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Review

Electrophoretic methods in the analysis of beverages

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Abstract

A review of the applications of electrophoresis to the determination of various compounds in beverage samples, namely beer, hard drinks, juice, milk, soft drinks, tea and wine, is presented.

Keywords: Reviews; Food analysis; Beer; Fruit juices; Milk; Soft drinks; Tea; Wine; Artificial sweeteners; Carbohydrates; Alcohols; Amino acids; Amines; Phenolic compounds; Organic acids; Proteins; Inorganic cations; Inorganic anions; Anthocyanins; Antibiotics; Catechins

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1. Introduction

Until recently, high-performance capillary chromatography (HPLC) and gas chromatography (GC) have been the main tools in beverage analysis. The earliest commercial form of capillary electrophoresis (CE), capillary isotachophoresis (cITP) has been used for determining numerous inorganic and organic ions in food and beverages. Extensive applications of cITP were found from its development in the mid-1970s through the 1980s [1–4]. During the past decade, CE emerged as a promising, effective and economic approach for the separation of a large variety of substances, including those encountered in beverages. Automated CE instruments became commercially available and promoted the exploration of an increasing number of CE methods for food and beverage analysis. The CE technique is becoming a viable alternative to ion chromatography (IC) for the determination of inorganic and organic ions in food, as evidenced by the substantial number of reviews in this area of analysis [5–20]. The relative properties of CE and HPLC are now often discussed [21–23].

This review covers the developments mainly concerning sensitivity and matrix interference for the determination of compounds in the following beverage samples: beer, hard drinks, juice, milk, soft drinks, tea and wine, in the references published mainly from 1996 to 1998. For each matrix surveyed methods are tabulated (Tables 1–7) in order to assist the method selection. Mineral water analysis is not included in the present review as this group is generally included in the environmental samples. Recently, the use of CE for the determination of inorganic species in environmental samples including mineral water was reviewed [24].

2. Beer

The principal components in beer are ethanol and other alcohols, CO_2, organic acids (e.g., acetic, formic acid), bitter acids (isohumulones), amino acids, proteins, polyphenols, inorganic ions and vitamins (A, B complex, C, D, E and K).

Table 1
Beer samples

Analyte	Carrier electrolyte composition, voltage applied, effective capillary length×I.D., injection, detection	Sample preparation	Validation	Ref.
Alditols and alcohols	250 m*M* NaOH, 20 kV, 50 cm×5 μm, electrokinetic at 20 kV for 5 s, amperometric	Degassed and diluted	Linearity 1.05–105 mg/l, LOD 0.1 fmol, RSD in peak current 2.2–4.7%, RSD in migration time 0.5–1.4%	[29]
Amino acids	10 m*M* phosphate, 30 m*M* octanesulfonic acid, 5% ACN, pH 2.36, 30 kV, 92 cm×50 μm, hydrostatic 10 cm for 15 s, UV 185 nm	Diluted and degassed	Linearity 5 (50)–1000 mg/l, LOD 0.5–50 ppm, RSD in peak area 3.5–9% for aliphatic amino acids	[31,32]
Chiral determination of D,L-aspartic acid, D,L-glutamic acid	40 m*M* phosphate, 100 m*M* octylglucoside, 5% ACN, pH 6.5, 15 kV, 40 cm×50 μm, hydrodynamic 20 mbar for 8 s, UV 230 nm or fluorescence (He–Cd 325 nm)	Centrifuged, diluted and derivatized	LOD 98 nmol, RSD in peak area 1.6–2.3%, RSD in migration time 0.3%	[33]
Amines	10 m*M* borate, 50 m*M* SDS, pH 9.3, 24 kV, 57.5 (74.5) cm×75 μm, vacuum 3.4 Pa for 2 s, fluorescence, excitation 488 nm, emission 540 nm	Derivatized and diluted with water or SDS	LOD 0.01–0.13 m*M*, RSD 10–19%	[35]
Inorganic and organic anions	0.5 m*M* CTAB, 5 m*M* PDC, pH 5.6, −25 kV, 72 cm×75 μm, pressure 50 mbar for 2.0 s, UV 350 nm, reference at 200 nm	Degassed and diluted	Linearity 5–50 mg/l, LOD 0.9–2.5 mg/l., RSD in peak area <3.4%, RSD in migration time <0.3%	[36,37]
Inorganic and organic anions	7.5 m*M* 4-aminobenzoic acid, 0.12 m*M* TTAB, pH 5.75, −30 kV, 48 cm×50 μm, pressure 25 mbar for 0.2 min, conductivity and UV 254 nm	Degassed and diluted	LOD 0.02–0.41 mg/l, RSD in peak area 0.5–6.6%	[32,38]
Total ascorbic acid	20 m*M* borate, 20 m*M* phosphate, 50 m*M* deoxycholate, pH 8.6, 25 kV, 75 cm×75 μm, vacuum level 2, 10 kPa s, UV 254 nm	Degassed	Compared with HPLC	[39]
Carbonate	6 m*M* chromate, 3 m*M* boric acid, 2.3 μ*M* CTAB, pH 8.75, 25 kV, 45 cm×50 μm, FIA–CE interface, electrokinetic, UV 372 nm	On-line gas diffusion	RSD in peak area 1.8%, RSD in migration time 0.43%	[40]

Table 1. Continued

Analyte	Carrier electrolyte composition, voltage applied, effective capillary length×I.D., injection, detection	Sample preparation	Validation	Ref.
Six hop bitter acids	10 m*M* borate, 40 m*M* SDS, 3% 1-butanol, 0.3% *n*-heptane, pH 9.2, 20 kV, 52.8 cm×50 μm, hydrodynamic 10 cm for 5 s, UV 214 nm	Extracted under reflux	Linearity to 3 mg/ml, RSD in peak area <5%, Compared with HPLC	[45]
Six iso-α-acids	65 m*M* phosphate, 40 m*M* SDS, pH 7.6, 18 kV, 50 cm×50 μm, hydrodynamic 25 s, UV 254 nm		Linearity to 30 mg/l, LOD<0.38 ppm, RSD in peak area <5%	[47]

Table 2
Hard drink samples

Analyte	Carrier electrolyte composition, voltage applied, effective capillary length×I.D., injection, detection	Sample preparation	Validation	Ref.
25 polyphenolic compounds	10 m*M* borate, 5% ethanol, pH 9.2, 25 kV, 85 cm×75 μm, pressure 10 mbar for 12 s, UV 280 nm	Filtered	Linearity 2.5–50 ppm, RSD in peak area 0.14–0.38%, RSD in migration time 0.06–0.67%, compared with HPLC	[57]
Phenolic compounds	25 m*M* phosphate, 50 m*M* borate, 25 m*M* SDS, pH 7.0, 15 kV, 31.4 cm×50 μm, pressure 350 mbar for 1.0 s, UV 280 nm	Solid-phase extraction	Linearity 0.1–5.0 μg/ml, LOD 0.04 μg/ml, RSD in peak area 0.98–1.34% (intra-day) and 2.55–3.46% (inter-day), RSD in migration time 0.15–0.41 (intra-day) and 0.87–1.67 (inter-day), compared with HPLC	[58]
Tyrosol, tryptophol and ferrulic acid	30 m*M* borate, 20 m*M* SDS, pH 8.5, 15 kV, 31.4 cm×50 μm, pressure 350 mbar for 1.0 s, UV 280 nm	Solid-phase extraction	Linearity 0.1–200 μg/ml, LOD 0.05 μg/ml, RSD in peak area 0.31–0.69% (intra-day) and 0.94–1.09% (inter-day), RSD in migration time 0.18–0.35% (intra-day) and 0.69–1.54% (inter-day), compared with HPLC	[59]

Table 3
Juice samples

Analyte	Carrier electrolyte composition, voltage applied, effective capillary length×I.D., injection, detection	Sample preparation	Validation	Ref.
Organic acids	5 m*M* TMA, 1 m*M* TTAB, pH 9.0, −20 kV, 63 cm×75 μm, hydrodynamic 3 s, UV 220 nm	Filtered and degassed	Linearity 0.01–1 m*M*, LOD 0.002 m*M*, RSD in peak area 1–4%, RSD in migration time <1%	[60]
Organic and inorganic acids	3 m*M* PMA, 3 m*M* DETA, pH 7.5 adjusted with Tris, −20 kV, 37 cm×75 μm, hydrodynamic 2 s, UV 220 nm	Diluted	Linearity 0.1–100 mg/l, LOD 0.006–1.072 mg/l, RSD in peak area 1–4%, RSD in migration time <0.55%	[61]
Small anions	6 m*M* chromate, 0.032 m*M* CTAB, 3 m*M* boric acid, 0.3% ACN, pH 8.0, 25 kV, 45 cm×50 μm, FIA–CZE interface, electrokinetic, UV 372 nm	On-line dialysis	RSD in peak height 1.6–3.3%, RSD in peak area 3.2–4.8%	[62]
Total ascorbic acid	20 m*M* phosphate, 20 m*M* borate, 50 m*M* CTAB, pH 8.6, 25 kV, 75 cm×75 μm, vacuum level 2, 10 kPa s, UV 254 nm	Filtered	Compared with HPLC	[39]
L-Ascorbic acid	100 m*M* borate, pH 8.0, 15 kV, 27 cm×57 μm, pressure 3.45 kPa for 3 s, UV 245 nm	Centrifuged and filtered	Linearity 0.5–500 μg/ml, LOD 0.1 μg/ml, RSD in peak area 1.2% (day-to-day), 0.8% (run-to-run), RSD in migration time 0.5% (day-to-day), 0.5% (run-to-run), compared with HPLC and DNP	[63]
Vitamins	100 m*M* phosphate, 500 m*M* taurine, 75 m*M* cholate, 2% 1-propanol, 17 kV, 56 cm×50 μm, pressure 4 kPa for 1 s, UV 214 nm	Solid-phase extraction	RSD in migration time 0.5–1.2%,	[64]
Amino acids	100 m*M* phosphate, 30 m*M* octanesulfonic acid, 5% ACN, pH 2.36, 30 kV, 92 cm×50 μm, hydrostatic 10 cm for 15 s, UV 185 nm	Filtered	Linearity 5 (50)–1000 mg/l, LOD 0.5 ppm or 10–50 ppm, RSD in peak area 3.5–9%	[31]
Sorbic acid	100 m*M* MES, 10 m*M* Bis-Tris, 0.2% PEG, pH 5.2, 150 μA, hydrodynamically closed 20 cm×0.3 mm, 90 nl valve, UV 254 nm	Diluted and filtered	Linearity 5–70 μ*M*, LOD 0.5 μ*M*, RSD in peak area <7%, RSD in migration time 0.61%	[67]

Table 3. Continued

Analyte	Carrier electrolyte composition, voltage applied, effective capillary length×I.D., injection, detection	Sample preparation	Validation	Ref.
Blackcurrent anthocyanins	25 m*M* phosphate, 30% ACN, pH 1.5, 25 kV, 70.4 cm×50 μm, hydrostatic for 4 s at low pressure, Vis at 520 nm	Extracted and filtered	LOD 25 μg/ml	[70]
Elderberry anthocyanins	30 m*M* phosphate, 60 m*M* borate, 30 m*M* SDS, pH 7.0, 15 kV, 31.4 cm×50 μm, pressure 350 mbar for 1.0 s, Vis at 510 and 560 nm	Solid-phase extraction	Linearity 5–200 μg/ml, LOD 0.5 μg/ml, RSD in peak area <5%, RSD in migration time 0.5%, compared with HPLC	[71]
Carbohydrates	6 m*M* sorbate, pH 12.2, 230 V/cm, 35 cm×50 μm, pressure 105 mbar for 1.0 s, UV 256 nm	Diluted and filtered	CE: Linearity 0.1–1 g/l, LOD 0.23–0.29 m*M*, RSD in peak area <2.5%, RSD in migration time 0.3%. Compared with HPAEC–PAD: Linearity 1–50 mg/l, LOD 0.5–1 μ*M*, RSD in peak area <1.5%, RSD in retention time <1%	[74]
Carbohydrates, sugar acids and alditols	50 m*M* NaOH, 15 kV, 80 cm×25 μm, electromigration 15 kV for 5 s, electrochemical	Diluted with buffer	Linearity μ*M*–m*M*, LOD fmol, RSD in peak area <10%.	[75]
K, Na, Ca and Mg	5 m*M* imidazole, H_2SO_4, pH 4.5, 20 kV, 60 cm×75 μm, hydrostatic 10 cm for 30 s, indirect UV 214 nm	Diluted and filtered	Linearity 0.5–20 μg/ml (K, Na, Ca), 0.5–10 μg/ml (Mg), 0.5–6 μg/ml (Mn), LOD 100 μg/ml (K, Na, Ca, Mn), 50 μg/ml (Mg), RSD<5%	[76]

2.1. Alditols and alcohols

The polyhydric compounds such as xylitol, sorbitol, mannitol, etc., (known as alditols), and alcohols such as ethanol, methanol, glycerol are known to be of industrial, clinical and forensic interest [25–27].

Chen and Huang developed [28] an end-column amperometric detector based on an incorporated Ni-microelectrode and used [29] this detector for the determination of 10 alditols and alcohols with CE. Satisfactory performance with respect to the stability of background current, analysis time, low detection limit (down to the sub-fmole level), and reproducibility was obtained. Application of this detection system was demonstrated by analyzing the alditols and alcohol content in two alcoholic beverages. Ethanol, glycerol, myo-inositol, erythritol, xylitol, arabitol and mannitol were found to be contained in Taiwan beer.

