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Analytical Methods

Unsupervised pattern recognition methods in ciders profiling based on GCE voltammetric signals

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ABSTRACT

This work presents a complete methodology of distinguishing between different brands of cider and ageing degrees, based on voltammetric signals, utilizing dedicated data preprocessing procedures and unsupervised multivariate analysis. It was demonstrated that voltammograms recorded on glassy carbon electrode in Britton–Robinson buffer at pH 2 are reproducible for each brand. By application of clustering algorithms and principal component analysis visible homogenous clusters were obtained. Advanced signal processing strategy which included automatic baseline correction, interval scaling and continuous wavelet transform with dedicated mother wavelet, was a key step in the correct recognition of the objects. The results show that voltammetry combined with optimized univariate and multivariate data processing is a sufficient tool to distinguish between ciders from various brands and to evaluate their freshness.

1. Introduction

Nowadays food authenticity is a relevant quality criterion and an essential challenge that must be faced in many different quality control tasks. Quality control should be able to establish the actual origin of a product and detect deliberate or accidental adulteration of valuable food components. The food industry, regulatory authorities and consumers are all interested in authentication of raw materials and verification of the origin, or the specific parameters of the product (Ashurst & Dennis, 1996, 1998; Lees, 2003). The combination of modern analytical techniques and chemometric pattern recognition is a powerful strategy which greatly contributes to promotion and quality assurance in the food industry. Food quality evaluation becomes more complex in the case of natural products of local origin, characterized by considerable diversity, resulting from the conditions of cultivation, plant varieties, different treatments or weather. Useful strategy relies on application of the specific markers, which allow for rapid identification of food products. This approach may be performed by investigation of the profile of selected compounds, for example biologically active ingredients, such as antioxidants. The profile of natural antioxidants may be source of information, useful for identification of the plant species, geographical region of cultivation, and manufacturing or storing processes.

Cider is popular alcoholic beverage produced by the fermentation of the apple juices. In Europe, its consumption in 2014 was close to 14 million hectoliters (Association of the Cider and Fruit Wine Industry of the European Union). Ciders have very complex composition – more than 60 different organic compounds have been found in these beverages (Burroughs, 1957; Williams, 1974; Williams & Tucknott, 1971). Ethanol content varies from 1.2% to 12% while the content of total phenols – from 200 to 3800 mg L^{-1} depending on the used apple variety (Riekstina-Dolge, Kruma, Dimins, Straumite, & Karklina, 2014). Major polyphenols present in cider are phenolic acids (hydroxy- and dihydroxycinnamic acids, among others: caffeic acid, chlorogenic acid, *p*-coumaric acid, syringic acid, hydrocaffeic acid and ferulic acid), flavanols (catechin, epicatechin and procyanidins), volatile phenols (catechol and tyrosol), dihydrochalcones and flavonols (Alonso-Salces, Guyot, et al., 2004; Alonso-Salces et al., 2006; Peng, Liu, Peng, & Ye, 2005; Picinelli Lobo, Diñeiro García, Mangas Sánchez, Rodríguez Madrera, & Suárez Valles, 2009; Rodríguez Madrera, Picinelli Lobo, & Suárez Valles, 2006) which are potentially important to the antioxidant activity of cider. From various polyphenols dominating is chlorogenic acid, and also caffeic acid, catechin, syringic acid, and epicatechin (Riekstina-Dolge et al., 2014). The phenolic profile of cider is influenced by several factors, such as the specimen of the apples used as raw material, climate and maturity in which they were cultivated (Alonso-Salces, Herrero, et al., 2005; Mangas, Rodríguez, Suárez, Picinelli, & Dapena, 1999), as well as by the manufacturing and storing processes (Lea & Timberlake,

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1978). On the other hand, polyphenols affect the quality of ciders, i.e. the organoleptic properties such as color, aroma and flavor (bitterness and astringency) (Alonso-Salces, Herrero, et al., 2005; Lea & Timberlake, 1978; Peng et al., 2005). The main components of ciders (i.e. alcohol, amino acids and carbon hydrates) are electrochemically active at glassy-carbon electrode (Sánchez Arribas, Martínez-Fernández, & Chicharro, 2012), while the oxidation potential of phenol derivatives stays within the range of the working potential window of GCE (−1.0 V to +1.4 V). The density of the ciders is between 0.997 and 1.013 g mL^{-1} (Riekstina-Dolge et al., 2014).

Some papers present application of the various analytical and physical methods of distinguishing ciders according to their geographical origin (Alonso-Salces, Guyot, et al., 2005; Alonso-Salces et al., 2006; García-Ruiz, Moldovan, Fortunato, Wunderli, & García Alonso, 2007) or characteristic of apples which have been used in the ciders production (Arias Abrodo et al., 2010; Lea & Drilleau, 2003). In each case multivariate data analysis was an important tool which enabled achieving the final effect. Table 1 gives a summary of these papers.

