Federico J. V. Gomez[1]
Romina P. Monasterio[1,2]
Verónica Carolina Soto Vargas[1]
María F. Silva[1]

[1]Instituto de Biología Agrícola de Mendoza (IBAM-CONICET), Facultad de Ciencias Agrarias, Universidad Nacional de Cuyo, Mendoza, Argentina
[2]Departamento de Química Analítica, Facultad de Ciencias Agrarias, Universidad Nacional de la Pampa, La Pampa, Argentina

Received November 2, 2011
Revised February 18, 2012
Accepted March 12, 2012

Review

Analytical characterization of wine and its precursors by capillary electrophoresis

The accurate determination of marker chemical species in grape, musts, and wines presents a unique analytical challenge with high impact on diverse areas of knowledge such as health, plant physiology, and economy. Capillary electromigration techniques have emerged as a powerful tool, allowing the separation and identification of highly polar compounds that cannot be easily separated by traditional HPLC methods, providing complementary information and permitting the simultaneous analysis of analytes with different nature in a single run. The main advantage of CE over traditional methods for wine analysis is that in most cases samples require no treatment other than filtration. The purpose of this article is to present a revision on capillary electromigration methods applied to the analysis of wine and its precursors over the last decade. The current state of the art of the topic is evaluated, with special emphasis on the natural compounds that have allowed wine to be considered as a functional food. The most representative revised compounds are phenolic compounds, amino acids, proteins, elemental species, mycotoxins, and organic acids. Finally, a discussion on future trends of the role of capillary electrophoresis in the field of analytical characterization of wines for routine analysis, wine classification, as well as multidisciplinary aspects of the so-called "from soil to glass" chain is presented.

Keywords:
Amino acids / Capillary electromigration methods / Elemental species / Mycotoxins / Phenolic compounds
DOI 10.1002/elps.201100595

1 Introduction

The scientific community has found wine to be a very worthy subject for investigation in view of the health benefits associated with moderate wine drinking. Historically, there is evidence that wine has been used as a medicine from ancient times in countries like China and India. Vast scientific evidences have explained the "French paradox" [1]; that is the ability to consume high-fat diet while maintaining a low incidence of atherosclerosis and other coronary diseases in populations that drink red wine daily. Consumption of about 250 mL/d of red wine for 2 months has been shown to significantly increase antioxidant status and decreases oxidative stress in circulation.

While the initial interest in red wine and health was directed toward cardiovascular disease, increasingly wine has been linked with other positive health outcomes. Biological properties of wine are widely diversified, residing in the antioxidant, antihypertensive, cardioprotective, antiinflamatory, bactericide, antimutagenic, and antitumoral activities of its pharmaconutrients [2]. Among the functional ingredients found in wine, red grapes are particularly rich in bioavailable phenols that are rapidly absorbed as intact molecules and delivered into the brain within minutes from their ingestion [3]. Based on nearly two decades of research since the term "French paradox" was first coined in 1992, wine fits the definition of a functional food [4].

During oxidative-stress events, cells respond by increasing the expression and activity of endogenous antioxidant enzymes. Nevertheless, this response may not be enough to scavenge and buffer the reactive species. Therefore, exogenous antioxidant compounds should be included in the diet. In this regard, phenolic compounds in wines represent a suitable source of this exogenous protection.

Wine is a hidroalcoholic solution containing hundreds of compounds; this complexity originates from three major sources: the raw material, which originates from thousands of grape varieties growing on a wide array of geological formations in different climates and altitudes, the fermentation process accomplished by a multitude of yeast and malolactic bacteria species and strains, and the ageing process, which varies as a result of different storage methods, container size and material, such as oak barrels of varying origin, but also owing to stocking time, which may range from a few weeks to more than several decades [5]. Thus, many factors influence the chemical composition if wine, such as grape variety, degree of grape ripeness at harvest, environmental and climatic

Correspondence: Dr. María Fernanda Silva, Instituto de Biología Agrícola de Mendoza (IBAM-CONICET), Facultad de Ciencias Agrarias, Universidad Nacional de Cuyo, Mendoza, Argentina.
E-mail: msilva@fca.uncu.edu.ar
Fax: +54-261-4960469

Abbreviations: BA, biogenic amine; **CHO**, carbohydrate; **MT**, melatonin

Colour Online: See the article online to view Figs. 2 and 3 in colour.

conditions, viticultural practices, and technology, all of them affecting the quality of the final product.

The international market related to wine is exceedingly competitive, so wine producers need to invest in technology and research in order to improve production and product quality. Consequently, it is important to recognize the relationship between the chemical nature and sensory properties of wines, and therefore the enologic and viticultural practices determining the chemical profile of the final product. Taken together, wine analysis has a great impact on diverse areas of knowledge as can be seen in Fig. 1.

As a consequence, a great deal of effort is being carried out in recent years for the development of accurate, sensitive, robust, versatile, and cost-effective analytical methodologies for the simultaneous determination of analytes of enological interest in wine and its precursors. Over the past 10 years, a number of interesting articles describing the separation of compound in wine by CE have been reported (Fig. 2). Capillary electromigration techniques have emerged as a powerful tool, allowing the separation and identification of highly polar compounds that cannot be easily separated by traditional HPLC methods, providing complementary information and permitting the simultaneous analysis of analytes with different nature in a single run. In the case of vegetal matrices related to the wine industry, the use of CE typically excludes complicated sample treatment.

2 Phenolic compounds

Phenolic compounds play an important role in plants, foods, and humans. They are one of the most important, numerous, and ubiquitous groups of compounds in the vegetable kingdom, being synthesized by plants during normal development and in response to different situations (biotic and abiotic stress, UV radiation, etc.) [6]. They can be classified in two groups: flavonoids and nonflavonoids (Fig. 3). The major flavonoids in wine include conjugates of the flavonols: quercetin and myricetin; the flavan-3-ols, (+)-catechin and (-)-epicatechin; and anthocyanins. The nonflavonoids include the hydroxybenzoates: *p*-hydroxybenzoic acid and gallic acid; the hydroxycinnamates: caffeic, caftaric, and *p*-coumaric acids; and the stilbenes: *trans* (t)-resveratrol, *cis* (c)-resveratrol, and t-resveratrol glucoside [7].

Wine is considered as a rich source of polyphenols and their contents vary depending on wine and grape origin, the amount of phenolic compounds in red wine is about six times higher than that in white wine because red juice has longer contact time with the grape skins and seeds [8]. Wine makers have to make choices at crushing and pressing stage that will affect the style of wine. Both color and astringency derive from polyphenols, which are concentrated particularly in the stems, seeds, and skins [9].

The content of phenolic compounds is an important indicator of wine quality. These substances influence sensory attributes of wine and they also play a principal role in the color chemistry of red wine during ageing [10]. Phenolic compounds come from various parts of grape bunches and are extracted during winemaking process. Their structure varies a great deal from grape to bottle as well as with age [11].