2.2. Amino acids and amines

Free amino acids can also be found in beer beside proteins and peptides, mainly originating from the malt component of this alcoholic beverage. In beer

Table 4
Milk samples

Analyte	Carrier electrolyte composition, voltage applied, effective capillary length×I.D., injection, detection	Sample preparation	Validation	Ref.
Polymorphism of ovine α_{S1}-CN and α_{S2}-CN	320 m*M* citric acid, 20 m*M* citrate, 6 *M* urea, 0.05% MHEC, pH 3.0, 25 kV, 50 cm×50 μm, pressure 3.4 kPa for 15 s, UV 214 nm	Precipitated, fractionated by FPLC, dissolved in sample buffer		[89]
α-Lg, β-Lg A, β-Lg B, α_S-casein complex, β-casein and κ-casein in ewes milk	320 m*M* citric acid, 20 m*M* citrate, 6 *M* urea, 0.05% MHEC, pH 3.0, 25 kV, 50 cm×50 μm, pressure 3.4 kPa for 8 s, UV 214 nm	Precipitated, fractionated by FPLC, dissolved in sample buffer		[91]
Polymorphism of caprine milk caseins	320 m*M* citric acid, 20 m*M* citrate, 6 *M* urea, 0.05% MHEC, pH 3.0, 25 kV, 57 cm×50 μm, pressure 3.4 kPa for 15 s, UV 214 nm	Precipitated, fractionated by FPLC, dissolved in sample buffer	SD in migration time <0.08%	[92]
Bovine whey proteins α-Lg, β-Lg, BSA and IgG	150 m*M* borate, 0.05% Tween 20, pH 8.5, 20 kV, 50 cm×50 μm, vacuum 17 kPa for 10 s, UV 215 nm	Caseins precipitated and removed by ultrafiltration		[93]
Bovine whey proteins α-Lg, β-Lg A, β-Lg B, BSA and IgG	150 m*M* borate, 0.05% Tween 20, pH 8.5, 20 kV, 50 cm×50 μm, vacuum 17 kPa for 10 s, UV 215 nm	Caseins precipitated and removed by centrifugation		[94]
Bovine α-Lg, β-Lg A, β-Lg B and BSA (standard mixture)	180 m*M* phosphoric acid, pH 3.6, 22 kV, 72 cm×50 μm, hydrodynamic 1 s, UV 214 nm	Diluted		[96]
Bovine α-Lg, β-Lg A, α-CN and β-CN	250 m*M* borate, pH 10.0, 10 kV, 18.5 cm×20 μm, pressure for 10–30 s, UV 200 nm			[98]
Bovine α-Lg, β-Lg A, β-Lg B, α_{S2}-CN A, α_{S1}-CN C, α_{S1}-CN B, κ-CN A, κ-CN B, and β-CN B, β-CN A^1, β-CN A^2 and β-CN A^3	10 m*M* citrate, 6 *M* urea, 0.05% MHEC, pH 2.45, 25 kV, 50 cm×50 μm, pressure 10–30 s, UV 214 nm	Incubated with reduction buffer	RSD in peak area 2–4%, RSD in migration time <0.08%	[101]

Table 4. Continued

Analyte	Carrier electrolyte composition, voltage applied, effective capillary length×I.D., injection, detection	Sample preparation	Validation	Ref.
Genetic variants A and D of bovine α_{S2}-CN, β-CN A^1, β-CN A^2, β-CN A^3, β-CN B, β-CN C and α_{S1}-CN B and C	20 m*M* citrate, 320 m*M* citric acid, 6 *M* urea, 0.05% MHEC, pH 3.0, 25 kV, 57 cm×50 μm, pressure 3.4 kPa for 15 s, UV 214 nm	Incubated with reduction buffer		[103]
Furosine	300 m*M* MOPSO, pH 7.0, 25 kV, 57 cm×50 μm, pressure 3.36 kPa for 5 s, UV 280 nm	Hydrolyzed and filtered	LOQ 4.7 mg/100 g, RSD in peak area 2.6%, compared with HPLC	[115]
Caseinglycomacropeptide (standard solution)	20 m*M* citrate, pH 3.5, 30 kV, 56 cm×50 μm, pressure 50 mbar for 20 s, diode-array		Linearity 0.1–2 mg/ml, LOD 30 μg/ml, RSD in peak area <3%, RSD in migration time <1%	[118]
Milk mixtures	120 m*M* borate, pH 9.2, 6 kV, 61 cm×50 μm, hydrodynamic 10.34 kPa for 0.3 s, UV 200 nm	Precipitated and filtered	RSD in peak area <3.5%, RSD in migration time <1%, 2% cows milk in mixture	[125]
Small cations and anions	6 m*M* aminopyridine, 2.7 m*M* H_2CrO_4, 30 μ*M* CTAB, pH 8.0, 20 kV, 30 cm×50 μm, hydrodynamic 40 s, UV 262 nm	Off-line dialysis	RSD in peak area 1.7–5.5%, RSD in migration time <3%	[128]
Oxytetracycline, chlortetracycline, tetracycline and doxycycline	50 m*M* borate, 50 m*M* phosphate, 10 m*M* SDS, pH 8.5, 15 kV, 50 cm×75 μm, pressure for 5 s (5 nl), UV 370 nm	Extracted	LOD 1.3–5.3 ng/ml	[131]
Tetracycline, chlortetracycline and oxytetracycline	500 m*M* magnesium acetate tetrahydrate in *N*-methylformamide, 15 kV, 20 cm×75 μm, pressure 3.5 kPa for 25 s, UV 280 nm, fluorescence, excitation 325 nm, emission 514 nm	Precipitated, centrifuged and extracted (solid-phase extraction)	Linearity 50–1000 ng/ml, LOD 25 ng/ml, RSD in peak area <5.5%	[132]
Cyclopiazonic acid	10 m*M* phosphate, 6 m*M* borate, 50 m*M* deoxycholate, pH 9.3, 20 kV, 60 cm×50 μm, pressure 50 mbar for 7 s, UV 225 nm	Extracted	Linearity 40–100 ppb, LOD 20 ppb, compared with RPLC	[135]

Table 5
Soft drink samples

Analyte	Carrier electrolyte composition, voltage applied, effective capillary length×I.D., injection, detection	Sample preparation	Validation	Ref.
Aspartame, benzoic acid and caffeine	20 m*M* glycine, pH 9.0, 20 kV, 44 cm×50 μm, hydrodynamic 1 s, UV 215 nm	Mixed with buffer and filtered	Linearity to 300 μg/ml (caffeine), 400 μg/ml (benzoic acid), 1500 μg/ml (aspartame), LOD 1.6 μg/ml (caffeine), 4.0 μg/ml (benzoic acid), 18 μg/ml (aspartame), RSD in peak area 2–3.8%, RSD in migration time 0.13–0.37%	[138]
Aspartame, benzoic acid and caffeine	25 m*M* borate, pH 9.4, 20 kV, 33 cm×50 μm, UV 272 nm, 229 nm and 210 nm for caffeine, benzoic acid and aspartame	Filtered	Linearity 40–200 mg/l (caffeine), 25–150 mg/l (benzoic acid), 75–600 mg/l (aspartame), LOD 1.7 mg/l (caffeine), 0.29 mg/l (benzoic acid), 2.2 mg/l (aspartame)	[139]
Caffeine and its metabolites	20 m*M* phosphate, 40 m*M* SDS, pH 11.0, 27 kV, 25 cm×75 μm, vacuum (2 nl), UV 250 nm	Degassed and filtered	Linearity 1–200 mg/l, LOD < 1 mg/l, RSD in peak area <5%, RSD in migration time <2%	[140]
Chiral resolution of pantothenic acid	60 m*M* phosphate, 60 mM 2-hydroxypropyl-β-CD, 10% methanol, pH 7.0, 20 kV, 56 cm×75 μm, pressure 50 MPa for 4 s, UV 200 nm	Degassed and diluted	Linearity 3–300 μ*M*, LOD 3% L-isomer in total acid, RSD in peak area <0.7%, RSD in migration time <1.2%	[142]
Cyclamate	10 m*M* benzoate, 1 m*M* CTAH, pH 6.6, −20 kV, 50 cm×75 μm, vacuum level 2, 20 kPa s, UV 254 nm	Diluted	Compared with AOAC	[143]
Artificial sweeteners	10 m*M* borate, 10 m*M* phosphate, 50 m*M* deoxycholate, 20 kV, 50 cm×75 μm, vacuum level 2, 20 kPa s, UV 220 nm	Diluted	Linearity to 200 μg/ml (aspartame), 50 μg/ml (caffeine and saccharine), 100 μg/ml (sorbic and benzoic acid), RSD between instruments <2.6%, compared with HPLC	[144]
Synthetic food colorants	30 m*M* TES, 8 m*M* imidazole, 0.2% PEG, 6 m*M* β-CD, pH 6.84, 150 μA, hydrodynamically closed 24 cm×0.3 mm, 90 nl valve, UV 254 nm	Diluted	LOD 10–300 ppb, RSD in peak area 0.3–6%, RSD in migration time 0.5–1%	[148,149]

Table 5. Continued

Analyte	Carrier electrolyte composition, voltage applied, effective capillary length×I.D., injection, detection	Sample preparation	Validation	Ref.
Class IV caramels	50 m*M* hydrogencarbonate, pH 9.5, 20 kV, 40 cm×50 μm, pressure 50 mbar for 5 s, UV 200, 280, 360 and 460 nm	Degassed and diluted	Linearity 0.1–10 g/l, LOD 0.1 g/l	[153]
Ammonium, K, Na and Ca	0.5 m*M* Ce(III) sulfate, 2.5 m*M* 18-crown-6, 30 kV, 55 cm×75 μm, electrokinetic at 20 (5) kV for 10 s, hydrostatic 10 cm for 30 s, fluorescence, excitation 251 nm, emission 345 nm		Linearity 1–1200 μ*M*, LOD 1–3 μ*M* (hydrostatic), 0.1–0.3 μ*M* (electrokinetic)	[154]
Na, K, Ca and Mg	5 m*M* 4-aminopyridine, 0.007 m*M* CTAB, pH 5.0, 25 kV, 50 cm×50 μm, hydrodynamic, UV 262 nm		Linearity to 100 mg/l	[155]

biogenic amines are usually generated by microbial decarboxylation of amino acids [30].

Underivatized amino acids (lysine, histidine, arginine, glycine, alanine, serine, tryptophane, phenylalanine, tyrosine and proline) can be determined in beer samples by CE [31,32] with direct UV detection at 185 nm using a 10 m*M* phosphate buffer containing 30 m*M* octanesulfonic acid (pH 2.36). Main advantages are the simplicity and the rapidness of the method, allowing a fast screening of the amino acids patterns. No sample pretreatment as well as no derivatization steps are necessary. However, the limits of detection (LODs) are relatively high for the aliphatic amino acids (10–50 ppm). The aromatic amino acids can be detected in low ppm concentrations.

Tivesten et al. [33] developed a CZE method for chiral determination of aspartic and glutamic acid. Aspartic and glutamic acid were derivatized using a fluorogenic reagent, *o*-phthaldialdehyde–2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranose. With a neutral surfactant, (octylglucoside), the D- and L-aspartic and glutamic acid derivatives could be resolved outside the micellar retention window creating a high selectivity towards other amino acids. With laser-induced fluorescence (LIF) detection, a LOD of 98 nmol was estimated. The method was applied to beer samples; both aspartic and glutamic acid in their D- and L-forms were found in the beer samples.

Sodium phosphate buffer at a concentration of 25 m*M* (pH 6.5) was used for the determination of histamine in non-alcoholic malt beer and beer samples [34]. The results agree well with those obtained by photometry in combination with solid-phase extraction.

CE with simultaneous UV and LIF detection was applied [35] to identify and quantify selected amines (ammonia, ethylamine, isoamylamine and dibutylamine) in beer following derivatization with 7-chloro-4-nitrobenzo-2-oxa-1,3-diazole. The fluorescence detection method was found to be more selective and sensitive for the determination of aliphatic amines in beer than UV–Vis absorbance detection.

2.3. Inorganic and organic anions

The measurement of the concentrations of inorganic and organic anions, in all phases of beer production, can be used to help track metabolic products of fermentation and correlate beer flavor trends.

