

Vinegar is produced from the alcoholic and subsequent acetous fermentations of carbohydrate sources under highly aerobic conditions wherein the ethanol is oxidized to acetic acid [1,2]. Depending on the source materials, many different types of vinegar are produced, as the former do not only provide different acidity and sour taste to the latter, but also play a key role in vinegar flavour as well as in its chemical composition.

As for many other food products, several frauds have been perpetrated in the production and commercialization of vinegar given the huge variety of vinegars available in the market in terms of quality, types and prices [2]. Unfortunately there is not a specific methodology that allows the detection of such adulterations with traditional methods, but current approaches rely on the quantification of certain physical properties or chemical compounds which have been reported as genuineness indicators [3]. In this direction, the application of a voltammetric electronic tongue (ET) towards the classification and authentication of vinegar is presented herein [4]. The proposed approach is based on the coupling of cyclic voltammetric responses obtained from an array of three chemosensors, with chemometric tools such as PCA and LDA for building the qualitative prediction models.

Experimental

ET approach

Vinegars were analysed with a three-sensor array consisting of a Au, a Pt and a glassy carbon electrode (GCE), without performing any sample pre-treatment, but only an electrochemical cleaning stage between sample measurements to avoid fouling onto the electrode surfaces (Fig. 1&2). Next, voltammetric responses were compressed employing discrete cosine transform (DCT), being the number of coefficients optimized through its inverse transform (Fig. 5). Finally, the obtained coefficients were analysed by principal component analysis (PCA) to attempt the discrimination of the different vinegars (Fig. 6) and by linear discriminant analysis (LDA) to build a model that allows its categorization (Fig. 7).

Vinegar samples

A set of 44 vinegar samples were purchased so as to cover the main varieties as per: red wine (7), white wine (7), apple cider (9), balsamic vinegar of Modena (8), sherry vinegar (8) and rice (5). Additionally, 4 extra vinegar samples were also purchased to further evaluate the performance of the proposed approach: 1 balsamic vinegar without the Italian IGP or PDO (C1); 1 red wine vinegar with 1% of raspberry aroma (C2); 1 vinegar from la Rioja analogous to sherry vinegar from Jerez, but not belonging to such class (C3); and 1 white wine vinegar from Italy containing some must (C4).

Voltammetric measurements

A complete voltammogram was recorded for each sample by cycling the potential between -1.0 V and +1.2 V vs. Ag/AgCl with a step potential of 5 mV and a scan rate of 100 mV·s⁻¹ (Fig. 3). A conditioning potential of +1.25 V was applied during 60 sec in a 0.5 M NaOH solution after each measurement to electrochemically clean the electrodes surfaces.