Flavonoids constitute the most important group of polyphenols; actually more than 5000 different compounds are known [12]. These constituents of wine are responsible for color, astringency, and bitterness [9]. Flavonoids differ

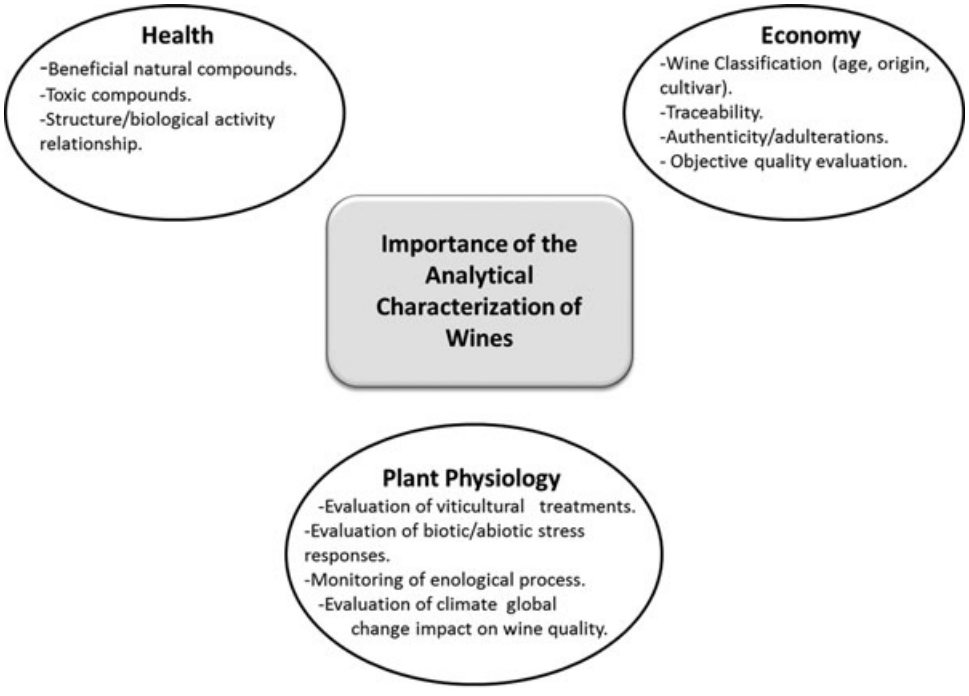


Figure 1. Importance of the analytical characterization of wines.

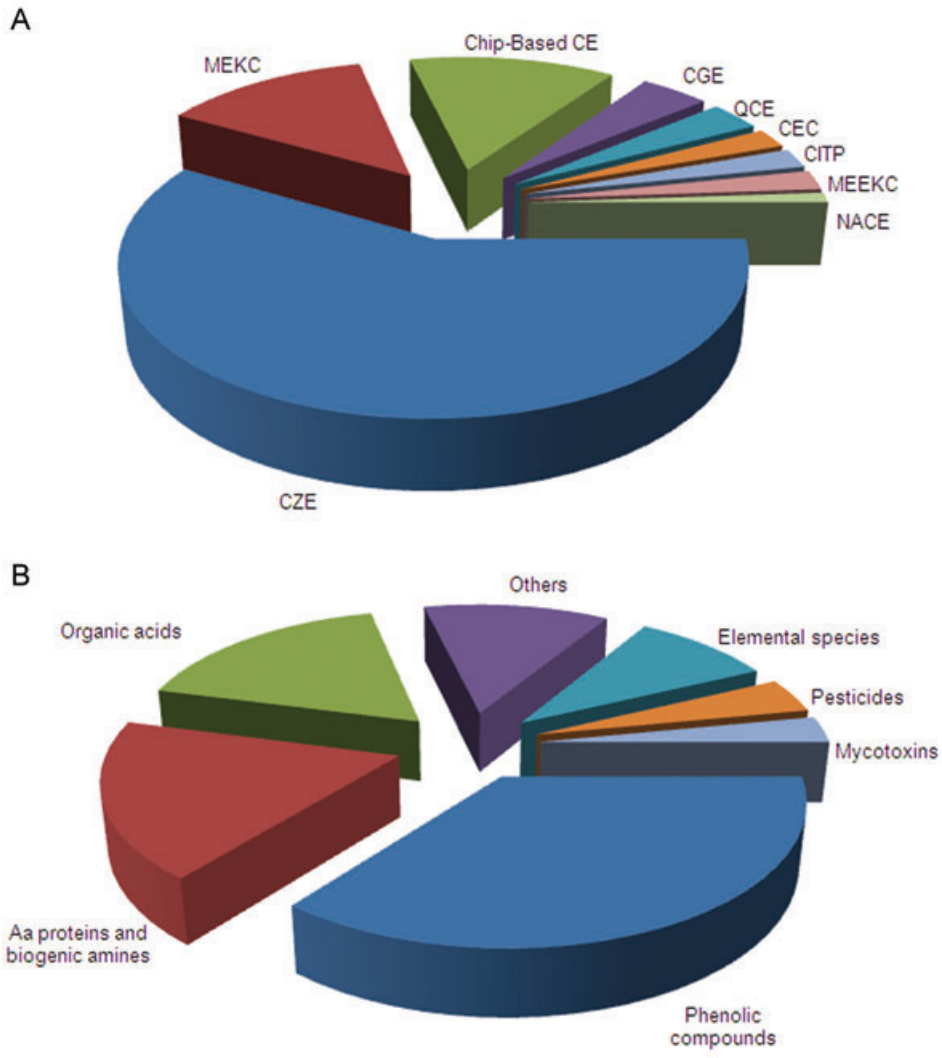


Figure 2. Pie charts showing capillary electromigration techniques for wine analysis. (A) Contributions according to operation modes. (B) Contributions according to the analytes determined.

greatly in their chemical structures and biological properties. Some flavonoids, such as quercetin, have free-radical scavenger properties and are considered as dietary antioxidants [12]. The color and the quality of wine depend to a large extent on the anthocyanins present in grapes. Nevertheless, the winemaking and maturation processes also influence on the concentration and the type of anthocyanins in wine [13–16].

The nonflavonoids constituents such phenolic acids are important in the wine industry due to their profound effect upon the sensory characteristics of wine (including flavor, color, and bitterness). In particular, hydroxycinnamic acids are present as tartaric esters in vacuoles of grape skin and pulp cells of wine grapes and are named caftaric, *p*-coutaric, and fertaric acid. The reaction between anthocyanins and hydroxycinnamic acids has gained importance, since it causes the stabilization of colored forms of anthocyanins and consequently enhances their color [17].

Resveratrol (3,5,4′-trihydroxystilbene) is an antioxidant compound belonging to the family of stilbenes. It exists in *cis*- and *trans*-isomer forms, being the trans isomer the most common in natural sources [8]. It is an antioxidant compound belonging to the family of stilbenes. This compound can be produced as an antifungal agent; therefore it can be found in healthy grapes as well as infected ones. Resveratrol content in wines can vary as a function of viticultural and enological practices. Wines produced with long maceration times were found to show much higher resveratrol content. Red wines contained higher levels of resveratrol than white wines regardless of maceration duration [18].

Due to the health significance of phenolic compounds, over the last decades numerous analytical methods have been developed for their separation, identification, and quantitation in natural products. Total phenols and polyphenols are usually quantified by employing Folin–Ciocalteu's reagent. This procedure is also employed in the wine industry, where gallic acid is usually selected as a standard [12]. Such analyses provide a rapid and appropriate response, but it cannot be used as a tool to identify and quantify individual phenolic

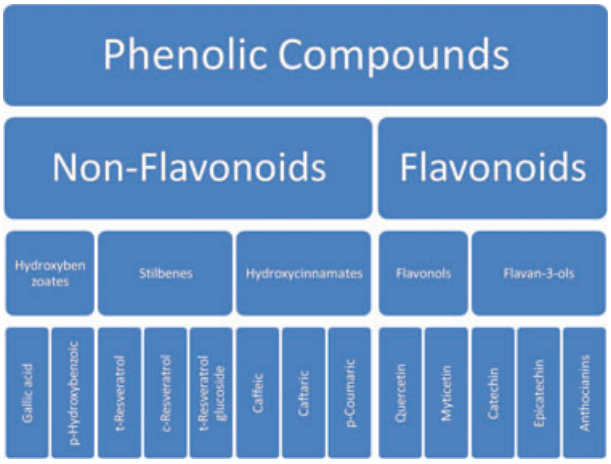


Figure 3. Graphical list of phenolic compounds.

compounds. Furthermore, since other compounds present in the matrix may contribute to the absorbance, these methods are characterized by poor selectivity.