Table 6
Tea samples

Analyte	Carrier electrolyte composition, voltage applied, effective capillary length×I.D., injection, detection	Sample preparation	Validation	Ref.
Caffeine	50 m*M* borate, pH 8.5, 25 kV, 100 cm×75 μm, gravity for 5 s, UV 214 nm	Diluted	Linearity 17–370 mg/l, LOD 1.9 mg/l	[158]
Caffeine, theanine, ascorbic acid and five catechins	20 m*M* borate, pH 8.0, 30 kV, 70 cm×50 μm, pressure for 5 s, UV 200 nm	Boiled, diluted and filtered	LOD 10 mg/l	[159]
Caffeine, theohylline and polyphenols	150 m*M* borate, pH 8.5, 20 kV, 57 cm×75 μm, FIA–CE interface, hydrodynamic 10 s, UV 210 nm	Extracted, filtered and diluted in FIA system	Linearity 0.1–1 μg/ml, LOD 0.04–1.2 μg/ml	[160]
Theanine, caffeine, ascorbic acid and catechins	80 m*M* borate, 50 m*M* SDS, pH 8.4, 25 kV, 70 cm×75 μm, pressure 5 s, UV 194 nm	Extracted, diluted and filtered		[165]
Caffeine, theobromine and theophylline	20 m*M* borate, 40 m*M* SDS, 10% methanol, pH 8.25, 17 kV, 50 cm×50 μm, pressure 3.45 kPa for 3 s, UV 214 nm.	Boiled, filtered and diluted	Linearity 0.001–0.5 mg/l	[166]
Caffeine and 6 catechins	20 m*M* borate, 110 m*M* SDS, 1.5 *M* urea, 14% methanol, 1 m*M* β-CD, 20 kV, 60 cm×50 μm, pressure 3.4 kPa for 4 s, UV 280 nm	Boiled and filtered		[167]
Caffeine and catechins	20 m*M* phosphate–borate, 25 m*M* SDS, pH 7.0, 30 kV, 70 cm×50 μm, hydrodynamic (25 nl), UV 200 nm (caffeine, catechins), UV 266 nm (ascorbic acid)	Boiled and diluted	Linearity 15–300 ppm, LOD<5 ppm, RSD in peak area <3%, RSD in migration time <3%	[168]
Polyphenols	50 m*M* phosphate, 50 m*M* borate, 20 m*M* SDS, 10% ACN, pH 6.0, 30 kV, 56 cm×50 μm, pressure 50 mbar for 15 s, UV 278 nm	Extracted		[169]

Table 6. Continued

Analyte	Carrier electrolyte composition, voltage applied, effective capillary length×I.D., injection, detection	Sample preparation	Validation	Ref.
Organic anions	10 m*M* chromate, 0.5 m*M* TTAB, 0.1 m*M* Na_2EDTA, −20 kV, 57 cm×75 μm, pressure for 5 s, UV 254 nm	Boiled, filtered and diluted	RSD in peak area 0.93–3.53%, RSD in migration time 0.4–0.8%	[170]
K, Na, Ca, Mg and Mn	5 m*M* imidazole, 6.5 m*M* HIBA, 20% (v/v) methanol, 0.55 m*M* 18-crown-6, pH 4.5, 20 kV, 60 cm×75 μm, hydrostatic 10 cm for 20 s, UV 214 nm	Boiled, filtered and diluted	LOD μg/ml	[171]
K, Na, Ca, Mg and Mn	5 m*M* imidazole, 6.5 m*M* HIBA, 20% (v/v) methanol, 0.55 m*M* 18-crown-6, pH 4.5, 20 kV, 60 cm×75 μm, hydrostatic 10 cm for 20 s, UV 214 nm	Microwave digested and diluted	Linearity 0.5–10 μg/ml, LOQ<600 μg/ml, except for K (2 mg/l)	[172]
Vanilla constituents	10 m*M* borate, 100 m*M* SDS, pH 8.7, 25 kV, 50 cm×75 μm, pressure 1.5 s, UV 254 nm	Filtered	Linearity 1–100 mg/l, LOD 0.3–0.9 mg/l, RSD in peak area <3.45%, RSD in migration time <1%	[173]

Inorganic and organic anions – chloride, sulfate, phosphate, oxalate, formate, malate, citrate, succinate, pyruvate, acetate, lactate and pyroglutamate – have been determined [36] in beer by means of 5 m*M* 2,6-pyridinedicarboxylic acid (pH 5.6) containing 0.5 m*M* cetyltrimethylammonium bromide as carrier electrolyte and indirect UV detection at 350 nm. The LODs for all analytes were in the range 0.9 to 2.5 mg/l.

This method was later validated and compared [37] with IC and HPLC analysis of beer samples. The concentrations of anions in the beer and wort were in good agreement with the current techniques. In conventional techniques, 20 min is needed for inorganic anion analysis by IC, and more than 40 min is needed for organic acid analysis by HPLC. However, using the CE method, three inorganic anions and nine organic acids were analyzed simultaneously in 7 min.

For the determination of inorganic and organic anions in different types of beer, it proved to be advantageous to use CZE with conductivity detection in series with UV detection at 254 nm [32,38]. With a running buffer composed of 7.5 m*M* 4-aminobenzoic acid and 0.12 m*M* tetradecyltrimethylammonium bromide (pH 5.75 adjusted by the addition of histidine), conductivity detection proved to be more sensitive for the faster migrating anions, whereas UV detection was found to be superior for analytes with mobilities similar to that of 4-aminobenzoic acid. By the use of both detection methods simultaneously, it was possible to perform quantification using the best suited method of detection for each type of analyte, namely, conductivity detection for chloride, sulfate, oxalate, formate, malate, citrate and succinate and UV detection for pyruvate, acetate, lactate, phosphate and pyroglutamate. This approach resulted in excellent LODs for all analytes. They

Table 7
Wine samples

Analyte	Carrier electrolyte composition, voltage applied, effective capillary length×I.D., injection, detection	Sample preparation	Validation	Ref.
Ethanol	20 m*M* barbital, 200 m*M* SDS, pH 8.6, 5 kV, 25 cm×25 μm, pressure 300 mbar s, Vis 510 nm, reference λ 230 nm	Diluted and filtered	Linearity 5–30%, RSD in peak area 0.069–0.140% (intra-day) and 0.20% (inter-day), RSD in migration time 0.10–0.62% (intra-day) and 1.04% (inter-day), compared with GC	[174]
Total sulfite	5 m*M* chromate, 0.5 m*M* OFM-Anion BT, pH 8.0, −15 kV, 50 cm×75 μm, vacuum level 2, 10 kPa s, UV 254 nm	Distilled, oxidated and filtered	Linearity to 50 μg/ml, LOD 5 mg/kg, SD in peak area 1.4–8.5%, compared with titrimetry	[175]
Total and free sulfite	6 m*M* chromate, 3 m*M* boric acid, 23 μ*M* CTAB, pH 8.75, 25 kV, 45 cm×50 μm, FIA interface, UV 372 nm	On-line gas diffusion	RSD in peak area 2.7%, RSD in migration time 0.35%.	[40]
Inorganic and organic anions	7.5 m*M* 4-aminobenzoic acid, 10.5 m*M* Bis-Tris, 0.1 m*M* TTAB, pH 7.0, −30 kV, 48 (60) cm×50 μm, pressure 25 mbar for 0.2 min, conductivity and UV 254 nm	Diluted and filtered	Linearity 1–100 mg/l, except for chloride (1–25 mg/l) and sulfate (1–50 mg/l), LOD 0.05–2.75 mg/l (conductivity) 0.13–0.51 mg/l (UV)	[177]
Total ascorbic acid	20 m*M* borate, 20 m*M* phosphate, 50 m*M* deoxycholate, pH 8.6, 25 kV, 75 cm×75 μm, vacuum level 2, 10 kPa s, UV 254 nm		Compared with HPLC	[39]
Free amino acids	20 m*M* borate, pH 9.5, 21 kV, 80 cm×50 μm, gravity at 10 cm for 15 s, fluorescence, excitation 340 nm, emission 455 nm	Diluted	Linearity 1–500 μ*M*, LOD glycine 0.67 μ*M*	[181]
Biogenic amines	40 m*M* copper(II) sulfate, formic acid, 18-crown-6, pH 4.5, 15 kV, 57 cm×75 μm, high pressure 10 s, UV 214 nm	Solid-phase extraction in FIA system	Linearity 0.1–10 μg/ml, LOD 0.05–0.1 μg/ml	[182]
Biogenic amines	100 m*M* borate, 50 m*M* SDS, 10% ACN, pH 8.9, 15 kV, 30 cm×50 μm, hydrodynamic for 5 s, UV 254 nm	Derivatized	Linearity 0.05–1 μmol/ml, LOD 0.05–2 μ*M*, RSD in peak area 3–5%, RSD in migration time <2%, except histamine (RSD 3.44%)	[183]
28 biogenic amines and amino acids	100 m*M* boric acid, 20 m*M* SDS, pH 9.3, +20 kV, 42 cm×50 μm, hydrodynamic for 2 s (15 nl), fluorescence 488 nm	Derivatized		[184]

Table 7. Continued

Analyte	Carrier electrolyte composition, voltage applied, effective capillary length×I.D., injection, detection	Sample preparation	Validation	Ref.
Monosaccharide enantiomers	50 m*M* borate, 23% ACN, pH 10.3, 30 kV, 100 cm×50 μm, pressure 3.45 kPa for 3.0 s, UV 200 nm	Derivatized	RSD in migration time 0.9%	[185]
Reducing sugars	50 m*M* borate, pH 8.8, 28 kV, 70 cm×50 μm, pressure 3.45 kPa, UV 200 nm	Evaporated, redissolved and derivatized		[186]
11 phenolic compounds	100 m*M* borate, pH 9.5, 20 kV, 50 cm×75 μm, hydrodynamic for 2 s (9 nl), UV 280 nm	Liquid–liquid extraction	Compared with HPLC	[189,190]
Catechin, epicatechin, rutin, quercetin and myricetin	30 m*M* phosphate, pH 8.85, 30 kV, 80 cm×50 μm, pressure 35 mbar for 5 s, UV 220 nm		LOD 3 pmol, RSD in migration time 1.5–2.6% (5–7% for incompletely dissociated)	[191]
Phenolic acids	50 m*M* hydrogencarbonate, pH 8.3, 15 kV, 36 cm×50 μm, hydrodynamic 2–5 s, spectrophotometric	Liquid–liquid extraction	RSD in peak area 1.0–2.2%, RSD in migration time <1%.	[192]
Separation of *cis*- and *trans*-resveratrol	10 m*M* phosphate, 6 m*M* borate, 50 m*M* deoxycholate, pH 9.3, 20 kV, 60 cm×50 μm, pressure 50 mbar for 7 s, UV 220 nm	Diluted and filtered	Linearity 8–1000 ppm	[197]
Determination of *trans*-resveratrol	25 m*M* borate, 25 m*M* phosphate, 75 m*M* SDS, pH 9.0, 16 kV, 30 cm×50 μm, UV 310 nm		Linearity 1.25–25 μ*M*, LOD 1.25 μ*M*	[198]
Determination of *cis*- and *trans*-resveratrol	40 m*M* borate, pH 9.5, 5 kV, 25 cm×75 μm, hydrodynamic for 5 s, UV 320 nm	Solid-phase extraction	Linearity 0.5–20 mg/l, LOD 0.08 mg/l (*cis*-isomer) and 0.06 mg/l (*trans*-isomer), RSD in peak area 1.3–1.8%, RSD in migration time 0.2–0.8%.	[199]
Proteins	100 m*M* Tris–HCl, pH 8.0, 12 kV, 50 cm×75 μm, pressure 3.4 kPa for 5 s, UV 214 nm		RSD in peak area 4.5–10.6%, RSD in migration time 2.6–3.3%	[206,207]

were found to be in the range of 0.02 mg/l for chloride using conductivity detection and 0.41 mg/l for phosphate using UV detection.

L-Ascorbic acid is often added to beer as an antioxidant. D-Erythorbic acid has the same antioxidative properties as L-ascorbic acid and is sometimes substituted for L-ascorbic acid because it is cheaper. Baseline separation of L-ascorbic and D-erythorbic acid was achieved [39] using a buffer consisting of 0.05 *M* SDS–0.005 *M* dipotassium hydrogenorthophosphate (pH 9.2) Ten beers were analyzed for total L-ascorbic acid using this buffer. The results were compared with those obtained by HPLC. Baseline separation of L-ascorbic and D-erythorbic acid was also maintained when sodium deoxycholate was substituted for SDS. Replacing the 0.005 *M* phosphate buffer (pH 9.2) with a 1:1 mixture of 0.02 *M* tetraborate–0.02 *M* phosphate buffer (pH 8.6) resulted in enhanced separation of the two isomeric acids and a much shorter run time. This MEKC method has the same order of precision as the HPLC method, however, the run time for the analytes were reduced from 25 min to 6 min when MEKC procedure was used.

Carbonate was determined [40] in beer sample using on-line gas diffusion coupled to CE in a flow arrangement.

2.4. Hop and beer bitter acids

The main characteristics of beer are derived from hops. The essential components of hops are hop bitter acids: the α-acids (humulone, cohumulone and adhumulone) and the β-acids (lupulone, colupulone and adlupulone). The α-acids are tasteless, but upon prolonged boiling in the wort they are isomerized to the bitter-tasting iso-α-acids or isohumulones (beer bitter acids) [41,42].

The successful separation of the six main α- and β-acids have been reported by Vindevogel et al. [43]. By using a carrier electrolyte consisting of 15 m*M* borate (pH 9.2), only the group separation of α- and β-acids is realized. By addition of a 40 m*M* SDS to the buffer (40 m*M* borate, pH 8.5), the six major α- and β-acids can be separated. Some difficulties in reproducing the separation between lupulone and adlupulone have been reported [44]. These problems were ascribed to the extremely narrow pH interval (0.1–0.2 pH unit) where separation is observed. When 3% (v/v) 1-butanol and *n*-heptane (0.3%) were added to the micellar buffer (10 m*M* borate, pH 9.2, 40 m*M* SDS) complete separation of all six hop acids was observed [45]. Separation between adlupulone and lupulone is obtained over a sufficient wide pH interval This microemulsion electrokinetic chromatography (MEEKC) method of hop acids has been applied to the characterization of hop cultivars and compared to HPLC analysis. MEEKC also provides more information as all six homologues are separated. Quantitative data obtained by HPLC and MEEKC are in good agreement.

