A single screen-printed electrode in tandem with chemometrics tools for the forensic differentiation of Brazilian beers

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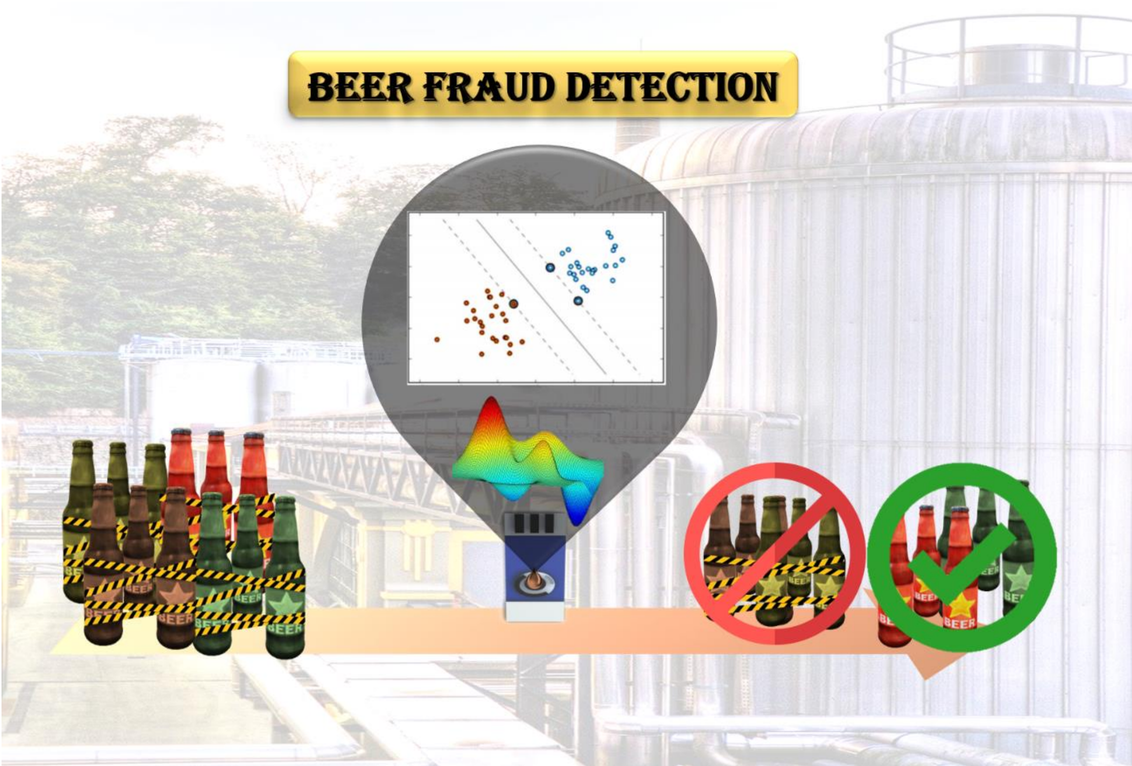
Abstract:

There is a need for fast and efficient beer fraud detection methods to increase product safety for the beer industry and beer consumers. In the present study, an electronic tongue based on cyclic voltammetry using a single commercial screen-printed carbon electrode (SPCE) and chemometric techniques were used for forensic differentiation of Brazilian American lager beers. To perform a differentiation of the beers at manufacturer and brand level the classification techniques: soft independent modeling of class analogy (SIMCA), partial least squares regression discriminant analysis (PLS-DA), and support vector machines discriminant analysis (SVM-DA) were tested. In total, 240 beers comprising 19 distinct brands either from the three major Brazilian manufacturers (Ambev, Heineken, Petropolis) or from other producers were used to construct the models. The linear techniques (SIMCA and PLS-DA) did not perform well on the classification of the beers according to the manufacturers. PLS-DA model presented an inconclusive assignment ratio of 20%. On the other hand, Simca models had a 0 inconclusive rate, but a moderate classification performance, with low overall sensibility (85%). SVM-DA, the non-linear technique, has shown the best overall classification results with an overall 98% of accuracy 95% of sensitivity, and 98% of specificity. The coupled SPCE-SVM-DA technique was then used to create a model that distinguishes two highly frauded beer brands (Amstel and Brahma). The technique was performed with high accuracy of 97% for the classification of both brands. Therefore, as the most common beer fraud practice in Brazil is the label switch, the proposed e-tongue was deemed an appropriate tool to evaluate this type of counterfeit.