In this work we propose the methodology of distinguishing of the cider samples based on chemometric analysis of differential pulse (DP) voltammograms recorded on the unmodified glassy carbon working electrode. The overall voltammogram is the colligated result related to various components in the tested sample, which have different redox potentials. The advantage of this approach is that only one working electrode is needed, which facilitates the implementation of electronic tongue. Nevertheless, information available for further chemometric analysis is somehow limited. Therefore the selection of a suitable signal processing strategy plays an important role in this approach.

Unsupervised multivariate methods, utilizing preprocessed voltammetric spectrum of polyphenolic compounds are used in order to characterize ciders on the basis of their brand. The possibility of using the voltammetric signal to evaluate the freshness of the cider was also investigated.

2. Materials and methods

2.1. Instrumentation

Electrochemical experiments were carried out in a three-electrode quartz cell with a multipurpose electrochemical analyzer 8KCA (mtm-anko, Poland). The working electrode was glassy carbon disk electrode (BAS, USA), of the geometrical surface area of 7 mm^2. The reference electrode was double-junction $Ag|AgCl|KCl_{sat}$ electrode. The counter electrode was platinum wire with geometrical area >2 cm^2. Magnetic Teflon-coated bar was used for the solution stirring (approx. 400 rpm) except while the measurements were being taken. All experiments were carried out in the room temperature. Prior to use, the glassware and, if necessary, also the electrodes bodies were cleaned by immersion in a 1:1 aqueous solution of HNO_3, followed by copious rinsing with distilled water.

2.2. Reagents and solutions

All measurements were carried out in 5 mL cell with Britton–Robinson buffer (pH = 2.0). The B–R buffer was prepared by diluting H_3PO_4 (⩾99.99%, Aldrich) and CH_3COOH (⩾99.7%, Sigma–Aldrich), and dissolving H_3BO_3 (99.97%, Aldrich) to the final concentrations of 0.04 mol L^{-1} each. The pH was adjusted with 0.02 mol L^{-1} NaOH solution (prepared from NaOH ⩾ 98%, Sigma–Aldrich) to the required value of 2. In every step the double-distilled water was used.

2.3. Samples

The studied samples were 5 different ciders of 2014 vintage, produced in Poland, which were purchased in local supermarkets. The measured ciders were: *Warka* (W), *Smile* (S), *Lubelski na miodzie* (L), *Dobroński* (D) and *Meli Melum* (M). For majority of ciders,

Table 1
Review of the examples of ciders profiling supported by multivariate methods.

Ciders origin	Profile of studied parameters	Research method	Reference
Spain	Volatile compounds (aromatic and spirit profile during aging)	GC–MS	Mangas, Rodríguez, Moreno, & Blanco (1996)
Asturias Country (Spain)	Volatile compounds Total polyphenol content Nonvolatile Acids	GC-FID Folin–Ciocalteu method HPLC-DAD	Picinelli et al. (2000)
Basque Country (Spain)	Polyphenolic composition Total polyphenol content Total Acidity	Thiolysis, RP-HPLC-DAD Folin–Ciocalteu method NaOH Titration	Alonso-Salces, Herrero, et al. (2004)
Basque Country (Spain), France	Polyphenolic composition	Thiolysis, HPLC-DAD	Alonso-Salces, Guyot, et al. (2004)
Basque Country (Spain), France	Total polyphenol content Color parameters	Folin–Ciocalteu method CIELab	Alonso-Salces, Guyot, et al. (2005)
Basque Country (Spain)	Polyphenolic composition	Thiolysis, HPLC-DAD	Alonso-Salces et al. (2006)
Asturias Country (Spain)	Polyphenolic composition	RP-HPLC-DAD	Rodríguez Madrera et al. (2006)
England, Switzerland, France, Asturias and Basque Country (Spain)	$^{87}Sr/^{86}Sr$ isotope abundance ratios Minor and trace elements	MC-ICP-MS ORS-ICP-MS, ICP-AES	García-Ruiz et al. (2007)
Asturias Country (Spain)	Volatile compounds (aromatic profile)	SPME with HSGC-FID, GC–MS	Arias Abrodo et al. (2010)
Ireland, UK, France, Spain, Belgium, Sweden, Australia, New Zealand	δ^2H and $\delta^{18}O$ composition $\delta^{13}C$ and $\delta^{18}O$ composition Sugar analysis	IRMS IRMS HPLC-RID	Carter, Yates, & Tinggi (2015)