The MEKC separation of the six main iso-α-acids poses less problems and is easily achieved [46] using 30 m*M* phosphate buffer (pH 7.6) containing 40 m*M* SDS. The total iso-α-acid concentration in beer is approximately 20 ppm, which is too low for direct determination. Therefore, the iso-α-acids are preconcentrated [47] by solid-phase extraction followed by MEKC analysis. However, this method is labor intensive and difficult to automate. Therefore, a second approach, involving direct injection of beer with on-column focusing, was investigated. Finally, 40 m*M* SDS, 65 m*M* phosphate and a 25 s injection time were selected for quantitative analysis.

2.5. Phenolic acids

CE using amperometric detection and a pH 7.2 run buffer was used [48] to detect phenolic acids in beer samples. Cationic and neutral compounds in the beer samples interfered with electrochemical detection by passivating the electrode surface. These compounds were removed using a reversed-polarity injection technique to elute them from the separation capillary into the sample reservoir prior to the electrophoretic separation. Electrophoretic peaks in the samples were identified by both matching their migration time and electrochemical properties with standards. The use of voltametric characterization provided improved peak identification for complex samples.

2.6. Proteins

Beer contains about 500 mg/l of proteinaceous material, including variety of polypeptides with molecular masses ranging from <5000 to $>100\,000$.

These polypeptides, which mainly originate from barley proteins, are the product of the proteolytic and chemical modifications that occur during brewing. In particular, the polypeptides are thought to be involved in the mechanisms of both haze formation and foam stabilization [49].

The major protein of beer is actually formed by two molecules, which are separable by SDS–PAGE [50–52]. The two proteins present in beer are derived, with minor modifications, from two corresponding proteins of the barley endosperm, which are resistant to drastic thermal treatments; and both are present in beer, although one is glycated and other is not. Moreover, they are immunologically related. Finally, they have a similar molecular mass (about 40 000). All of these characteristics are typical of barley protein Z, suggesting that the proteins described [52] are related to protein Z.

3. Hard drinks

3.1. Phenolic and polyphenolic compounds

Phenolic compounds found in alcoholic beverages are produced by the yeast from raw materials [53]. Ferulic acid, vanillin and vanillic acid are major phenolic compounds found in an alcoholic beverages [54].

Polyphenolic compounds are widely distributed in nature as they are important components of plants [55]. Some distilled drinks must be aged for a certain period in wood barrels (usually oak). Complex phenolic substances as tannins are extracted from wood, structural molecules (lignin and hemicellulose) are depolymerized and extracted to the distillate; and reactions may occur between components of wood and distillate [56].

Twenty-five polyphenolic compounds in spirits and ethanolic oak extracts were studied by CE and results were compared with reversed-phase HPLC analysis [57]. Both borate, phosphate and mixtures of phosphate and borate buffers have been used in the separation of phenolic compounds. Borate buffer gave a better separation of standard compounds and it was usually preferred in analysis of samples. In order to improve separation, additives (5% ethanol and 0.1 *M* SDS) were added to the borate buffer. The buffer containing 5% ethanol presented a better separation of standards. The use of surfactant made possible the separation of furfural which is an important component of brandies and is a neutral compound. The results obtained with this method may be used for comparison with complementary HPLC in order to get a full characterization of these samples. Characterization by this method may contribute to the study of the quality and authenticity of brandies.

Phenolic compounds (ferulic acid, vanillin, vanillic acid and 4-vinylguaiacol) found in Japanese spirituous liquor have been analyzed by MEKC [58]. These phenolic compounds were extracted by solid-phase extraction. Compared to the HPLC method, MEKC method is advantageous due to its low running cost, and shorter analysis time requirements.

MEKC was applied [59] to the simultaneous analysis of tyrosol, tryptophol and ferulic acid in sake, using an uncoated fused-silica capillary with SDS solution in borate buffer at pH 8.5 and UV detection at 280 nm. The MEKC method can be applied to the routine quality control of sake brewing. In sake brewing, the analysis of tyrosol, tryptophol and ferulic acid from sake is very important for quality control, as these tree compounds taste bitter.

4. Juice

4.1. Inorganic and organic anions

Organic acids – oxalic, citric, acetic, tartaric, malic, succinic, lactic, carbonic, aspartic, glutamic, ascorbic and gluconic – could be separated by CE [60] with indirect UV detection (220 nm) using 5 m*M* trimellitate as the BGE and 1 m*M* tetradecyltrimethylammonium bromide as the EOF modifier. For the simultaneous determination of all analytes, the optimum pH is 9.0, at which all peaks except for malate and succinate are baseline resolved within 9.5 min. The detection limit for most analytes is of the order of 2 μmol/l. With this method, citrate, tartrate and malate were determined in artificially flavored grape juice.

Eight anions – chloride, sulfate, malate, succinate, citrate, phosphate, acetate and lactate – were identified in apple juice [61].

On-line coupling of dialysis in an flow-injection analysis (FIA) system to a CE system was used [62] for the determination of chloride, sulfate, citrate, hydrogencarbonate and benzoate in orange juice containing fruit pulp.

Near baseline resolution of L-ascorbic acid and D-erythorbic acid in fruit juices was observed [39] using a buffer consisting of 0.05 *M* SDS–0.005 *M* K_2HPO_4 (pH 9.2) The resolution of the two analytes diminished with increasing amounts of tartaric acid, whereas, the acetic acid had very little effect on the separation. Replacing the 0.005 *M* phosphate buffer with a 1:1 mixture of 0.02 *M* tetraborate–0.02 *M* phosphate buffer (pH 8.6) resulted in a much shorter run time and baseline separation of L-ascorbic and D-erythorbic acid was maintained when sodium deoxycholate or cetyltrimethylammonium bromide was substituted for SDS. In addition, the separation was not affected by the presence of citric or tartaric acid. The levels of total L-ascorbic acid in the fruit juices determined by MEKC and the instrument repeatability showed good agreement with the HPLC procedure. The run time for the analytes of the juices was reduced from 25 min to 6 min when the MEKC procedure was used.

Choi and Jo developed [63] a CZE method to measure the L-ascorbic acid in juices and compared it with HPLC and 2,4-dinitrophenylhydrazine (DNP) method of the Korean Food Codex. The run times for the DNP, HPLC and CZE methods were 6 h, 15 min and 2.0 min, respectively. The LODs for the DNP, HPLC and CZE methods were 2.5 μg/ml, 1.2 μg/ml and 0.06 μg/ml, respectively.

Recently Buskov et al. [64] achieved the separation of 14 water-soluble vitamins and vitamins cofactors by MEKC and diode-array detection using a buffer consisting of 100 m*M* Na_2HPO_4, 500 m*M* taurine, 75 m*M* sodium cholate and 2% 1-propanol. Mixtures of vitamins from natural sources were obtained from freeze–dried orange juice. Fat and other lipid-soluble substances were removed by solid-phase extraction. Direct analysis of the defatted orange juice resulted in an electropherogram with many peaks. Therefore MEKC analysis of original extracts needs further purification. However, thiamine, pyridoxine and ascorbic acid were identified and quantified from direct analysis of defatted orange juice. Correlation coefficients (R^2) from linear regression analysis on normalized peak area for the varying vitamin concentrations ranged from 0.986 to 0.997. The linearity for ascorbic acid was not good ($R^2=0.971$) may be due to its rather poor stability in the applied system, but antioxidants may be added [65] to diminish the degradation.

Benzoic and ascorbic acids are probably the only among current food additives [66], which could interfere in the analysis of sorbate by CE. A selective and rapid CZE method performed in a hydrodynamically closed separation compartment was described [67] for the determination of sorbic acid in juice concentrates. Using a carrier electrolyte consisting of 100 m*M* MES, 10 m*M* Bis-Tris, 0.2% PEG (pH 5.2), benzoate and ascorbate migrated with higher effective mobilities and did not disturb the analysis of sorbic acid.

4.2. Amino acids

Underivatized amino acids (arginine, alanine, serine, asparagine, tryptophan, glutamic acid, phenylalanine, tyrosine and proline) can be separated [31] in orange juices by CE with direct UV detection at 185 nm. The content of free amino acids was investigated in two types of orange juice, a freshly prepared one and a canned one. It can be seen that these two juices showed significant differences. The amount of proline found in the canned juice was 500 ppm, the highest concentration of a free amino acid occurring in this study. Looking at the freshly prepared juice, only one-quarter of this quantity could be detected. Notable differences between the two investigated sample could also be found for tryptophan, whereas arginine and asparagine could be identified as main compounds in both juices.

4.3. Anthocyanins

Anthocyanins are water-soluble pigments that are responsible for the red, purple and blue colors of flowers and fruits of higher plants.

Recently, Bridle and co-workers [68,69] reported on the separation of anthocyanins by CZE with a pH 8.0 running borate buffer. The applicability of this method is limited in part by the fact that anthocyanins are not stable under alkaline conditions.

One usual way to prevent the chemical degra-

dation of the anthocyanin compounds during CZE analysis is to separate them using an acidic running buffer [70]. The four major anthocyanins present in blackcurrent juice were separated with CZE with a sodium phosphate buffer containing 30% (v/v) acetonitrile at an apparent pH of 1.5. Using the acidic buffer conditions, cyanidin 3-glucoside, cyanidin 3-rutinoside and delphinidin 3-glucoside were detected at concentrations of 25 μg/ml, whereas under basic conditions, 40 μg/ml were required for detection.

A CZE separation of the four main anthocyanins, which are present in elderberry juice, with a 100 m*M* phosphate buffer at pH 2.5 gave only one peak [71]. MEKC with SDS solution in a phosphate buffer at pH 7.0 was successful for the separation of these elderberry pigments [71]. The MEKC technique was compared with a HPLC method. Although both HPLC and MEKC gave good separations of these four pigments, the HPLC method required longer analysis time using gradient elution, whereas the MEKC analysis was much shorter not only in separation time, but also in reconditioning the column or capillary.

The yellow safflower pigment was extracted from juice samples by solid-phase extraction cartridges and analyzed by MEKC with 2.0% butyl acrylate–butyl methactrylate–methacrylic acid copolymer sodium salts [72].

4.4. Carbohydrates

As it can be generally expected that sugar contents in fruit juices will be in the range 10–100 g/l, a dilution of 1:50 to 1:100 should allow a CE analysis [73].

A CZE method with indirect UV detection (256 nm) was adapted for the routine determination of carbohydrates in a variety of fruit juices [74]. The optimized CZE method was compared with a routine method for the determination of sugars in fruit juices, a high-performance anion-exchange chromatographic method with pulsed amperometric detection (HPAEC–PAD). The CZE method showed a 10–20-fold increase in separation efficiency compared with HPAEC–PAD. However, PAD was able to detect as little as 0.5–1 μ*M*, whereas indirect UV detection with sorbate as the BGE resulted in LODs of 0.23–0.29 m*M*. Sucrose, glucose and fructose were determined in apple and orange juice; glucose and fructose in grape juice.

A better LOD (<10 μ*M*) for a wide range of carbohydrate compounds including simple sugars, sugar acids and alditols was achieved by CE combined with electrochemical detection copper electrodes [75]. Glucitol, sucrose, glucose and fructose were found in apple juice.

4.5. Metals

Baseline resolution of K, Na, Ca and Mg in orange juice was obtained [76] using a buffer consisting of 5 m*M* imidazole–H_2SO_4 (pH 4.5). A comparison with flame atomic spectrometry (FAS) was carried out in terms of sensitivity, limit of detection, linearity, accuracy and precision. The accuracy and precision of capillary ion electrophoresis (CIE) with hydrostatic injection are acceptable but that of FAS is better. A wider linear range is obtained in CIE than in FAS, however, the limit of detection for CIE is poorer than that for FAS.

4.6. Monitoring

New trends in adulteration monitoring favor the development of methods analyzing simultaneously as many compounds as possible. A CE method has been developed to analyze simultaneously most citrus juice components in a single procedure. Depending on the conditions up to 30 components could be separated [77]. The identified molecules included phenolic amines, amino acids, flavonoids, polyphenols and vitamin C. Samples can be analyzed without specific preparation. This method was recently modified and used [78] to develop a method for detection and quantitation of pulp wash added to citrus juice. Compounds monitored regularly were the biogenic amine synephrine, some flavonoids (didymin, hesperidin, narirutin, neohesperidin and naringin), the polyphenol phlorin, amino acids (tryptophan, phenylalanine, and tyrosine) ascorbic acid and the preservatives sorbate and benzoate. Didymin, narirutin and phlorin peaks were used with an artificial neural network to assess the volume of added pulp wash, a by-product of juice preparation. This method allows rapid monitoring of citrus juices (20 min), giving information on quality, freshness,

and possible adulteration of the product. The total analytical time is one-half that of the previous procedure involving pulp wash determination and liquid chromatographic measurement of flavonoids and preservatives.

Recently, it was found [79] that the 1,2-dimethylimidazole–trimellitic acid combination was the most suitable BGE for the simultaneous separation of alkali metals and organic acids. 18-Crown-6, added as an organic additive for resolving NH_4^+ and K^+ peaks, had no influence on the separation and detection of the organic acids. Under optimal conditions, NH_4^+, K^+, Na^+, Li^+, ascorbate, sorbate, benzoate, lactate, acetate, succinate, malate, tartrate, maleate, malonate, perchlorate and oxalate could be separated and detected within 6 min with LODs ranging from 0.08 to 5 μg/ml. The method was applied to the analysis of apple, orange and grape juices.

5. Milk

For humans milk is an excellent source of essential nutritional components (proteins, fats, carbohydrates, minerals and vitamins). Humans consume milk of many animal species; cow's milk is the most intensively studied [80].

