Discrimination of monovarietal Italian red wines using derivative voltammetry

Identification of specific analytical fingerprints associated to grape variety, origin, or vintage is of great interest for wine producers, regulatory agencies, and consumers. However, assessing such varietal fingerprint is complex, time consuming, and requires expensive analytical techniques. Voltammetry is a fast, cheap, and user-friendly analytical tool that has been used to investigate and measure wine phenolics. In this work linear sweep voltammetry with different multivariate analysis tools (PCA, LDA, KNN, Random Forest, SVM) has been exploited to discriminate and classify Italian red wines from 10 different varieties.A total of 131 monovarietal Italian red wines vinified in 2015 or 2016 were collected from wineries across Italy. The varieties are: Aglianico, Cannonau, Corvina, Montepulciano, Nebbiolo, Primitivo, Raboso, Sagrantino, Sangiovese, and Teroldego. The wines of the same variety came from the same region. Linear sweep voltammograms were collected using a PalmSense3 potentiostat and disposable Screen-Printed Carbon Electrodes. The derivative voltammograms were obtained with a Savitzky Golay smoothing filter.The results obtained indicated a great diversity of voltammetric responses, but with raw data it was not possible to identify electrochemical features that discriminated the varieties. To obtain a higher discriminant ability first and second order derivative voltammogram were built.The second order derivative voltammograms (2DV) show similar trends within the same variety, in particular the varieties appear to be divided by the potential and intensity of the first peak (180-370 mV).From the PCA of 2DV (explained variance 78% with the first two components) 3 regions of the voltammograms that mainly contribute to PC1 and 4 to PC2 can be identified. Five of these regions (3 for PC1 and 2 for PC2) are at potentials lower than 600 mV, the region associated to the more easily oxidizable compounds. PC1 vs PC2 of the second order derivative voltammetry shows 3 groups with a visible separation of Nebbiolo and Teroldego from the other varieties.The best classification result has been obtained with a PCA-LDA of 2DV using the first 5 PC scores as predictors with an overall accuracy in calibration of 77.9% and an overall accuracy in prediction of 66.7%. The best accuracy has been obtained for varieties Nebbiolo, Teroldego and Sangiovese. The classification of two varieties (Cannonau and Primitivo) resulted problematic both in calibration and in prediction. To conclude, linear sweep voltammetry coupled to chemometric can be a suitable analytical tool technique for the classification of monovarietal red wines in a fast, cheap, and easy-to-use way. In addition, second-order derivative deconvolution of the voltammograms has been proven to be a suitable data pre-processing method for the interpretation of voltammograms from complex matrixes that are rich in oxidable compounds such as red wine.

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