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Application and potential of capillary electroseparation methods to determine antioxidant phenolic compounds from plant food material

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ABSTRACT

Antioxidants are one of the most common active ingredients of nutritionally functional foods which can play an important role in the prevention of oxidation and cellular damage inhibiting or delaying the oxidative processes. In recent years there has been an increased interest in the application of antioxidants to medical treatment as information is constantly gathered linking the development of human diseases to oxidative stress.

Within antioxidants, phenolic molecules are an important category of compounds, commonly present in a wide variety of plant food materials. Their correct determination is pivotal nowadays and involves their extraction from the sample, analytical separation, identification, quantification and interpretation of the data.

The aim of this review is to provide an overview about all the necessary steps of any analytical procedure to achieve the determination of phenolic compounds from plant matrices, paying particular attention to the application and potential of capillary electroseparation methods. Since it is quite complicated to establish a classification of plant food material, and to structure the current review, we will group the different matrices as follows: fruits, vegetables, herbs, spices and medicinal plants, beverages, vegetable oils, cereals, legumes and nuts and other matrices (including cocoa beans and bee products). At the end of the overview, we include two sections to explain the usefulness of the data about phenols provided by capillary electrophoresis and the newest trends.

Abbreviations: ACN, acetonitrile; Ac Pin, (+)-1-acetoxypinoresinol; AD, amperometric detection; AHBA, 4-amino-2-hydroxy-benzoic acid; ASE, accelerated solvent extraction; BHT, butilated hydroxytoluene; [Buffer], buffer concentration; CCE, chiral capillary electrophoresis; CD, cyclodextrin; CE, capillary electrophoresis; CEC, capillary electrochromatography; CGE, capillary gel electrophoresis; CIEF, capillary isoelectric focusing; CITP, capillary isotachophoresis; CZE, capillary zone electrophoresis; DAD, diode array detection; DHPE, 2,3-dihydroxyphenylethanol; DOA, decarboxymethyloleuropein aglycon (3,4-DHPEA-EDA); EA, elenolic acid; ED, electrochemical detection; EDTA, ethylenediaminetetraacetic acid; EOF, electroosmotic flow; EtOAc, ethyl acetate; EtOH, ethanol; Et_2O, diethyl ether; ESI, electrospray ionisation; EVOO, extra virgin olive oil; FT-ICR, fourier transform ion cyclotron resonance; GC, gas chromatography; GPC, gel permeation chromatography; HPLC, high performance liquid chromatography; HYTY, hydroxytyrosol; i.d., internal diameter of capillary; IR, infrared radiation; IS, internal standard; IT-OT, ion trap-orbitrap; L_{ef}, effective length of capillary; Lig Agl, ligstroside aglycone; LLE, liquid–liquid extraction; MAE, microwave-assisted extraction; MEEKC, microemulsion electrokinetic capillary chromatography; MEKC, micellar electrokinetic chromatography; MeOH, methanol; MS, mass spectrometry; NACE, non-aqueous capillary electrophoresis; NIR, near infrared; NMR, nuclear magnetic resonance; Ol Agl, oleuropein algycone; OT, orbitrap; PLE, pressurized liquid extraction; QQQ, triple-quadrupole; Q-TOF, quadrupole-time of flight; SC, sodium cholate; SDS, sodium dodecyl sulphate; SFE, supercritical fluid extraction; SLE, solid–liquid extraction; SPE, solid phase extraction; SWE, subcritical water extraction; T, temperature; TBAOH, tetrabutylammonium hydroxide; t_{inj}, injection time; TLC, thin layer chromatography; TOF, time of flight; Tween 20, polyoxyethylene sorbitan monoalurate; TY, tyrosol; UV, ultraviolet; V, voltage; VA, vanillic acid; VOO, virgin olive oil.

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1. Introduction

Phytochemicals are a big group of non-nutrient substances present in plants, which are biologically active and have an important role in the interaction of plants with their environment as well as reveal health promoting impacts [1]. Several compounds included in this group are considered antioxidants, owing to the fact that these compounds have a capacity to protect cells and biomacromolecules [2] neutralising free radicals and, for this reason, they may prevent against oxidative degradation and certain human diseases (cancer, inflammatory disorders, neurological degeneration, coronary heart diseases, etc.) [3]. As a consequence, antioxidant compounds are nowadays gaining more and more interest and the consumption of food rich in antioxidants is increasing. Vegetables, fruits and other plant matrices are some of the most important sources of natural antioxidants [4].

Antioxidants can be classified taking into account their mechanism of action, although there are other possible classifications. Bearing in mind the mechanism of action, they can be divided into primary antioxidants, synergistic and secondary antioxidants [5]. Some substances considered as antioxidants are ascorbate, tocopherols, some enzymes, carotenoids and bioactive plant phenols. The health benefits of fruits and vegetables are largely due to the antioxidant vitamin content supported by a large number of phytochemicals, some with greater antioxidant properties. Sources of tocopherols, carotenoids and ascorbic acid are well-known and there is a great number of publications related to their role in human health. However, plant phenols have not been completely studied because of the complexity of their chemical nature and the extended occurrence in plant materials.

Phenolic compounds are one of the most important, numerous and ubiquitous groups of compounds in the vegetable kingdom, being synthesised by plants during normal development and in response to different situations (stress, UV radiation, etc.) [6]. These substances are obtained from carbohydrates via the shikimate pathway and phenylpropanoid metabolism [7,8] and there are more than 8000 different known structures [3]. However, this large range of structures possess a common structural feature: an aromatic ring with one or more hydroxy substituents. The way to classify these components it is not clearly established; a possible classification can be based on the number of constitutive carbon atoms in conjunction with the structure of the basic phenolic skeleton, including for instance, simple phenols, phenolic acids, coumarins, flavonoids and stilbenes. [9] (see Fig. 1).

Phenolic compounds play an important role in plants, foods and humans. In plants, these compounds carry out diverse functions, such as protective agents against UV light, take part in growth and reproduction, components of pigments, essences, flavours, etc. In food and beverages, phenolic compounds may contribute to the oxidative stability and organoleptic characteristics (bitterness, flavour, astringency ...) [10]. Phenols act in human bodies providing numerous beneficial effects, due to the fact that they have anti-microbial [11], cardioprotectives, anti-allergenics and anti-inflamatories activities [12,13]. Since 1980, several studies have shown that lower risk of chronic diseases was correlated with a diet rich in fruits and vegetables [14,15].

Therefore, the determination of this family of compounds is of special relevance. In principle, a wide range of analytical methods can be used to determine these natural compounds, but it is important to bear in mind that the complexity of the matrix, which generally contains these compounds, makes mandatory the use of separative techniques with high resolving power. The most used techniques have been chromatographic techniques (TLC, HPLC, GC), electroseparation methodologies (MEKC, CITP, CE, CZE), combined methods (CEC) and spectroscopic methods (MS, NMR, UV, IR, NIR) [16].

The aim of this review is to describe the different CE methods that have been used so far to carry out the determination of phenolic compounds in plant food matrices. Since, in general, any analytical procedure for the determination of individual phenolic compounds involves four basic steps: extraction from the sample, analytical separation, quantification and interpretation of generated data (achieving worth conclusions). These steps will be explained in later sections of this article, paying particular attention to the separation step and the different CE methodologies (coupled to several detection systems) reported to date. In Fig. 2, a valid scheme for any method developed for the isolation and determination of polyphenols from plant food material using CE as analytical tool is presented.

2. Sample preparation

Although the advances in modern analytical techniques have led to significant improvement in the quality of analysis, the importance of sample peparation should not be underestimated; isolation of the phenolic compounds from the sample matrix is generally necessary to succeed in any analysis. The ultimate goal when the analyst face the sample preparation step is clear: to achieve the preparation of a sample extract uniformly enriched in all compo-

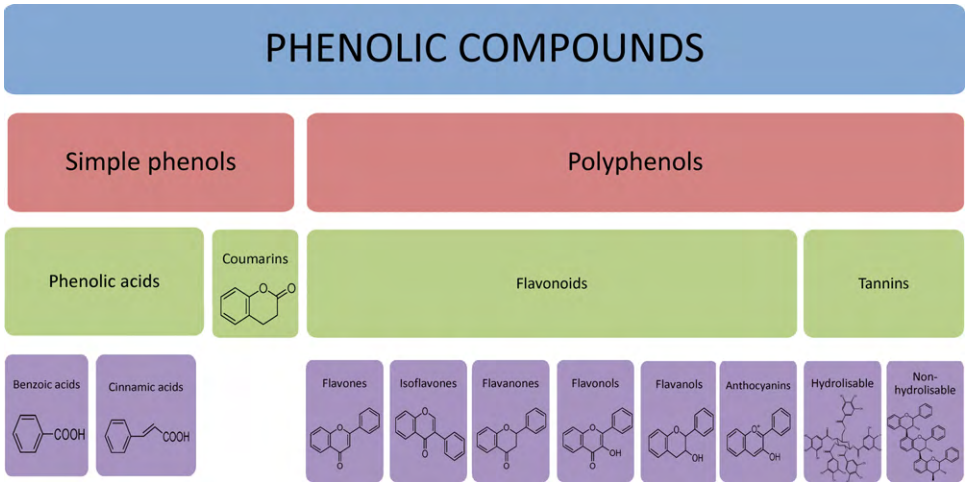

Fig. 1. A simplified classification of phenolic compounds and representative structures belonging to benzoic acids, hydroxycinnamic acids, flavones, isoflavones, flavanones, flavonols, flavanols, anthocyanins and tannins. Only the basic skeletons from where phenolic compounds of vegetal origin are derived are shown.

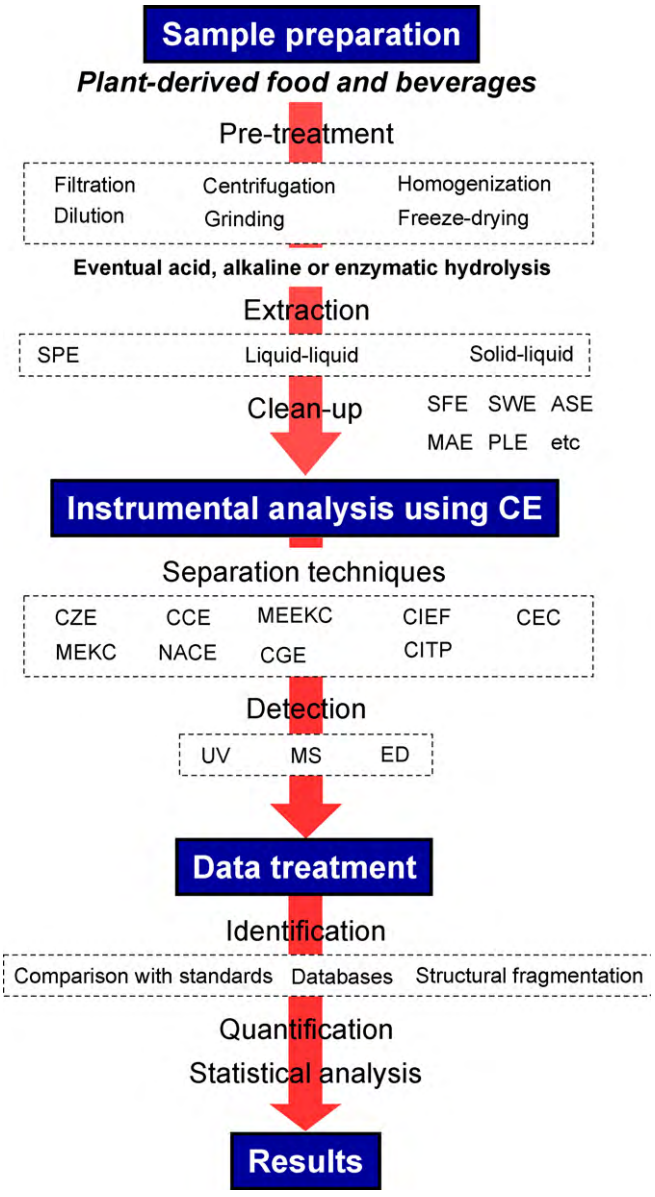

Fig. 2. Complete analytical procedure to achieve the determination of phenolic compounds present in plant food material, including sample preparation, instrumental analysis (by means of electroseparation methods) and data treatment.

nents of interest and free from interfering matrix components [17]. It covers several steps ranging from exhaustive solvent extraction and preconcentration procedures to simple LLE or filtration [9]. The precise procedure will depend on the nature of both the analyte (for instance, total phenols, *o*-diphenols, specific phenolic classes or individual antioxidants), and the sample (fruit or vegetable type, or portion (skin, leaf, seed. . .)).

Traditional procedures include homogenisation, filtration/centrifugation, distillation, solvent and Soxhlet extraction, among others. The introduction of SPE, supercritical fluid extraction (SFE), solid-phase microextraction, pressurized liquid or fluid extraction (PLE), subcritical water extraction (SWE), microwave-assisted extraction (MAE), membrane extraction and surfactant cloud point extraction have met the increasing demand for new and more sofisticated techniques, which can be fully automated and consume less amount of solvent [8,18].

Isolation of phenolic compounds from fruits is further complicated by the unequal distribution in various structural forms; accumulation of soluble phenols is greater in the outer tissues (epidermal and subepidermal layers) of the fruit than in the inner tissues (mesocarp and pulp) [19].

Usually solid samples are first homogenised, which may be preceded by (freeze-) drying or freezing with liquid nitrogen. The next step is the analytical isolation; to achieve that purpose, solvent extraction, which may be followed by SPE, is still the most widely used technique due to its ease of use and wide-ranging applicability. In the case of liquid matrices, they are usually filtered and/or centrifugated; afterwards the sample is either directly injected into the separation systems or, more often, the sample undergo to LLE or SPE procedures.

Solubility of antioxidants is governed by their chemical nature in the plant that may vary remarkably; moreover there is a possibility of interaction between phenols and other plant components, such as carbohydrates and proteins. Solubility of phenolic compounds is also affected by the polarity of the solvent(s) used; therefore it is very difficult to develop an extraction procedure suitable to recover all plant phenols [6].