Key-words: Support Vector machines, Classification methods, Cyclic voltammetry, Electrochemical analysis, PLS-DA, SIMCA, Beer fraud



Graphical Abstract

1 Introduction

Beer is one of the most popular alcoholic beverages worldwide with a US$ 612 billion revenue in 2021 and a 10% annual growth projected for this market between 2021 and 2025 (Statista, 2021). In 2018, Brazil was the third-biggest producer, with a production of 14 billion liters, only behind China and United States (Report, 2019). Similar to the global market, the Brazilian beer market is dominated by few large breweries. Currently, three companies, namely Ambev (a subsidiary of the AB InBev), Heineken group, and Petropolis group account for 96% of the Brazilian beer market share where the most commercialized style is the American lager (CervBrasil, 2020). In such a competitive market beers from these manufacturers are commercialized with higher value due to their effective market presence, consumer loyalty, and the quality attributed to the brand's name. However, these characteristics make these brands subject to fraud practices.

Due to the pandemic's lowering in surveillance, recent reports revealed an increasing trend in beer fraud and counterfeiting practices (Valor, 2020). The most common type of fraud is switching the label and cap of lower-value brands for higher-value ones (Civil, 2020; Extra, 2021; Globo, 2020). Detection of this type of fraud is analytically challenging as the distinctions among beers from the same style can be very subtle. Therefore, the development of a fast and reliable, and portable technique to classify American lager beers from distinct manufacturers and brands is necessary to ensure product security.

However, the challenge of classification amongst the same style as required for the detection fraud was only approached with advanced analytical techniques such as ^{1}H NMR (da Silva, Flumignan, Pezza, et al., 2019) and paper spray mass spectrometry

(Pereira et al., 2016). Although these techniques are very sensible, they rely on expensive equipment, use of solvents, and lack portability. In this regard, the use of electronic tongues (ET) is regarded, as they offer a fast, reliable, and portable option for the fingerprint of several food matrices. ETs are analytical systems composed of unspecific electrochemical sensors coupled with chemometric techniques to identify the characteristics of a complex system (Galvan et al., 2021).

The use of ET in beer science is described for classification among beers from distinct styles (Blanco et al., 2015; Gutiérrez et al., 2013; Roselló et al., 2021) and distinct raw materials (Mutz et al., 2021). Since each beer will present chemical variation related to its manufacturing process and employed raw materials the use of ETs emerges as a viable option for forensic tasks (Mutz et al., 2020). Indeed, in our previous work, we developed an ET based on commercially available SPE's and chemometric techniques capable of discriminate between Premium and standard and American lager beers. However, a further challenge would be to discriminate between beers of the same style from distinct brands, as it offers great forensic potential. Therefore, regarding the need for rapid, reliable, and portable methods with forensic potential for beer classification, the present study evaluates the potential use of cyclic voltammetry coupled with classification methods to discriminate among American lagers from the three major Brazilian producers.

2. Material and methods

2.1 Beer samples

In total, 240 beer samples were purchased at local supermarkets in the metropolitan region of Espírito Santo State (Brazil). The sampling comprised 19 different brands from the three major commercialized groups that in the Brazilian market (Ambev, Petropolis group, Heineken group), and from other manufacturers.

2.2 Instrumentation and voltammetric measurements

Cyclic voltammetry measurements were performed on a portable potentiostat/galvanostat μSTAT 400 (Metrohm DropSens, Oviedo, Spain) controlled by Dropview 8400® software using a disposable SPCE made by Metrohm-Dropsens (Oviedo, Spain). The SPCE used were a DS-110 carbon working electrode with dimensions of 3.4 x 1 x 0.05 cm containing three electrodes printed on the same planar ceramic platform: a working electrode, a pseudo reference electrode (Ag/AgCl), and an auxiliary electrode manufactured in the same material as the working electrode. In this work, there was not necessary the use of supporting electrolytes, once the samples (beers) present electrolytes that become make possible the electrochemical measurements

Before electrochemical measurements, the beer samples were opened for 30 minutes for the removal of excess CO_2. Voltammetric measurements were performed at room temperature (25 ºC) in triplicate dropping a 40 μL aliquot on the surface of the electrode. The cyclic voltammetry scan was performed following the settings from a previous experiment (Mutz et al., 2021), using the range of between −1.0 V and 1.0 V, with a scan rate of 100 mV s^{-1}, totaling 40 seconds per scan, without the need for support electrolyte.

2.3 Chemometric procedures

2.3.1 Data treatment

The beer samples voltammograms were concatenated in a matrix (240 x 2000), with each line corresponding to a sample and the columns corresponding to the current signals. The dataset was then preprocessed by mean-centering. To construct the classification models according to the manufacturer, samples were labeled for each of the manufacturing groups (Ambev, Petropolis, Heineken, Other). Furthermore, for the brand challenge, the samples were labeled as either Brahma, Amstel, or other. All statistical analyses were performed using the Matlab 2016a software (The MathWorks, Massachusetts, USA).

2.3.2 Classification techniques

The linear classification techniques used were partial least squares discriminant analysis (PLS-DA) and soft independent modeling of class analogies (SIMCA) using the classification toolbox of the Milano chemometrics and QSAR research group (Ballabio & Consonni, 2013). The non-linear technique support vector machines discriminant analysis (SVM-DA) was employed using the Gamma toolbox (Bona et al., 2017).