A great number of publications concerning phenolic compounds of wine can be found, however, only few (less than 10%) are referred to electrophoretic methods. Several articles compare chromatographic techniques [5], usually HPLC, with CE [9, 16, 21]. The most used methodologies are capillary zone electrophoresis (CZE) [15–17, 19, 20] and micellar electrokinetic chromatography (MEKC) [17, 21, 22], although capillary isotachophoresis (CITP) [10] is also used and, in a lesser extend nonaqueous CE (NACE) [23]. A number of selected approaches regarding the determination of phenolic compounds in samples of viticulture interest is presented in Table 1.

Havel and co-workers have used CZE with preconcentration by solid-phase extraction (SPE) and they applied neural networks to predict cultivars and vintage of samples of young wines [24]. Berli et al. developed a simple, accurate, and rapid method for the separation and simultaneous determination of representative phenolic compounds in grape treated with different solar UV-B radiation levels by CZE [20]. Silva and co-workers studied the effects of combined in field treatments (water-stress and exogenous ABA) on phenolic accumulation for berries and wine. The responses were assessed by UV–Vis and CZE [15]. Peres et al. developed and validated a method for the simultaneous determination of the stilbene resveratrol, four phenolic acids (syringic, coumaric, caffeic, and gallic acids), and five flavonoids (catechin, rutin, kaempferol, myricetin, and quercetin) in wine by CZE [25].

It has to be pointed out that phenolic analysis is by far the most developed strategy for wine characterization due to their great importance on wine quality, health properties, and potentiality of wine classification (origin, cultivar, and age). The main advantages of CE over other techniques are versatility, rapidness, reproducibility, low cost per analysis, and, specially, lower matrix effects.

3 Amino acids, proteins, and biogenic amines

Amino acids found in grape musts are important as nutrients for the growth of yeasts, since they are consumed as a nitrogen source during the alcoholic fermentation [31]. However, they are not only nutrient substances in wine, but also are precursors for aroma compounds and directly contribute to the bouquet, taste, and appearance of wine. Regardless wines are not rich in protein, they contain free amino acids. Several of these amino acids undergo a series of biotransformation, yielding higher alcohols, aldehydes, esters, or ketonic acids. Therefore, amino acids have a significant impact on the organoleptic properties of wine and some researchers have employed the composition in amino acid for purposes of differentiating wines [31, 32]

CE has been used to separate and detect amino acids, peptides, and proteins in different food samples. Methods of detection used to detect amino acids include laser-induced fluorescence (LIF), which has limits of detection of about 10^{-20} M for derivatized amino acids. One drawback of this technique is the length of time taken in sample preparation, since it requires a process of derivatization and preconcentration prior to analysis [31].

Treilhou et al. [32] reported that detection selectivity of amino acid in wine is poor because of multiple molecules that absorb in the UV range (e.g., flavonoids, peptides, nucleotides, etc.) so that, they used LIF detection, labeling wine samples using a concentrated fluorescein isothiocyanate (FITC) solution . According to these authors the sensitivity of the LIF detection for labeled amino acids (fluoresceine isothiocarbamyl amino acids) was approximately 10^{-12} M. The concentration of amino acids in wine was in the micromolar range. On the other hand, Martinez-Giró et al. [33] optimized an in-capillary derivatization method by CE for the determination of chiral amino acids. The enantiomers of arginine, lysine, and ornithine were determined. The enantiomeric determination of these amino acids showed that higher concentrations of L-lysine were present in the rose wine (1.6×10^{-4} M) than in the red wine (6.6×10^{-5} M). Similar concentrations of L-arginine were obtained in both wines (6.6×10^{-5} and 7.5×10^{-5} M, respectively). However, the highest concentrations of L-orninthine were found in the red wine (6.2×10^{-5} M) in comparison with the rose wine (2.0×10^{-5} M) [33].

Proteins are commonly present in wines at low levels, most of them having a remarkable and economical relevance. As proteins form complexes with tannins or polyphenols, they can influence wine stability and clarity. Thus, a variety of procedures has been developed for their removal from wines [33].

Exogenous proteins are frequently added to wines for clarification purposes. Fining agents typically used for clarification of wine include milk proteins, egg proteins, and/or fish gelatin. Among milk proteins, caseins are universally known as suitable agents for binding phenolic compounds and reducing off-flavor ingredients that may affect wine taste and

Table 1. Phenolic compounds present in wine and its precursors by CE

Compounds	Mode	Sample	Comments	Ref.
Phenolic compounds	CZE	Red, white, and rose wines	Relationship between total phenolic content and total antioxidant potential	[12]
		Red and white musts	Evaluation of the effects of the enzyme laccase used for clarification	[9]
		Red and white wines	Prediction of cultivars and vintage using artificial neural networks (ANN)	[24]
		Red, white and rose wines	λ=190 nm, three-dimensional electropherograms used as fingerprints	[26]
		Berries and wine	Evaluation of the effects of water deficit and exogenous abscisic acid	[15]
	CZE-ITP	Red wine	Online combination of CZE with ITP	[10]
	CE	Red, white, and blended wines	Multivariant optimization	[25]
Flavonoids	CZE	Grape wine	Separation of luteolin and quercetin	[13]
	MEKC	Red and white wines	Anticarcinogenic flavonoids for fingerprinting of wines from different regions	[27]
	NACE	Red and white wines	BGE = malonate(pH 13.5), capillary coated with poly(GMA-co-NVP) copolymer	[8]
Anthocyanins	CZE	Red wine	Minimal sample setup time with the addition of SO_2	[21]
		Tannat wine	Analytes isolated by LC fractionation and concentrated by lyophilization	[22]
Phenolic acids	Microchip CE	Red wine	Microchip protocol with amperometric detection	[28]
	ASEI-sweeping MEEKC	Red wine	96,000- to 238,000-fold increases in detection sensitivity	[29]
Polymeric pigments	CZE	Red wine	Characterization of different red, white, and aged wines	[14]
		Wine	GPC fractionation	[30]
Antioxidants	CSEID and IAD	Red and white wines	Microfluidic platforms	[23]

color. The analysis of fining agents like caseins, that might be present as residues in wines, is of importance to safeguard allergic consumer's health and to comply with the legislation issued on food allergens of many countries. Monaci et al. [34] studied a method using a capillary separation combined with mass spectrometry (MS) for the identification of peptides from caseins, which was applied to white wine fined with caseinate. With the proposed method it was possible to detect and identify some peptides arising from α and β caseins present as residues in wine extracts.

Biogenic amines (BA) derive essentially from the decarboxylation of the respective precursor amino acids through substrate-specific enzymes resulting from the microorganisms present [35]. They are a group of low-molecular mass organic bases that are formed from the degradation of the amino acids by the action of microorganisms. In wine they can be formed by various microorganisms associated with the different stages of wine production and storage (e.g., grape variety, skin maceration, microorganism strains, levels of sulfur dioxide, pH, duration of wine contact with yeast lees, or aging process). Moreover, BA content in wines is dependent on climatic and geological factors of the producing regions [35–38].

The most important BAs found in wine are histamine, tyramine, putrescine, cadaverine, and β-phenylethylamine, which are products of the decarboxylation of histidine, tyrosine, ornithine, lysine, and β-phenylalanine, respectively [39, 40]. The concentration of histamine, tyramine, and putrescine are low after alcoholic fermentation, and increase in most wines during malolactic fermentation to a very variable extent. Putrescine in grapevines has been associated with the potassium deficiencies of the soil. Viticulture practices that do not prevent potassium deficiency may contribute to higher contents of putrescine in wine [35].

Wines with too high levels of BA may be harmful and poisoning on susceptible individuals. BA such as histamine, tyramine, and phenylethylamine are known to induce nausea, headaches, and respiratory disorders in sensitive individuals, particularly when accompanied by alcohol and acetaldehyde [41]. In addition to toxicological issues, BA such as putrescine and cadaverine seem to modify negatively the taste properties of wines as they have been associated to dirty and rancid flavors [38]. Therefore, their presence is considered as marker molecules of quality loss. Several European countries have made recommendations for the amount of BA acceptable in wine, though each country has

different values as maximum acceptable levels (e.g., Germany 2 mg/L, Belgium 5–6 mg/L, Switzerland and Austria 10 mg/L, France 8 mg/L, and Holland 3 mg/L) without reaching a consensus on this parameter [42]. The latter has a great economic impact on countries that export wines to European countries [43].