Solvents, such as methanol, ethanol, propanol, acetone, ethyl acetate, dimethylformamide and their combinations, have also been used for the extraction of phenolics, often with different proportions of water [8]. In those cases, the recovery of polyphenols from the plant material under study was influenced by the extraction time, number of extraction stages, ratio of solvent-to-sample, sample particle size, temperature, etc., and thus the analyst should check the influence of all the mentioned parameters to assure high recoveries.

Interesting applications can be mentioned as well for SPE [20,21], SWE [22,23], ASE or PLE [24,23] or MAE [25].

In a number of instances, an hydrolysis step has to be included, mainly as an aid to structural elucidation and characterisation of phenolic glycosides and phenolic choline esters [26]. Three types of hydrolytic treatment are used for this purpose: acidic, enzymatic and alkaline. Hydrolysis could also be used to minimise interferences in subsequent analytical separation and to simplify the data obtained.

An in-depth discussion about the diverse extraction systems, which can be used to carry out the sample preparation, is beyond the scope of this manuscript (please, check the following comprehensive reviews [6,8,9,17,18,27]).

3. CE methods

CE is a micro-analytical technique applicable for analyses of a great range of analytes, above all polar and charged compounds [28]. The electrophoretic process is a differential movement or migration of solutes caused by the attraction or repulsion in an electric field [29]. The term "electroseparation methods" includes a wide variety of separation methodologies, which present different operational characteristics and are based on different mechanisms of separation. In general, these methods can replace chromatographic methods (such as HPLC) owing to the fact that they represent useful and powerful tools to analyse simultaneously several kinds of analytes [3], as well as they provide some advantages dealing with high efficiency, short analysis time, low solvent volume consumption, versatility and simplicity [15,30]. To understand the reason of the great versatility that CE offers to the analyst, Table 1 includes the different CE separation techniques [29,31]:

Several publications describe that CZE and MEKC are the "classical" CE modes and the most used to analyse phytochemicals in different plant materials [30,32], and probably CZE is more widely used for its simplicity and versatility [33]. After carrying out the separation of the sample components (regardless the CE mode used), the detection of the analytes has to be made. Different detec-

Table 1
Capillary electroseparation techniques, their acronym and separation principle.

Separation technique	Acronym	Separation principle
Capillary zone electrophoresis	CZE	Charge/size
Non-aqueous capillary electrophoresis	*NACE*	*(different physicochemical properties of organic solvents)*
Micellar electrokinetic chromatography	MEKC	Interaction hydrophobic/ionic with surfactant micelles
Capillary electrochromatography	CEC	Mobility in a free solution and chromatographic retention
Capillary isotachophoresis	CITP	Migration capacity between tampons of different nature
Capillary isoelectric focusing	CIEF	Isoelectric point
Capillary gel electrophoresis	CGE	Molecular size
Chiral capillary electrophoresis	CCE	Formation of stereospecific complex
Microemulsion electrokinetic capillary chromatography	MEEKC	Hydrophobicities and electrophoretic mobilities

tion systems can be coupled to CE; they can be classified in three groups: detection based on optical techniques (fluorescence, phosphorescence, UV–vis absorption, chemiluminiscence [34], infrared spectroscopy, NRM [35,36], Raman spectroscopy, refraction, etc.); electrochemical techniques (such as conductometric [37], potentiometric, amperometric [38] and voltametric detection [39]); and other techniques like MS [38,40–42] and radiochemical techniques.

UV–vis absorption is clearly the detection tecnique most widely used [32,38,41], although nowadays, CE coupled to MS is getting more popular and affordable. MS has a great potential and the advantages of MS detection include the capability for both determining molecular weight and providing structural information. In general, if a separation technique is coupled with MS the interpretation of the analytical results can be more straightforward.

For obtaining a good separation in CE it is necessary to optimise several parameters, such as buffer type, pH and concentration, type and dimensions of capillary, additives (type and concentration), temperature, voltage and injection mode, etc. The influence of every parameter on the separation will be evaluated by the analyst and will depend on the CE methodology used, the kind of phenolic molecule under study and the matrix analysed.

In the rest of the review we will try to summarise some of the most relevant applications in the field of capillary electroseparation methods to determine phenolic compounds from plant food material, as well as give to the reader an idea about the usefulness of the data achieved and the new trends in CE analytical separations.

4. CE analysis of plant food material

As was already mentioned, the phenolic compounds are characteristic of many plants, and they are found practically in all food of vegetable origin constituting an integral part of our diet. Nevertheless, it is not easy to establish a phenolic distribution owing to the fact that the quantity of phenols depends on the site of their ultimate accumulation in the fruit as well as on the type of the fruit we wish to study. This variability in terms of distribution and concentration is essentially due to a variety of factors such as climatic conditions, genetics, and cultivation treatment. Moreover, in the case of plant-derived food origin that have undergone a certain technological treatment or more specifically food processing, the qualitative and quantitative variability is intimately related to the nature of the mentioned process.

It is really complicated to establish a classification of plant food material, since there are several ways of doing it. For instance, there are a culinary classification which is not the same as the botanical distinction [43,44]. Trying to structure properly the current review and do it easy to understand to the reader, we will divide this section in the following parts: fruits, vegetables, herbs, spices and medicinal plants, beverages, vegetable oils, cereals, legumes and nuts and other matrices (including cocoa beans and bee products).

4.1. Fruits

Botanically, a fruit is a ripened ovary with seeds and any other structure that enclose it at maturity. This definition of a fruit means that many 'vegetables' are fruits (squash, tomatoes, beans, corn) and many 'grains' are also fruit (rice, wheat, etc.). Although this definition is correct, we are going to consider the "culinary" distinction. Traditionally, "fruits" are the edible pulpy tissue without seeds that are used as desserts or as sweet side dish to a meal, among others, due to their sweet or tart taste [44].

Fruits can be classified on the basis of their seeds, the harvest, the number of ovaries and the number of flowers involved in their formation, and other characteristics. The easiest classification could be the one which is based on common characteristics, finding: citrus fruits, pome fruits (apples and pears), stone fruits, tropical fruits, berries and others.

All of them are rich in vitamins, minerals and water, whereas they contain a few amount of fibre, proteins and fat. Carbohydrates vary in each fruit (5–20%) and the majority are sugars. Fruits have also an important content of antioxidants, specifically, phenolic compounds. According to Robards et al. [7], fruits are a great source of cinnamic acids (chlorogenic, ferulic, sinapic, *p*-coumaric and caffeic acids) and flavonoids (flavanols, flavonols and anthocyanins), finding mainly the glycoside forms of these compounds.

Paying attention to the different groups, citrus fruits are quite rich in cinnamic acids, which are conjugated with glucaric, galactaric acid, some lactones and other sugars more common. Specifically, they have a big amount of ferulic acid. Stone fruits, such as apricots, peachs, plums, etc., have significant amounts of kaempferol, quercetin, caffeoylquinic acids and *p*-coumaroylquinic acids; whereas pome fruits contain chlorogenic acids, caffeoylquinic acids and *p*-coumaroylquinic acids, but smaller amounts of caffeoyl-, *p*-coumaroyl- and feruloyl-glucoses. Anthocyanins are the predominant group of flavonoids present in berries and the rest of phenolic compunds depend on the variety and the family of berry fruits [45,46].

The following table (Table 2) shows some of the most relevant articles where phenolic compounds were determined in fruits by using CE methods. All the optimum parameters used to carry out the analysis (instrumental and experimental variables), the extraction system used (initial amount of sample and final amount of solvent) and the name of the compounds under study are included.

4.2. Vegetables

The term "vegetable" usually refers to the fresh edible portion of a herbaceous plant (fruits, tubers, bulbs, leaves) consumed either raw or cooked. Vegetables generally contain little amount of protein or fat and varying proportions of minerals, fibre, carbohydrates or antioxidant phytochemicals, such as polyphenolic compounds.

Table 2
Summary of the most relevant articles where phenolic compounds were determined in fruits by using CE methods. The optimum parameters used to carry out the analysis (instrumental and other variables), the extraction system used (initial amount of sample and final amount of solvent) and the name of the compounds under study are included.

	References	Sample	Extraction system	Initial quantity→Final quantity of solvent in the extraction process	Instrumental variables						Chemical variables			Detected compounds
					λ_d [nm]	V [kV]	T [°C]	i.d. [μm]	L_{ef} [cm]	t_{inj} [s]	Type of buffer	[Buffer] [mM]	pH	
Citrus fruits	Kanitsar et al. [47]	Orange Grapefruit	– (dilution)	Fruits were hand-squeezed, centrifuged and supernatant diluted. Sample cleanup process with continuous flow system	200	20	20	75	67	5	Boric acid	100	9.5	Hesperidin, sinapic acid, ferulic acid, *p*-coumaric acid, caffeic acid
	Wu et al. [48]	Grapefruit	SLE	1 g peel → 10 mL 99.7% EtOH (3 times) → 80 μL → 1 mL 60 mM borate buffer 80 μL pulp juice → 1 mL 60 mM borate buffer	– (ED)	12	Room temp.	25	75	6	Borate	60	9.0	Hesperidin, naringin, hesperedin, naringenin, rutin
	Herrero-Martínez et al. [49]	Orange	SLE	3.5 g → 4 mL MeOH + 1 mL 12 M HCl + 12 mg BHT → 10 mL MeOH	295	20	25	50	40	5	Phosphate + SDS + SC + MeOH	50 + 25 + 25 + 10%	7.0	Naringenin
	Sawalha et al. [50]	Orange	SLE	0.2 g dried simple → 10 mL MeOH → 2 mL MeOH:H_2O (50:50, v/v) → diluted 1:1 in water	– (MS)	25	Room temp.	50	100	5	Boric acid	200	9.5	Naringin, neohesperidin, hesperidin, narirutin
Tropical fruits	Kofink et al. [51]	Guaraná	SLE	50 mg seeds → 5 mL purified water 50 mg powder extract → 5 mL puriefied water	280	18	20	75	40	3	Borate + (2-hydroxypropyl)-γ-CD	100 + 12	8.5	(−)-catechin, (+)-catechin, (+)-epicatechin, (−)-epicatechin
	Fukuji et al. [52]	Abiu-roxo Wild mulberry	SLE	Whole fruit → 1 mL 1:1 EtOH:deionized water Same process described above + hydrolisation in 4 M NaOH + 10 mM EDTA + 1% ascorbic acid	200	30	25	50	30	5	Sodium tetraborate + MeOH	50 + 7.5% (v/v)	9.2	Chlorogenic acid, ferulic acid, *p*-coumaric acid, caffeic acid, gallic acid, protocatechuic acid
Berries	Bridle et al. [53]	Strawberries Edelberries	SPE	Pigments eluted 3% formic acid in MeOH → dissolved in 25 mM phosphate buffer (pH 2.5) + MeOH (3:1)	560	25	25	75	50	2	Sodium borate	150	8.0	Cyanidin 3-glucoside, pelargonidin 3-glucoside, pelargonidin 3-rutinoside, pelargonidin 3-succinylglucoside, cyanidin 3-sambubioside-5-glucoside, cyanidin 3,5-diglucoside, cyanidin 3-sambubioside
	da Costa et al. [54]	Blackcurrant	SLE	1 g powder → 25 mL water → partitioned against 50 mL $CHCl_3$, Et_2O, EtOAc and MeOH → redissolved in 30 mL water	520	25	20	50	70.4	4	Sodium phosphate + ACN	25 + 30% (v/v)	1.5	Cyanidin 3-glucoside, cyanidin 3-rutinoside, delphinidin 3-glucoside
	Watson et al. [55]	Cranberries	SLE SPE	5 g → 20 mL 95% EtOH:1.5 M HCl 85:15 (v/v) (3 times) → 3 mL + 15 mL 1% HCl in MeOH → cartridge → elution with 2 mL 1% HCl in MeOH → dried → 2 mL 50:50 water:MeOH	525	20	27	75	48	5	Phosphoric acid + Urea + β-CD	150 + 3000 + 50	2.11	Peonidin, cyanidin

Ehala et al. [56]	Bilberry Cowberry Cranberry Strawberry Blackcurrant Redcurrant	Ultrasonic extraction	50 g frozen berries → 100 mL MeOH/H_2O (70:30) + 1% HCl + 20 mg L-ascorbic acid (3times) → Final amount extracts 150 mL	210	20	25	50	39	20	Sodium tetraborate	35	9.3	*Trans*-resveratrol, cinnamic acid, chlorogenic acid, ferulic acid, *p*-coumaric acid, quercetin, (+)-catechin, caffeic acid
		SPE	(off-line preconcentration) 5 mL sample solution (ultrasonic extraction) → 0.5 mL MeOH										
Dadáková et al. [57]	Apple	SLE	0.5 g grinded freeze-dried + ascorbic solution (80 mg in 7.5 mL water) → 12 mL MeOH + 5 mL 6 M HCl → Neutralised with 2 g $NaHCO_3$ → 7.5 mL MeOH and 100 mL water → made up to 200 mL by water	270	20	25	75	67	2	Boric acid + sodium tetrabo-rate + SDS + MeOH	10 + 10 + 20 + 15% (v/v)	9.2	Quercetin
Huang et al. [58]	Grape Apple	SLE	25 g fresh fruit milled and blended → 25 mL MeOH	200	−27	30	50	40	3	Phosphate + Heptane + Cyclohexano + SDS + ACN	25 + 1.36% (w/v) + 7.66% (w/v) + 2.89% (w/v) + 2% (w/v)	2.0	(+)-catechin, (−)-epicatechin, caffeic acid, (−)-epigallocatechin, gallic acid
Priego Capote et al. [59]	Grape	Superheated ethanol-water leaching	1–3 g milled skins → extracting with 0.8% HCl in different EtOH–water mixtures	220 285 (Fluor.)	25	15	50	56	6	Sodium tetraborate + MeOH	50 + 10% (v/v)	8.4	Resveratrol, (−)-epicatechin, (+)-catechin, malvidin-3-glycoside, peonidin-3-glycoside, cyanidin-3-glycoside, delphinidin-3-glycoside, kaempferol, myricetin, quercetin
Berli et al. [60]	Grape	SLE	50 g skin grape berries → 50 mL EtOH 12% + tartaric acid 6 mg/mL + SO_2 100 μg/mL → supernatant diluted 1:100 (v/v)	280	30	15	75	50	5	Sodium tetraborate + MeOH	20 + 30% (v/v)	9.0	Resveratrol, catechin, quercetin