SIMCA is a class modeling technique that relies on PCA to model a class with reduced dimensionality. SIMCA constructs individual models for each of the sample's categories. Therefore, as classes are independently modeled, new samples are predicted as belonging to the class or not. Further, class assignment relies on a distance measure to interpret if the samples belong or not to the modeled class. In the implemented SIMCA, the distance measure is a combination of the normalized T^2 statistics and normalized Q residuals (Ballabio & Consonni, 2013).

A multi-class PLS-DA model was built to simultaneously define class boundaries between the distinct categories. The techniques focus on the dissimilarities between the different classes to find class belonging traits. PLS-DA uses the PLS2 algorithm to search for latent variables that maximize the correlation between independent and dependent variables. A class threshold is defined for each class to minimize the number of incorrect assignments. Thus, based on the probability of class belonging and class threshold the samples are assigned to a class. Furthermore, samples can also be non-assigned in the case of their calculated estimates being higher or lower than all the calculated class thresholds (Ballabio & Consonni, 2013).

SVM-DA is a non-linear discriminant technique. The technique employs kernels to map data from linearly inseparable problems into high dimensional feature spaces and then perform classification (Argyri et al., 2013). In the present study radial basis function (RBF) was chosen as the kernel function. In this technique the dimensionality of the feature space that performs the samples separation is determined by the RBF γ parameter, while the complexity of the model is set by the penalty parameter C. Together the γ and C parameters control a trade-off between the model generalization ability and its complexity (Bona et al., 2017).

2.3.3 Optimization of the model parameters

The optimization of the number of principal components for SIMCA and latent variables for PLS-DA was done with 10-fold cross-validation in the calibration dataset. For this cross-validation, the calibration set was divided into ten subgroups and one subgroup at a time was removed from the data set and used for external validation for the constructed model. At the end of the process, the number of components or latent variables that minimize the classification error was chosen.

The SVM parameter C and the RBF kernel parameter γ were simultaneously optimized using particle swarm optimization (PSO) and 10-fold cross-validation to maximize the classifier performance. The PSO was executed with a swarm of 2000 particles and a maximum convergence error tolerance of 1×10^{-3} between the calculated value at an interaction stall of 20 subsequent iterations (Galvan et al., 2020). The restrictions of the PSO algorithm were set in the form of lower and upper bounds were (1 x 10^{-8} to 1 x 10^{-4}) for γ and (1 x 10^{2} to 1 x10^{5}) for C. For the brand challenge, the optimization interval was 1 x 10^{-7} to 1 x 10^{-3} for γ and 1 x10^{0} to 1 x 10^{4} for the C parameter.

2.3.4 Validation, and performance of the models

To perform the external validation first the dataset (240 beer samples) was split into a validation set with 30% of the samples and a calibration set with the remaining 70%. Separation of the datasets was performed using the duplex algorithm (Snee, 1977) to obtain a more conservative separation of the samples (Westad & Marini, 2015). Then, the validation was performed by calculating the performance parameters of the obtained classification models.

The performance figures of merit (FOM) for validation of the models were calculated for the model prediction in the calibration and test datasets. The calculated FOM were: accuracy, sensitivity, specificity, and inconclusive ratio (IR), Equations 1, 2, 3, and 4 respectively.

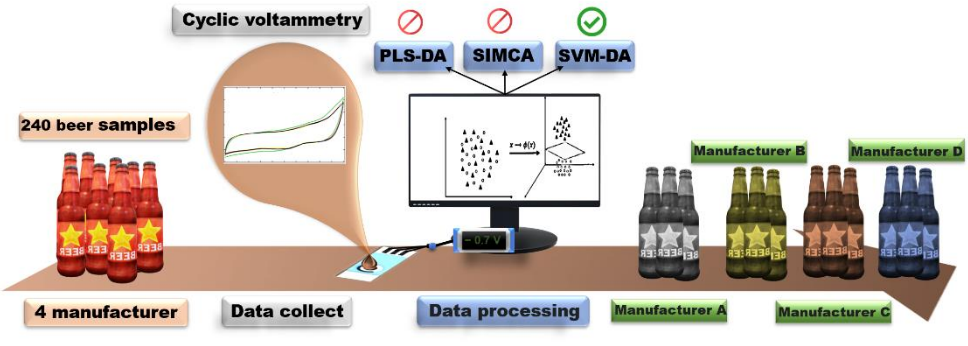
$$Sensitivity = \frac{TP}{TP+FN} \tag{2}$$

$$Specificity = \frac{TN}{TN+FN} \tag{3}$$

$$Accuracy = \frac{TN+TP}{TN+TP+FN+FP} \tag{4}$$

$$IR = \frac{NA}{N} \tag{5}$$

TP, FN, TN, and FP indicate the number of true positive, false negative, true negative, false-positive, samples respectively. Further, IR is the inconclusive rate, NA is the number of non-assigned samples, and N is the number of samples belonging to the class. A summary of the implemented procedure is shown in scheme 1.