Although HPLC is the most common method for the analysis of BA, CE has recently become attractive since it is one of the most powerful separation techniques for the analysis of BA in wine because of its speed, high resolving power, and extremely small sample requirement [44]. As most BA are protonated under physiological conditions, they are cations and thus their separations by CZE can be carried out under acidic conditions in the presence of small EOF. Nevertheless, CZE does not provide enough resolving power for the separation of the analytes, especially because the BA have low hydrophilic properties, similar dissociation constant (Ka) values, and the tendency to be adsorbed on the capillary wall. In order to overcome the solubility problem and improve resolving power, MEKC is preferred [45]. A number of selected approaches regarding the determination of biogenic amines and amino acids in wine are presented in Table 2.

CE with UV–Vis detection is widely used for the analysis of samples such as foods and beverages that contain high concentrations of amines of interest. Nonetheless, derivatization is required for wine analysis when conducting UV–Vis absorption and fluorescence detection [46]. Recent advances in derivatization strategies and innovative online preconcentration procedures have contributed dramatically to enhance the sensitivity of the methods [38]. Derivatization procedures can be classified in three different modes based on the analytical stage where derivatization takes place: before (precapillary), during (in-capillary), or after (postcapillary) the electrophoretic separation [33]. The technique is chosen depending on the reaction speed and conditions, as well as whether the labeling agents and side products have unfavorable effects on the separation resolution and detection sensitivity [45]. In 2006, García Villar et al. [46] introduced hydrodynamically reagent and buffer solutions into the capillary whereas the sample was injected electrokinetically, thus allowing a selective preconcentration of the analytes by field-amplified sample stacking. Afterwards, amines were labeled inside the capillary using a zone-passing derivatization approach in mixed tandem mode. According to Martínez-Girón et al. [33], in-capillary derivatization procedures offer many advantages over conventional pre- and postcapillary derivatization modes. They can allow a full automatization of the derivatization step without additional equipment, minimize sample preparation, sample dilution is reduced to a minimum, and a low consumption of sample and derivatizing reagent is required. Despite of this, low concentrations of BA show poor sensitivity to UV absorption detection. A combination of LIF detector and MS with capillary electrophoretic separations provided a remarkable improvement in detection limits [44]. Laser-induced native fluorescence (LINF) detection provides selectivity and at least ten times greater sensitivity for aromatic and heterocyclic amines. Generally, the CE-LINF electropherograms of biological samples are relatively simple when compared to those of CE UV–Vis, mainly because of fewer analytes having intrinsic fluorescence properties. Alternatively,

Table 2. Biogenic amines and amino acids present in wine by CE

Analyte	Mode	Sample	Comments	Ref.
Biogenic amines	CZE	Red wine	Field-amplified simple stacking and in capillary derivatization. Multivariate optimization. LODs = 0.02–0.91 mg/L	[46]
	CZE	Red wine, sake, beer, and musts	Microfabricated glass CE device with fluorescence detection	[41]
	CZE	Red and white wine, beer, salami, cheese	BGE: histidine - adipic acid - sulfuric acid - ethylenediaminotetraacetic acid - hydroxyethylcellulose - methanol (pH 5.8). Conductometric detection	[48]
	Cyclodextrin-modified-CE	Fish, wine, and urine	BGE: borate, methyl-β-cyclodextrin, sulfobutylether-β-cyclodextrin and 10% ethanol (pH 9.0)	[47]
	CE-IT-MS CE-TOF-MS	Red and white wines	LODs = 0.08–2.81 mg/L	[39]
	MEKC	Wine, pomegranate juices, and pomegranate molasses	LIF detection LODs = 0.42–1.26 nM. BGE = Brij 35 and borate (pH 9.6)	[44]
Amino acids	Cyclodextrin-modified-CE	Dietary supplements and wines	BGE: phosphate buffer - Highly sulfated-β-ciclodextrin and acetylated-β- ciclodextrin (pH 2.0). Amino acid enantiomers determination	[33]

electrochemiluminescence (ELCL) is a good choice for the analysis of tertiary amines, mainly because of its sensitivity and selectivity [45].

Male and Luong [47], using CE-LIF, reported noticeable levels of putrecine and cadaverine in both white and red wines. Putrescine levels were higher at 45 and 84 μM compared to cadaverine levels at 6.4 and 11 μM for the white and red wines, respectively.

Kvasnčka and Voldřich in 2006 [48] developed a direct sensitive and quick electrophoretic method for the determination of BA in selected food (salami, cheese, wine, and beer). They used a CZE with conductometric detection and reported that this method is able to detect BA in beer or wine at ppm levels without any pretreatment, just dilution with water, within 10 min. According to these authors, putrescine and histamine had higher levels among the BA studied in wine samples.

On the other hand, Jayarajahet et al. [41] determined BA in fermented beverages using a portable microchip CE system. Tyramine was found mainly in red wines at 1–3.4 mg/L, while the histamine content of these samples ranged from 1.8 to 19 mg/L.

Simó et al. [39] reported that ion-trap and time-of-flight MS coupled to CE, (CE-IT-MS) and (CE-TOF-MS) respectively, allowed both the identification of BA in wines without any previous treatment and the quantitation of these compounds with limits of detection as lower as 10 ng/mL.

Regarding sensitivity and limits of detections, CE methods are suitable for quantifying the most relevant amines such as histamine, tyramine, putrescine, and cadaverine. Although improvements for increasing the robustness of the CE methods are still required, the combination of electrophoretic preconcentration based on stacking with in-capillary derivatization is recognized as a highly attractive option for straightforward analysis of BA in wines [38].

One of the most successful application areas of CE is the chiral analysis of amino acids. In the CE analysis of amino acid enantiomers, the selection of the separation mode is one of the most important issues to obtain good resolution of target enantiomers. Among various modes in CE, cyclodextrin-modified CZE (CD-CZE), CD EKC (CDEKC), MEKC, CD-modified MEKC (CD-MEKC), ligand-exchange CE (LE-CE), affinity CE (ACE), and NACE have been applied to the separation of racemic amino acids [49].

4 Elemental species

Knowledge of the accumulation of mineral elements in plants and their distribution in the different vegetal tissues has been considered to be essential for biochemical and physiological studies and is a fundamental tool for supporting traceability studies on the geographical origin of food commodities, table grapes, and wine [50]. The presence of macro–micro and trace elements in wine is a contribution to the organoleptic, nutricional, and toxicological profile of wines [51]. On the other hand, minerals seem to be the primary candidates for a fingerprint due to their stability. The metallic composition of wine depends on many factors, some of which are related to the specific production area, grape varieties, soil and climate, culture and winemaking practices, and yeasts. Taking into account the influence of all these factors, a great variability in the metal content in wines from different areas, regions, and countries is observed. Determination of typical levels of metal in wines is a very useful tool to differentiate wines from different geographic origins as well as to detect adulterations and falsifications [52].

CE is an effective tool for separating metal ions [53]. Taking into account that most of the metal species are not or weakly UV active, cationic chromophores are usually added to the running buffer for their detection. Most of the currently used cationic chromophores are compounds with atoms that can be protonated [54].

The metals most commonly analyzed by CE in wine are: K, Na, Ca, and Mg [52, 54–56] because these are the most abundant elements in this beverage. Other metals that have been determined in wine by CE are Ba, Li, Co, Cu, Ni, Fe, and Mn [2–4, 7]. Qin et al. [54] reported the CZE separation of K, Na, Li, Ca, Mg, and Ba in red wine with reversed electroosmotic flow on a room-temperature ionic liquid coated capillary. Sirén and co-workers [55] used CE for determination of inorganic alkali and alkali earth metal cations in six Pinot Noir grape red wines. Spectrum analysis was applied to evaluate chemical differences between the wines from different geographic origin. Tang et al. [53] developed the application of the cloud point extraction (CPE) technique as a preconcentration step for NACE determination of trace metal ions in commercial flavor wines. Ming Fu and co-workers [56] presented an innovative design and fabrication method for semicircular detection electrodes designed for CE microchips. The developed detector comprises microchannels for sample injection and separation, and side channels for two buried detection electrodes. They identified four metal ions in six commercial beverages including red wine.