4.2.1. Fruit as the edible part of the vegetable

Solanaceae represents one of the largest and most diverse plant families including vegetables (tomato, potato, capsicum, eggplant) and commercial (tobacco) and ornamental (petunia) crops. The plant species of Solanaceae used as food are rich in healthy components and therefore they are also widely consumed. Tomato consumption, either fresh or processed, is higher than that of all other fruits and vegetables. Helmja et al. [61] have determined the phenolic composition and vitamin content of the skin extracts of tomato, chilli pepper, eggplant and potato (the latter not being a fruit, but a tuber) by CZE with UV detection at 210 nm. The separation of polyphenols was performed in a 75 cm × 75 μm i.d. fused-silica capillary (effective length 50 cm) using 25 mM sodium tetraborate (pH 9.3) as separation buffer and 25 kV. Different phenolic acids and flavonoids were identified with the spectra of the reference compounds and by spiking the standard solutions in the extracts: genistein, rutin, naringenin, myricetin, quercetin and chlorogenic and caffeic acids were identified in tomato; cinnamic, chlorogenic, caffeic and ferulic acids were detected in eggplant, and luteolin, quercetin and caffeic acid in chilli pepper. Additionally, the antioxidative capability of the phenolic compounds in the tomato skin extract was monitored and evaluated by CZE. The electropherogram recorded 5 min after the reaction between the free radical 2,2-diphenyl-1-picrylhydrazyl (DPPH) and the tomato extract was compared with the electropherogram of the original tomato extract. In later studies, using the same CZE conditions, these researchers were able to identify additional phenolic compounds: naringenin chalcone in the tomato skin [62] and dihydroxycinnamoyl amide, cinnamic acid derivative and isomers of chlorogenic acid in the eggplant skin extract [63]. In both extracts, the evaluation of the antioxidative capability was also carried out by HPLC-DAD-ESI-MS/MS. Due to MS detection, HPLC proved to be advantageous over CE, enabling the identification of a higher number of phenolic compounds in the original extracts (16 and 10 in tomato and eggplant, respectively). Nonetheless, the speed, resolution and low amount of sample and reagents consumed on CE, made it an attractive method for reaction monitoring.

The composition of tomato extracts is very complex. Simplification of the electropherograms and a higher sensitivity and selectivity were achieved coupling CZE to ED [4] since only electroactive analytes could be detected. Peng et al. [4] accomplished the quantitative analysis of ascorbic acid, naringenin, rutin, myricetin and chlorogenic acid in the peel, pulp and seeds of three tomato varieties. Separations were undertaken in a 80 cm × 25 μm i.d. fused-silica capillary maintained at 20 °C, under the following conditions: 50 mM borate (pH 8.7) running buffer; 16 kV separation voltage; and potential of the working electrode 0.90 V (vs SCE).

4.2.2. Tubers

In the global diet, potato is another important species of the Solanaceae family. These carbohydrate-rich tubers are a staple food in many places, being one of the most grown crops today, with over 100 edible varieties. Nevertheless, the sweet potato is not one of them, belonging to a different plant family, the Convolvulaceae.

CZE coupled to UV detection [64,65] has been applied to quantify several phenolic acids (chlorogenic acid and some of its positional isomers, caffeic and ferulic acids) in different potato varieties, giving comparable results to those found analysing the same samples by HPLC. Fernandes et al. [64] tested several electrophoretic conditions. Chlorogenic acid isomers separation was carried out in a fused-silica capillary (72 cm × 50 μm i.d.; effective length 50 cm) maintained at 30 °C, applying a voltage of 20 kV with a 100 mM sodium dihydrogen phosphate buffer (pH 4.44). The method was applied as well in a preliminary study to evaluate the effect of light on potato tubers. The results indicated that prolonged exposure to light resulted in a significant change in the isomeric ratios and in an increase in the total chlorogenic acid content.

As already described in the previous section [61], potato skin has been as well analysed by CZE-UV detection, identifying catechin, rutin, chlorogenic acid, quercetin and caffeic acid in the methanol/water extract.

On the other hand, CZE coupled to ED [66] has been used for the quantification of rutin, quercetin and chlorogenic and caffeic acids together with vitamin C in sweet potato. In particular, the quantity difference in the peel and pulp and the variation between fresh and cooked sweet potato of these active compounds were investigated, finding lower contents in the pulp and when the samples were cooked (except for quercetin). All five analytes were well-separated within 20 min utilizing 18 kV and a 60 mM borax running buffer (pH 9.0) in a 75 cm × 25 μm i.d. fused-silica capillary. The applied voltage to the working electrode was 0.95 V (vs SCE).

4.2.3. Bulbs

The bulb onion (Alliaceae family) constitutes a key part of the daily diet in most countries for its distinctive taste and flavour. The number of studies using CE for the detection of phenolic compounds in onion has been scarce; however, they revealed the presence of several flavonoids.

The major flavonoids of mature onion bulb are quercetin 3,4′-diglucoside and quercetin 4′-monoglucoside [67,68]. As could be expected, significant differences in the levels of both flavonols were observed between the six onion varieties analysed (including white, red and brown bulbs); concretely, only trace amounts were detected in the white variety [67]. Separations were performed in a 57 cm × 75 μm uncoated fused-silica capillary (effective length 49.4 cm) at 25 °C and applying a voltage of 25 kV. The buffer consisted of 10 mM boric acid, 10 mM sodium tetraborate and 15 mM EDTA dissolved in 15% v/v methanol/water (pH 10.2 adjusted with 1 M hydroxide solution) and the detector was set at 280 nm. The use of HPLC-UV and ^{1}H NMR confirmed the identification of both flavonols and allowed the identification of two minor isorhamnetin derivatives. Price and Rhodes [68] investigated the changes in composition resulting from autolysis experiments during 24 h in four different onion varieties (white, brown, hybrid pink and red skinned). HPLC-UV was used to study the onion extracts before autolysis, identifying 17 additional minor components (representing only 16% of the total peak area) besides the two main quercetin derivatives mentioned. During the autolysis period, a small loss in the total flavonol content and a significant change in the flavonols conjugation were observed. The deglucosidation products were studied in more detail using CE-UV.

The second most important class of flavonoids in pigmented onion varieties are anthocyanins. Petersson et al. [69] developed a CE-ESI-TOF-MS method for the identification of anthocyanins employing silica capillaries coated with poly-LA 313 (polycationic amine-coating polymer) and an MS-compatible volatile separation buffer, consisting in 15 mM formic acid (pH 1.9). A total of 10 anthocyanins, containing the aglycon ion of either cyanidin, peonidin, delphinidin, petunidin or malvidin, were identified. CE was coupled to ESI-TOF-MS by a sheath–flow interface with acidified methanol/water as sheath liquid. Positive detection was used due to the better ionisation of the analytes in this ion mode.

4.2.4. Leaves

A validated method for the determination of quercetin was applied to two plant species from the Brassicaceae family, white cabbage and cauliflower [57]. Due to their four-petaled flowers, which look like a cross, this family is also known as Cruciferae. Typically, the flower heads of cauliflower and the leaves of cabbage are the parts of the plant eaten. The method was based on the acid hydrolysis of bonded quercetin in the samples followed by SPE and

Table 3
Important aspects involved in the electrophoretic determination of phenols in herbs and spices: extraction system, separation and detection optimum parameters and compounds under study.

References	Sample	Extraction system	Initial quantity→Final quantity of solvent in the extraction process	Instrumental variables						Chemical variables			Detected compounds
				λ_d [nm]	V [kV]	T [°C]	i.d. [μm]	L_{ef} [cm]	t_{inj} [s]	Type of buffer	[Buffer] [mM]	pH	
Ibañez et al. [74]	Rosemary	SFE	60 g → unspecified	230	10	25	50	20	1	Sodium deoxycholate + boric acid-sodium tetraborate + ACN	50 + 20 + 15% (v/v)	9.0	Rosmanol, carnosol, carnosol isomer, carnosic acid, methyl carnosate
Sáenz-López et al. [75]		SLE	150 mg → 2 mL MeOH	250	30	25	50	56	3	Disodium tetraborate	50	10.1	Carnosol, carnosic acid
Bonoli et al. [76]		SLE	1 g → 10 mL organic solvent ($MeOH/CHCl_3$/isopropilic alcohol and 1:1 $MeOH:CHCl_3$, v/v) → four 100 fold diluted extract in isopropanol	200	30	35	50	40	3	Sodium tetraborate	20	9.0	Carnosol, carnosic acid, rosmarinic acid
Crego et al. [77]		SWE	1 g → 3.47 mL water → freeze-drying	200	30	25	50	45	10	Sodium tetraborate + ACN	50 + 10%	9.5	Carnosol, rosmarinic acid, carnosic acid, genkwanin, rosmanol
Herrero et al. [78]		PLE (SWE)	2 g → 6.6 mL water → freeze-drying → 10 mg dry extract → 1 mL water	200	20	Room temp.	50	67	10	Ammonium acetate	40	9.0	Isoquercetin, homoplantagenin, gallocatechin, carnosic acid, rosmarinic acid
Peng et al. [79]		SLE	2 g → 10 mL 70% EtOH	– (ED)	16	Room temp.	25	75	8	Borate buffer	80	9.0	Hesperetin, acacetin, diosmetin, ferulic acid, apigenin, luteolin, rosmarinic acid, caffeic acid
Ben Hameda et al. [80]	Sage	SLE	Leaf + water 1:10 w/w ratio	280	20	25	75	35	5	Borate buffer	40	9.2	Epicatechin, catechin, vanillic acid, rosmarinic acid, caffeic acid, galli acid
Başkan et al. [81]		SLE	1 g → 10 mL MeOH	210	28	25	50	45	5	Borate buffer	40	9.6	Carnosic acid, rosmarinic acid
Petr et al. [82]	Marjoram	PSE	1 g dried plant → 22 mL acetone → diluted in water-MeOH (90:10, v/v) → diluted in 50 mM sodium borate, pH 9.5 (electrokinetic accumulation CE injection)	200	−10	20	50	40	1800	Sodium phosphate + SDS	50 + 60	2.5	Sinapic acid, ferulic acid, coumarinic acid, caffeic acid, syringic acid, vanillic acid, 4-hydroxybenzoic acid
Nhujak et al. [83]	Turmeric	SLE	100 mg → 10 mL EtOH → ethanolic extract diluted 1 mL solution containing 300 mg/L dodecylbenzene and 300 mg/L 2,4-dinitrophenyl phthalimide	214 425	−15	25	50	30	3	Phosphate buffer + n-octane + SDS + 1-butanol + 2-propanol	50 + 1.1% (v/v) + 180 + 890 + 25% (v/v)	2.5	Curcumin, demethoxycurcumin, bis-demethoxycurcumin
Chu et al. [84]	Dandelion	SLE	2 g dried powder → 10 mL anhydrous EtOH and deionized water (4:1) → 5 mL in volume 3 g powder granules → 10 mL anhydrous EtOH and deionized water (4:1) → made up to 5 mL in volume	– (AD)	16	Room temp.	25	75	8	Borate buffer	50	8.0	Diosmetin, ferulic acid, chlorogenic acid, luteolin, caffeic acid

Table 3 (*Continued*)

References	Sample	Extraction system	Initial quantity→Final quantity of solvent in the extraction process	Instrumental variables						Chemical variables			Detected compounds
				λ_d [nm]	V [kV]	T [°C]	i.d. [μm]	L_{ef} [cm]	t_{inj} [s]	Type of buffer	[Buffer] [mM]	pH	
Fonseca et al. [85]	Chamomile	SLE	16 g dried plant → 400 mL 1:1 MeOH:H_2O (3 times) → residue of recovered fractions → 24 mL MeOH (solution) 10 mL solution → 20 mL H_2O (stock solution) 2.5 g stock solution → 10 mL 1:1 MeOH:H_2O	337	25	25	50	25	CZE 3 CEC 24	Phosphate buffer + ACN	50 + 50%	2.8	Herniarin, umbelliferone, chlorogenic acid, caffeic acid, apigenin, apigenin-7-*O*-glucoside, luteolin, luteolin-7-*O*-glucoside, quercetin, rutin, naringenin
Kulomaa et al. [86]	*Eucommia ulmoides*	LLE Soxhlet SFE	Mixture of boiling water–MeOH (30:70, v/v) Boiling water 3.5 g leaves → acetone-dichloromethano 1 g powder → MeOH–water (2:1, v/v) → extracts collected into 3.5 mL acetone	220	30	25	50	80	5	Sodium dihydrogen phosphate + disodium hydrogen phosphate	30 + 30	7.0	Flavone, rutin, quercitrin, chlorogenic acid, ferulic acid, caffeic acid, protocatechiuc acid
Cheung et al. [87]		SLE	10 g (bark/leaves) → 150 mL MeOH → 0.2 g dried bark/0.1 g dried leaves → 50 mL MeOH	214	20	20	50	50	5	Boric acid + SDS + 1-butanol	50 + 50 + 4%	9.5	Geniposide, geniposidic acid, pyrogallol, rutin, chlorogenic acid, ferulic acid, *p*-coumaric acid, quercetin, caffeic acid, protocatechuic acid
Šafra et al. [88]	*Melissae herba*	SLE	1 g dried pulverized plant → 50 mL MeOH → Supernatant diluted with water to contain 20% (v/v) MeOH	270/320	–	Room temp.	300	16	–	MOSPO + Tris + Hydroxyethylcellulose + boric acid + MeOH (for CZE) (electrolyte system for ITP–CZE in column coupling mode)	25 + 50 + 0.2% + 40 + 20%	8.1	Protocatechuic acid, caffeic acid, rosmarinic acid, *p*-coumaric acid, chlorogenic acid, ferulic acid, quercitrin, apigenin
Chen et al. [89]	Sophora flower *Ligustrum lucidum* Camphor laurel	SLE	0.5 g Sophora flower → 50 mL MeOH 2 g *Ligustrum* and camphor → 50 mL MeOH Residues → washed with 20 mL MeOH Extracts + washings → concentrated to 40 mL → diluted to 50 mL with MeOH Extracts diluted with running buffer	– (ED)	12	20	25	40	6	Borate buffer	100	9.0	Daidzein, rutin, quercetin
Helmja et al. [90]	Hop	SLE (SFE as well)	0.7 g → 7 mL MeOH:water 70:30	210	20 or 30	Room temp.	75	50	15	Sodium tetraborate	25	9.3	Naringin, resveratrol, catechin, rutin, naringenind, chlorogenic acid, quercetin, myricetin, *p*-coumaric acid, caffeic acid
Arráez-Román et al. [91]		SLE	2.5 g hop pellets → 30 mL hexane (×3) → 30 mL MeOH (×3) → combination extracts → evaporation organic solvent → residue + 2 mL MeOH:water 50:50 v/v	– (MS)	25	Room temp.	50	100	10	Ammonium acetate/ammonium hydroxyde	80	10.5	Kaempferol-3-*O*-rutinoside, hesperidin, rutin, luteolin-7-*O*-glucoside, kaempferol-3-*O*-glucoside, quercetin-4′-*O*-glucoside, chlorogenic acid
Pomponio et al. [92]	Echinacea	LLE	Sample solution (prepared in MeOH–water 70:30, v/v) → diluted with water to obtain a final MeOH–water ratio of 10:90	300	20	20	50	43.5	2	Sodium tetraborate + sodium deoxycholate	40 + 70	9.2	*p*-nitrobenzoic acid, vanillic acid, caffeic acid, cichoric acid, caftaric acid