Scheme 1. Schematic illustration of the analysis and differentiation procedure of beer samples. Data collection was performed by cyclic voltammetry with SPCE from a drop (40µL) of the samples and data treatment using the PLS-DA, SIMCA, and SVM-DA techniques to differentiate the manufactures.

3 Results and discussion

3.1 Electrochemical profile

Cyclic voltammetry is the most used technique for the acquisition of qualitative information on the electrochemical properties of a food system (Hoyos-Arbeláez et al., 2017). It consists of a linear scan of the potential of a working electrode thus providing information on the redox process and electron-transfer reactions of a matrix (Vilas-Boas et al., 2019). As beer is a matrix that possesses several molecules susceptible to undergo redox processes, the collected information becomes useful for the construction of classification models (Mutz et al., 2021).

All voltammograms and average voltammograms of the samples discriminate by the manufacturer are shown in Figure 1. Although a great similarity between the voltammograms obtained can be observed (Figure 1a-d), it is also noticeable that each manufacturer shows its peculiarities. The voltammograms of samples from producer Ambev show a slight "peak" of reduction around 0.1 V in practically all samples, which does not appear with such intensity in the other groups of samples. The samples from the Heineken group showed a great variation within the voltammograms from the producer.

Furthermore, it is observed that the voltammograms of the Heineken group present a slight "peak" of oxidation around 0.8 V, distinct from the others. The samples from the Petropolis groups present voltammograms with good reproducibility between the samples themselves. Finally, the voltammograms obtained from the samples of the "others" group present a good variety of profiles obtained, with samples generating responses similar to all three groups discussed above.

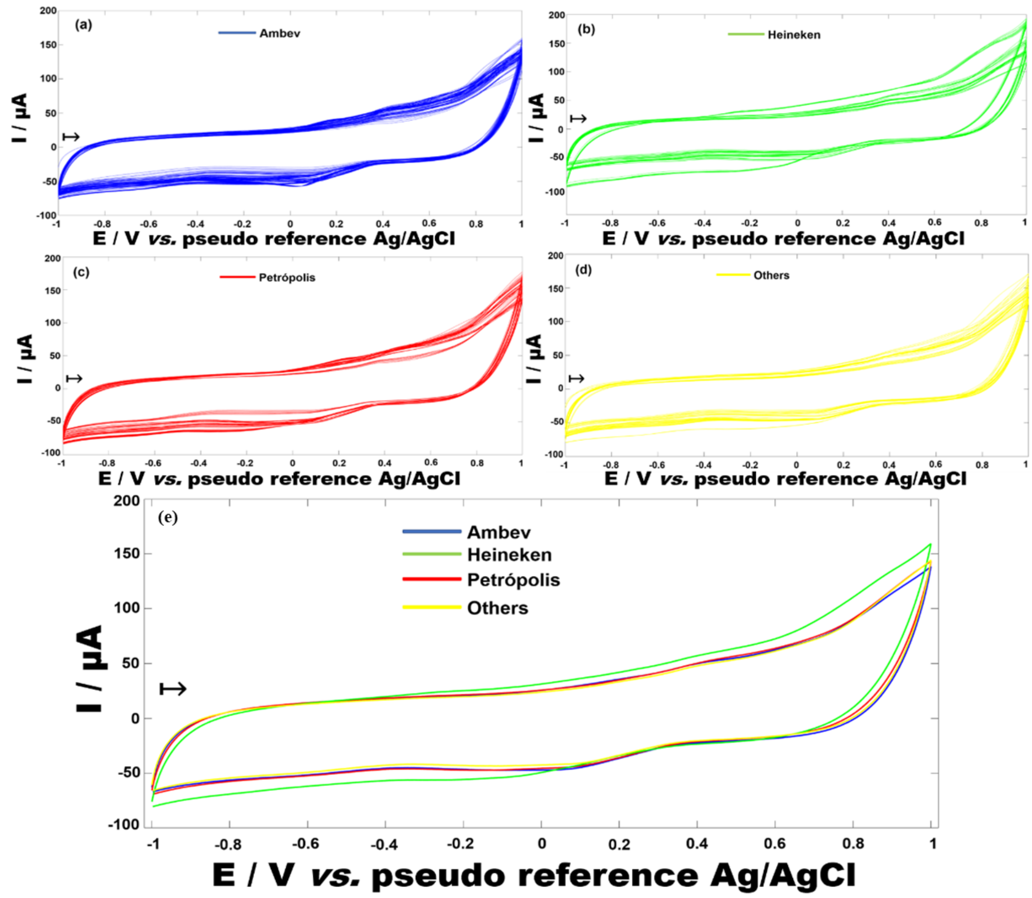


Figure 1. (a-d) All cyclic voltammograms of Brazilian American lager beer discriminated by manufacturers and (e) average cyclic voltammograms from the 240 beers obtained with screen-printed carbon electrodes. Scan rate: 100 mV s^{-1}. Scan direction (→).