5.1. Proteins

5.1.1. Proteins and protein polymorphism

About 80% the bovine milk proteins consists of caseins, a heterogeneous fraction which is insoluble at pH 4.6 and 20°C. The casein fraction can be subdivided into the α_{S1}-, α_{S2}-, β- and κ-casein components (α_{S1}-CN, α_{S2}-CN, β-CN and κ-CN). Proteolytic products of the four primary caseins are also present in milk. The remaining 20% of the milk protein fraction is formed by the whey proteins (soluble at pH 4.6 and 20°C). Whey proteins include β-lactoglobulin, α-lactoglobulin, bovine serum albumin and immunoglobulins (β-Lg, α-Lg, BSA and Igs) [81]. The minor proteins are also present: lactoferrin, lactoperoxidase, proteose–peptone components, glycomacropeptide and protein components of the milk fat globule membrane [82].

The analysis of milk proteins has traditionally been performed by PAGE (native and sodium dodecyl sulfate SDS–PAGE) and isoelectric focusing (IEF) [83]. Combinations of techniques providing two-dimensional electrophoresis have been commonplace.

CZE is an alternative separation technique that has the potential for the analysis of milk proteins and its application to milk protein analysis has been recently reviewed [84].

Milk proteins are usually separated into casein and whey protein fraction before CE analysis. Whey proteins can be prepared [85] from milk by acid precipitation of casein at pH 4.6 using mineral acid. The casein is removed by centrifugation and the whey is filtered (0.45 μm) to remove any residual casein precipitate and fat.

Relating to casein. various conventional electrophoretic techniques have been employed to detect genetic polymorphism of bovine (PAGE) [86,87] and ovine (PAGE, SDS–PAGE, PAGIF) [88–90] milk caseins. Bovine milk caseins polymorphism is usually studied by alkaline electrophoresis where α_S-, β- and κ-CN migration zones are well defined [86]. Although these methods achieve excellent separation, they do not permit good quantitative analysis.

To study ovine caseins polymorphism is much more difficult because κ-CN migrated together with β-CN (PAGE) [89,90], moreover, α_{S2}-CN could not be detected in the SDS–PAGE analysis of whole casein because it migrated together with α_{S1}-CN [89].

The potential of CE for the characterization of ewe's milk proteins has been demonstrated by Cattaneo et al. [91]. This CE method was later used to the identification of the α_{S1}-CN variants A, B and C and the fast moving α_{S2}-CN variant in ovine α_S-CN [89]. The rapid (30 min) and easy identification of the ovine genetic variants makes this method suitable for screening and complementary to other phenotyping methods. It may be particularly useful because of the complexity of the genetic polymorphism ovine α_S-CN associated with different levels of phosphorylation and non-allelic form.

Recently, the main protein fractions had been identified in caprine milk by CE and subsequently genetic polymorphism in caprine α_{S1}-CN, α_{S2}-CN, β-CN and κ-CN has been determined. κ-CN A and B, β-CN A and null, α_{S2}-CN A, B and C, α_{S1}-CN A,

B, C and null and other forms with intermediate and low α_{S1}-CN content have been identified [92]. The method was rapid and allowed the analysis of whole caprine milk using simple sample preparation. This method may also permit the quantitation of different protein fractions.

Bovine whey proteins – α-Lg, β-Lg, BSA and IgG – have been separated [93] by CE in an uncoated capillary using sodium borate (150 m*M*, pH 8.5), containing 0.05% Tween 20, separation buffer. This method was used to quantitate α-Lg, β-Lg, BSA and IgG in a liquid whey sample and a reconstituted whey protein concentrate powder. The results were compared with those obtained by HPLC, SDS–PAGE and SDS–CGE. The values obtained for α-Lg and β-Lg were consistent throughout the various methods, however, there was considerable variation in the values for the BSA and IgG. The authors concluded that these variations were due to the low concentration of these proteins in the whey and also to their heterogeneous nature. The reproducibility of the CE method results was as good as those for HPLC and better than could be obtained by PAGE.

This CE method was later studied in detail [94]. A sample buffer and separation buffer system was developed which eliminated an initial solvent trough that coincided with the IgG peak. This made it possible to quantify the IgG protein. Optimum resolution and analysis time (10 min) for the α-Lg, β-Lg A, β-Lg B, BSA and IgG was achieved with a sample buffer consisting of 10 m*M* phosphate (pH 7.4) and a separation buffer consisting of 150 m*M* sodium borate (pH 8.5) containing 0,05% Tween 20. This method was successfully used to separate a mixture of commercially purified whey proteins and an acid whey sample.

Paterson et al. [85], using an uncoated capillary and a 50 m*M* MES running buffer (pH 8.0) with the addition of 0.1% Tween 20, achieved the separation of β-Lg A, B and C variants from both each other and from the other bovine whey proteins – α-Lg and BSA. The method was then used to phenotype β-Lg in a sample population of New Zealand Jersey cows.

In CE non-ionic long-alkyl-chain surfactants such as Brij and Tween have been successfully used as agents of capillary coating in order to eliminate the adsorption of protein on the capillary wall. The effect of surfactant type and concentration on the migration behavior of α-Lg, β-Lg A and β-Lg B was recently studied [95] by CE using a poly(ethylene glycol) coated capillary column. Three surfactants – Tween 20, Brij 35 and Brij 78 – were used as buffer additives. There are distinct differences in behavior between α-Lg and β-Lg A in the presence of surfactants selected. β-Lg appears to form a complex with these surfactants by hydrophobic binding, whereas some structural modifications of α-Lg occur within the concentration range employed (Brij 35, 0–80 μ*M*). The value of pH has an influence on the magnitude of the binding of the surfactant to the protein.

CE using an untreated fused-silica capillary filled with solution of 0.18 *M* phosphoric acid (pH 3.6) allowed the separation of α-Lg, β-Lg A, β-Lg B and BSA in a single run of 8 min without the presence of polymeric additives [96].

Although most research has centered on the separation of the four major whey proteins, Riechel et al. [97] have used CE for the determination of the minor whey protein bovine lactoferrin in cheese whey concentrates. To enhance the detection sensitivity, the affinity interactions in combination with LIF detection, were used.

Simultaneous separation of the major milk proteins – α-CN, β-CN, α-Lg and β-Lg – have been assayed using uncoated fused-silica capillaries and high pH running buffer [98] containing urea or high ionic strength buffer [99,100] to overcome the adsorption of proteins to the capillary wall and to eliminate the casein aggregation problems.

A better resolution was obtained by using a hydrophilically coated capillary and low pH citrate buffer (pH 2.5) containing urea and methylhydroxyethylcellulose [101]. Casein micelles were disrupted by the incubation of skim milk with reduction buffer (citrate buffer, 6 *M* urea, D,L-dithiothreitol) for 1 h at room temperature. The resulting clear solution was used for CE analysis. The reformation of micelles during electrophoresis was prevented by using 6 *M* urea in the electrophoresis buffer.

This method was later optimized by Recio and co-workers [102,103] and was applied to the analysis of genetic variants of milk proteins from different species (cow, goat and ewe) [103]. Genetic variants A and D of bovine α_{S2}-CN, β-CN variants A^1, A^2,

A^3, B and C and α_{S1}-CN variants B and C were determined. In addition, the different casein fractions including some genetic variants of ovine and caprine milk were identified by CE. Moreover, variants which differ only in a single amino acid (e.g., ovine β-Lg variants) could be separated. However, bovine κ-CN variants could not be separated.

Cattaneo et al. [91], using the same method, identified the major components of ewe's milk. Identification was carried out by analysis of individual samples and comparison with the results obtained by HPLC, FPLC and PAGE. The major protein components of ewe milk were well resolved within 45 min. Identification of α-Lg, β-Lg genotypes, α_S-CN complex, κ-CN and β-CN fractions was possible by their characteristic migration times. The CE results showed good correlation with those obtained by HPLC and PAGE. CZE separations permit the simultaneous determination of whey proteins and caseins. Sample preparation for CZE was easier than that for HPLC and PAGE.

Separation of a_S-CN, β-CN, κ-CN, α-Lg and β-Lg was achieved by MEKC [104]. These proteins are separated successfully after complete denaturation with SDS and D,L-dithiothreitol.

The procedure for phenotyping of most genetic variants in cow milk was optimized for IEF of camel milk proteins and milk from individual camels of different breeds was screened [105]. The caseins obtained from IEF bands were also investigated by N-terminal sequencing.

5.1.2. Effect of heat and pressure treatments

To render milk safe and to extend its shelf life, raw milk is commonly processed prior to human consumption. It undergoes several treatments including heat-processing to eliminate micro-organisms, inactivate enzymes and alter chemical and/or physical properties for further processing. Changes in the amounts of whey proteins are a good indicator of the thermal damage undergone by milk. Changes in the amounts of α-Lg and β-Lg during storage of direct and indirect ultra high treated milks were studied by RP-HPLC and CE [106]. Both methods provided comparable results at the beginning of the storage period. However, the CE analysis of α-Lg and β-Lg in stored milk allowed a more accurate quantification.

A direct method [102] to measure heat-denatured whey proteins in the casein fraction of heat-treated milk allowed a more accurate assessment of the pasteurization processes than procedures based on measurements of the native whey proteins.

The heat-induced binding of whey proteins to milk fat globule membranes in whole milk was investigated by electrophoresis and laser scanning densitometry [107]. Both α-Lg and β-Lg bound to the surfaces of fat globules when milk were heated in the temperature range 65–85°C. The interaction behavior of α-Lg did not seem to change with the temperature; the quantity of β-Lg interacting with the milk fat globules increased with temperature between 65 and 85°C.

The amounts of α-Lg and β-Lg which interacted with the casein micelles in skim milk during heat treatment at temperatures in the range 75–90°C at pH values of 5.8, 6.2 and 6.8 were determined by SDS–PAGE [108]. In general, faster reaction of the whey proteins with the micelles was found at low pH and higher temperatures. The reaction between α-Lg and casein micelles depended to a relatively small extent upon environmental variations (pH and temperature), while β-Lg interactions were more affected.

Oldfield et al. [109] used PAGE to determine the extent of denaturation of α-Lg and β-Lg and their association with the casein micelles in skim milk heated in the range 80–130°C. A pseudo-first-order model was used to calculate the reaction kinetics of the association of β-Lg with the casein micelle.

CE allows a fast and easy determination of the ratio of native (unmodified) to total β-Lg for monitoring storage conditions of milk powders [110].

During milk processing and storage free amino groups of proteins are glycated by lactose according to the Maillard reaction yielding Amadori compounds. Furosine, obtained by acid hydrolysis of these products, has been proven to be a suitable indicator of the presence of Amadori compounds in milk. As the temperature and water activity are among the most important parameters that affect the Maillard reaction, the furosine content of milk can provide information on milk quality such as the addition of reconstituted milk powders to liquid milk [111–113].

CE separation of furosine in milk [114] in fused-

silica capillary was successfully obtained using 60 m*M* *N*,*N*,*N*′,*N*′-tetramethyl-1,3-butanediamine as the run buffer additive, which prevented interactions of furosine with the capillary wall and reversed the EOF. However, the reliable quantitative data are obtained only for standard solution of furosine and only the analysis of one sample of dried milk is reported.

A different CE method for furosine determination was described by Tirrelli [115]. The separation was performed using a 3-(*N*-morpholino)-2-hydroxypropanesulfonic acid solution at pH 7.0 as run buffer. The data obtained on 48 samples including heat-treated milk, cheeses and drum wheat products were compared with those obtained by HPLC.

When analyzed by CE, certain skimmed milk powders are seem to exhibit additional peaks migrating after the whey protein-β-Lg. Using a model reaction between β-Lg and lactose, and studying the reaction products using electrospray MS, it was demonstrated that these protein peaks are almost certainly due to a Maillard reaction between lactose and the ε-amino group of lysine. This results in the formation of a series of lactose–protein conjugates exhibiting throughout molecular mass increments of 324, which is sufficient to allow their separation by CE [116].

SDS–PAGE was used [113] to investigate the effect of the glycation conditions (dry and aqueous system) on both the association behavior and the conformational changes of the glycated Lg formed.

SDS–PAGE and PAGEIF with immunodetection were used to specifically detect the Amadori compounds in milk [112]. Polyclonal antibodies raised against a synthetic lactosylated peptide were found to be specifically directed against the carbohydrate moiety of the immunogen, recognizing, in addition to the Amadori compound, lactose, and, to a lesser extent, lactose and galactose. These antibodies were effective in detecting lactosylated proteins both on a model system containing β-CN and on milk subjected to different thermal treatments.

The potential of high-pressure treatments as an alternative to thermal treatments is currently a focus of major investigators. The microbiological and biochemical changes during storage of high-pressure treated (400 MPa at 25°C for 30 min) whole and skim milk at refrigeration temperatures (7°C) were studied by CE [117]. CE of the casein fraction showed a negligible degradation of κ-CN and a considerable β-CN, α_{S2}-CN and α_{S1}-CN hydrolysis during storage, which can be responsible for flavor defects, during prolongated refrigerated storage. The results showed that pressurization of milk at 400 MPa for 30 min led to milk with extended shelf life from a microbiological point of view.

5.1.3. Adulteration

Adulteration of milk by addition of rennet whey solids is usually based on detection and quantification of caseinoglycomacropeptide (CGMP). Several reports have shown CE to be a powerful method for CGMP. CE at acidic pH and in the presence of sodium citrate buffer, offers a suitable and rapid method for the determination of CGMP and its several subcomponents [118]. Selectivity was demonstrated for all other major whey protein. This method has been validated and the authors concluded that the method may be used to assess the component identity (percentage of the various glycoforms) and to check the CGMP purity when yielded by different methods or batches.