Pomponio et al. [93]	*Cistus*	SLE	4 g → 150 mL boiling water (3 times) → Lyophilized residues dissolved in water	200	−10	40	50	19.5	1	Heptane + SDS + Butan-1-ol + Sodium phosphate	1.36% (w/v) + 2.31% (w/v) + 9.72% (w/v) + 50	2.5	Catechin, gallocatechin
Wang et al. [94]	*Cortex fraxini*	SLE	1.250 g → 10 mL 80% (v/v) MeOH → precipitated → 8 mL 80% (v/v) MeOH Filtration residue → 5 mL 80% (v/v) MeOH Collected solution → diluted to 25 mL 80% (v/v) MeOH → diluted with running buffer	214	22	25	50	50	15	Sodium tetraborate + Tween 20 + MeOH	20 + 64 + 9% (v/v)	9.3	Scopoletin, rutin, esculetin, chlorogenic acid, caffeic acid
Peng et al. [95]	Honeysuckle	SLE	0.2 g → 10 mL 80% EtOH	– (ED)	16	Room temp.	25	75	8	Borax	50	8.7	Hyperoside, chlorogenic acid, luteolin, caffeic acid
Hamoudová et al. [96]	St. Johnïs wort	SLE	0.5 g → 50 mL MeOH 0.5 mL supernatant → 2 mL IS stock solution (50 μg/mL kaempferol in MeOH) and diluted with water to 10 mL	270	Driving current 200 mA	Room temp.	300	16	–	MOSPO + Tris + Boric acid	25 + 50 + 65	8.3	Quercetin, quercitrin, chlorogenic acid, isoquercitrin, hyperoside, rutin
Segura-Carretero et al. [97]	*Hibiscus sabdariffa* L.	SPE	25 g homogenized dried calyces → 1 L acetic acid (15% v/v) → filtrate mixed 40 g Amberlite XAD-2 → Amberlite particles packed into a glass column → washed with deionized water → Anthocyanins renained absorbed on the column → eluted with 1 L ethanol (70% v/v)–acetic acid (1% v/v) Red solution → concentrated to dryness → 2 mL water	– (MS)	25	25	50	80	20	Boric acid + ammonia	200	9.0	Delphinidin-3-sambubioside, cyanidin-3-sambubioside, cyanidin-3-*O*-rutinoside, delphinidin-3-*O*-glucoside, cyanidin-3,5-diglucoside, chlorogenic acid
Sheu et al. [98]	Artemisiae capillaris herba	SLE	4 g → 20 mL MeOH (2 times) → combined extract → reduced to 5 mL	254	20	25-26	75	MEKC 92.4 CZE 72.4	2	MEKC Sodium borate + SDS CZE Sodium borate + 2,3,6-tri-*O*-methyl-β-ciclodextrin	MEKC 20 + 20 CZE 25 + 6.75 mg/mL	9.82 –	Scopoletin, 6,7-dimethyl esculetin, chlorogenic acid, caffeic acid,capillaris in.
Šafra et al. [99]	Herba Epilobi	SLE	1.5 g → 50 mL MeOH → Supernatant diluted with water + 20% (v/v) MeOH	270	ITP–CZE driving current 50–200 mA	Room temp.	300	16	30 μl	MES + Tris + Boric acid + α-CD + HEC + MeOH	25 + 50 + 30 + 10 + 0.2% + 20% (v/v)	8.31	Protocatechuic acid, caffeic acid, gentisic acid, cinnamic acid, coumaric acid, ferulic acid
Vaher et al. [100]	Sweet gale Sea buckthorn Hiprose Knotweed	SFE	Unspecified	240	18	Room temp.	50	70	–	Disodium tetraborate in water	25	9.4	Resveratrol, catechin, quercetin, flavone
Yue et al. [101]	*Hippophae rhamnoides* (sea buckthorn)	Soxhlet extraction	2 g air-dried podwer → 50 mL MeOH (with or without 5 mL 25% (v/v) hydrochloric acid)	270	15	25	50	30	1	Borate	20	10.0	Quercetin, kaempferol, isorhamnetin

Table 3 (*Continued*)

References	Sample	Extraction system	Initial quantity→Final quantity of solvent in the extraction process	Instrumental variables						Chemical variables			Detected compounds
				λ_d [nm]	V [kV]	T [°C]	i.d. [μm]	L_{ef} [cm]	t_{inj} [s]	Type of buffer	[Buffer] [mM]	pH	
Gorbatsova et al. [102]		SLE	10 g frozen squeezed berries → 20 mL CH_3OH/H_2O (70:30)	210 265 280	16	25	50	35	20	Borate	20	9.3	Myricetin, *trans*-resveratrol, catechin, quercetin, caffeic acid, *p*-coumaric, gallic acid
Vaher et al. [103]		SLE	50 g raw material squeezed → 50% MeOH	210 265	+20	25	50	41	–	Sodium tetraborate	20	9.3	Rutin, chlorogenic acid, quercetin, caffeic acid, gallic acid
Chen et al. [104]	Puerariae Radix *Pueriae lobata*	SLE	2 g → 50 mL 95% EtOH Residues → 10 mL 95% EtOH (2 times) Extract + washings → concentrated to 40 mL and diluted to 50 mL with 95% EtOH Extracts diluted with running buffer	–	9	20	25	40	6	Borate	50	9.0	Puerarin, daidzein, rutin
Li et al. [105]	Scute-coptis herb	SLE	0.4 g pulverized herb couple → 10 mL 70% MeOH (3 times) → extracts combined → addition 2 mL IS solution (5.2 mg umbelliferone in 1 mL 70% MeOH) → diluted to 50 mL with 70% MeOH	270	30	30	50	71.5	5	Sodium borate + sodium dihydrogenphosphate + SC + ACN	5 + 15 + 50 + 65%	6.97	Wogonin 7-*O*-glucuronide, oroxylin A-7-*O*-glucuronide, baicalin, oroxylin A, wogonin, baicalein
Okunji et al. [106]	*Garcinia kola* seed	SLE	2.15 g ground sample → 110 mL water at 90 °C	325	28.5	25	50	55	2	Borate	100	9.5	Biflavanones (GB1, GB2, GB1-glycoside, kolaflavanone)

(ASE → Dionex commercial name for PLE (Pressurized liquid extraction)).

a MECK-UV determination at 270 nm. Separations were achieved in fused-silica capillaries of 70 cm (67 cm effective length) × 75 μm i.d. maintained at 25 °C and applying a voltage of 20 kV. The running buffer consisted of 10 mM boric acid, 10 mM sodium tetaborate, 20 mM SDS and 15% methanol (pH 9.2). The quercetin content in cabbage was 7 ± 1 mg/kg, whereas the cauliflower samples did not contain detectable amounts of that compound.

4.3. Herbs, spices and medicinal plants

Spices are natural and common food additives, which have been used, throughout thousand of years, to increase or to improve the food flavour, colour and taste, as well as to preserve the quality of food [70,71]. Several spices possess beneficial effects on human health, so they can be used, besides flavouring/colouring/seasoning, like natural treatment in different diseases [72].

On the other hand, for centuries, medicinal plants have been used to treat human health problems in many countries of Asia, specifically in China [73]. Almost all these plants are consumed as beverages, i.e. the leaves or other parts of the plants are mixed, usually, with hot water for extracting the compounds which could have beneficial properties [70,72] and people drink the infusion originated.

The number of articles related to phenolic compounds present in different spices or plant matrices is quite impressive, although the percentage of papers in which electroseparation methods were used is quite low (in most cases, HPLC was the method of choice).

The following table (Table 3) contains information about different important aspects involved in the determination of phenols in these matrices, such as extraction system and separation and detection optimum parameters, compounds under study, etc. Considering the fact that plants, herbs and spices contain very similar compounds or closely related ones, only some examples have been included in order to contain the size of this review.

4.4. Beverages

Since we are aware that the current review can not cover all the developments concerning the determination of antioxidants in all the beverages consumed nowadays, we will focus on those beverages which could be consider more important. Therefore, we include the following beverage samples: tea, coffee, juice, wine and beer. In the last part belonging to this section, we include some interesting methods developed to carry out the determination of antioxidants in other beverages, such as cider, cognac and other liquors. For each matrix surveyed, methods are tabulated (or at least described in detail) in order to assist the method selection.

4.4.1. Tea

The term "tea" is referred to the plant, leaf, or beverage originated from the species *Camellia sinensis*. There are a lot of types of commercial tea, but the most abundant are two: *sinensis* and *assamica* [107]. One of the most significant differences between them is the size of its leaves, being *assamica* leaves bigger than *sinensis* leaves. Despite that the origin of this plant is the Southeast of Asia, it is cultivated in about 30 countries in the tropical and subtropical regions [107]. It is consumed by a large number of people and, after water, is one of the most important or relevant beverages [43].

Tea is an excellent natural source of antioxidants, and phenolic compounds represent the most abundant group. Indeed, tea is particularly rich in terms of flavanoids, such as flavanol monomers (catechin, epicatechin) and flavanol gallates (epicatechin gallate, epigallocatechin gallate) [108,109]. Apart from the mentioned analytes, tea contains as well other polyphenols to a lesser amount, such as gallic acid, coumaric acid and caffeic acid, as well as purine alkaloids, theobromine and caffeine [110].

There are different types of tea according to the manufacture: green, black, white and oolong teas. Green tea (non-fermented beverage) is elaborated with young leaves which are submitted to several processes, like withering, steaming or pan firing, drying and grading in order to deactivate the enzymes which are responsible for the degradation of catechins in thearubigins and theaflavins [111]. White tea (considered non-fermented or semi-fermented beverage) is produced using leave buds with white trichomes. In black tea production the leaves undergo plucking, withering, maceration and drying. This type of tea is fermented for several hours and during this step occurs the oxidation of polyphenols, altering the chemical composition and changing leaf colour and aroma. Oolong tea is a semi-fermented tea, owing to the fact that the manufacture includes a short period of oxidation. There are different methods for carrying out its production, and thus, a wide variety of products on the basis of the catechins oxidation degree [107,108].

Liquid chromatography with UV absorbance or MS detection has been the method selected more often for analysing phenolic compounds in tea [112], but there are several publications in which CE methods (such as CZE or MEKC) are used to determine the compounds mentioned above. The best resolution, separation and quantitation for catechins are usually achieved by MEKC methods, whereas CZE methods are more rudimentary [113,114].

Table 4 summarises some of the CE methods regarding determination of phenolic compounds from tea. Information about the type of samples used in every study, separation and detection optimum parameters, detected compounds, etc. are included.

4.4.2. Coffee

Coffee is an alcohol-free beverage and one of the most important natural drinks widely consumed in the world [131]. There are many species of coffee, but as far as commercial production is concerned, the most important are *Coffea arabica* (Arabica) and *Coffea canephora* (Robusta) [43]. Brazil is one of the main producer and exporter (35% world production) [132], followed by Colombia, Indonesia, Mexico and Uganda [133].

Coffee is a natural source of antioxidants and contains plenty of phenolic compounds, being chlorogenic acid the most abundant [134].

Chromatographic techniques have been traditionally used for determining these compounds in coffee samples; electrophoretic methods only represent the 1% of total number of publications found in the scientific literature. Risso et al. [135] developed a method by MEKC to determine some phenolic acids, such as chlorogenic acid (resolving two positional isomers), caffeic acid and ferulic acid. The optimum conditions were a capillary of 22.5 cm × 75 μm i.d., 10 mM phosphate + 70 mM SDS + 5% MeOH like running buffer, pH 2.5, voltage applied of −17 kV, 22 °C, hydrodynamic injection at 25 mbar for 3 s. The results obtained were satisfactory and the method allowed the rapid and simultaneous determination of the phenolic acids previously mentioned.

Zhu et al. [136] investigated two stacking methods in MEKC in an attempt to increase the amount of sample injected, as well as to focus analytes onto a small zone; one employed a "high-conductivity zone", which was inserted between the sample zone and background solution to build an unequal conductivity gradient. The other employed a "low-temperature bath". Doing that they were able to separate three phenolics acids (ferulic, caffeic and chlorogenic).

Chu et al. [131] determined catechin, rutin, *o*-dihydroxybenzene and ferulic, chlorogenic, caffeic, gallic and protocatechuic acids in samples of instant coffee by CE with AD. They used a voltage of 16 kV for the separation and 80 mM borate (pH 8.4) as running buffer. The dimensions of capillary were 75 cm length and 25 μm i.d. The injection was made by means of electrokinetic injection at 16 kV for 8 s. The results proved that the method was accurate, reproducible and sensitive for the analysis of natural antioxidants in coffee samples.