In Figure 1e is observed that the average voltammograms from the manufacturers are similar with subtle distinctions, with an exception for the Heineken group voltammogram that stands out. Each beer is unique, varying on the type of fermentation, style, ingredients, and manufacturing process (Mutz et al., 2020).

In the present study, the challenge is to gather electrochemical information about beers of the same style from distinct producers. The electrochemical distinctions at the manufacturer or brand level between beers of the same style can be attributed to several electroactive molecules such Na^+/K^+ adducts of oligosaccharides(Pereira et al., 2016), phenolic acids, esters, higher alcohols, and organic acids (Alcázar et al., 2012; da Silva, Flumignan, Pezza, et al., 2019; da Silva, Flumignan, Tininis, et al., 2019; Fernández Pierna et al., 2012; Lunte et al., 1988; Pereira et al., 2016). Therefore, as these classes of molecules can be detected by the employed cyclic voltammetry technique (Cetó et al., 2013; Deo & Wang, 2004; Mutz et al., 2021), it can be assumed that difference in the voltammograms to be related to their contents.

The content of organic acids and higher alcohols in beer relates to several distinctions in beer manufacturing. Higher alcohols are byproducts of yeast metabolism, either in anabolic or catabolic pathways (Lodolo et al., 2008). As for the organic acids, although they may be a product of yeast metabolism, their majority is produced during the malt's germination step (Li et al., 2007; Xiang et al., 2006). Indeed organic acids are very important to beer flavor, as they directly influence its sourness (Saison et al., 2009). Due to their importance, there are classification studies based on the beer's organic acid profile (da Silva, Flumignan, Pezza, et al., 2019; Li et al., 2007). Furthermore, the distinction in phenolic acids, esters, aldehydes, ketones, and other electroactive molecules is multifactorial, from the raw ingredients employed, to the conduction of the variables of the brewing process, and its quality control (Paiva, Mutz & Conte-Junior, 2021).

3.2 Classification according to manufacture

The task of classifying the beers according to their distinct manufacturers was approached with supervised pattern recognition techniques (PLS-DA, SIMCA, SVM-

DA) (Table 1). The first approach was made using the linear classification methods: SIMCA and PLS-DA.

Table 1

		LV		Training				Test		
Technique	**Beer**		**Sensitivity**	**Specificity**	**Accuracy**	**NA**	**Sensitivity**	**Specificity**	**Accuracy**	**IR**
	Ambev		0.94	0.96	0.91	0.17	0.95	0.92	0.83	0.20
PLS-DA	Petropolis		1	0.96			1	0.96		
	Heineken		0.74	1			0.43	1		
	Casa DiConti		0.91	0.95			0.90	0.90		
	Overall		0.90	0.97		0.17	0.82	0.94		
	Ambev		0.97	0.96	0.96		0.82	0.89	0.86	
SIMCA	Petropolis		1	0.99	0.99		0.84	0.96	0.93	
	Heineken		0.94	0.93	0.93		0.76	0.93	0.89	
	Casa DiConti		1	0.97	0.98		1	0.95	0.96	
	OVERALL		0.98	0.96	0.96		0.85	0.93	0.91	
SVM-DA	Ambev		100	0.9908	0.9943		0.9333	0.9778	100	
	Petropolis		100	100	100		100	0.9824	94,67	
	Heineken		0.9756	0.9854	0.9831		0.8823	0.9655	98,67	
	Casa DiConti		100	100	100		100	100	96	
	OVERALL		0.99	0.99	0.99		0.95	0.98	0.98	

* PLS-DA: Partial least squares discriminant analysis; SIMCA: Soft independent modeling of class analogies; SVM: Support Vector machine discriminant analysis; Inconclusive rate

In the present study, the PLS-DA constructed model with 4 classes (Ambev, Heineken, Petropolis, and others) presented an accuracy of 83%. The PLS-DA FOM was above or equal to 90% for all classes except for the Heineken group's beer, which presented a sensitivity of 43% (Table 1). PLS-DA is a discriminant technique that focuses on the distinction among the defined classes to define a separation threshold among them (Brereton et al., 2018). The low sensitivity of this class may indicate a high intra-class variation, i.e., a distinct electrochemical profile among samples from the Heineken group. On the other hand, the distinction that the Heineken group samples showed in their voltammograms when compared to the other manufacturers (Figure 1) corroborate the 100% specificity achieved in this class.