Soya protein is probably the most common non-milk protein used in milk replacers and it is likely to be a major adulterant. 5% (w/w) processed soya milk in pasteurized skim milk can be detected by SDS–PAGE [119]. By introducing a selective sample pretreatment which removed soluble casein from insoluble soya protein, 0.06% soya protein was detected in total protein of melted cheese [120].

Recently, two different commercial kits for SDS–CE were evaluated for the detection of the presence of soya protein in milk powder [121]. The use of a tetraborate–EDTA sample treatment minimized interferences from milk proteins, allowing the detection at least 1% (w/w) of soya protein in total protein. SDS–CE affords less resolution than SDS–PAGE for the separation of soya and milk proteins, but allows a more accurate quantitation of the resulting data.

Bovine β-Lg is a major cow's milk allergen. Other whey proteins such as α-Lg or Ig could be also allergenic. Soya proteins are a suitable replacement for milk proteins from animal species when individuals are allergic to these animal proteins [122]. The use of very highly sensitive technique is needed

to prevent food adulteration and to safeguard food quality. Recently, a Western blotting method for the detection of whey milk proteins in commercial soya milks was applied to assess the food safety [123]. Soya proteins and milk proteins were separated by SDS–PAGE followed immunodetection with anti-bovine β-Lg or anti-bovine α-Lg antisera. Adulteration with bovine protein (0.1%) in soya protein can be detected. The sensitivity is about 300-times higher than that obtained by chromatographic method. The method was applied to detect adulteration of bovine milk proteins in different soya milks, powdered soya milk and soya infant formulas. The soya milk powder studied includes whey milk proteins α-Lg and β-Lg.

Adulteration of milk with milk from different species could be detected by CE [124], as, in fact, each kind of milk (cow, goat and ewe) gave typical electropherogram. The analysis of different milk mixtures gave the possibility of detecting 8% cow milk added to ewe or goat milk, according to the different migration times of the α_{S1}-CN fractions of different species.

Recently, the detection and quantification of cow's milk in goat's milk, based on the presence of the specific whey proteins, was described [125]. The minimum amount detectable of cow's milk was 2% in milk mixtures and 4% in cheeses. Qualitative analysis of goat–ewe–cow and goat–ewe samples was also reported.

5.2. Small ions

The inorganic cations most frequently determined in milk are Na^+, K^+, Ca^{2+} and Mg^{2+}. The comparison of CZE and atomic spectroscopy for the determination of the cation content of a standard reference material, IAEA-A-11, milk powder indicated that there is no systematic differences between the methods [126].

The simultaneous analysis of anions (chloride, sulfate, citrate and phosphate) by CE with indirect UV detection was described [127]. With a BGE based on chromate and borate, the interference of system peaks with those of sample anions was shown. When the location of the system peaks are optimized, the quantification of citrate can be achieved. This method was used for determination of anions in milk.

Recently, a CE system for the simultaneous determination of small cations and anions have been developed [128]. The system uses one capillary and one detector. The sample is first injected into one end of the capillary and subsequently into the other end. The detector is placed in the center of the capillary. The system allows excellent separation of 22 small inorganic and organic cations and 1A and 2A class cations within 5 min. Milk samples were analyzed after off-line dialysis pretreatment. Chloride, sulfate, citrate, phosphate, lactate, K^+, Na^+, Ca^{2+} and Mg^{2+} were separated in milk.

5.3. Antibiotic residues

The monitoring of milk for antibiotic residues is an area of increasing concern and importance due to the potential impact on human health. Although many of the separation modes used for antibiotic analysis are well developed, separations based on CE methods have much potential in the field of antibiotic analysis.

Electrophoretic separation of antibiotics and detection by bioautography has been evaluated by several researchers [129,130]. A CE method was developed for simultaneous determination of oxytetracycline, chlortetracycline, tetracycline and doxycycline levels in cow milk [131]. The tetracyclines were extracted specifically with a metal-chelating affinity column.

Metal complexation in non-aqueous CE systems was evaluated [132] for the separation and improved detection of tetracycline antibiotics using LIF detection. The method can be used for the detection of tetracyclines at the ppb level in milk.

The application of CE coupled with nano-electrospray Quasi-MS–MS–MS to the multiresidual analysis of a large number of sulfonamide antibiotics in milk extracts were reported [133]. The residues at the ppb level to the ppt level were identified.

5.4. Mycotoxins

Milk contamination with mycotoxins is a serious threat to public health. Most of the reported incidence of mycotoxins in milk was due to aflatoxin

M_1. The occurrence of another mycotoxin, cyclopiazonic acid (CPA), in animal products and its carryover into the milk emphasized the potential risk to dairy consumers [134]. However, the presence of CPA in milk is not well studied in the literature as for aflatoxins.

Prasongisdh et al. [135] recently published a MEKC method to detect CPA in milk and compared its quantifying efficiency to the RPLC. MEKC was capable of isolating of the CPA peak at lower quantity, although the sample injection volume was several times lower than that of RPLC. This method was later used to assess the stability of CPA during cold storage and processing of milk [136]. It has been found that the potential of CPA to reach milk consumers appeared to be high since it persisted in all forms of processed milk products including liquid, frozen, freeze–dried and spray–dried milk. Simulation of heat-treatments used by the dairy industry also induced no significant degradation of CPA [137].

6. Soft drinks

Soft-drink beverages are common everyday products, which are produced regionally. Generally, concentrated syrups, aspartame, caffeine and preservatives such as benzoic acid are mixed with water followed by carbonation and bottling.

Three of the more important beverage components which require routine testing are caffeine, benzoate and aspartame. These three substances exhibit strong UV absorptivity and are easily detected by most commercially-available HPLC and CE instruments [138,139].

Rapid analysis of carbonated beverages by CE [138] allows the simultaneous determination of aspartame, benzoic acid and caffeine in 2 min using 20 m*M* glycine buffer at pH 9.0 and direct detection at 215 nm. Aspartame is also well resolved in a mixture of synthetic standards containing phenylalanine and its demethylated dipeptide degradation product, aspartylphenylalanine. In general, glycine buffers offer more rapid migration times than borate buffers, but also reduce resolution of phenylalanine and aspartylphenylalanine.

The physiological effects produced by many non-alcoholic beverages such as tea, coffee and coca depend mainly on their natural xanthine content. The MEKC separation of caffeine and its metabolites, theobromine, paraxanthine, theophylline and 1,3,7-trimethyluric acid was investigated using SDS as the micellar phase [140]. Caffeine and its three analogues were resolved within 2 min with LODs less than 1 μg/ml. No sample preparation other than filtration was necessary for analysis of non-carbonated beverages. For carbonated beverages degassing by purging with argon was required prior to filtration. The only xanthine detected in beverage samples (Pepsi-cola, Coca-cola) was caffeine.

6.1. Inorganic and organic ions

Soft-drinks generally contain high concentration of salts, chloride being a predominant anion. Citrate, lactate and ascorbate are also commonly found in these drinks. The contents of nutrient-added drinks vary; beside citrate, malate and ascorbate, the amino acids aspartate and glutamate are also commonly found [60].

Carbonate was determined in soft drink samples using on-line coupling of gas diffusion to a CE system [40].

CZE performed in a hydrodynamically closed separation compartment offers a rapid and reproducible alternative to the determination of sorbic acid in soft drink [67]. Benzoic and ascorbic acid did not interfere in the analysis of sorbate by the CZE.

Pantothenic acid is a member of the B complex vitamins. Using a CE method, pantothenic acid could be separated [141] from ascorbic acid and pyridoxine in commercial soft drinks. Chiral resolution of D,L-pantothenic acid in soft drink was also studied [142]. The optimum running conditions were found to be 60 m*M* phosphate buffer (pH 7.0) containing 60 m*M* 2-hydroxypropyl-β-CD and 10% (v/v) methanol. The CE analysis of a soft drink showed the presence of only D-pantothenic acid.

6.2. Artificial sweeteners

The artificial sweeteners (cyclamate, aspartame, acesulfame-K, alitame) and sorbic acid are well separated [143] from the other compounds in the diet soft drinks in less than 5 min using an electrolyte

consisting of 1 m*M* hexadecyltrimethylammonium hydroxide and 10 m*M* sodium benzoate. The levels of cyclamate determined by CZE were in good agreement with those determined by the AOAC gravimetric method, Saccharin, benzoic acid, and caffeine, which are added to low Joule colas containing cyclamate, cannot be determined with this system as saccharin appears as a broad peak in the electropherogram, caffeine does not migrate with this system and benzoic acid cannot be determined as the electrolyte contains sodium benzoate.

Saccharin, caffeine, benzoic acid, sorbic acid and a number of other artificial sweeteners (aspartame, acesulfame-K, alitame and dulcin) were separated and determined in low-Joule drinks by MEKC [144]. The levels of artificial sweeteners, preservatives and caffeine were in good agreement with those obtained by the HPLC procedure.

A rapid and selective method for the determination of aspartame in diet cola samples using CE with a pH 2.14 buffer and detection at 211 nm has been developed [145]. No other sample constituents are detected in this method. The analysis time (4 min) is faster than that reported for the HPLC methods (14 min).

The chiral separation of aspartame and several decomposition products namely L-β-aspartame, L-α-aspartyl-L-phenylalanine, L-β-aspartyl-L-phenylalanine and diketopiperazine was accomplished by HPLC and CZE methods [146]. The presence of any of these decomposition products in diet soft drinks labeled to contain the sweetener.

6.3. Carbohydrates

A method for the rapid quantitative analysis of underivatized acidic sugars, monosaccharides and disaccharides using co-electroosmotic CE was developed [147]. Indirect UV detection at 254 nm using sorbate as BGE was employed. A highly alkaline pH value of the electrolyte system was chosen in order to achieve an electrophoretic mobility of the saccharides towards the anode. A codirectional movement of the negatively charged analytes and the electroosmotic flow is accomplished by employing a polycationic surfactant (hexadimethrine bromide), which is added to the BGE. To improve the resolution, acetone is added as organic modifier. A practical application of the developed method for the fast determination of fructose, glucose and sucrose in various soft drinks is provided.

6.4. Colorants

Although the number of permitted food colorants was reduced for food safety reasons in recent years, many kinds of synthetic food colorants are still widely used all over the world because of their low price, effectiveness and stability.

Separation conditions enabling the complete resolution of 11 permitted synthetic food colorants and some of their subspecies by CZE in a hydrodynamically closed separation compartment were investigated [148]. A complete CZE resolution of these analytes requires a proper pH of the carrier electrolyte to eliminate adsorption of erythrosine combined with complexing effects of β-CD. Under optimized conditions, the CZE separation times were in the 2.5–10.5 min range. The quantitative aspects and practical applicability of this CZE method to the determination of the permitted colorants in soft drink concentrates and liqueurs were also studied [149]. In general, the determination of the dyes at 4 and 32 ppm concentrations exhibit high reproducibilities. This CZE procedure required only minimal sample pretreatment in the analysis of practical samples.

A CE method with diode-array detection has been developed for the analysis of synthetic food colorants in fruit soda drinks [150]. Eight food colorants were separated within 10 min using pH 9.5 borax–NaOH buffer containing 5 m*M* β-CD.

The caramels used in soft drinks are classified as Class IV caramels. Class IV caramels are prepared by the controlled heat treatment of sugars in the presence of both sulfite and ammonium compounds, which produces caramels with low isoelectric points and therefore negatively charged above pH 3.0.

The established method for determination of caramel is a simple spectrometric measurement at 610 nm. This method cannot distinguish between caramel classes nor between caramel and other compounds which absorb at 610 nm [151].

Coffey and Castle [152] have used CE at acid pH to discriminate between Class I, III and IV caramels. A reliable, robust method for the analysis of Class IV caramels by CE has recently been developed

[153]. The migration time of the colored ''caramel'' peak was shown to be related to its sulfur content. A high-nitrogen, high-sulfur content Class IV caramel was found to be used in the majority of the soft drinks investigated. This caramel was quantified with less than 5% uncertainty when using either of two high-nitrogen, high-sulfur caramels from different manufactures as a standard. Production batch samples made over a 12-month period of these two caramels showed less than 3% variation.

6.5. Metals

The separation of ammonium, potassium, calcium and sodium in a cola beverage was obtained [154] using a carrier electrolyte consisting of 500 μ*M* cerium(III) sulfate–2.5 m*M* 18-crown-6. The LODs were in the range 0.1–0.3 μ*M* for electrokinetic injection.

Recently a flow injection analysis–capillary electrophoresis system with hydrodynamic injection has been developed and used to determine common inorganic cations (Na, K, Ca and Mg) in water and soft drink samples [155]. The developed FIA–CE system with hydrodynamic injection offers several advantages, such as automated sample pretreatment and simple calibration, independent on differences in sample conductivity. Quantitative analysis with a precision about 3% can be completed in a time which is about five fold shorter than that required by corresponding conventional CE systems.

Simultaneous detection of small cations and organic acids by CE with indirect UV detection has recently been reported [79].