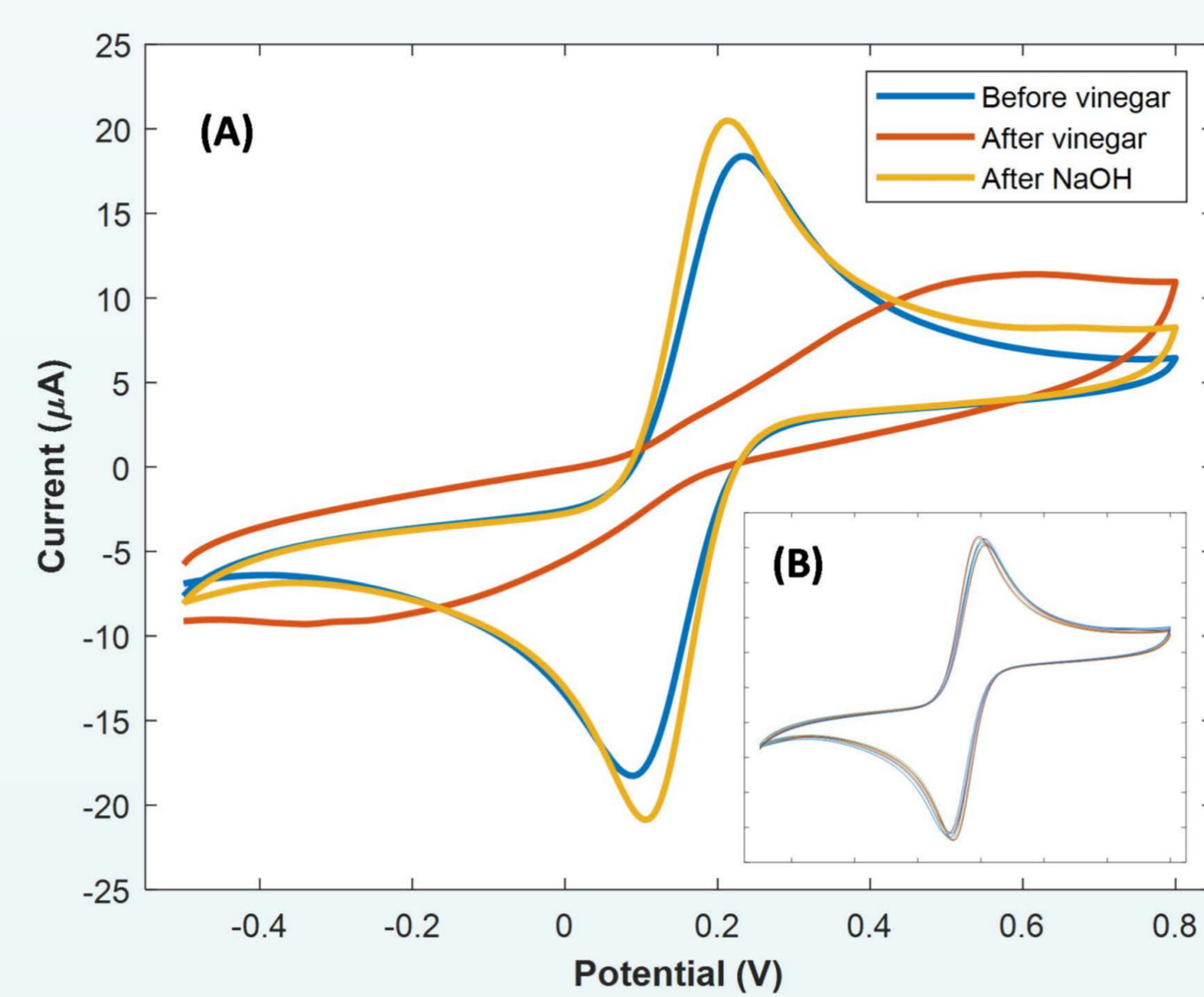


Fig. 1. Changes in the voltammetric response of the GCE towards a 2 mM [Fe(CN)₆]^{3/4-} in phosphate buffer (pH 7.4): (A) with/without the electrochemical cleaning and (B) during the measurement of all the 48 vinegar samples.