Nonetheless, the use of PLS-DA to classify the beer manufacturers was not considered satisfactory, once the built model could not assign 15 out of the 75 samples of the test samples, leading to an inconclusive rate (IR) of 20%. Corroborating our findings (da Silva, Flumignan, Pezza, et al., 2019) approached the classification of Brazilian beers by its manufacturers (Ambev, Heineken, and Petropolis) using ^{1}H NMR spectroscopy and PLS-DA, and also found a non-assignment rate of 6.89% for the Petropolis and Ambev groups. A non-assignment by the PLS-DA model is achieved when a sample is perceived as belonging to multiple classes, or none of the classes at all (Ballabio & Consonni, 2013). Therefore, it can be implied that the PLS-DA model does not have sufficient discriminative power to separate the manufacturers based on their electrochemical information.

On the other hand, the SIMCA models did not present non-assigned samples, leading to an inconclusive rate of 0. In addition, the model's achieved an overall accuracy of 96 %, superior to the PLS-DA model. In contrast to PLS-DA, a discriminant method, SIMCA is a one-class-classifier (OCC) technique that focuses on the class similarities to individually model class boundaries (Oliveri & Downey, 2012)). SIMCA models presented good values for specificity, with an average value of 91%. Specificity represents the model's ability to reject samples from other classes from being classified as the observed class (Ballabio & Consonni, 2013). This metric is specifically important when dealing with authentication or forensic tasks as their objective is to rule out out-of-pattern samples caused by fraudulent practices (Biancolillo et al., 2014). For this reason, the use of class modeling techniques is regarded (Rodionova et al., 2016). Indeed, SIMCA is widely adopted for the goal of the authenticity of food and beverages (Oliveri & Downey, 2012). However, except for the group of other manufacturers, the SIMCA models' sensitivity was low. Therefore, pointing to an inefficient recognition of the samples as true belonging to the tested class.

The overall low performance of the PLS-DA and SIMCA models can be indicative that the brands could not be linearly separated. Therefore, SVM-DA, a non-linear classification technique was employed. First, the SVM-DA parameters γ and C were adjusted using particle swarm optimization. The parameters were chosen after a 10-fold cross-validation process to minimize classification error. The manufacturer model optimized parameter was $\gamma = 8.90 \times 10^{-7}$ and $C = 4.85 \times 10^{3}$.

The accuracy of the SVM-DA technique was superior to the linear methods, with an overall of 98% (Table 1). SVM-DA separation was performed with an overall specificity of 98% and sensitivity of 95%. The model's prediction for the beer samples of all the defined classes can be seen in Figure 2.

