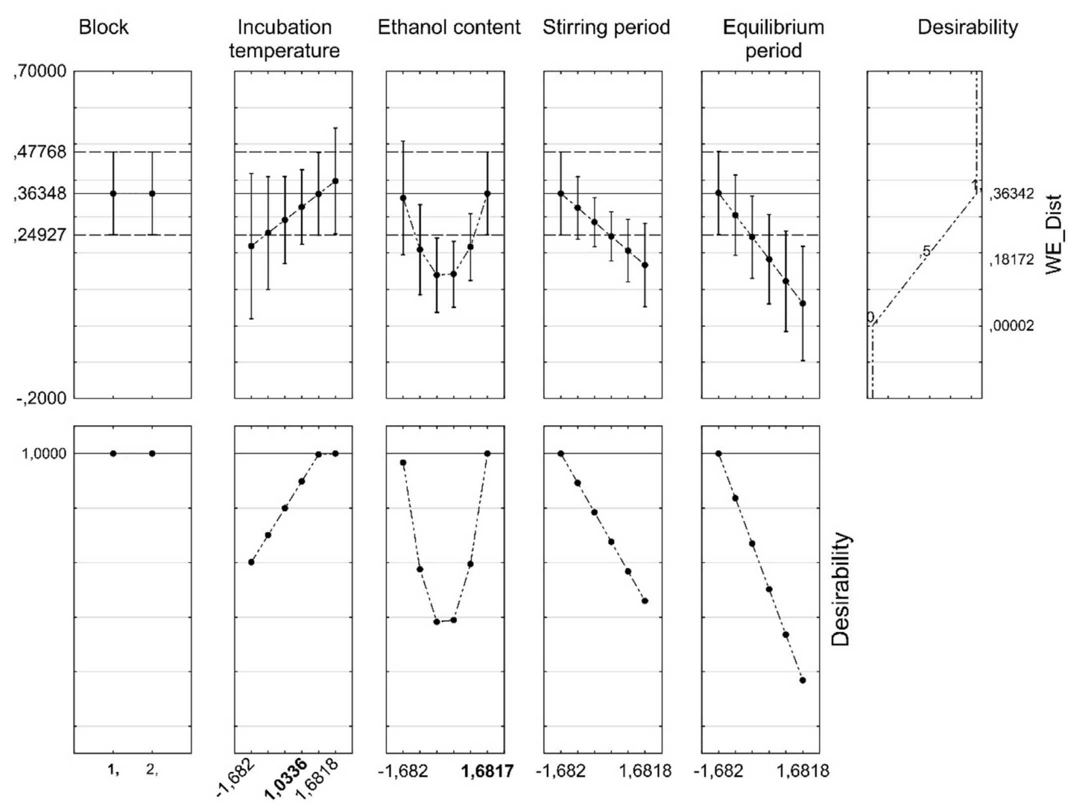

Fig. 6. Desirability profile obtained for factors explored in RCCD.

desirability for the model obtained. Ethanol content behavior, on the other hand, present a quadratic displaying higher desirability for 40% ($v \cdot v^{-1}$), although, the level of 10% ($v \cdot v^{-1}$) displayed a closely high desirability level (0.967).

The adoption of lower level of ethanol content for optimized sample preparation for electronic nose readings, may not only influence positively on aging compounds' solubility [58] but also avoiding sensors poisoning effect as well. The diluted sample preparation matches the approach describe for human panel sensory analysis in whisky quality assessment, where samples are standardized at around 20% alcohol by volume in order to avoid burning sensation caused by ethanol [16] and increase the level of certain volatile compounds in headspace [59].

Even though the isolated effects of incubation temperature were not significant for modeling, an optimum condition was observed regarding the established conditions for its interactive factors (stirring and equilibrium period). The desirability for incubation temperature reached a maximum at 49.2 °C, same value obtained at higher incubation temperature, which may indicate a saturation behavior of volatile compounds in headspace during sample preparation for electronic nose injection. It is known that cold temperature of samples during sensory analysis decreases flavor intensity perceived by panel of tasters due to direct impact on volatility of compounds of interest [60]. Dilution warms whisky samples because of exothermic reaction that occurs during mixture of ethanol and water, enhancing the spirits' flavor for the panel evaluation [61].

The results for stirring and equilibrium period lead to dismissing those sample preparation procedures, which may increase analysis productivity by eliminating time-consuming steps for electronic nose system. Moreover, a part of hardware - namely a magnetic stirring plate - is dismissed according to the desirability profile. Stirring and equilibrium period optimized at lower level may be related to headspace composition equilibrium achieved in absence of heating, due to the fact of sample preparation being sequential.

As expected, this fact points for an important role of molecules volatility in electronic nose differentiation between samples. The volatilization phenomenon is based on saturated vapor pressure physicochemical characteristic, that corresponds to the measurable ability of compounds to migrate from a liquid matrix to vapor phase [23]. Once the total energy contained in a system under heating process is higher, it turns possible to enhance the headspace concentration of volatile compounds previously linked by low energy bond to nonvolatile molecules from samples [23,62].

5. Conclusions

Choosing the appropriate experimental design may contribute to feasibility of optimization experiments by reducing the number of trials needed to determine processing optimal conditions. The RCCD enabled, through desirability analysis over a fitted model surface result, stablishing condition for sample preparation in order to maximize the differentiation power of an electronic nose system based on MOS sensors.

Injection response data must undergo pretreatment for signal noise reduction and variance feature extraction. The chemometric tools and analysis employed in this experiment were effective to extract variance causes from the electronic nose readings and the multivariate distance was an efficient metric to explore samples differentiation in this system.

The performance of distinction between two samples of cachaça using the electronic nose device was more associated to incubation temperature and ethanol content of samples than stirring and equilibrium time. So that, further electronic nose analysis over aged sugar cane spirits will be driven according to the sample preparation procedure based on dilution of spirits to 10% ($v \cdot v^{-1}$) of ethanol content, followed by incubation at 49 °C during 8 min.

A broader investigation into headspace composition after the present sample preparation procedure may be achieved considering further GC-MS analysis, which may possibly aid to determine new aging-markers and detail the potential of the electronic-nose response to specific flavor compounds found in wood-aged distilled beverages.

Author contributions

Giovanni Casagrande Silvello: Conceptualization; Formal analysis; Investigation; Methodology; Project administration **André Ricardo Alcarde:** Funding acquisition; Resources; Supervision; Validation; Writing - review & editing.

Declaration of competing interest

The authors declare no competing financial interest.

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