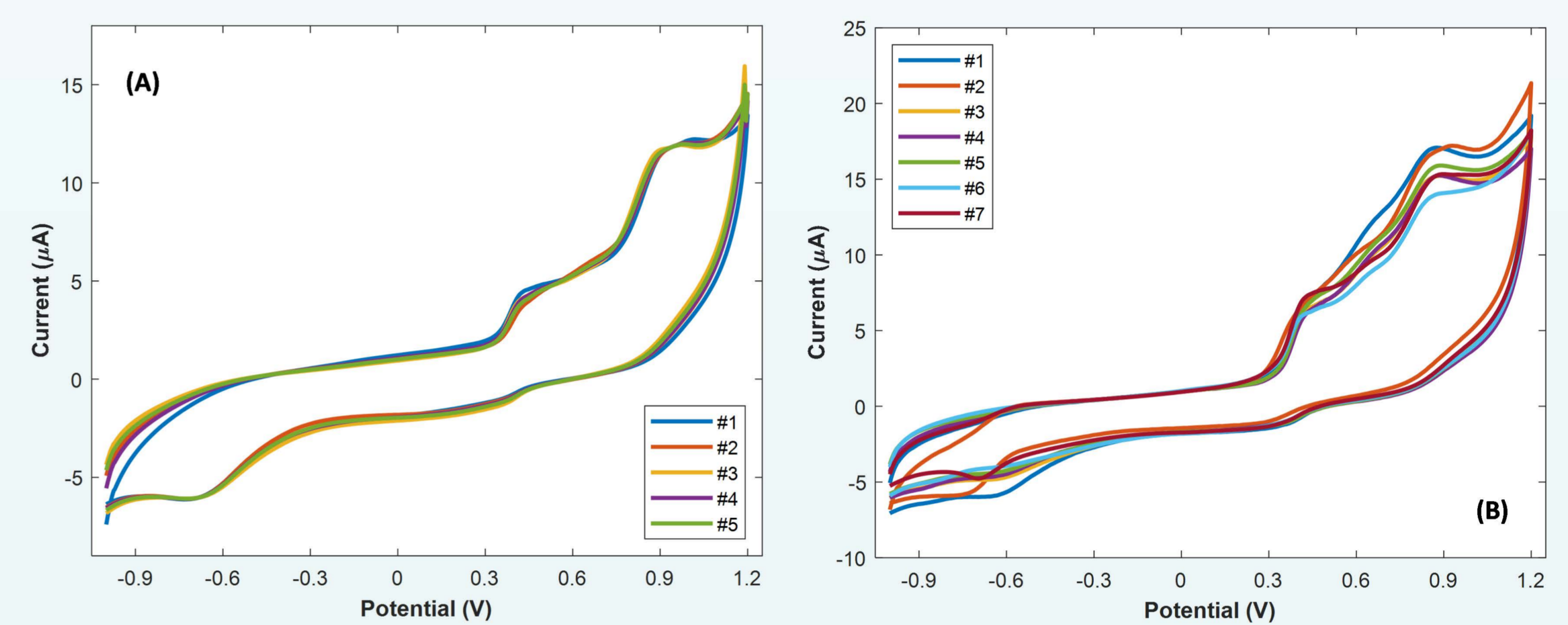


Fig. 2. Voltammetric responses obtained with the GCE towards (A) an arbitrary white wine vinegar for several consecutive measurements and (B) the seven red wine vinegars considered in this study.

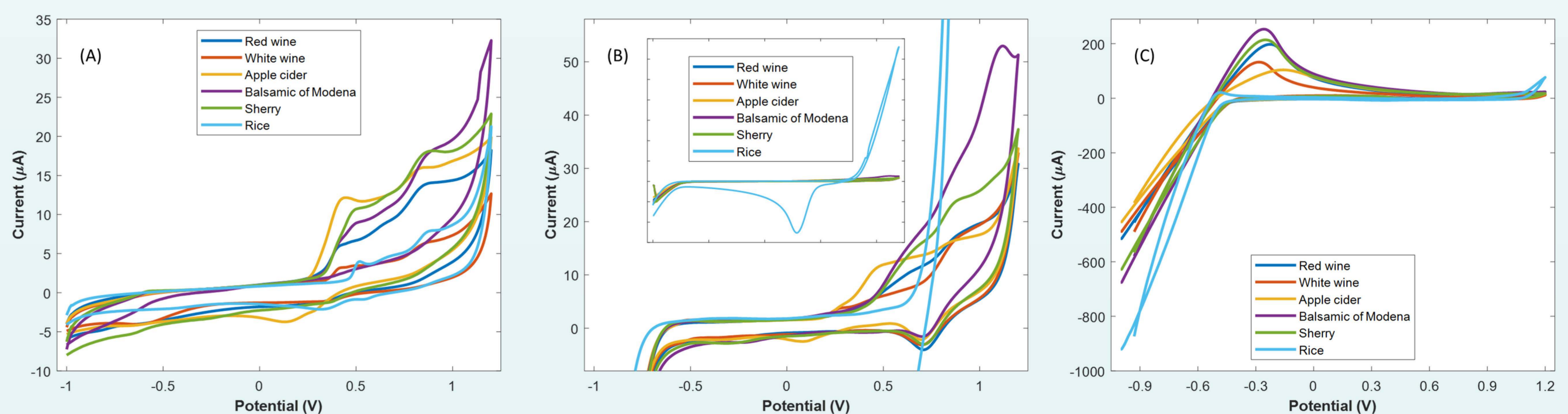


Fig. 3. Representative voltammetric fingerprints obtained for the different vinegar varieties with the different sensors: (A) GCE, (B) Au and (C) Pt.

Signal compression

Discrete cosine transform

To fully exploit all the information obtained from each voltammogram and to prevent the saturation of the associated chemometric model with excessively complex data, obtained responses were compressed down to 64 coeffs. without any loss of relevant information by means of DCT [5,6].