5 Organic acids

In the wine industry, the monitoring of organic acids is of principal importance for quality and process control. Organic acids have a major role in the microbiological and physicochemical stability and sensory properties of wines [57,58]. The analysis of organic acids allows controlling the evolution of the acidity during the different steps of the winemaking process (alcoholic and malolactic fermentation, aging process, etc.). Some sensory properties of organic acids are characteristic acidity (pleasant and refreshing sourness), astringency, taste, smell, color, etc. [59–62]. This pleasant and refreshing sourness of organics acid in wines have a limit; in excess, they promote an unpleasant acidity, suppressing the perception of other desirable flavor and mouth-feel attributes, especially the perception of sweetness. An example is tartaric acid, the most abundant acid in wines, which, in high concentrations, gives a sharp, unpleasant taste to the beverage.

Malic acid promotes an additional taste described as harsh that can be reduced via the malolactic fermentation, which transforms malic acid into lactic acid. Succinic acid promotes a bitter note in the wine, causing salivation and accentuating the overall flavor of the beverage. Citric acid is occasionally added to wines as an acidifying agent, but since this acid is not dominant in grapes, large additions may result in what many would regard as a citrus-like flavor. Other fixed acids, such as fumaric and pyruvic acids, are generally found in minor amounts in wines, and do not usually cause any sensory impact on the beverage [61, 63]. The acids come from the grapes, such as tartaric, citric, and malic acids, or are produced during fermentation (lactic, acetic, and succinic acids) [63]. These compounds also have great importance in the detection of wine alterations and/or illnesses, because they suppose a modification of acid content. For example, some wine alterations (bacterial participation) are related to increase in the levels of acetic and lactic acids (acetic or lactic sharpness, respectively) [64]. Also, there are small amounts of other acids, like galacturonic, glucuronic, citramalic, dimethylglyceric, pyruvic, ketoglutaric present in wine [65]. Table 3 lists the contents of principal organic acids present in wine with their chemical structure together with some important information.

The application of CE for organic acids analysis has been growing in the last years. Compared with other techniques, like HPLC, CE offers several unique characteristics that make it particularly attractive for analysis of wine, such as high resolving power, minimal reagent consumption, rapid and low-cost analyses. The CE methods reported for organic acids are mainly by CZE. The detection system used for determination of organic acid in wine is mainly UV spectrophotometry. Detection systems such as conductivity and MS have been used in few methodologies using different sample or other analytes [66, 67]. Whereas, UV detection is employed principally due to its nearly universal detection nature [68, 69]. The CE-UV methodologies encompass two modes, direct detection and indirect detection [68,69]. In indirect detection, chromophoric reagents more used in organic acids present in wine are 3,5-dinitrobenzoic acid (DNB) [8], 2,3-pyrazinedicarboxylic acid [70], 2,6-pyridinedicarboxylic acid (PDC) [71, 72], 1,2,4,5-benzene-tetracarboxylic acid (pyromellitic acid or PMA) [73], 1,3,5-benzenetricarboxylic acid (BTA) [74] among other.

In order to separate anionic analytes in a short time and adequate resolution it is necessary to reversal the direction of EOF. Different electrolyte systems have been proposed, generally comprising of quaternary ammonium salts (cetyltrimethylammonium bromide (CTAB) [64, 70, 72, 75], cetyltrimethylammonium hydroxide (CTAH) [66], tetradecyltrimethylammonium hydroxide (TTAOH) [57], tetradecyltrimethylammonium bromide (TTAB) [76], myristyltrimethylammonium bromide (MTAB) [21]), amines (bis-(2-aminoethyl)-amine (DETA) [68]), and alkylamines (tetraethylenepentaamine (TEPA) [74]) as EOF reversers.

The most representative: tartaric, malic, succinic, acetic, citric, and lactic acid [57, 64, 71–73, 75–78]. Taking into account the LODs of the different methodologies published, interestingly the values are very different for each one (Table 3). For the majority of them, the separations are optimized to obtain fast analyses, separation, and determination of main organic acids that can be achieved between 3 and 18 min. Considering the analytical performance of the reported methodologies and the great economic impact of the analysis of organic acids in wine and its precursors, CE can be surely considered as a routine technique for these analytes in wineries.

6 Mycotoxins

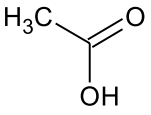
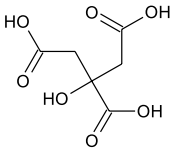
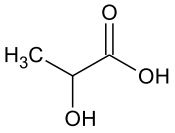
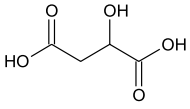
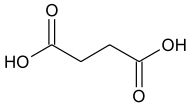
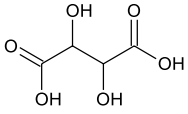
Mycotoxins are toxic secondary metabolites produced by about 200 identified filamentous fungi, as for example, *Fusarium, Aspergillus,* and *Penicillium* species, growing under a wide range of climatic conditions on agricultural commodities (grains, spices, fruits, coffee, nuts, etc.) in the field and during storage [79–81]. These toxics compounds are of low molecular weight and nonproteinaceous. Some mycotoxins have been mentioned in grape products (patulin, aflatoxins, trichothecenes). However, mycotoxins such as these are seldom detected in wine and other grape products and are currently of little concern for the grape and wine industries. In wine, the most important mycotoxin is the ochratoxin A (OTA) that is not appreciably degraded during winemaking, fermentation process, and storage [81–83]. OTA is known to have nephrotoxic, immunotoxic, teratogenic, and carcinogenic effects [84]. The maximum permitted level for wine (white wine, rose wine, and red wine) is 2.0 $\mu g\ L^{-1}$ [85]. Wine is considered the major source of OTA intake after cereals [86].

Patulin is an unsaturated heterocyclic lactone, produced by certain fungal species growing on fruit [87]. Patulin has been mainly found in apple and apple products and occasionally in pears, grapes, apricots, strawberries, blueberries, and peaches. This mycotoxin is destroyed by the fermentation process during cider or wine production [79]. Another important group of mycotoxins are trichothecenes. These are responsible for a wide range of disorders in animals, including feed refusal, weight loss, and vomiting. These toxin mainly occurs in grains such as barley, corn, and cereal-based products [86].

CE has been recognized as a suitable separation technique that offers the advantages of faster method development, higher efficiency, and lower consumption of solvents and reagents. Some methods using CE have been developed for mycotoxin analysis: fumonisin B1 in corn [88], aflatoxins in corn [89], patulin in apple juice [90], and OTA in coffee, corn, and sorghum [91]. However, up to now only a few methods for the determination of micotoxins in wine using CE have been reported [92].

MEKC and CZE in combination with different detection schemes have been the main CE modes applied for mycotoxin analysis [88–93]. While the development of MEKC methods has been devoted to detect mostly fumonisins and aflatoxins, CZE method has been developed for the detection of OTA [92].