4.4.3. Juice

Juice is a beverage obtained from fruits or vegetables, since it is the liquid naturally contained in their tissues. The traditional way to extract the juice is mechanically squeezing or macerating fresh fruits/vegetables (without heat or solvents). The juice is composed by different substances, such as amino acids, carbohydrates, organic acids and phenolic compounds, among others.

OïShea et al. [137] used CE with ED and employing an on-column Nafion joint to identify chlorogenic, *p*-coumaric and caffeic acids in samples of apple juice. The conditions were: 10 mM sodium borate (pH 9.5) as running buffer, capillary of 65–70 cm effective length and 50 μm of i.d., a effective voltage of 425 V/cm (≈28 kV) and detection potential of 650 mV.

Cancalon and Bryan [138] resorted to CE for the determination of flavonoids such as didymin, hesperidin, narirutin, neohesperidin and naringin in citrus juice, specifically this method was applied to compare pure orange juice and pulpwash (a major adulterant of orange juice). The capillary used had 70 cm of effective length and 50 μm i.d. The optimum conditions were sample injection for 15 s, a voltage of 21 kV, 25 °C of temperature and 35 mM solution of borax at pH 9.3 as background electrolyte. The detection range wavelength was set between 200 and 500 nm. The addition of pulpwash, a lower-quality juice product, by comparison with a pure citrus juice, can be detected with this method.

Gel-Moreto et al. [139] analysed the diastereomers of naringin, prunin, narirutin, hesperidin, neohesperidin and eriocitrin in lemon juice. They used CCE for being a good method for the separation of stereoisomers. The running background electrolyte was 200 mM borate buffer with 5 mM γ-CD, pH 10.0. Uncotaed, fused-silica capillary had an effective length of 60 cm and an internal diameter of 75 μm. The separation voltage was 15 kV, the detection was carried out at 290 nm and the temperature was maintained at 25 °C. Finally, the samples were injected by pressure during 2 s. This method highlighted that CCE could achieve the separation of the diastereomers, above all of eriocitrin and hesperidin. Following the same approach, Aturki and Sinibaldi [140] determined the aforementioned compounds (flavanone-7-*O*-glycosides) in citrus juices. This type of compounds can be separated only if there was a chiral environment. Lemon, orange and grapefruit juices were the samples used, which were extracted by SPE. They carried out the optimisation of different electrophoretic parameters and, finally, the best conditions were: capillary of 50 μm i.d. × 40 cm effective length, thermostated at 20 °C, the applied voltage was 20 kV, samples were injected by pressure (5 kPa × 10 s), and the background electrolyte consisted of 20 mM of sodium tetraborate buffer pH 7.0 containing 5 mg/mL of sulfobutyl ether-β-CD. The analyses were recorded at 205 nm, providing this wavelength the highest sensitivity for these compounds. The method allowed a qualitative analysis of the diastereomers of naringin, neohesperidin, narirutin, eriocitrin and hesperidin contained in several citrus juices, and the results showed good resolution in less than 10 min and high peak efficiency.

Simó et al. [141] used a combination of MEKC and reverse-phase liquid chromatography for analysing narirutin, hesperidin, naringin, benzoic acid and a compound belonging to the family of flavanones (no fully characterised). The orange juice samples were injected at pressure (0.5 psi for 2 s) and analysed in a capillary of 20 cm effective length × 50 μm i.d., using a buffer of 50 mM boric acid/sodium tetraborate and 100 mM SDS at pH 8.0. The temperature was 25 °C and the detection system was set at 280 nm. The best results were obtained with those conditions for MEKC and they could identify several compounds, although with LC-DAD-MS a higher number of analytes could be detected. LC method showed

Table 4
CE methods developed to carry out the determination of phenolic compounds from tea. Information about the type of samples used in every study, separation and detection optimum parameters and detected compounds has been included.

References	Sample tea	Extraction system	Initial quantity → Final quantity of solvent in the extraction process	Instrumental variables						Chemical variables			Detected compounds
				λ_d [nm]	V [kV]	T [°C]	i.d. [μm]	L_{ef} [cm]	t_{inj} [s]	Type of buffer	[Buffer] [mM]	pH	
Wright et al. [115]	Black	SLE	CZE 6 g → 5 mL aqueous MeOH	280 380	CZE 22.5	CZE 25	50	CZE 51	5	Boric acid + potassium sulfate	600 + 50	7.0	Theaflavin-3,3′-digallate, free theaflavin, theaflavin-3-monogallate, theaflavin-3′-monogallate
			NACE 2 g → 100 μL ACN–MeOH–acetic acid (74.5:25:0.5, v/v)		NACE 27.5	NACE 18.5		NACE 32		ACN + MeOH + acetic acid + ammonium acetate	71 v/v + 25 v/v + 4 v/v + 90		
Horie et al. [116]	Green Oolong Black	SLE	250 mg → 50 mL ACN–2% metaphosphoric acid (1:1, v/v) → diluted 10 times with water	194 270	25	30	75	70	5	Sodium tetraborate + Boric acid + SDS	20 + 80 + 50	8.4	(−)-Epigallocatechin, (−)-epicatechin, (−)-epigallocatechin gallate, (−)-epicatechin gallate
Bonoli et al. [117]	Green	SLE	100 mg → 100 mL water–formic acid solution (99.7/0.3, v/v) 99 mL green tea extract → 1 mL acetone	200	30	29	50	40	1	Potassium dihydrogen phosphate + sodium tetraborate + SDS	20 + 50 + 200	7.0	(−)-Gallocatechin, (+)-catechin, (−)-epigallocatechin, (−)-epigallocatechin-3-gallate, (−)-gallocatechingallate, (−)-epicatechingallate, (−)-epicatechin, gallic acid
Huang et al. [118]	Tea beverage Tea leave	Direct injection SLE	– 1 g → 20 mL 100 °C hot water	200	−27	30	50	40	3	MEEKC Heptane + cyclohexanol + ACN + SDS + phosphate solution MEKC SDS + MeOH + phosphate solution	1.36% + 7.66% + 2.0% + 2.89% + 25 2.89% + 2.0% + 25	2.0	(−)-epigallocatechin gallate, (−)-epicatechin, (−)-epigallocatechin
Stach et al. [109]	Green Black	SLE	1.4 g → 400 mL 90 °C hot water 1 mL → 50 μL 80 mM HCl + 20 μL AHBA	200	18.2	25	50	45.4	1	SDS + sodium phosphate buffer + MeOH	100 + 20 + 10% (v/v)	2.7	(−)-epicatechin, (−)-epigallocatechin, (+)-catechin, (−)-catechin gallate, (−)-epicatechin gallate, (−)-epigallocatechin gallate
Arce et al. [114]	Green	SLE	1.75 g → 100 mL boiling water	210	20	20	75	57	10	Boric acid	150	8.5	(−)-epicatechin, (+)-catechin, gallic acid, (−)-epigallocatechin, (−)-epigallocatechin-3-gallate, (−)-epicatechin-3-gallate
Barroso et al. [119]	Green Black	LLE	0.5% solution → diluted 1:2 with Mili-Q water	200	30	21	50	70	–	Borate-phosphate + SDS	20 + 25	7.0	(+)-catechin, (−)-epigallocatechin, (−)-epigallocatechin gallate, (−)-epicatechin, (−)-epicatechin gallate
Gotti et al. [120]	Green	SLE	1 g → 60 mL 85 °C hot water → diluted 1:2 with IS (syringic acid) aqueous solution (100 μg/mL)	200	15	25	50	8.5	2	Borate-phosphate buffer + SDS + hydroxypropyl-β-CD	25 + 90 + 25	2.5	(−)-epicatechin, (+)-catechin, (−)-catechin, (−)-epigallocatechin, (−)-epicatechin gallate, (−)-gallocatechin gallate, (−)-epigallocatechin gallate
Kodama et al. [121]	Green Oolong Black	SLE	1 g → 60 mL 85 °C hot water → diluted five times with purified water	210	25	20	50	56	2	Borate + phosphate + 6-*O*-α-D-glucosyl-β-CD + SDS	200 + 20 + 25 + 240	6.4	(−)-catechin, (+)-catechin, (−)-catechin gallate, (−)-epigallocatechin gallate, (−)-epicatechin gallate, (−)-epigallocatechin, (+)-epicatechin, (−)-epicatechin

Kartsova et al. [122]	Green Black	SLE	200 mg → 20 mL hot water	200	20	20	75	50	10	Phosphate buffer + SDS + Urea	25 + 20 + 10	7.0	(+)-Catechin, (−)-epigallocatechin, (−)-epigallocatechin gallate, (−)-epicatechin, gallic acid, (+)-gallocatechin gallate, (−)-epicatechin gallate
Bonoli et al. [123]	Green Black	Dilution/normal infusion (to drink)	1 mg green tea extract → 1 mL water/formic acid solution (99.7:0.3 v/v) 2 g dried leaves → 250 mL boiling water All samples → diluted two times with destilled water → additon of acetone (1%, v/v)	200	30	29	50	40	1	Potassium dihydrogen-phosphate + sodium tetraborate + SDS	10 + 8.3 + 66.7	7.0	(−)-gallocatechin, (+)-catechin, (−)-epigallocatechin, (−)-epigallocatechin-3-gallate, (−)-gallocatechingallate, (−)-epicatechingallate, (−)-epicatechin, gallic acid
Zhang et al. [124]	Jasmine Green	SLE	3 g → 10 mL EtOH (3times) → 20 mL water	211	27.5	25	50	40	99	Borate buffer + SC + ethylene glycol	10 + 90 + 40% v/v	–	(−)-epigallocatechin, (−)-epicatechin, (+)-catechin, (−)-epigallocatechin gallate, (−)-epicatechin gallate
Larger et al. [125]	Green Black	SLE	0.2 g → 100 mL boiling water → 5 mL ACN 4 g → 500 mL boiling water 100 mL → 5 mL ACN	278	30	25	50	56	15	Monosodium dihydrogenphos-phate + sodium tetraborate + SDS + ACN	50 + 50 + 20 + 10%	6.0	(−)-epigallocatechin, (+)-catechin, (−)-epicatechin, (−)-epigallocatechin gallate, (−)-epicatechin gallate, chlorogenic acid, kaempferol derivative, diverses flavonoids and their glycosides
Watanabe et al. [126]	Green Black	Direct injection	–	280	15	20	50	32	1	Phosphate + borate + SDS	25 + 50 + 25	7.0	(+)-catechin, (−)-epigallocatechin, (−)-epicatechin, (−)-epigalocatechin gallate, (−)-gallocatechin gallate, (−)-epicatechin gallate, (−)-catechin gallate
Aucamp et al. [127]	Black	LLE	1% (w/v) tea solution → 0.5% (w/v)	200	14	25	50	50	2	Phosphate + MeOH + SDS	25 + 6% (v/v) + 100	7.0	(+)-catechin, (−)-epigallocatechin, (−)-epigallocatechin gallate, gallic acid, (−)-epicatechin, (−)-epicatechin gallate
Chi et al. [128]	Chinese herbal	LLE	150 mL → 1000 μL 20% 500 mM KH_2PO_4–250 mM $Na_2B_4O_7$ and 30% EtOH	– (AD)	15	Room temp.	25	60	12	Potassium dihydrogen-phosphate + sodium tetraborate + β-CD	400 + 200 + 0.20	7.6	Kempferol, apigenin, rutin, ferulic acid, quercetin, luteolin
Horie et al. [129]	Green	SLE	3 g → 180 mL boiling water → diluted 10 times with 0.1% metaphosphoric acid	280	30	23	50	70	5	Borax buffer	20	8.0	(−)-epigallocatechin gallate, (−)-epicatechin gallate, (−)-epigallocatechin, (−)-epicatechin, (+)-catechin
Nelson et al. [130]	Green	SLE	0.2 g → 20 mL water + L-tryptophan (IS)	280	20	20	50	60	4	Tetraborate buffer + SDS + MeOH + Urea + β-CD	20 + 110 + 14% + 1500 + 1	8.0	(−)-epigallocatechin, (−)-epicatechin, (−)-epigallocatechin gallate, (−)-epicatechin gallate

better peak area reproducibility than MEKC, but the later presented the highest analysis speed. Both of them had similar analysis time reproducibility, and could be used as complementary techniques.

Desiderio et al. [142] determined several flavanone-7-*O*-glycosides in orange, lemon and grapefruit juice by isocratic reversed-phase CEC using a 75 μm i.d. silica fused column packed with 5 μm ODS silica gel. Optimum separation conditions were found using a mixture of ammonium formate (pH 2.5)-acetonitrile (8:2, v/v) as the mobile phase by the short-end injection mode. Under these conditions all the investigated flavanones were baseline-resolved within short analysis time (between 5 and 10 min).

Peng et al. [143] evaluated the analytical performance of CE with ED for analysing phloridzin, epicatechin, chlorogenic acid and myricetin in apple juice. The capillary used had 75 cm and 25 μm i.d., and CE was performed using a running buffer of 50 mM borate buffer (pH 8.7) at 18 kV. The apple juice was electrokinetically injected at 18 kV for 6 s. They saw that the amounts of phenolic compounds in different juices were not the same, because, according with literature, the levels of phenolic compounds in juices had an enormous dependence on the fruit varieties used and the process to obtain the juice. CE-ED demonstrated to be a very powerful technique which had high resolution and sensitivity and good reproducibility.

Other phenolic compounds identified in juice were anthocyanins, which are responsible of their different colours (red, purple, blue, yellow). Sádecká and Polonský [144] enclosed several publications about determination of anthocyanins by electrophoretic methods, specifically, CZE and MEKC. One of these articles was published by Watanabe et al. [145] who identified cyanidin-3-sambubioside-5-glucoside, cyanidin-3-glucoside-5-glucoside, cyanidin-3-sambubioside and cyanidin-3-glucoside in elderberry juice using MEKC with SDS solution in a phosphate buffer at pH 7.0.

4.4.4. Wine

Wine is a fermented beverage with a minimal alcohol level (8.5–17% by volume) obtained from grape juice. There are a wide range of varieties of grapes, such as Merlot, Pinot Noir, Cabernet Sauvignon, Syrah, Cinsault, Rondinella, Sangiovese, Nebiolo, Grenache, Tempranillo, Carignan, etc [43]. In spite of the different grape varietals grown all over the world that produce hundreds of types of wine, these may be grouped into a small list of basic categories: red, white, sparkling, rosé and fortified wine.