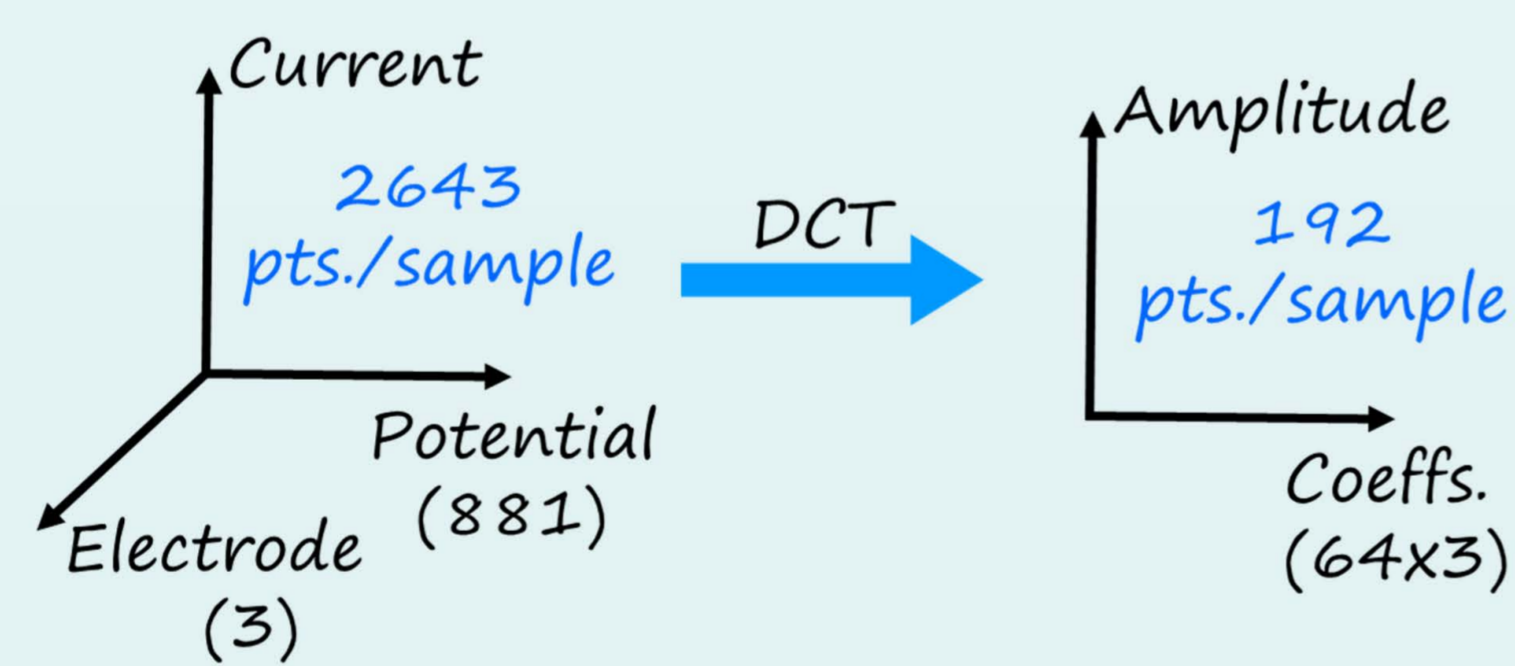


Fig. 4. Voltammetric signals are unfolded and compressed by means of DCT, achieving a reduction of ca. 96.4%.