Table 3. Organic acids present in wine by CE

Organic acids	Chemical structure	General information	Origin	Analytical performance		Ref.
				LOD (mg L^{-1})	RSD (%)	
Acetic acid ($C_2H_4O_2$)		MW: 60.05 pKa: 4.75	Fermentation	0.9	1.4	[52]
				0.054	0.40	[72]
				0.12	-	[69]
				46.4	4.9	[67]
				1.78	-	[70]
				0.93	5	[59]
				1	6.4	[65]
				0.29	2.69	[52]
Citric acid ($C_6H_8O_7$)		MW: 192.12 pKa: 3.08; 4.74; 5.4	Grape	2.2	1.0	[66]
				0.38	-	[69]
				75.0	5.0	[67]
				1.55	5	[59]
				1	4.8	[65]
				0.23	2.39	[52]
Lactic acid ($C_3H_6O_3$)		MW: 90.07 pKa: 3.86	Fermentation	1.2	1.8	[66]
				0.032	0.58	[72]
				0.27	-	[69]
				28.5	5.1	[67]
				36.74	-	[70]
				0.70	5	[59]
				1	8.1	[65]
				0.10	1.87	[52]
Malic acid ($C_4H_6O_4$)		MW: 118.08 pKa: 3.45; 5.09	Grape	1.2	1.5	[66]
				0.037	0.74	[72]
				0.27	-	[69]
				30.6	1.5	[67]
				19.68	-	[70]
				0.64	5	[59]
				1	4.9	[65]
				0.05	2.56	[52]
Succinic acid ($C_4H_6O_5$)		MW: 134.08 pKa: 4.20; 5.63	Fermentation	1.2	1.5	[66]
				0.015	0.82	[72]
				0.24	-	[69]
				37.8	5.0	[67]
				6.13	-	[70]
				0.86	5	[59]
				1	6.8	[65]
				0.05	1.78	[52]
Tartaric acid ($C_4H_6O_6$)		MW: 150.08 pKa: 3.03; 4.36	Grape	1.4	2.2	[66]
				0.040	0.96	[72]
				0.3	-	[69]
				25.0	1.2	[67]
				19.92	-	[70]
				1.02	5	[59]
				1	4.4	[65]
				0.38	0.81	[52]

Separation conditions	
[66]	5 mM PDC, 0.5 mM CTAB (pH 5.6); indirect detection; time: 15 min
[72]	3 mM phosphate, 0.5 mM MTAB (pH 6.5); direct detection; time: 6 min
[69]	3 mM BTA, 15 mM Tris, 1.5 mM TEPA (pH 8.4); indirect detection; time: 14 min
[67]	7.5 mM PDC, 0.5 mM CTAB, 0.5 mM EDTA (pH 5.6); indirect detection; time: 18 min
[70]	5 mM PDC, 0.5 mM CTAB (pH 5.6); indirect detection; time: 10 min
[59]	20 mM 2,3-pyrazinedicarboxylic acid, 65 mM Tricine, 2 mM $BaCl_2$, 0.5 mM; time: 5.5 min
[65]	CTAB, 2 M urea (pH 8.06); indirect detection; time: 10 min
[52]	7.5 mM NaH_2PO_4, 2.5 mM Na_2HPO_4, 2.5 mM TTAOH, 0.24 mM $CaCl_2$; (pH); direct detection; time: 3 min

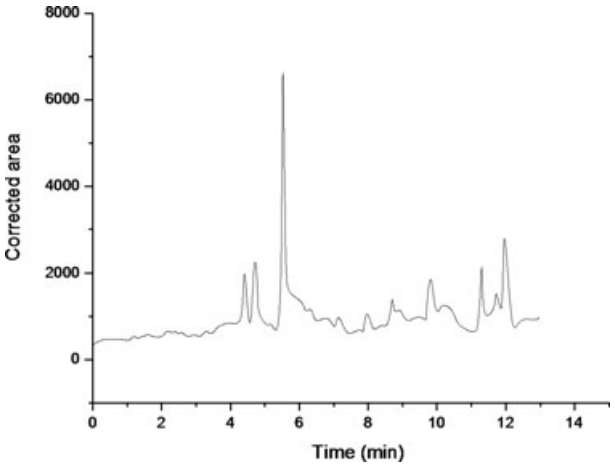


Figure 4. Electropherogram of a red wine (cv Malbec) sample by CEC with immobilized c-MWNT as stationary phase (reprinted with permission from reference [95]).

The detection methods employed in CE methodologies for mycotoxins analysis are mainly LIF. Most of the mycotoxins have own fluorescence or are easily derivatized, so LIF is the detection most used. The LODs and LOQs achieved with LIF (ng L^{-1}) are compatible with legislation. Gonzalez-Peña et al. reported a methodology to determine OTA in wine by CE-DAD, but the LOD achieved is not consistent with legislative requirements [92]. CE-ESI-MS was reported by Hines et al. to analyze fumonisin in corn [94].

7 Miscellaneous

Melatonin (MT), the often called "hormone of darkness" is a ubiquitous molecule widely distributed in nature. It plays a decisive role in the regulation of circadian and seasonal rhythms. MT is beneficial for the immunological system, enhancing resistance to infection and diseases, presenting inhibitory activity on some cancer forms, and inducing beneficial effects on neuronal disorders. Stege et al. [95] implemented a new method for the determination of MT in red and white wines, grape skin, and plant extracts by CEC with immobilized carboxylic multiwalled carbon nanotubes (c-MWNT) as stationary phase (Fig. 4). The straightforwardness and reproducibility of the extraction procedure is accompanied by the high electrochromatography resolution, robustness, and high sensitivity obtained, providing a useful tool for further research into MT in foods of vegetal origin.

The determination of sulfite (or sulfur dioxide) is important in many environmental and industrial situations, particularly when monitoring atmosphere, food and beverages, process liquors and wastewaters from paper mills, photographic laboratories, mining sites, and mainly in the wine industry. Jankovskiene and co-workers [96] developed a capillary electrophoretic method for the simple and selective determination of free sulfite in wines. The analysis does not require any preliminary treatment of the samples except dilution. The proposed CE method appears to be a good alternative to iodometric and colorimetric procedures for determining sulfite in samples containing interfering substances.

The analysis of carbohydrates (CHOs) in foods has extreme nutritional importance since they contribute with 40–50% of the caloric intake of human beings. The constant increase in obesity indices, diabetes, and some CHO intolerances intensify the necessity of their rigorous control. In wines, the quantification of CHOs is correlated with final product conservation. Studies indicate that the majority of microorganisms used for the fermentation process consume more glucose than fructose. So, high contents of fructose in wine can compromise its preservation. Also, the control of CHO compositions in wine is fundamental for the standardization of its alcoholic content. The determination of different CHOs is a significant challenge, since they are analytes of difficult separation and present similar physicochemical characteristics. CE is an ascending technique for this type of analysis, since the fused-silica capillary withstands highly alkaline pHs, above 11.5, allowing the ionization of CHOs, which facilitates separation. Meinhart et al. [97] developed a MEKC technique with anionic surfactant, combined with multivariate modeling to study the effects of pH, electrolyte, and surfactant concentrations on peak pair resolutions.

Ravelo-Perez et al. [98] proposed a MEKC approach using reversed electrode polarity stacking mode (REPSM) as online preconcentration strategy for the determination of pesticides in rose wines. Pesticides were previously extracted by means of a solid-phase microextraction (SPME) procedure.

8 Conclusions and future outlooks

A major advantage for analysis by CE over traditional methods for wine analysis is that in most cases samples require no treatment other than filtration. The latter is extremely important for wine classification and speciation analysis. Capillary electromigration methods have the advantages of high speed, high resolution, low operational cost, low consumption of chemicals, and robustness. Selection of the technique depends on chemical nature and concentration levels of the target analytes. Wine matrix affects can be mitigated by the appropriate selection of electrophoretic variables and calibration strategy. However, to determine low concentrated analytes presented in the sample, some preconcentration technique is still required prior to the analysis. This issue can probably be addressed by means of new devices for online sample pretreatment or new in-capillary preconcentration strategies. In this sense, in-capillary derivatization procedures offer many advantages over conventional pre- and postcapillary derivatization modes.

Chemometric pattern recognition techniques have been widely applied in wine chemistry to elucidate the chemical information provided for the different multicomponent analytical techniques. Nevertheless, very few reports have been proposed by capillary electromigration techniques combined with multivariate analysis. The development of

combined CE/MS-chemometric methodologies is undoubtedly a promising area of research for wine classification as well as for unraveling the biological role of newly discovered chemical species in wine.