Wine is considered as a rich source of flavonoids and resveratrol and its contents vary depending on the wine origin [146], but it is well-known that red wine has higher amounts of phenolic compounds than white or rosé wine.

A huge number of worth publications about wine and phenolic compounds can be found, however, only few of them (less than 10%) are referred to electrophoretic methods. Several articles compare chromatographic techniques, usually HPLC, with CE. The most used methodologies are CZE and MEKC, although CITP is also used and, in a lesser extend, NACE.

The next table (Table 5) outlines some publications including information about the different methodologies used, with the most important parameters and the compounds identified in each case.

4.4.5. Beer

Beer is one the most ancient alcoholic beverages in the world. It was consumed by Mesopotamian, Egyptians, Greeks and Romans. Nowadays, the consumption of beer in the world continues increasing, because several studies over the last years have shown the beneficial effects of this beverage [172–174]. It is a fermented and flavoured alcoholic drink [175] made from malted grains, hops, yeast and water [43]. Beer components are ethanol and other alcohols, polyphenols, organic acids, vitamins, inorganic ions and bitter acids, among others [144].

In literature, only about 2% of the total number of scientific papers regarding phenolic compounds used electrophoretic methods as analytical tools.

Moane et al. [176] described the use of CE with ED and they achieved the separation of seven phenolic acids (chlorogenic, sinapic, ferulic, caffeic, *p*-coumaric, vanillic, and protocatechuic acids) in different types of beer. To achieve that purpose, they used the following capillary electrophoretic conditions: a running buffer 25 mM sodium phosphate and 1 M nitric acid pH of 7.2, a fused-silica capillary of 65 cm length × 50 μm i.d., voltage of 25 kV and hydrodynamic injection (applying 20 psi for 30 s). The described method demonstrated to be a very useful and powerful tool in the determination of active compounds in complex samples.

Holland et al. [177] carried out the detection of phenolic acids by CE-ED on-capillary dual electrode system consisting of two platinum wires. The integrated dual electrode configuration was evaluated for direct AD in which the current response at both electrodes was monitored, using phenols as model analytes. The method demonstrated high effectiveness and selectivity, and good collection efficiencies for chemically reversible compounds. The CE separation conditions were: 25 μm i.d. × 32 cm fused-silica capillary, 20 mM phosphate, pH 7, applied voltage of 15 kV, hydrodynamic injection at 10 psi, for 1 s.

According to Hernández-Borges et al. [171], a beer sample was analysed by coelectroosmotic CE method and they could identify five phenolic compounds, particularly, salicylic, *p*-hydroxybenzoic, vanillic, *p*-coumaric and ferulic acids. They used the following conditions: 75 μm i.d. capillary with 40 cm of effective length, run potential 15 kV, temperature 20 °C, hydrodynamic injection for 2 s, buffer formed by 125 mM borate, 49 mM phosphate, 0.002% (w/v) hexadimethrine bromide, 2.5 mM α-CD, at pH of 7.5. The method achieved, in less than 3.5 min, the separation of the phenolic compounds with a good resolution.

4.4.6. Other beverages

In this section we include some other beverages, like cider, cognac and other liquors; only a few papers in which phenols were analysed in the mentioned samples can be found. Other infusions/tisanes besides tea could be included, but the most part of the plants used for doing these beverages are medicinal; therefore we have already spoken about them in Section 4.3.

Peng et al. [143] described the use of CE with ED for the analysis of myricetin, chlorogenic acid, (−)-epicatechin and phloridzin in cider. The fused-silica capillary had a dimension of 75 cm length × 25 μm i.d. CE was carried out in a 50 mM borate buffer with pH of 8.7 and the separation voltage applied was 18 kV. The injection of cider samples was electrokinetically for 6 s. The results showed that this method was optimum to determine the compounds mentioned above and each variety had the same phenolic acid and flavonoid profile (qualitative profile), but the amount of them was different on the basis of the fruit varieties and the process.

Panosyan et al. [178] carried out the detection of phenolic aldehydes, which could serve as quality and age markers of cognac. These phenolic aldehydes (vanillin, syringaldehyde, coniferaldehyde and sinapaldehyde) were determined by HPCE, using a 50 mM borate buffer with pH 9.3 and a capillary of 45 cm × 50 μm i.d. The temperature was maintained at 20 °C and the voltage was 30 kV. Detection was performed at different wavelengths: 348, 362, 404 and 422 nm. The duration of the analysis was 10 min, time enough to obtain good separation and reasonably high detection sensitivity.

Watanabe et al. published two articles related to Japanese liquors, such as sake and sochu. In the first one [179], the author determined tyrosol, tryptophol and ferulic acid in different commercial sake samples by MEKC, using the following conditions:

Table 5
Summarised information about different methods to determine phenolic compounds in several wine beverages.

References	Sample wine	Extraction system	Initial quantity → final quantity of solvent in the extraction process	Instrumental variables						Chemical variables			Detected compounds
				λ_d [nm]	V [kV]	T [°C]	i.d. [μm]	L_{ef} [cm]	t_{inj} [s]	Type of buffer	[Buffer] [mM]	pH	
Sáenz-López et al. [147]	Red	–	Centrifugation → upernatant isolated and Potassium metabisulphite added (amounts non specified)	280	25	10	75	56	6	Sodium tetraborate + MeOH	50 + 10%	9.4	Malvidin-3-*O*-(6-coumaroyl)-glucoside, malvidin-3-*O*-(6-acetyl)-glucoside, malvidin-3-*O*-glucoside, peonidin-3-*O*-glucoside, malvidin-3-*O*-glucoside catechin dimer, malvidin-3-*O*-glucoside and pyruvic acid derivative, petunidin-3-*O*-glucoside, delphinidin-3-*O*-glucoside, cyanidin-3-*O*-glucoside
García-Viguera et al. [148]	Red	LLE	5 mL extracted with diethyl ether → 0.5 mL MeOH	280	20	30	75	50	2	Sodium borate	100	9.5	Gallic acid, 3,4-dihydroxybenzoic acid, 4-hydroxyphenethyl alcochol, *cis*-CAFTA, catechin, vanillic acid, *trans*-COUTA, caffeic acid, syringic acid, *p*-coumaric, epicatechin, myricetin, quercetin, kaempferol, isorhamnetin
Andrade et al. [149]	Port	LLE	20 mL → 0.5 mL MeOH	280	20	30	75	50	2	Sodium borate	100	9.5	Tyrosol, epicatechin, catechin, syringic acid, *p*-coumaric acid, caffeic acid, gallic acid, 3,4-diOH-benzoic, *cis*-COUTA, *trans*-COUTA
Andrade et al. [150]	White	LLE	20 mL extracted with diethyl ether → 1 mL MeOH	280	20	30	75	50	2	Sodium borate	100	9.5	Tyrosol, epicatechin, syringic acid, ferulic acid, *p*-coumaric acid, caffeic acid, 3 nonidentified hydroxycinnamic esters, gallic acid, 3,4-diOH-benzoic, *cis*-COUTA, *trans*-COUTA, *trans*-CAFTA.
Gil et al. [151]	Red	LLE	5 mL → 1 mL MeOH	280	20	30	75	75	2	Sodium borate	100	9.5	Epicatechin, catechin, epigallocatechin, syringic acid, *p*-coumaric acid, vanillic acid, caffeic acid, gallic acid, cis-COUTA, 3,4-diOH-benzoic acid, *trans*-COUTA, *cis*-CAFTA
Guadalupe et al. [152]	Red	GPC	2 mL → 500 μL 12% (v/v) EtOH in aqueous solution containing 6 g/L tartaric acid, pH 3.5	280 420 520 599	25	10	75	56	6	Sodium tetraborate + MeOH	50 + 10%	9.4	Malvidin-3-*O*-(6-coumaroyl)-glucoside, malvidin-3-*O*-(6-acetyl)-glucoside, malvidin-3-*O*-glucoside, peonidin-3-*O*-glucoside, malvidin-3-*O*-glucoside catechin dimer; malvidin-3-*O*-glucoside, pyruvic acid derivative, petunidin-3-*O*-glucoside, delphinidin-3-*O*-glucoside, cyanidin-3-*O*-glucoside
Pazourek et al. [153]	Red White	SPE	2 mL → 0.2 mL MeOH	305	20	25	75	30	4	Borate	25	9.4	*Cis*-resveratrol, t*rans*-resveratrol
Gu et al. [154]	Red	Direct injection	–	310	20	Room temp.	50	30	–	Sodium borate + sodium phosphate + SDS	25 + 25 + 75	9.0	*Trans*-resveratrol
		SPE	1 mM in ACN	200–400	25	20	50	30	3	Boric acid + dibasic phosphate + SDS + ACN	30 + 30 + 75 + 15%	9.2	*Cis*-resveratrol, *trans*-resveratrol
Hamoudová et al. [155]	Red	–	Diluted with water and directly injected (30 μL)	254	– –	25	ITP 800 CZE 300	ITP 9 CZE 16	–	Water–MeOH + MOSPO + Tris + Boric acid + 2-HEC + β-CD	4:1 + 25 + 50 + 15 + 0.2% + 5	8.5	Protocatechuic acid, gallic acid, caffeic acid, vanillic acid, syringic acid, ferulic acid, *p*-coumaric acid, quercitrin, rutin, kaempferol, quercetin.

Table 5 (*Continued*)

References	Sample wine	Extraction system	Initial quantity → final quantity of solvent in the extraction process	Instrumental variables						Chemical variables			Detected compounds
				λ_d [nm]	V [kV]	T [°C]	i.d. [μm]	L_{ef} [cm]	t_{inj} [s]	Type of buffer	[Buffer] [mM]	pH	
Prasongsidh et al. [156]	Non specified	–	Dilution of 100 μL sample in 900 μL buffer	220	20	40	50	60	7	Sodium deoxycholate + disodium hydrogen phosphate + disodium tetraborate + phophoric acid	0.05 + 0.01 + 0.006 M each	9.3	*Cis*-resveratrol, t*rans*-resveratrol, quercetin, catechin, gallic acid
Cartoni et al. [157]	Red	LLE	2 mL → 50 μL water–MeOH 1:1	210	15	25	50	36	2–5	Hydrogencarbonate	50	8.3	Syringic acid, *p*-coumaric acid, vanillic acid, caffeic acid, 3,4-diOH-benzoic acid, gallic acid
Vanhoenacker et al. [158]	Red	LLE	50 mL → 2.5 mL MeOH-water 1:1	280	20	25	50	65	5	Ammonium tetraborate	18.75	9.3	Gallic acid, 3,4-diOH-benzoic acid, catechin, caffeic acid, epicatechin, *p*-coumaric acid, myricetin, quercetin, kaempferol, vanillic acid, syringic acid, trans-polydatin, ferulic acid, rutin, cis-polydatin
Wang et al. [159]	Grape	SPE	20 mL → 3 mL ACN	250	16.8	Room temp.	75	45	1	Borax	35	8.9	Myricetin, luteolin, quercetin, apigenin, naringenin, kaempferol, hesperetin, baicalein, galangin
Peng et al. [160]	Red	LLE	1 mL → 2 mL buffer	– (ED)	12	Room temp.	25	70	6	Borate	100	9.2	*Trans*-resveratrol, epicatechin, catechin
Arce et al. [161]	Red White	SPE	2 mL → 2 mL MeOH	280	20	20	75	67	5	Sodium borate	100	9.5	*Trans*-resveratrol, epicatechin, catechin, *p*-coumaric, caffeic acid, gentisic acid, quercetin, salycilic acid
Saénz-López et al. [162]	Red	–	Centrifugation → upernatant isolated and Potassium metabisulphite added (amounts non specified)	599	25	10	75	46	6	Sodium tetraborate + MeOH	50 + 15%	8.4	Malvidin-3-*O*-glucoside, peonidin-3-*O*-glucoside, petunidin-3-*O*-glucoside, delphinidin-3-*O*-glucoside, cyanidin-3-*O*-glucoside
Chu et al. [163]	Red	LLE	30 μL → 5 μL 2-[(2-aminoethyl)amino]-5-nitropyridine hydrochloride	310	20	20	50	30	–	Sodium borate + sodium phosphate + SDS	25 + 25 + 75	9.0	*Trans*-resveratrol
Peres et al. [164]	Red White Blended	LLE	1 mL → 2.5 mL EtOH–water 60:40 v/v	280	25	25	75	40	3	Sodium tetraborate + MeOH	17 + 20%	Sodium tetraborate range	Resveratrol, catechin, rutin, syringic acid, kaempferol, p-coumaric acid, myricetin, quercetin, caffeic acid, gallic acid
Demianová et al. [146]	Red White	LLE	1 mL → 2 mL MeOH	230	30	25	50	8.5	1.5	Malonic acid + TBAOH in MeOH	5 + 9.6	13.5	Resveratrol, quercetin, myricetin, catechin, epicatechin
Rodríguez-Delgado et al. [165]	Spanish (commercial, no type specified)	LLE	5 mL → 0.5 mL MeOH	280	20	25	75	50	2	Boric acid + SDS + MeOH	150 + 50 + 5%	8.5	Catechin, epicatechin, quercetin, rutin, protocatechuic-aldehyde, syringic-aldehyde, ferulic acid, *p*-coumaric acid, vanillic acid, myricetin, kaempferol, caffeic acid
Woraratphoka et al. [166]	Red White Blended	LLE	1 mL → 1 mL EtOH (50%)	206 217	15	25	50	56	7	Phosphate + Borate	25 + 10	8.5	Resveratrol, epicatechin, catechin, rutin, quercetin, syringic acid, cinnamic acid, *p*-coumaric acid, gentisic acid, *p*-hydroxybenzoic acid, salicylic acid, caffeic acid, gallic acid, protocatechuic acid
Minussi et al. [167]	Red Rosé White	LLE	1 mL/2 mL → 100 μL buffer + 10% MeOH	206 217 312	15	20	75	50	7	Phosphate + borate	25 + 10	8.8	Tyrosol, *cis*-resveratrol, *trans*-resveratrol, catechin, epicatechin, hydroxytyrosol, sinapic acid, epicatechin gallate, syringic acid, *o*-coumaric acid, p-coumaric acid, vanillic acid, gentisic acid, *p*-hydroxybenzoic acid, salicylic acid, caffeic acid, gallic acid, protocatechuic acid

Pazourek et al. [168]	Red White Rosé	Direct injection	Diluted 5 times with water	190	20	25	75	36.5	5	Sodium tetraborate	25	9.5	Epicatechin, catechin, gentisic acid, *p*-coumaric acid, caffeic acid, gallic acid
		SPE	5 mL→2 mL MeOH + 5 mL water										
Berzas Nevado et al. [169]	Red	SPE	25 mL→4 mL ACN–water (3 + 7)	320	5	25	75	25	5	Sodium tetraborate	40	9.5	*Cis*-resveratrol, *trans*-resveratrol
Dobiášová et al. [170]	Red White	SPE	2 mL→0.3 mL 100% MeOH	305	20	25	75	36.5	5	Sodium tetraborate	25	9.5	*Trans*-resveratrol
Hernández-Borges et al. [171]	Red	SPE	5 mL→1 mL MeOH	280	15	20	75	40	2	Borate + phosphate + Hexadimethrine bromide + α-CD	125 + 49 + 0.002% (w/v) + 2.5	7.5	Protocatechuic acid, salicylic acid, *p*-hydroxybenzoic acid, vanillic acid, syringic acid, ferulic acid, sinapic acid

fused-silica capillary (50 μm × 31.4 cm) thermostated at 20 °C, potential of 15 kV, injection of samples by pressure at 350 mbar for 1 s, UV detection at 280 nm. The running buffer used was 20 mM SDS solution in 30 mM borate buffer (pH 8.5). The second article [180] showed the application of the same method (MEKC) to determine vanillic acid, vanillin, ferulic acid and 4-vinylguaiacol in sochu samples. The conditions were exactly the same apart from the running buffer, which in this case consisted on 25 mM SDS solution in 25 mM phosphate–50 mM borate buffer (pH 7.0).