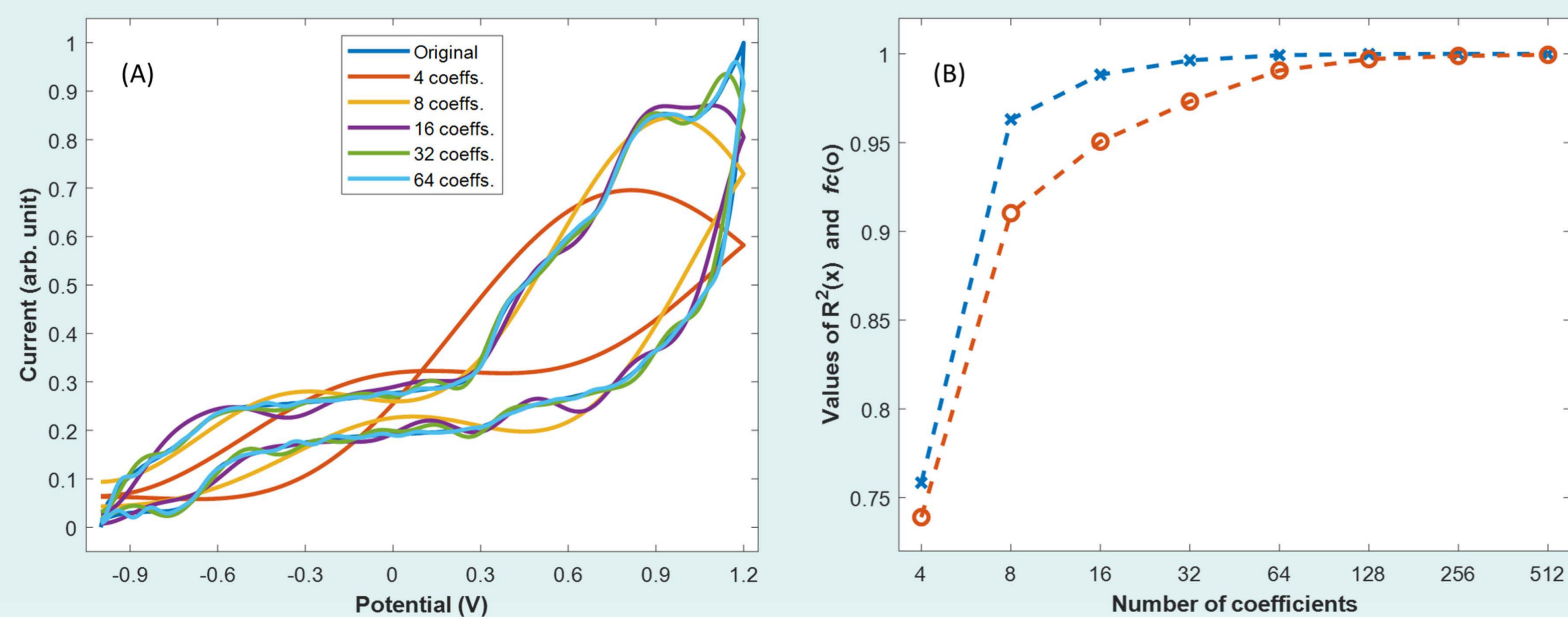


Fig. 5. Selection of the optimal number of coefficients for signal compression with DCT; GCE signal for an arbitrary vinegar shown as example. Changes in (A) the reconstruction of the voltammetric signal and (B) in the coefficient of determination (R^2 , \times) and $f_0(c)$.

Discrimination of vinegar varieties

Principal component analysis

As a first attempt, discrimination of white wine, apple cider, balsamic of Modena and rice vinegar samples was attempted by means of PCA. The advantage of using an unsupervised pattern recognition method at this initial stage is that it provides a better representation of samples' (dis)similarities based only on the measurements' variance, but not any prior expected similarities.