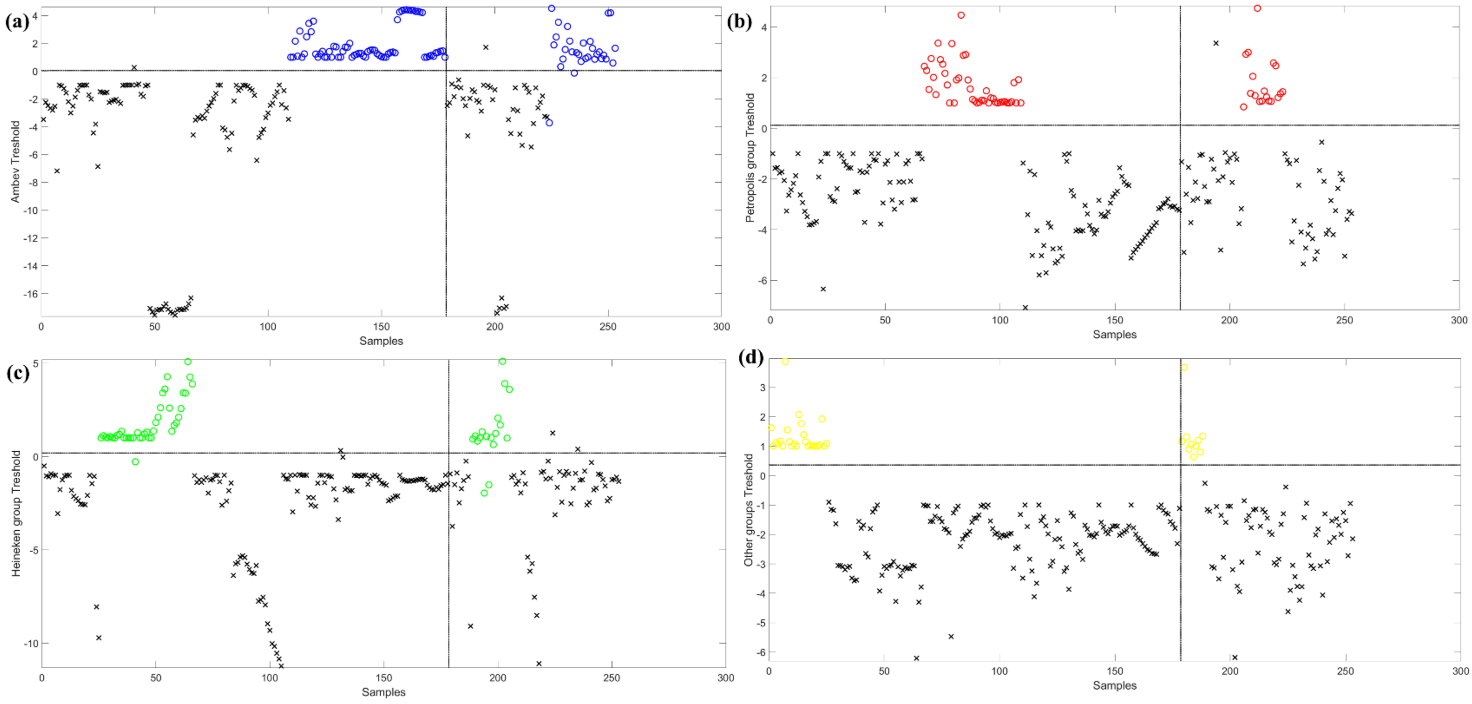


Figure 2 SVM-DA prediction showing the calculated threshold for discrimination (horizontal dashed line) of (A) Ambev samples. (B) Petropolis group samples. (c) Heineken group samples. (D) Other manufacturers samples. The horizontal dashed line separates the calibration dataset (left side) and the validation dataset (right side)

Although requiring higher computing power, these techniques allow for the separation of seemly inseparable overlapping classes (Argyri et al., 2013). Indeed, the use of SVM-DA for beer classification is successfully described in the literature as differentiation of geographical origin (Alcázar et al., 2012) and authentication of Trappist beers (Fernández Pierna et al., 2012). Moreover, in accordance with our study (Roselló et al., 2021) also found that SVM-DA led to lower (5.3%) classification error than PLS-DA (23.6%) when discriminating among beers with distinct fermentations using a carbon SPE and cyclic voltammetry.

SVM-DA maps the input data into higher dimensional feature spaces and then performs classifications (Alcázar et al., 2012; Bona et al., 2017). In the present approach, the performed SVM-DA classification of multiple manufacturing brands was made with the one versus all (OVA) approach. In this approach, the targeted class is separated from the rest of the samples which is grouped as the foreign sample. For being a discriminant technique, the use of the OVA approach means that the hyperplane designed to classify the beer brand takes into account all the other manufacturers as outsiders. Based on the model results, such a technique was considered suitable for the proposed classification task.

Such promising results raised the question of whether the developed SVM-DA-cyclic voltammetry ET is suitable to be employed in forensic tasks. The most simple and common method of beer fraud in Brazil is to switch caps or labels of a beer (da Silva, Flumignan, Tininis, et al., 2019). Therefore, to test if the technique developed was indeed suitable for fraud detections, we tested its ability to differentiate beers at the brand level. To perform the brand challenge two frequently reported frauded brands within the Brazilian big producers, Brahma from Ambev group and Amstel from Heineken group were selected (Civil, 2020; Extra, 2021; Globo, 2020).

The optimization of the SVM parameters for this challenge was performed for the manufacturer models. The optimum values were $\gamma = 3.52 \times 10^{-6}$ and $C = 1.48 \times 10^{1}$.
The tuning of the γ and C parameters defines the classification boundaries of the SVM model. While γ defines the influence of each selected support-vector, and therefore the smoothness of the classification surface, C controls the model complexity in a trade-off between the number of incorrect classifications and the model margin (Bona et al., 2017). Thus, a higher C means that the dataset is reliable and a higher penalty is given to classification error in exchange for a lower margin for the decision boundary is employed (Papadopoulou et al., 2013). Therefore, for the beers classification, the brand separation had a smoother classification boundary but a noisier dataset when compared to the

manufacturers production. This can be attributed to the possibility of some of the sampled beers being electrochemically close to the profile of the Brahma and Amstel studied beers.

The SVM-DA model constructed for the brand challenge presented no un-assignments leading to an inconclusive rate of 0. The separation between the two tested brands versus other beers is shown in Figure 3. Similar to the results found for the manufacturer test, the SVM-DA models presented high accuracy (97% for the Brahma and 96% for the Amstel). Further, the sensitivity of the models ranges from 87-90% and specificity from 97-98%.