Both of them proved to be a very useful tool for the analysis of phenols in comparison with other techniques, as HPLC, and for this reason they can be applied to routine quality control of liquors. The major difference with other research works is the sample preparation, since in these two papers the extraction of phenolic compounds was performed by solid-phase instead of liquid–liquid.

4.5. Vegetable oils

Among the different vegetable oils, VOO is unique because it is obtained from the olive fruit (*Olea europaea L.*) solely by mechanical means, without further treatment other than washing, filtration, decantation, or centrifugation [181].

Its chemical composition consists of major and minor components.

The major components, that include glycerols, represent more than 98% of the total weight. Abundance of oleic acid, a monounsaturated fatty acid, is the feature that sets olive oil apart from other vegetable oils. In particular, oleic acid (18:1 $n-9$) ranges from 56 to 84% of total fatty acids [182], while linoleic acid (18:2 $n-6$), the major essential fatty acid and the most abundant polyunsaturate in our diet, is present in concentrations between 3 and 21% [183].

Minor components, that amount to about 2% of the total oil weight, include more than 230 chemical compounds, e.g., aliphatic and triterpenic alcohols, sterols, hydrocarbons, volatile compounds and antioxidants [184]. The main antioxidants of VOO are carotenes and phenolic compounds, including lipophilic and hydrophilic phenols [185]. While the lipophilic phenols, such as tocopherols, can be found in other vegetables oils, some hydrophilic phenols of VOO are not generally present in other oils and fats [185,186].

The phenolic fraction of VOO consists of a heterogeneous and very complex mixture of compounds, mainly simple phenols, lignans, flavonoids and secoiridoids each of which varies in chemical properties and impacts in different ways on the quality of VOO [184,187]. There is evidence that phenolic compounds could play a major role in the healthy effects of VOO, besides to be responsible of its antioxidant activity and organoleptic properties (flavour, astringency, ...) [188–190]. Therefore, the determination of this family of compounds in olive oil is of special relevance.

So far, different analytical methods (GC, HPLC, CE) coupled to different detectors (UV, fluorescence, MS) have been developed to analyse olive oil phenolic compounds. Although HPLC is the most frequent method of choice, very interesting results have been achieved by using other analytical techniques; obviously in the current review we focus on CE methodologies.

CE was used for the first time in 2003 for analysing extracts from VOO by Bendini et al. [191]; they published a very interesting paper in which LLE and SPE were compared and the analytical separations were made by HPLC and CZE. Since that moment, CE has become more and more popular in the analysis of phenols from vegetable oils (mainly olive oils) [192,193]. Table 6 summarises the most important applications in the field; the differences in internal diameter of the capillary and time of injection, as well as the extraction system (the quantity of olive oil used in the extraction protocol and the volume of solvent for redissolving the phenolic compounds extracted) cause the differences in sensitivity among these methods.

Table 6
Relevant examples of separation of phenolic compounds from the polar fraction of olive oil using CE methods.

References	Extraction system and amounts	Detected compounds in olive oil	Instrumental variables						Chemical variables			Other relevant aspects
			λ_d [nm]	V [kV]	T [°C]	i.d. [μm]	L_{ef} [cm]	t_{inj} [s]	Type of Buffer	[Buffer] [mM]	pH	
Bendini et al. [191]	LLE (Pirisi et al. [194]) 2 g → 1 mL	HYTY, TY, unidentified secoiridoids compounds	200	27	30	50	40	3 s (0.5 p.s.i)	Sodium tetraborate	45	9.6	1st paper where CE is used for the analysis of phenolic compounds from oils
Bonoli et al. [195]	LLE (Pirisi et al. [194]) 2 g → 1 mL	HYTY, TY, DHPE, unidentified oleuropein aglycone derivatives	CZE method of Bendini et al. [191]									
Bonoli et al. [196]	LLE (Pirisi et al. [194], modified by Rotondi et al. [197]) 2 g → 0.5 mL	HYTY, TY, VA, DAOA, Ac Pin	CZE method of Bendini et al. [191]									
Carrasco-Pancorbo et al. [198]	60 g → 0.5 mL	13 phenolic acids + taxifolin (flavanonol)	210	25	25	75	50	8 s (0.5 p.s.i)	Sodium tetraborate	25	9.6	Potent extraction system which permits to detect little quantities of phenolic acids
Buiarelli et al. [199]	10 g → non specified (Combination of LLE-SPE)	5 phenolic acids	200	18	25	50	36	2 s (1.5 p.s.i)	Sodium tetraborate	40	9.2	
Carrasco-Pancorbo et al. [200]	60 g → 0.5 mL [198]	13 phenolic acids + taxifolin (flavanonol)	210	−25	25	75	50	8 s (0.5 p.s.i)	Sodium tetraborate (20% 2-propanol)	50	9.6	Co-electroosmotic CE
Gómez-Caravaca et al. [201]	60 g → 2 mL (SPE-Diol)	TY, Pin, Ac Pin, DOA, Lig Agl, HYTY, Ol Agl, EA	214/250	25	25	75	100	8 s (0.5 p.s.i)	Sodium Tetraborate	30	9.3	Use of standards obtained by semipreparative-HPLC
Carrasco-Pancorbo et al. [202]	60 g → 2 mL (SPE-Diol [201])	11 phenols (simple phenols, lignans, complex phenols and EA)	214/MS (ESI-IT)	25	25	50	100	10 s (0.5 p.s.i)	NH_4OAc (5% 2-propanol)	60	9.5	1st paper in which CZE-ESI-IT MS is used for the analysis of phenolic compounds from oils
Carrasco-Pancorbo et al. [203]	60 g → 2 mL (SPE-Diol [201])	26 compounds belonging to all the different families of phenolic compounds present in olive oil	200/240/280/330	28	22	50	40	8 s (0.5 p.s.i)	Sodium tetraborate	45	9.3	1st paper in which flavonoids are detected by CE, and 1st method "multicomponent" for the phenols of olive oil
Carrasco-Pancorbo et al. [204]	60 g → 2 mL (SPE-Diol [201])	Applicative work using a method previously described [203]	CZE method of Carrasco-Pancorbo [203]									Interesting from a quantitative and applicative point of view
Carrasco-Pancorbo et al. [205]	60 g → 2 mL (SPE-Diol [201]) and diluted 1:10	All the phenolic compounds "well-knonw" and other 28 analytes	MS (ESI-TOF)	30	25	50	85	10 s (50 mBar)	Ammonium hydrogen carbonate	25	9.0	1st paper in which CZE-ESI-TOF MS is used for the analysis of phenolic compounds from oils. TOF permits the "identification" of new compounds in the profile of the oils
Aturki *et al.* [206]	LLE (Pirisi et al. [194]) with minor modifications 2 g → 0.5 mL and diluted 1:5	7 phenolic acids and HYTY, TY and Oleuropein	200	22	20	75	33 (eff. packed lengths of 24.5 and 23 cm)	Combination of pressure and Voltage (10 bar × 10 kV × 0.5 min)	Mobile phase: ammonium formate buffer/water/ACN (5:65:30 v/v/v)	100	3.0	Reversed-phase capillary electrochromatography. Complete method validation
Carrasco-Pancorbo et al. [207]	60 g → 2 mL (SPE-Diol [201]) and diluted 1:8	Applicative work using a method previously described [203]	CZE method of Carrasco-Pancorbo [203]									Quantitative comparison of phenolic profiles of two PDOs and their relation to sensorial properties with statistical analysis
Gómez-Caravaca et al. [208]	60 g → 2 mL (SPE-Diol [201]) and diluted 1:10 or redissolved in 10 g oil+10 mL 1-propanol	All the phenolic compounds "well-knonw" and other 28 analytes	MS (ESI-TOF)	30	25	50	85	10 s (50 mBar)	NH4OAc/AcH in methanol/ACN (1/1 v/v)	25	5.0	Direct injection of the investigated matrix introducing a plug of olive oil directly into the capillary. Comparison between CZE and NACE

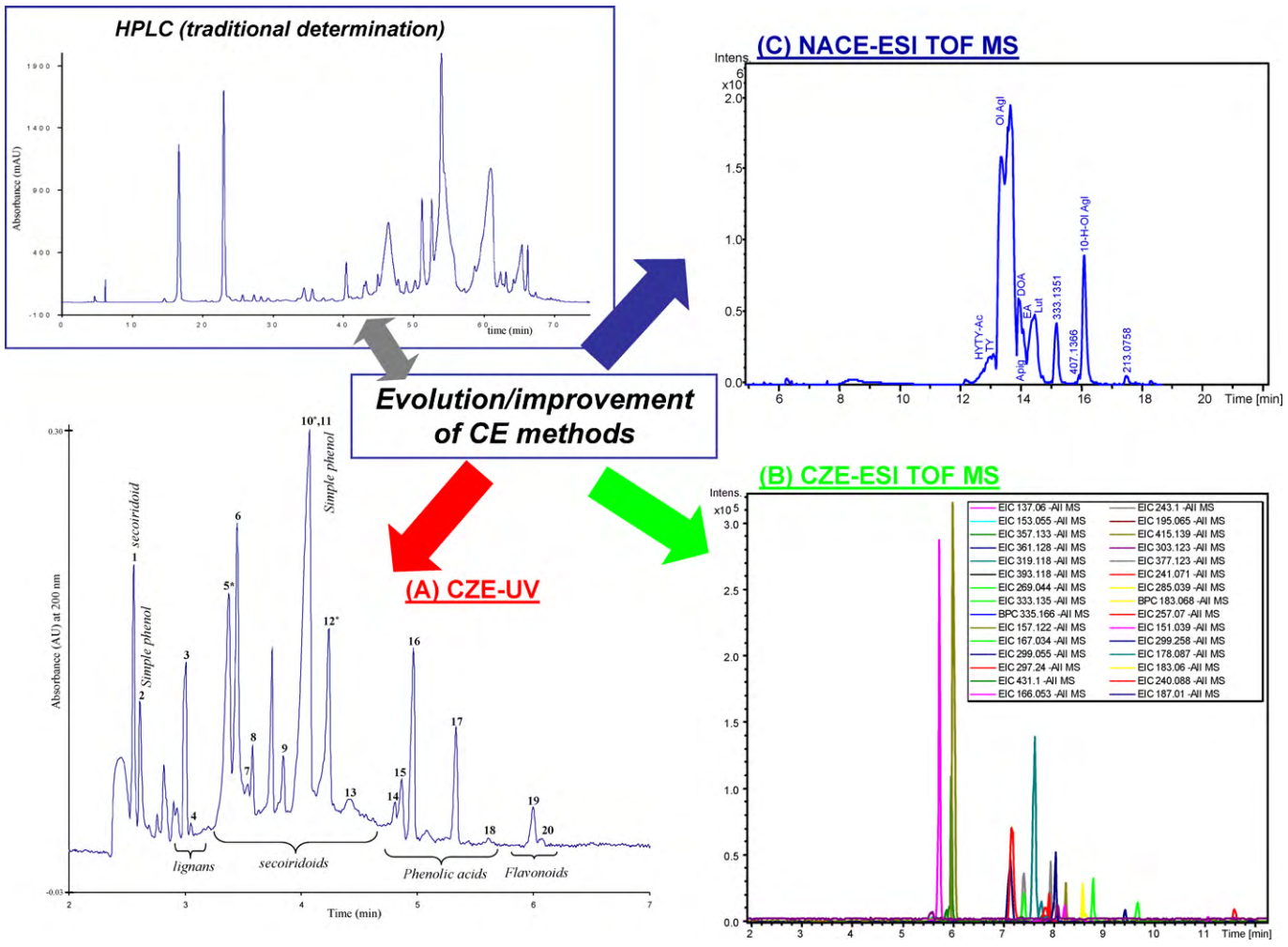

Fig. 3. Comparison between HPLC and CE as analytical tools for analysing polyphenols from EVOO. The figure shows as well the evolution/improvement of the CE methods. (A) CZE-UV analysis of an extract from an EVOO.
Peak identification numbers: 1, Lig Agl (a); 2, TY; 3, Pin; 4, Ac Pin; 5, Ol Agl (a) + DOA (a); 6, DOA (b); 7, Lig Agl (b); 8, Ol Agl (b); 9, EA (a); 10, Ol Agl (c) + Lig Agl (c) + DOA (c) + EA (b, c); 11, HYTY; 12, DOA (d) + EA (d); 13, EA (e); 14, trans-cinnamic acid; 15, 4-hydroxyphenylacetic acid; 16, sinapinic acid; 17, gentisic acid; 18, o-coumaric acid; 19, luteolin; and 20, apigenin.
(B) Extract Ion Electropherograms as obtained by CZE-ESI-TOF-MS of an extract from EVOO at the optimum electrophoretic and MS conditions.
(C) Base Peak Electropherogram obtained by NACE-ESI-TOF-MS after direct injection of EVOO sample inside the capillary.