CE will surely become a serious candidate for routine analysis in wineries. Although improvements for increasing the robustness of the CE methods are still required, the appropriate cost per analysis, separation efficiency, speed, and very low sample and reagent consumption related to electromigration techniques result extremely interesting for wine producers. In this sense, lab on a chip platforms are ideal for in-field analysis.

Finally, to make wine successful in the functional food market further studies are required in order to correlate consumer perception with chemical composition and viticultural and vinification practices influencing wine quality.

The authors have declared no conflict of interest.

9 References

[1] Renaud S., de Lorgeril M., *Lancet* 1992, *339*, 1523–1526.

[2] Castellarin S. D., Pfeiffer A, Sivilotti P, Degan M, Peterlunger E, Di Gaspero G., *Plant Cell. Environ.* 2007, *30*, 1381–1399.

[3] Corder R., Mullen W., Khan N. Q., Marks S. C., Wood E. G., Carrier M. J., Crozier, A., *Nature* 2006, *7119*, 444–566.

[4] Yoo, Y. J., Saliba, A. J., Prenzler, P. D., *Comp. Rev. Food Sci.* 2010, *9*, 530–531.

[5] Fischer, U., in: Berger, R. G. (Ed.), *Flavours and Fragrances: Chemistry, Bioprocessing and Sustainability*, Springer, Berlin, 2007, pp. 241–267.

[6] Hurtado-Fernández, E., Gómez-Romero, M., Carrasco-Pancorbo, A., Fernández-Gutiérrez, A., *J. Pharm. Biomed. Anal.* 2010, *53*, 1130–1160.

[7] Woraratphoka, J., Intarapichet, K., Indrapichate, K., *Food Chem.* 2007, *104*, 1485–1490.

[8] Demianová, Z., Sirén, H., Kuldvee, R., Riekkola, M. L., *Electrophoresis* 2003, *24*, 4264–4271.

[9] Minussi, R. C., Rossi, M., Bologna, L., Rotilio, D., Pastore, G. M., Durán, N., *J. Mol. Catal. B Enzym.* 2007, *45*, 102–107.

[10] Hamoudová, R., Urbánek, M., Pospíšilová, M., Polášek, M., *J. Chromatogr. A* 2004, *1032*, 281–287.

[11] Ribéreau-Gayon, P., Glories, Y., Maujean, A., Dubourdieu, D., *Handbook of Enology Volume 2*, John Wiley & Sons Ltd, Chichester, 2006.

[12] Minussi, R. C., Rossi, M., Bologna, L., Cordi, L., Rotilio, D., Pastore, G. M., Durán, M., *Food Chem.* 2003, *82*, 409–416.

[13] Wang, S.-P., Huang, K.-J., *J. Chromatogr. A* 2004, *1032*, 273–279.

[14] Sáenz-López, R., Fernández-Zurbano, P., Tena, M. T., *J. Chromatogr. A* 2004, *1052*, 191–197.

[15] Deis, L., Cavagnaro, B., Bottini, R., Wuilloud, R., Silva, M. F., *Plant Growth Regul.* 2011, *65*, 11–21.

[16] Bednar, P., Tomassi, A. V., Presutti, C., Pavlikova, M., Lemr, K., Fanali, S., *Chromatographia* 2003, *58*, 283–287.

[17] Sáenz-Navajas, M. P., Tena, M. T., Fernández-Zurbano, P., *Food Chem.* 2009, *115*, 766–774.

[18] Chu, Q., O'Dwyer, M., Zeece M. G., *J. Agric. Food Chem.* 1998, *46*, 509–513.

[19] Nicolaou, I. N., Kapnissi-Christodoulou, C. P., *Electrophoresis* 2010, *31*, 3895–3902.

[20] Berli, F., D´Angelo J., Cavagnaro, B., Bottini, R., Wuilloud, R., Silva, M. F., *J. Agric. Food Chem.* 2008, *56*, 2892–2898.

[21] Sáenz-López, R., Fernández-Zurbano, P., Tena, M. T., *J. Chromatogr. A* 2003, *990*, 247–258.

[22] Calvo, D., Sáenz-López, R., Fernández-Zurbano, P., Tena, M. T., *Anal. Chim. Acta* 2004, *524*, 207–213.

[23] Kovachev, N., Canals, A., Escarpa, A., *Anal. Chem.* 2010, *82*, 2925–2931.

[24] Pazourek, J., Gajdosová, D., Spanilá, M., Farková, M., Novotná, K., Havel, J., *J. Chromatogr. A* 2005, *1081*, 48–54.

[25] Peres, R. G., Micke, G. A., Tavares, M. F. M., Rodriguez-Amaya, D. B., *J. Sep. Sci.* 2009, *32*, 3822–3828.

[26] Pazourek, J., González, G., Revilla, A. L., Havel, J., *J. Chromatogr. A* 2000, *874*, 111–119.

[27] Sun, Y., Fang, N., Chen, D. D. Y., Donkor, K. K., *Food Chem.* 2008, *106*, 415–420.

[28] Scampicchio, M., Wang, J., Mannini, S., Chatrathi, M. P., *J. Chromatogr. A* 2004, *1049*, 189–194.

[29] Huang, H. Y., Lien, W. C., Huang, I. Y., *Electrophoresis* 2006, *27*, 3202–3209.

[30] Guadalupe, Z., Soldevilla, A., Sáenz-Navajas, M. P., Ayestarán, B., *J. Chromatogr. A* 2006, *1112*, 112–120.

[31] Callejón, R. M., Troncoso A. M., Morales M. L., *Talanta* 2010, *81*, 1143–1152.

[32] Treilhou, M., Bras, M. H., Siméon, N., Bayle, C., Poinsot, V., Couderc, F., *LC-GC Europe*, 2001, December, *14*, 1–6.

[33] Martínez-Girón, A. B., García-Ruiz, C., Crego, A. L., Marina, M. L., *Electrophoresis* 2009, *30*, 696–704.

[34] Monaci, L., Losito, I., Palmisano, F., Visconti, A., *J. Chromatogr. A*, 2010, *1217*, 4300–4305.

[35] Leitao, M. C., Marques, A. P., San Romao, M. V., *Food Control* 2005, *16*, 199–204.

[36] Smith, A. Y., du Toit, W. J., du Toit, M. S., *Afr. J. Enol. Vitic.* 2008, *29*(2), 109–127.

[37] Ancín-Azpilicueta, C., González-Marco, A., Jiménez-Moreno, N., *Crit. Rev. Food Sci. Nutr.* 2008, *48*, 257–275.

[38] Hernández-Cassou, S., Saurina, J., *J. Chromatogr. B* 2011, *879*, 1270–1281.

[39] Simó, C., Moreno-Arribas, M. V., Cifuentes, A., *J. Chromatogr. A* 2008, *1195*, 150–156.

[40] Beneduce, L., Romano, A., Capozzi, V., Lucas, P., Barnavon, L., Bach, B., Vuchot, P., Grieco, F., Spano, G., *Ann. Microbiol.* 2010, *60*, 573–578.

[41] Jayarajah, C. N., Skelley, A. M, Fortner, A. D., Mathies, R. A., *Anal. Chem.* 2007, *79*, 8162–8169.

[42] Izquierdo, P., Céspedes, E., Camacho, M., García, A., Torres, G., Piñero, M., *Multiciencias* 2008, *2*, 139–147.

[43] García-Ruiz, A., González-Rompinelli, E., Bartolomé, B., Moreno-Arribas, M., *Int. J. Food Microbiol.* 2011, *148*, 115–120.

[44] Uzaşçı, S., Başkan, S., Erim, F. B., *Food Anal. Methods* 2012, *5*, 104–108.

[45] Chiu, T. C., Yang-Wei, L., Yu-Fen, H., Huan-Tsung, C., *Electrophoresis* 2006, *27*, 4792–4807.