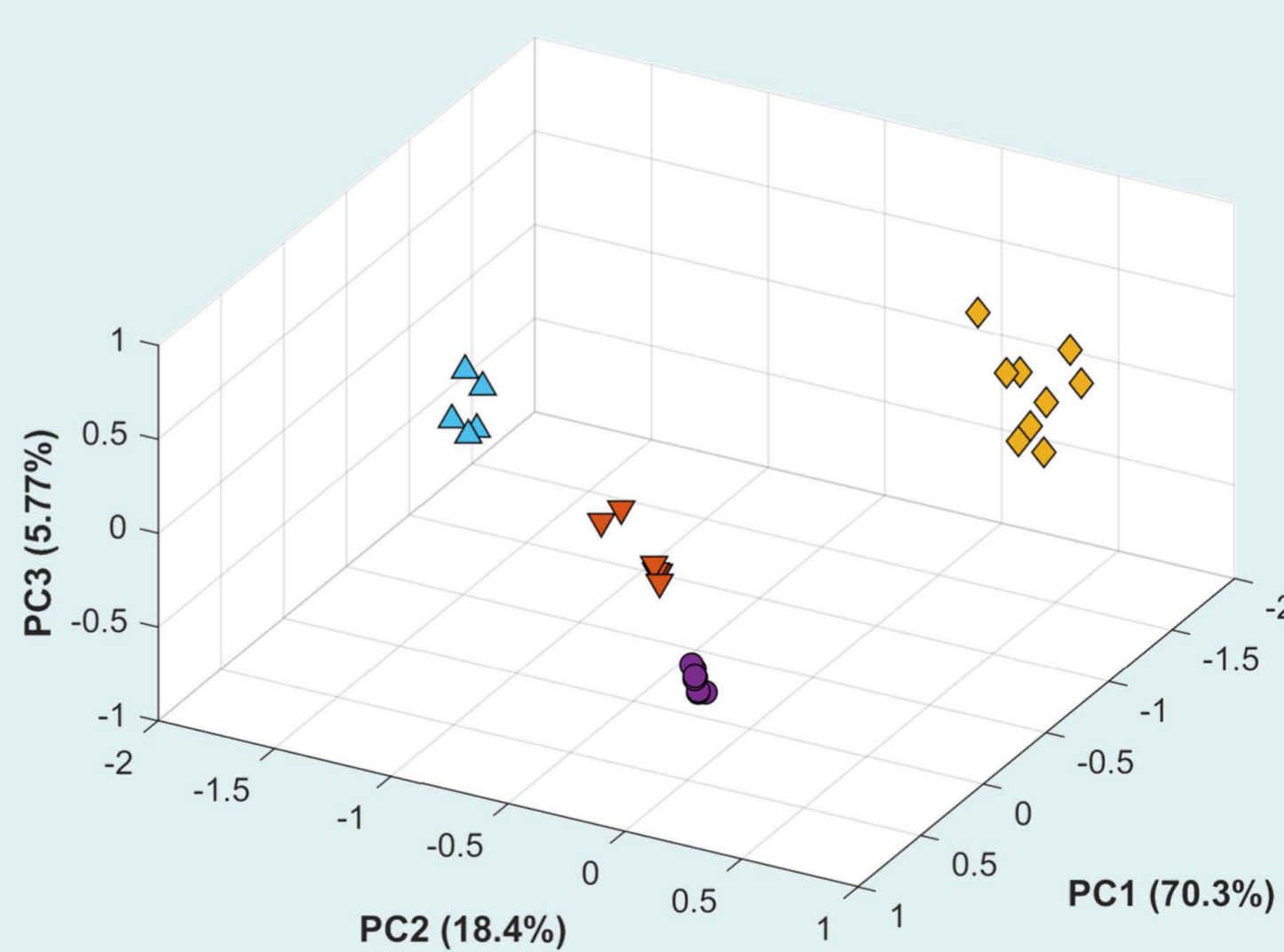


Fig. 6. PCA score plot of the different vinegar varieties: (▼) white wine, (♦) apple cider, (●) balsamic of Modena and (▲) rice.

Linear discriminant analysis

Next, classification of the different vinegar varieties was attempted by means of LDA. Furthermore, to better assess the performance of the model and its generalization ability towards new unknown samples, the set of samples was divided into two subsets (train and test) in the ratio 2:1.