6.6. Soluble dietary fiber

Many soft drinks containing such polysaccharides as Polydextrose, Pinefibre and guar gum are now commercially available. These polysaccharides are used as dietary fiber in soft drinks in Japan and are mainly used as bulking agents in the manufactures of reduced-calorie foods in America. A clean-up method using gel permeation chromatography (GPC), and a qualitative analysis involving the electrophoresis of soluble dietary fibers, including Polydextrose, Pinefibre, Cellace, Sunfiber and guar gum in soft drinks were both developed [156]. Impurities such as sucrose, glucose, fructose, coloring agents (grape skin pigment, carthamus yellow, carminic acid, gardenia yellow) acids and vitamins (citric, succinic, malic, ascorbic, nicotinamide, calcium pantothenate) were clearly eliminated by GPC. The solutions were then applied to the electrophoresis with a borate buffer (0.5 *M*, pH 9.0). The SDFs showed different migration distances and were detected colorimetrically with 4-aminopyrine. SDFs were also determined by a HPLC method.

6.7. Quinine

The separation and determination of quinine in bitter drinks by MEKC with UV detection is described [157]. The beverage is simple diluted, filtered and analyzed using a buffer containing of 15% methanol and 85% of a mixture of 0.05 *M* CTAB, 0.01 *M* sodium tetraborate and 0.01 *M* potassium dihydrogenorthophosphate, pH 8.6. The levels of quinine determined by MEKC were in good agreement with those determined by HPLC.

7. Tea

The principal components present in tea are cellulose, hemicellulose, lignin, alkaloids (caffeine, theophylline and theobromine), polyphenols (flavonols-catechins, flavon-3-ols, phenolic acids and esters), amino acids, metals and vitamins.

7.1. Alkaloids, polyphenols, amino acids and ascorbic acid

Several CE methods have been used to separate, and in some cases, quantify alkaloids [158–160,166] and polyphenols [159–169] either individually or as a part of standard mixtures.

Zhong et al. [161] developed two types of dual-electrode detectors for CE determination of phenolic acids (chlorogenic acid, caffeic acid and *p*-coumaric acid) in black tea. The first employs a ring-disk microelectrode placed in a wall-jet configuration and is used for the selective detection of substances undergoing chemically reversible oxidation. The second electrode design consists of two adjacent carbon fibers embedded in an epoxy matrix. This

configuration can be used to confirm pear identity and purity by operating the electrodes at two different potentials.

Using HPLC methods, several catechins and caffeine can be separated, but the time needed for one sample is more than 20 min, and neither theanine nor ascorbic acid could be simultaneously analyzed with catechins [164].

The CE method developed by Horie et al. [159] is more suitable than HPLC methods to estimate the quality and taste of green tea, in terms of a shorter analytical time (only 11 min) and a simultaneous determination of five catechins, caffeine, theanine and ascorbic acid. The limit of quantification (LOQ) of 10 mg/l was obtained.

A better LOQ was achieved by Arce et al. [160] who obtained LOQs in the range of 0.12 mg/l for flavonols to 4 mg/l for caffeine. In this method, the analysis was carried out after treatment (extraction, filtration and dilution) of the samples in a flow injection system which was coupled to a CE equipment. The compounds analyzed were caffeine, adenine, theophylline, epigallocatechin-3-gallate (EGCG), epigallocatechin (EGC), epicatechin gallate (ECG), epicatechin (EC), catechin (C), quercetin, gallic acid and caffeic acid.

However, although quantitative results were obtained in the analysis of tea catechins using borate buffer of the pH range of 8.0–8.5, poor resolution between EGC–C–EC (similarly EGCG–ECG) is evident. In addition, caffeine and theobromine could not be separated by CE [159,160].

To enhance the resolution and separation among alkaloids and catechin isomers, surfactant was added to the borate buffer, which facilitates the separation of analytes with MEKC [165,166].

The effect of several critical separation parameters (micelle charge type, surfactant type, organic solvent buffer modifier, micelle concentration, buffer pH and cyclodextrin buffer modifier) were evaluated for enhanced isomer separation and resolution [167]. Finally, six tea catechins: EGCG, ECG, gallocatechin gallate (GCG), EGC, EC and C and caffeine were effectively separated using 20 m*M* tetraborate, 110 m*M* SDS, 14% methanol, 1.5 *M* urea, 1 m*M* β-CD (pH 8.0). The developed MEKC system was applied to the determination of the catechins isomers in native samples of green tea. For comparative purposes, the analytical levels of the catechins in the Lung Ching green tea samples were determined using RP-HPLC with good agreement.

Barroso and van de Werken [168], using a 20 m*M* borate–phosphate buffer (pH 7.0) containing 25 m*M* SDS, achieved the separation of caffeine, catechin, EGC, EGCG, EC and ECG. The method was applied to the determination of the above components in green tea and black tea infusions. It was observed that in the case of black tea the baseline definition was not as good as for green tea. After injection of black tea, the capillary needed to be thoroughly cleaned (1 *M* H_3PO_4 before normal procedure) to again obtain similar peaks.

An optimized buffer consisting of 20 m*M* SDS, 50 m*M* phosphate, 50 m*M* sodium tetraborate and 10% acetonitrile (pH 6.0) has been developed and applied to the analysis of a range of tea types [169]. Most of the major classes of tea components were identified using diode-array detection. In an effort to improve the resolution of black tea components, solvent extraction was carried out on the infusion to provide three separate fractions: ethyl acetate fraction, methanol fraction and remaining water which could then be analyzed separately to permit simplification of this highly complex infusion. In many respects, MEKC can be considered complementary to RP-HPLC for tea separations. It is capable of separating the xanthine, catechin and flavonol classes, but in common with the latter, cannot resolve the highly complex thearubigens. Low-molecular-mass acidic species such as chlorogenic acid and 3-galloylquinic acid migrate late in MEKC and are more easily separated than by HPLC, where they elute close to the void volume. One particular drawback of MEKC is the adsorption of the theaflavins by the capillary wall.

7.2. Organic anions

Organic anions make an important contribution to the taste and quality of tea. However, data on these components are more scare than those of alkaloids and polyphenols. Gluconic, ascorbic, citric, malic and aspartic acid were found in honey tea by CE with indirect UV detection [60].

The organic acids – oxalic, malic, citric, quinic, aspartic and glutamic – are the major ones in tea

according to the literature. These acids in tea infusions were analyzed simultaneously using CZE with a chromate buffer containing tetradecyltrimethylammonium bromide and ethylenediaminetetraacetic acid disodium salt which was added to reduce the influence of metal cations [170].

7.3. Artificial sweeteners

A rapid method for the determination of the artificial sweetener aspartame in diet iced tea using CE [145] with a 30 m*M* phosphate–19 m*M* Tris (pH 2.14) buffer and detection at 211 nm has been developed. The analysis time is faster than that reported for HPLC methods. No other sample constituents are detected in this CE method.

7.4. Metals

Five metal cations (K, Na, Ca, Mg and Mn) were detected [171] in a Chinese tea infusion using CE in a BGE system composed of imidazole (5 m*M*)–2-hydroxyisobutyric acid (6.5 m*M*)–18-crown-6 (0.55 m*M*) and methanol (20%, v/v) at pH 4.5. A limit of detection at the μg/l level could be achieved using electromigration injection.

This method was later validated [172] for the determination of K, Na, Ca, Mg and Mn in food and botanical materials. Closed-vessel microwave acid digestion was used for the sample preparation. The LODs and LOQs in solution are below 600 μg/l, except for K, for which the LOQ is about 2 mg/l. The concentrations of the metals in tea with different geological origin were determined.

7.5. Adulteration

Natural vanilla extract has been widely replaced as a flavoring agent by the synthetic vanillin or ethylvanillin. MEKC can be used as a rapid screening method for the analysis of vanilla flavorings and vanilla extracts [173]. The method permits the direct injection of vanilla extracts and beverages. Under optimized conditions, baseline separation of nine vanilla constituents and three possible adulterants is possible within 9 min. The method was applied to additives in vanilla-flavored tea and vanilla-flavored coffee.

8. Wine

The main components present in wine are ethanol, SO_2, sugars, organic acids, proteins, amino acids, inorganic ions, fural and its derivatives and colorants.

8.1. Ethanol

Ethanol is present in wines as a by-product of the fermentation of sugars in grape juices by yeast. It contributes to the flavor of the wine, as well as its microbial stability.

Ethanol is routinely analyzed in wines for sensory and taxation purposes. Using a MEKC technique, ethanol could be determined [174] in wines with a per sample time of less than 5 min. The response was linear over a range of 5–30% (v/v) ethanol, with an average RSD of 1.38%. Glycerol and sugars did not interfere with the analysis. In a comparison with a GC method for ethanol analysis, the results for the two methods did not different significantly. This method offers the speed of the GC analysis and the versatility of CE, which can also be used for a number of other wine analysis.

8.2. Sulfite

Sulfite is added to the wine as an antioxidant and preservatives and is limited to 160 mg/l in red and to 225 mg/l in white wine.

The classical method is a titrimetric method using the reductive potential of this substance. Other components in wine with reductive potential (e.g., sugars) may falsify results.

Trenerry [175] described a CE method for the determination of sulfite as sulfate in wine using a Monier–Williams distillation to liberate SO_2, subsequent oxidation of SO_2 to H_2SO_4 followed by the determination of sulfate by CE. The LOD is 5 mg/kg. The levels of sulfite in the wines are in excellent agreement with those obtained by titrimetry.

On-line coupling of gas diffusion to a CE system in a flow arrangement, which is a suitable technique for automated pretreatment of wine samples, is very recent data [40]. The sample is merged with a 1 *M* H_2SO_4 to transform the anions into their gaseous

species. These gaseous analytes permeate through a PTFE membrane into an acceptor stream consisting of a 5 m*M* Tris buffer. The acceptor stream is led into an injector. A carrier electrolyte containing 6 m*M* potassium chromate, 3 m*M* boric acid and 2.3 μ*M* CTAB at pH 8.75 was found to be suitable for accomplishing baseline separation of $S_2O_3^{2-}$, Cl^-, SO_4^{2-}, NO_3^-, HS^-, SO_3^{2-}, citrate, formate, HCO_3^- and acetate in the model mixture. The technique has been applied to the determination of SO_2 (total and free), carbonate and acetate in wine samples.

8.3. Inorganic and organic anions

Measuring organic and inorganic acid levels in wine is important from the standpoint of monitoring the fermentation process, checking product stability and studying the organoleptic properties of products.

Generally, inorganic and organic ions could be analyzed with both, UV and conductivity detection. A new electrolyte system for indirect UV detection in CZE using a 1,2,4,5-benzene-tetracarboxylic acid buffer system with bis-(2-aminoethyl)-amine as EOF modifier, was applied [61,176] to the separation of 11 anions (chloride nitrate, sulfate, oxalate, tartrate, malate, succinate, citrate, phosphate, acetate and lactate). The LODs were from 0.006 to 1.072 mg/l. The method was applied to the determination of anions in red and white wine. Chloride, sulfate, tartrate, malate, succinate, citrate, acetate and lactate were identified and quantified in red wine. In white wine, in addition, phosphate were found.

Klampfl et al. [177] achieved the separation of chloride, sulfate, oxalate, tartrate, malate, succinate, adipate, glutarate, acetate, lactate, butyrate, valerate and shikimate. Simultaneous direct conductivity and indirect UV detection was used. Regarding conductivity detection, high sensitivity can be achieved for the fast migrating species, e.g., chloride, sulfate and oxalate, whereas indirect UV detection provides low LODs for analytes showing longer migration times like lactate and shikimate. The combination of direct conductivity and indirect UV detection is advantageous for the CZE analysis of wine samples, as only the combination of both detection techniques allowed the quantification of most of the analytes in a single CZE run. Only oxalate and valerate were below the LOQ and butyrate was not detected.

Baseline separation of L-ascorbic and D-erythorbic acid in wine was achieved [39] using a buffer consisting of 0.05 *M* sodium deoxycholate–0.02 *M* tetraborate–0.02 *M* phosphate (pH 8.6). The separation was not affected by the presence of citric or tartaric acid. Seven wines were analyzed for total L-ascorbic acid using this buffer. The results were compared with those obtained using the HPLC method. The run time for the analysis of wines were reduced from 25 min to 6 min when the MEKC was used. Replacing sodium deoxycholate with CTAB in the buffer resulted in baseline separation of L-ascorbic and D-erythorbic acid even in the presence of tartaric or citric acid. The statistical data also showed good agreement between both techniques.

Sorbic acid is a widely used preservative in wines. CZE performed in a hydrodynamically closed separation compartment offers a rapid and reproducible alternative to the determination of sorbic acid in wine as a very good reproducibility in the migration time of the analyte (RSD 0.6%) and 4 min analysis time is achieved [67].

Tartaric acid is an important by-product of wine preparation. Recently, Mallet et al. [178] described the fast and reproducible determination of tartaric acid in solid wine residues by CE and indirect UV detection.

8.4. Amino acids and amines

Amino acids are significant factors in the growth of yeast and bacteria that produce wine. It is generally accepted that free amino acids contribute to the wine's aroma and taste [179].

Biogenic amine can be present in the must, be formed by yeast during alcoholic fermentation. Histamine and tyramine in wines are products of microbial decomposition of histidine and tyrosine. Ethanol amine is one of several amines occurring in wine at low concentrations, it is formed from its precursor of 1,2-ethanediol. The wine produced under hygienically optimal conditions should be nearly free of amines [180].

Wei and Li [181] described the construction and performance of a new rugged device for post-column derivatization in CE. The device has been applied in fluorescence detection of amino acids in wine using a

mixture of *o*-phthaldialdehyde–2-mercaptoethanol as derivatizing reagent. The theoretical plate numbers for 11 amino acids separated in a pH 9.5 borate buffer were obtained in the range of 40 000–250 000. Wine samples could be analyzed without any sample pretreatment except for dilution. It was seen that the wine contain many kinds of amino acids in the concentration range of 2 m*M*.