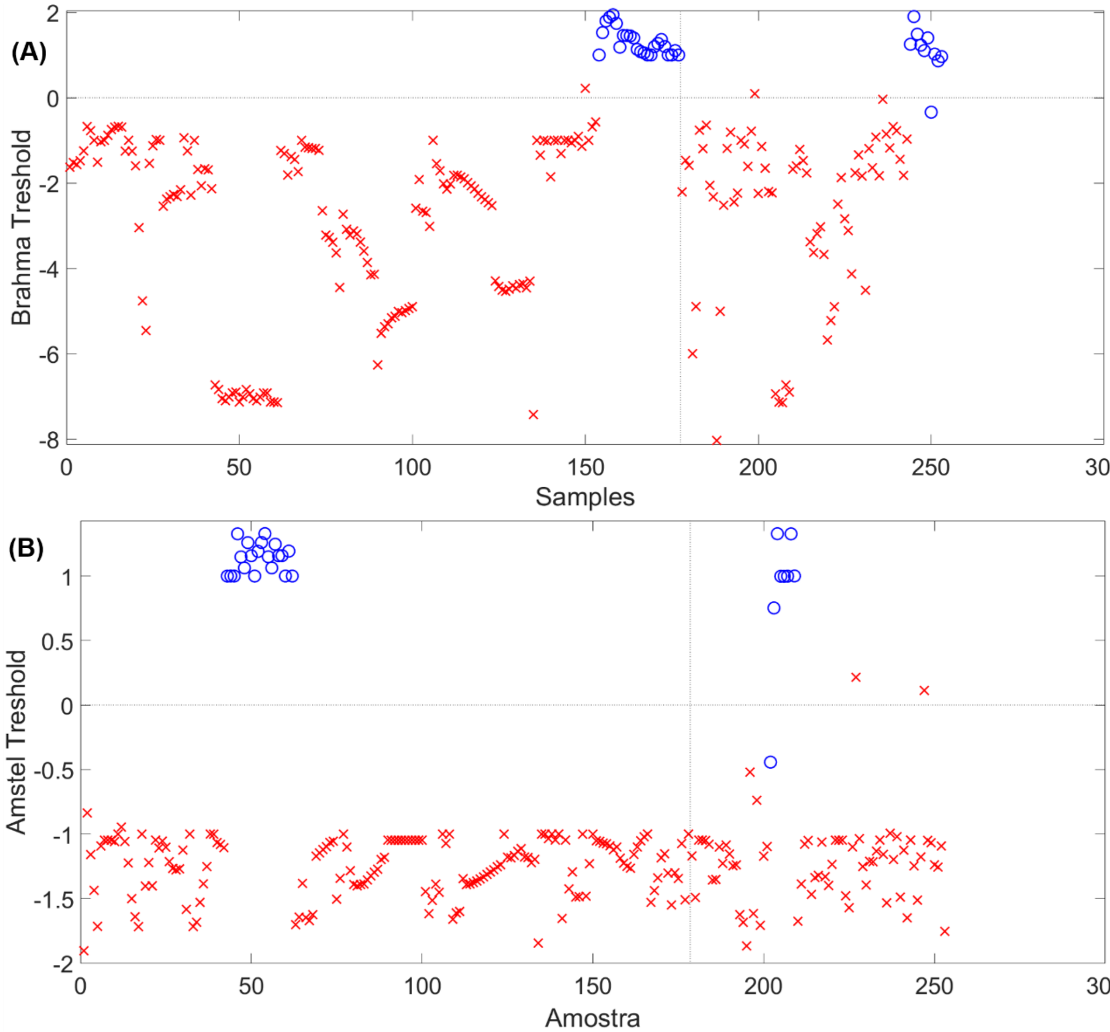


Figure 3. Samples Plot showing the calculated threshold for discrimination (grey line) for the support vector machines discriminant analysis model. Blue circles are (a)Brahma beer samples and (b) Amstel beer samples; Samples above the grey line are classified as Brahma or Amstel for the technique. Samples from the left side of the grey line are part of the calibration dataset and on the right side are part of the validation set.

This high performance works as a demonstration that after being suitable for differentiation at the manufacturers-level, a separation of brand level is achievable with the developed SPCE-SVM-DA configuration for the ET. Therefore, as depicted by its performance results the developed technique proves to be a rapid, costless, efficient method for fraud detection. Furthermore, it should be a highlight that the present technique is portable, presenting great potential for *in loco* analysis, which is attractive for government agencies, consumers, and even breweries.

4. Conclusion

A novel approach based on a single screen-printed electrode coupled with SVM-DA for rapid, direct, and effective differentiation of Brazilian's American lager beers has been developed. The proposed configuration for an electronic tongue has been shown to predict with great specificity and sensibility from the three major Brazilian manufacturers (Ambev, Heineken, Petropolis). Furthermore, the configured ET allowed for the differentiation at the brand level of two commonly frauded beers (Brahma and Amstel). Furthermore, the developed ET employs portable equipment and commercially available SPCE's. Therefore, the developed portable ET proved to be one useful tool for regulation purposes and forensic applications such as fraud and counterfeit surveillance. Future highlights for this field include exploring the potential of chemometric techniques coupled with homemade electrodes (3D printed, pencils, ink, among others electrodes) to help the field of forensic analysis.

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