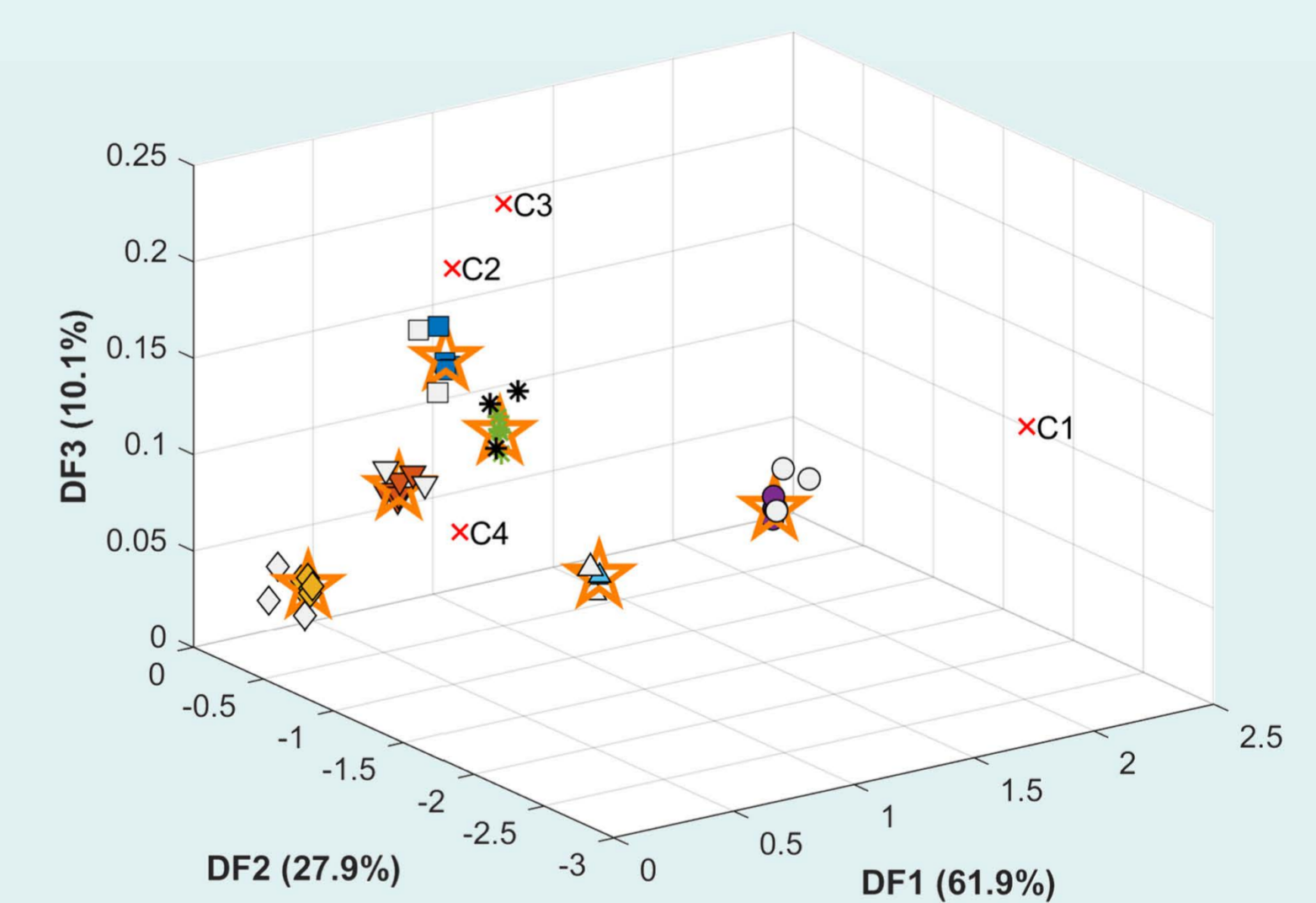


Fig. 7. LDA score plot of the different vinegar varieties: (■) red wine, (▼) white wine, (♦) apple cider, (●) balsamic of Modena, (✱) sherry and (▲) rice. Coloured symbols correspond to the samples of the training subset, while light grey ones to the testing subset. Additionally, the centroid (★) for each of the classes as well as the control samples are also plotted.

Conclusions

The use of a voltammetric ET was assessed as a tool to distinguish between different vinegar varieties. The proposed three-sensor array has shown to be sufficient to generate distinguished electrochemical fingerprints of the different vinegars, which in combination with pattern recognition methods allowed the correct discrimination of the different vinegar types. Moreover, analysis of some control samples confirmed the potential of the ET not to only carry out the classification of the different vinegars, but to also achieve the authentication of PDO/IGP protected varieties.

Overall, the reported approach herein demonstrates the potential of ETs as a viable option for the on-site authentication of food products, with the added advantages of their simplicity, low cost of both the system and the analysis, speed of response, versatility and simple measuring setup, between others.

References

- C.W. Ho, A.M. Lazim, S. Fazry, U.K.H.H. Zaki, S.J. Lim, *Food Chem.* 221 (2017) 1621
- A. Bekatorou (Ed.), *Advances in Vinegar Production*, CRC press, Boca Raton, 2019
- R.S. Singhal, P.R. Kulkarni, D.V. Rege (Eds.), *Handbook of Indices of Food Quality and Authenticity*, Woodhead Publishing, Cambridge, 1997
- X. Cetó, S. Pérez, *Talanta* 219 (2020) 121253
- X. Cetó, F. Céspedes, M. del Valle, *Microchim. Acta* 180 (2013) 319
- K.R. Pao, P. Yip, *Discrete Cosine Transform Algorithms, Advantages, Applications*, Academic Press, San Diego, 1990

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