To determine levels of histamine, two methods were used, photometry in combination with liquid–liquid extraction (LLE) and solid-phase extraction (SPE) clean-up procedure, and CZE [34]. Samples do not need to be cleaned up before CZE. The histamine contents of white wine determined by CZE, photometry after LLE and photometry after SPE were compared.

Technically, a new interface for coupling flow-injection with CE was developed in order to automate the treatment of wine samples and their transfer to the CE equipment [182]. The method allows the rapid determination of 10 biogenic amines in wine. The separation process is simpler than comparable to chromatographic methods. The FIA–CE method for determining amines in wine is good alternative to the conventional process where amines are manually extracted with a Vacuc/Elut system. Biogenic amines are separated in less than 15 min by CE, in contrast to the 25 min taken by HPLC. The limits of detection in the range 0.05–0.1 μg/ml were obtained with direct UV detection.

MEKC has been employed for separating seven biogenic amines in wine [183]. Derivatization of the amines were carried out using (6-aminoquinolyl-*N*-hydroxysuccinimidyl) carbamate. The LODs range from 0.05 μ*M* for tryptophan to 2 μ*M* for histamine in wines (UV detection at 254 nm). Complete separation of seven amines was achieved within 30 min with good reproducibility and linearity.

Nouadje et al. [184], using a buffer consisting of 20 m*M* SDS, 100 m*M* borate (pH 9.3) buffer and LIF detection of fluorescein thiocarbamate derivatives, quantified 28 biogenic amino acids and amines during wine ageing. Among the 28 biogenic amines or unusual amino acids, they found two correlations (taurine/cysteic acid; arginine/spermine) during time of quantity evolution of amino acids and their corresponding degradation product.

8.5. Sugar

Sugar content determines the classification of a wine as a Table wine or a wine of higher quality. Together with the percentage of ethanol this standard is dependent on the amount of natural sugar.

A CZE method for the separation of all 16 D- and L-aldohexoses in a single run was developed by Noe and Freissmuth [185]. Discrimination of sugar enantiomers was achieved by reductive amination with (*S*)-(−)-1-phenylethylamine. The BGE consisting of 50 m*M* borate (pH 10.3) and 23% acetonitrile was used. This method was recently adapted for the analysis of reducing sugars enantiomers in wine [186]. A BGE consisting of 50 m*M* borate, pH 8.8 was employed for the separation. To achieve a better D-glucose/D-mannose separation, the sample was derivatized with (*R*)-(+)-1-phenylethylamine. Thus, in the presence of D-glucose, estimation of D-mannose, D-xylose, L-arabinose, D-galactose and D-galacturonic acid was possible. Traces of D-xylose and D-ribose were also detected. Other sugars were found only in negligible amounts.

8.6. Phenolic compounds

Phenolic compounds, such as phenolic acids, catechins and other flavonoids have an important role in wine quality; they contribute to sensory attributes and are also important in the color chemistry of red wine during ageing. Phenolic compounds also inhibit the oxidative degradation of food products and are used for this purpose by the food industry [187].

HPLC has been the method of choice for analyzing theme compounds, but CE has also been used and comparisons of CE and HPLC for analysis of phenolic compounds in wines have also been published [188–199].

Garcia-Viguera and Bridle [189] quantified 10 non-colored phenolic compounds occurring in a Portuguese red wine. Comparison between the data obtained by HPLC and CZE showed minor anomalies in quantitation for certain wine phenols – catechin, epicatechin and caffeic acid gave greater values in CZE analysis than HPLC. Gallic acid, 3,4-dihydroxybutyric acid, 4-hydroxyphenyethyl alcohol, *cis*-CAFTA, catechin, vanillic acid, syringic

acid, *p*-coumaric acid and epicatechin separated well and were characterized by both methods. However, the flavonols, myricetin, quercetin, kaempferol and isorhamnetin detected and identified by HPLC, were not detected by CZE – which may be due to a sensitivity effect with CZE. This method was also applied to the determination of non-colored phenolics in port wines [190]. Also, other standard blended ports have been analyzed, as a preliminary study, to determine the influence of ageing on the phenolic compounds.

The CZE method, using phosphate buffer at pH 8.85 was used to separate the rutin, catechin, quercetin, epicatechin and myricetin in red wine [191]. The marker index technique, using organic carboxylic acids, was used to give indices for the flavonoids and phenolic compounds and for identification of the analytes. The detection limit for all of the compounds was 3 pmol.

The phenol, phytoalexin, resveratrol was first reported in the skins of grapes and later in wines [200]. Resveratrol has been found to be the most active cardioprotective agent in wines [201]. This phytoalexin in *cis*- and *trans*-isomer forms was found in wine with other antioxidants such as gallic acid, catechin and quercetin [200]. *cis*-Resveratrol, *trans*-resveratrol, gallic acid, catechin and quercetin have been separated [197] using a phosphate–borate buffer (pH 9.1), containing deoxycholate within 11 min. Standards and wine samples were directly injected into the CE system after a simple filtration. Probability of peak identity was done by using automated comparison to spectral libraries. However, no quantitative data were reported for wine samples.

Chu et al. [198], using a phosphate–borate buffer (pH 9.0) containing SDS, achieved the separation of *cis*- and *trans*-resveratrol within <15 min with a detection limit of 1.25 μM. The method was applied to the direct determination of *trans*-resveratrol in wines. However, *cis*-resveratrol could not be quantified.

The determination of *cis*- and *trans*-resveratrol in wine generally requires the use of extraction and preconcentration techniques prior to CZE [199] as those compounds are present in wine at very low concentrations and the matrix of the wines is highly complex. After solid-phase extraction, the detection limits of 0.06 mg/l for *trans*-resveratrol and 0.08 mg/l for *cis*-resveratrol were obtained using CZE with 40 m*M* borate buffer (pH 9.5). This method allows the simultaneous determination of *cis*- and *trans*-resveratrol in wine.

8.7. Proteins

Proteins are minor constituents of wine, but they contribute to wine quality. Proteins are partly responsible for the sensation of ''body'' in wines. They can also bind volatile compounds so that the aroma of the wine is retained, and they have a positive effect on foam stability in sparkling wines. However, they can cause a number of technological problems: difficult filtration, clarification and tartrate stabilization, and turbidity in boiled wine [202].

Most of the studies on wine proteins have been carried out using the conventional electrophoretic methods of native and SDS–PAGE and IEF [203–206].

Two different methods – ion-exchange fast-protein liquid chromatography (FPLC) and PAGE – were utilized to compare, analyze and fractionate the soluble proteins of four white wines [203]. Both methods are sensitive, but the electrophoresis gives a higher resolution, is time consuming, destructive and more complex to perform. In contrast, the FPLC technique is non-destructive and very simple and rapid to perform.

Qualitative effects of *Botrytis cinerea* infection on a must protein fraction were studied by comparing the electrophoretic patterns of musts obtained from healthy grapes or from grapes highly infected by *B. cinerea* [204]. It was found that proteins secreted by *B. cinerea* can degrade grape proteins.

The results obtained by Moreno-Arribas et al. [205] confirm that with PAGE it is possible to ascertain, in the majority cases, the grape variety from which the musts originate and that the technique can be used as a complement to classical morphological descriptions for varietal characterization of wines.

To date, there are only a few references in the literature above the application of CE technique to wine proteins [206,207]. The CE method of Luguera and co-workers [206,207] using a uncoated fused-

silica capillary at alkaline pH, was applied to the study of proteins during the manufacture of a sparkling wine made according to the Champenoise method with up to 24 months of ageing with yeast. The results were compared with those obtained by PAGE. The use of CE made it possible to present the protein profiles of sparkling wines, which would not have been possible using other electrophoretic techniques. No changes in the protein profiles of sparkling wines were observed during the first 18 months of ageing with yeast.

The oenological gelatins are mainly used for clarification and stabilization in order to reduce the turbidity and/or to decrease the astringency of musts and wines. Five oenological gelatins were characterized by analytical methods and used for clarification tests. Molecular mass of gelatins was obtained by SDS–PAGE [208].

8.8. Yeasts

An important phase in the elaboration of wines is fermentation and in recent years attention has also been paid to different aspects of this, such as the treatment of the must, the preparation of the inoculum of the selected yeasts, the quantity of SO_2 added, the selection of yeasts from wild biota, and so on [209].

The indigenous *Saccharomyces* yeasts are responsible for the alcoholic fermentation of grape must into wine, but indigenous yeasts from many other genera are always present in varying numbers, often throughout fermentation. It is still not well understood what affects the growth of different yeasts and how they contribute to the final wine flavor.

Studies of the succession of different yeasts in a fermentation using a classical physiological assays often gives ambiguous results. Molecular techniques, such as pulsed-field gel electrophoresis (PFGE) of entire or fragmental chromosomes and polymerase chain reaction (PCR)-based methods allow reliable discrimination of different *Saccharomyces* strains and various non-*Saccharomyces* yeasts [210–213].

Henick-Kling et al. [214], using PCR and PFGE, evaluated the contribution of indigenous microflora, starter cultures and sulfite treatments to the sensory character of the wine. The results showed that by using different yeast starter cultures and SO_2 additions to the must, sensorially recognizable different wines can be produced. Taste panel scores for ''overall'' quality indicated that the uninoculated wines were as acceptable as those fermented with a commercial starter culture.

In the recent years *Brettonomyces/Dekkera* yeasts are posing an increasingly severe quality problem in the wine industry. The DNA fingerprinting methods of electrophoretic karyotyping, restriction fragment length polymorphism analysis and random amplified polymorphic DNA-PCR were adapted with *Brettonomyces/Dekkera* reference strains and used to identify suspected *Brettanomyces/Dekkera* yeasts isolated from wine [215].

9. Conclusion

A study of the literature published over the last few years suggests that electrophoretic methods have become an indispensable tool for the rapid analysis of beverages. In CE, beverages can often be directly injected into the separation capillary or require only minimal pretreatment, such as dilution or filtration. Solutes, that cannot be determined by direct sample injection have to be extracted and often concentrated. For extraction, solid-phase extraction procedures are typically employed. Currently under investigation and thus not much in use as yet are approaches featuring in-column application of solid-phase material for on-line extraction and preconcentration of analytes. Furthermore, on-column preconcentration can also be attained by ''stacking'' procedures. A relative new approach to solving matrix problems is the use of on-line dialysis performed in a flow-injection analysis system.

Calibration graphs obtained with calibrator samples with the same or similar matrix as the sample show good linear correlations when assessed over a concentration range of not more than two to three orders of magnitude. The RSDs are typically on the 3–5% level for the peak area and 0.5–1% for the migration time. Moreover, high quality data obtained by CE have also been demonstrated by comparing the CE data to those obtained by other methods. However, as of today, only a few completely validated assays have emerged. Therefore, future investigations are needed to extend the generality of

these techniques and expand their into the field of beverage analysis.

10. Nomenclature

ACN	acetonitrile
β-CD	β-cyclodextrin
BGE	background electrolyte
Bis-Tris	2,2-bis(hydroxymethyl)-2,2′,2″-nitrilotriethanol
BSA	bovine serum albumin
C	catechin
CAFTA	caffeoyl tartaric acid
CGE	capillary gel electrophoresis
CGMP	caseinoglycomacropeptide
CIE	capillary ion electrophoresis
cITP	capillary isotachophoresis
CN	casein
CPA	cyclopiazonic acid
CTAB	cetyltrimethylammonium bromide
CTAH	hexadecyltrimethylammonium bromide
CZE	capillary zone electrophoresis
DETA	bis(2-aminoethyl)amine
EC	epicatechin
ECG	epicatechin gallate
EGC	epigallocatechin
EGCG	epigallocatechin-3-gallate
EOF	electroosmotic flow
FAS	flame atomic spectrometry
FIA	flow injection analysis
FPLC	fast-protein liquid chromatography
GCG	gallocatechin gallate
GPC	gel permeation chromatography
HIBA	α-hydroxyisobutyric acid
HPAEC	high-performance anion-exchange chromatography
IC	ion chromatography
IEF	isoelectric focusing
Ig	immunoglobulin
LIF	laser-induced fluoresence
Lg	lactoglobulin
LLE	liquid–liquid extraction
LOD	limit of detection
LOQ	limit of quantification
MEEKC	microemulsion electrokinetic chromatography
MEKC	micellar electrokinetic chromatography
MES	2-(*N*-morpholino)ethanesulfonic acid
MHEC	methylhydroxyethylcellulose
MOPSO	3-(*N*-morpholino)-2-hydroxypropanesulfonic acid
Na_2EDTA	ethylenediaminetetraacetic acid, disodium salt
PAD	pulsed amperometric detection
PAGE	polyacrylamide gel electrophoresis
PAGIF	polyacrylamide gel isoelectric focusing
PCR	polymerase chain reaction
PDC	2,5-pyridinedicarboxylic acid
PEG	polyethyleneglycol
PFGE	pulsed-field gel electrophoresis
PMA	1,2,4,5-benzenetetracarboxylic acid (pyromellitic acid)
RSD	relative standard deviation
SDF	soluble dietary fiber
SDS	sodium dodecyl sulfate
SPE	solid-phase extraction
TES	*N*-tris(hydroxymethyl)methyl-2-aminoethane
TMA	trimellitic acid
TTAB	tetradecyltrimethylammonium bromide

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