[46] García-Villar, N., Saurina, J., Hernández-Cassou, S., *Electrophoresis* 2006, *27*, 474–483.

[47] Male, K. B., Luong, J. H., *J. Chromatogr. A* 2001, *926*, 309–317.

[48] Kvasnčka, F., Voldřich, M., *J. Chromatogr. A* 2006, *1103*, 145–149.

[49] Kitagawa, F., Otsuka, K., *J. Chromatogr. B* 2011, *879*, 3078–3095.

[50] Bertoldi, D., Larcher, R., Bertamini, M., Otto, S., Concheri, G., Nicolini, G., *J. Agric. Food Chem.* 2011, *59*, 7224–7236.

[51] Tenore, G. C., Troisi, J., Di Fiore, R., Manfra, M., Novellino, *Food Chem.* 2011, *129*, 792–798.

[52] Núñez, M., Peña, R. M., Herrero, C., García-Martín, S., *Analusis* 2000, *28*, 432–437.

[53] Tang, A.-N., Jiang, D.-Q., Yan, X.-P., *Anal. Chim. Acta* 2004, *507*, 199–204.

[54] Qin, W., Wei, H., Li, S. F. Y., *J. Chromatogr. A* 2003, *985*, 447–454.

[55] Rovio, S., Sirén, K., Sirén, H., *Food Chem.* 2011, *124*, 1194–1200.

[56] Lee, C. Y., Chen, C. M., Chang, G. L., Lin, C. H., Fu, L. M., *Electrophoresis* 2006, *27*, 5043–5050.

[57] Mato, I., Suárez-Luque, S., Huidobro, J. F., *Food Chem.* 2007, *102*, 104–112.

[58] Pan, W., Jussier, D., Terrade, N., Yada, R. Y., Mira de Orduña, R., *Food Res. Int.* 2011, *44*, 660–666.

[59] Hufnagel, J. C., Hofmann, T., Agric J., *Food Chem.* 2008, *56*, 1376–1386.

[60] Arvanitoyannis, I. S., Katsota, M. N., Psarra, E. P., Soufleros, E. H., Kallithraka, S., *Trends Food Sci. Technol.* 1999, *10*, 321–336.

[61] Biasoto, A. C. T., Catharino, R. R., Sanvido, G. B., Eberlin, M. N., da Silva, M. A. A. P., *Food. Qual. Prefer.* 2010, *21*, 755–762.

[62] Kallithraka, S., Bakker, J., Clifford, M. N., *J. Food Sci.* 1997, *62*, 416–420.

[63] Garrido-Delgado, R., López-Vidal, S., Arce, L., Valcárcel, M., *J. Sep. Sci.* 2009, *32*, 3809–3816.

[64] Peres, R. G., Moraes, E. P., Micke, G. A., Tonin, F. G., Tavares, M. F. M., Rodriguez-Amaya, D. B., *Food Control* 2009, *20*, 548–552.

[65] Mato, I., Suárez-Luque, S., Huidobro, J. F., *Food Res. Int.* 2005, *38*, 1175–1188.

[66] Hagberg, J., *J. Chromatogr. A* 2003, *988*, 127–133.

[67] Kvasnicka, F., Voldrich, M., *J. Chromatogr. A* 2006, *1103*, 145–149.

[68] Weinberger, R., *Practical Capillary Electrophoresis*, Academic Press, London 2000.

[69] Baker, D. R., *Capillary Electrophoresis*, John Wiley & Sons, Inc, New York 1995.

[70] Rovio, S., Kalliola, A., Sirén, H., Tamminen, T., *J. Chromatogr. A* 2010, *1217*, 1407–1413.

[71] Soga, T., Ross, G. A., *J. Chromatogr. A* 1999, *834*, 65–71.

[72] Villiers, A., Lynen, F., Crouch, A., Sandra, P., *Eur. Food Res. Technol.* 2003, *217*, 535–540.

[73] Arellano, M., Andrianary, J., Dedieu, F., Couderc, F., Puig, P., *J. Chromatogr. A* 1997, *765*, 321–328.

[74] Fung, Y. S., Lau, K. M., *Electrophoresis* 2003, *24*, 3224–3232.

[75] Esteves, V. I., Lima, S. S. F., Lima, D. L. D., Duarte, A. C., *Anal. Chim. Acta* 2004, *513*, 163–167.

[76] Klampfl, C. W., Katzmayr, M. U., Buchberger, W., *Electrophoresis* 1998, *19*, 2459–2464.

[77] Castiñeira, A., Peña, R. M., Herrero, C., García-Martín, S., *J. Food Compos. Anal.* 2002, *15*, 319–331.

[78] Castiñeira, A., Peña, R. M., Herrero, C., García-Martín, S., *HRC-J. High Resolut. Chromatogr.* 2000, *23*, 647–652.

[79] Shibamoto, T., Bjeldanes, L. F., *Introduction to Food Toxicology*, Academic Press, San Diego, CA 2009.

[80] Zöllner, P., Mayer-Helm, B., *J. Chromatogr. A* 2006, *1136*, 123–169.

[81] García-Cañas, V., Cifuentes, A., *Electrophoresis* 2007, *28*, 4013–4030.

[82] Hocking, A. D., Leong, S.-l. L., Kazi, B. A., Emmett, R. W., Scott, E. S., *Int. J. Food Microbiol.* 2007, *119*, 84–88.

[83] Tessini, C., Mardones, C., von Baer, D., Vega, M., Herlitz, E., Saelzer, R., Silva, J., Torres, O., *Anal. Chim. Acta* 2010, *660*, 119–126.

[84] Pfohl-Leszkowicz, A., Manderville, R. A., *Mol. Nutr. Food Res.* 2007, *51*, 61–99.

[85] OIV, Code of sound vitivinicultural practices in order to minimise levels of ochratoxin A in vine-based products, Available at http://news.reseau-oncept.net /images/oiv_uk/Client/VITI -OENO_1-2005_EN.pdf 2005.

[86] Romero-González, R., Frenich, A. G., Vidal, J. L. M., Aguilera-Luiz, M. M., *Talanta* 2010, *82*, 171–176.

[87] Turner, N. W., Subrahmanyam, S., Piletsky, S. A., *Anal. Chim. Acta* 2009, *632*, 168–180.

[88] Maragos, C. M., Bennett, G. A., Richard, J. L., *Adv. Exp. Med. Biol.* 1996, *392*, 105–112.

[89] Maragos, C. M., Greer, J. I., *J. Agric. Food Chem.* 1997, *45*, 4337–4341.

[90] Murillo-Arbizu, M., González-Peñas, E., Hansen, S. H., Amézqueta, S., Østergaard, J., *Food Chem. Toxicol.* 2008, *46*, 2251–2257.

[91] Corneli, S., Maragos, C. M., *J Agric. Food Chem.* 1998, *46*, 3162–3165.

[92] González-Peñas, E., Leache, C., López de Cerain, A., Lizarraga, E., *Food Chem.* 2006, *97*, 349–354.

[93] Murillo, M., González-Peñas, E., Amézqueta, S., *Food Chem. Toxicol.* 2008, *46*, 57–64.

[94] Hines, H. B., Brueggemann, E. E., Holcomb, M., Holder, C. L., *Rapid Commun. Mass Spectrom.: RCM* 1995, *9*, 519–524.

[95] Stege, P. W., Sombra, L. L., Messina, G., Martinez, L. D., Silva, M. F., *Electrophoresis* 2010, *31*, 2242–2248.

[96] Jankovskiene, G., Daunoravicius, Z., Padarauskas, A., *J. Chromatogr. A* 2001, *934*, 67–73.

[97] Meinhart, A. D., Ballus, C. A., Bruns, R. E., Lima Pallone, J. A., Godoy, H. T., *Talanta* 2011, *85*, 237–244.

[98] Ravelo-Pérez, L. M., Hernández-Borges, J., Borges-Miquel, T. M., Rodríguez-Delgado, M.A, *J. Sep. Sci.* 2007, *30*, 3240–3246.