All the gathered methods without MS detection used simple CZE methodologies based on a borate run buffer at alkaline pH, since the most efficient operative mode to separate phenolic compounds has been found to be borate-based CZE.

In 2006, Carrasco-Pancorbo et al. [202] developed the first CE-ESI-IT MS method offering to the analyst the chance to study important phenolic compounds, such as phenolic alcohols (TY, HYTY and 2-(4-hydroxyphenyl)ethyl acetate), lignans ((+)-pinoresinol and Ac Pin), complex phenols (Lig Agl, Ol Agl, their respective decarboxylated derivatives and several isomeric forms of those compounds and 10-hydroxy-Ol Agl) and another phenolic compound (EA) in extra-virgin olive oil (EVOO), using a simple SPE before CE-ESI-MS analysis.

After showing the potential of ion trap as mass analyser, another publication compared the capabilities of a HPLC-ESI-TOF MS method with those of a CE-ESI-TOF-MS [205], showing that the two methodologies were able to determine many well-known phenolic compounds present in olive oil and provided information about the presence and relative concentration of minor phenolic compounds. Both CE-MS and LC-MS could determine more than 45 analytes in each run.

Aturki et al. [206] achieved the simultaneous separation of 10 phenolic compounds (protocatechuic, *p*-coumaric, *o*-coumaric, vanillic, ferulic, caffeic and syringic acids, HYTY, TY and oleuropein) in EVOOs by isocratic reversed-phase CEC, demonstrating that the mentioned methodology can be successfully employed for the separation of polar compounds with high precision, linearity and sensitivity.

One of the most promising newest applications involved the use of NACE-ESI-TOF-MS [208]; the authors compared the results achieved by NACE with those obtained by CZE (with aqueous buffers) both coupled to ESI-TOF MS. Both methods offer the chance to study phenolic compounds from EVOO belonging to different families by injecting methanolic extracts with efficient and fast CE separations. Apart from that, in the case of the NACE method, the direct injection of the investigated matrix introducing a plug of olive oil directly into the capillary was also checked, producing very interesting results.

In Fig. 3, a comparison of the analysis of the phenolic fraction of an EVOO analysed by HPLC (the technique most widely used) with the profiles achieved by three different CE methodologies are showed. The comparison between HPLC and CE results in terms of

analysis time is quite clear, although the truth is that nowadays the improvement in the chemistry of LC columns and LC systems (withstanding higher pressures) could provide shorter analysis time. Anyway, what is more interesting about Fig. 3 is to observe the evolution/improvement of the CE method. The first example (A) is the electropherogram obtained with a simple CZE-UV method [203]. The method was quite powerful, being able to separate, identify and quantify about 20 compounds in 6 min. The second example (B) [205] illustrates a CZE-ESI-TOF MS separation of the polar extract from an EVOO. TOF MS facilitated the identification of a great number of compounds. In (C), the reader can have a look at the profile achieved when direct injection of EVOO diluted in an organic solvent was introduced inside capillary and a NACE separation carried out. Despite that analysis time is still better for aqueous CE (B), the fact of doing direct injection of olive oil in NACE is one of the greatest advantages that can be mentioned.

4.6. Cereals, legumes and nuts

Cereals, legumes and nuts are matrices that have been studied together in some publications, which is why we decided to include them in the same section.

Cereals have an important role in human nutrition, since they constitute one of the most pivotal pillars on the diet. The term "cereal" includes wheat, barley, maize, oats, millet, rye, sorghum, malt and rice. Cereals are a source of phenolic acids [209] and flavonoids in the free and conjugated forms, which are usually located in the outside layers [210]. Maize, rice, wheat and sorghum have been described also for containing anthocyanins [211].

Several research groups have worked in the field of the determination of phenolic compounds from cereals by using electrophoretic methods. For instance, Hernández-Borges et al. [171] described a rapid separation by coelectroosmotic CE of seven phenolic acids (protocatechuic, salicylic, *p*-hydroxybenzoic, vanillic, syringic, ferulic and sinapic acids) present in corn flour samples. The phenols were extracted by LLE and these samples were hydrodynamically injected for 2 s. The separation was carried out with a fused-silica capillary of 75 μm i.d. × 40 cm effective length, at 20 °C, using as running buffer 125 mM borate, 49 mM phosphate, 0.002% (w/v) hexadimethrine bromide, 2.5 mM α-CD, at 7.5 pH and applying a separation voltage of 15 kV. Finally, compounds were detected at 280 nm by DAD. The same research group [212] developed a CE method to determine the phenolic acids mentioned above in gofio, a typical food produced in Canary Islands (Spain) that consists of roasted flours, alone or mixed, of barley, wheat and corn. In this case, they used the following conditions: 40 cm effective length × 75 μm i.d. capillary, run voltage −15 kV, temperature 20 °C, hydrodynamic injection for 2 s and detection at 280 nm. The running buffer was 125 mM borate, 48.6 mM phosphate, 0.002% (w/v) hexadimethrine bromide, 2.5 mM α-CD and pH 7.5. This method proved to be reproducible and provided good separation.

According to Vaher et al. [213], wheat is an important source of sinapic, syringic, ferulic, *p*-coumaric, vanillic and caffeic acids. The analyses were carried out at 25 °C with a fused-silica capillary (50 μm i.d. × 52 cm effective length), using 50 mM sodium tetraborate (pH 9.3) as separation buffer. Detection was made at 210 nm and the voltage was set at 20 kV. Several wheat samples were analysed and the method demonstrated its usefulness.

Peng et al. [214] analysed the hull and flour of buckwheat by CE-ED. They could identify (−)-epicatechin, rutin, hyperoside and quercetin using 50 mM borate buffer with pH 8.7 and a fused-silica capillary of 75 cm length and 25 μm i.d. Samples were injected for 6 s and the separation voltage was 16 kV. The method was satisfactory. A similar study was carried out by Kreft et al. [215] and they determined rutin in seeds of buckwheat, using an uncoated capillary of 50 μm i.d. × 57 cm effective length. The temperature was maintained at 18 °C and the applied voltage was 25 kV. Samples were injected for 20 s, the detection was carried out at 380 nm and the running buffer was 50 mM borate and 100 mM sodium dodecyl sulfate (pH 9.3).

Barley is other cereal which has been studied, indeed Samaras et al. [216], Kvasnička et al. [217] and Bonoli et al. [218] paid attention to it. The first author identified ferulic, *p*-coumaric, vanillic, homovanillic, and *p*-hydroxyphenyl-acetic acids, catechin and 4-vinylguaiacol in barley and different types of malts. For the CE analysis, they used a fused-silica capillary (40 cm effective length × 50 μm i.d.), the temperature was maintained at 25 °C, the applied voltage was 25 kV, the running buffer was formed by 50 mM borate containing 20% methanol (pH 9.5), samples were injected for 5 s and separations were monitored at 200, 280, 325 and 420 nm. Kvasnička et al. [217] resorted to CZE to identify *p*-coumaric, caffeic, ferulic and sinapic acids, using the following conditions: the background electrolyte was 50 mM acetic acid, 95 mM 6-aminocaproic acid, 0.1% polyacrylamide, 1% polyvinylpyrrolidone and 10% methanol; capillary of 28 cm effective length × 50 μm i.d.; constant voltage of −30 kV; temperature 30 °C; detection at 230 and 315 nm; and samples injection for 25 s by pressure. Finally, Bonoli et al. [218] analysed wholemeal barley flour using MEKC but, in contrast to the previous, they determined other different phenolic compounds besides phenolic acids. They carried out SLE and PLE, using different mixtures of solvents and methods. The electrophoretic conditions were: a 20 mM sodium tetraborate, 5 mM potassium dihydrogen phosphate and 10 mM SDS buffer (pH 9.0), 50 μm i.d. × 40 cm effective length capillary, voltage of 30 kV, temperature 30 °C, injection for 3 s and detection at 200 nm. Results showed that the method was efficient, reliable and suitable to determine some flavan-3-ol compounds, proanthocyanidins, hydrolysable tannins and hydroxycinnamic acids.

Nuts are a group of food consumed traditionally in the Mediterranean area, Asia and South America. Nowadays, they are eaten all around the world like snacks or appetizers, but they are also included in different desserts, sauces, etc. [219]. Nuts are a great source of energy, providing proteins, essential unsaturated fatty acids, vitamins and minerals [220]. They also contain several compounds with beneficial effects in human health, such as tannins and polyphenols, among others [221].

Cifuentes et al. [222] was one of the first authors who identified phenolic compounds in nuts, particularly in almond peels, by CE. They used MEKC with acidic buffers to determine procyanidins and other compounds. The optimum conditions used for the analyses were: fused-silica capillary 30 cm effective length × 50 μm i.d., applied voltage of 14 kV, sample injection for 1.5 s, temperature 25 °C, detection at 200 and 280 nm, and running buffer formed by 50 mM acetic acid/sodium acetate and 100 mM SDS (pH 5.0). The results showed the presence of catechin and procyanidin B2 in almond peel samples.

Cashew nut has been other matrix analysed, specifically by Česla et al. [223]. They used MEKC to carry out the separation of different anacardic acids and chose MS as detector. They employed two different methodologies, since they used bare fused-silica capillaries and polydimethylacrylamide-coated capillaries. Conditions were the same for both methodologies, except the effective length of capillaries, the applied voltage and the background electrolyte. The temperature was maintained at 15 °C, the detection was carried out at 214 and 305 nm, and samples were injected hydrodynamically for 10 s. Non-coated capillaries had an effective length of 40 cm, the voltage used with them was 20 kV and the running buffer was formed by 40 mM borate pH 9.2 with 1 M urea, 27 mM SDS and 24% acetonitrile. On the other hand, polydimethylacrylamide-coated capillaries had 50 cm of effective length, the separation voltage was −17.5 kV and the background electrolyte was 10 mM

phosphate, 1 M urea, 20% acetonitrile, 20 mM SDS, 10 mM β-CD and 1 mM heptakis-6-sulpho-β-CD. The best results were obtained with polydimethylacrylamide-coated capillaries, since separation selectivity and efficiency were better.

Gómez-Caravaca et al. [224] developed a CE method coupled to MS for determining catechin, digalloylglucose, glansreginin B, ferulic acid glucoside, vanillic acid glucoside, glansreginin A, cumaroylquinic acid, chlorogenic acid, ellagic acid and ellagic acid pentoside dimer. The optimum conditions were uncoated fused-silica capillary 50 μm i.d. × 90 cm effective length, voltage 30 kV, running buffer 40 mM ammonium acetate/NH_3 (pH 9.5) and sample injection for 20 s. The method proved to be successful, as it allowed to identify and quantify compounds which were present in the polar fraction of walnuts in a short analysis time (less than 15 min).

Karamać [225] resorted to CZE to separate tannin fraction of walnut, hazelnut and almond kernels. This author employed an uncoated silica capillary with 50 μm i.d. × 40 cm effective length, temperature 40 °C, a 100 mM boric buffer (pH 8.5), a constant voltage of 20 kV, injection for 3 s and detection at 280 nm. The results showed that the profiles of hazelnuts and almonds were quite similar, whereas the walnut analyses were qualitatively different. The tannin fraction of walnut mainly consisted of hydrolysable tannins, whereas condensed tannins were typical in the fractions of hazelnuts and almonds.

Legumes are dried seeds or fruit of different plants, which have been part of the human diet, together with the cereals, for centuries. There are a wide range of legumes, for instance, lentils, chickpeas, white and black beans, peas, soybean, lupin, etc. Only a few of them have been analysed by CE and soy is, undoubtedly, the most studied.

Shihabi et al. [226] used CE to identify daidzin, genistin, biochanin A, daidzein, genistein and coumestrol in samples of soybean. To carry out the separation, they employed a capillary of 50 cm × 50 μm i.d., a running buffer formed by 200 mM borate (pH 8.6) and a voltage of 13 kV. The samples were injected for 10 s by pressure and the detector set at 254 nm. The method proved to have good reproducibility in a short time.

The method developed by Cifuentes et al. [222] for determining procyanidins and other phenolic compounds in almond peels, was applied to lentils, white beans and black beans. The compounds under study were not found in white beans, while lentils presented six compounds (procyanidin B3, procyanidin B1, (+)-catechin, *cis p*-coumaric acid, *trans p*-coumaric acid and (−)-epicatechin) and black beans contained five of the analytes studied (procyanidin B1, (+)-catechin, procyanidin B2, *trans p*–coumaric acid, (−)-epicatechin). This method allowed a good separation and good reproducibility (intra- and interday) in less than 5 min.

Peng et al. [227] analysed different soy products by CE with ED. They achieved daidzein and genistein separation using the following conditions: capillary of 70 cm × 25 μm i.d., sample injection for 6 s, voltage of 12 kV and 100 mM borate buffer (pH 11.0). It proved to be a useful qualitative method, simple and rapid.

Dinelli et al. [228] developed a CE-DAD method to identify and quantify different flavonoids (daidzein, genistein, glycitein and kaempferol) in soybean and three common kinds of beans. The aim of this work was to compare the compositional changes in those samples when they were treated with UV-B radiation. CE analyses were carried out with capillaries of 75 μm i.d. × 30 cm effective length, at 25 °C, applying a voltage of 15 kV and using 50 mM ammonium acetate buffer (pH 10.5) with 20% (v/v) methanol. Samples were injected for 10 s and the electropherograms were recorded at 214 and 260 nm. The results showed that these common beans could be used as a potential dietary source of isoflavones.

García-Villalba et al. [229] carried out a comparison between transgenic and conventional soybean using CE-UV and CE-MS. They identified several plant metabolites and some of them were phenolic compounds, like genistein, daidzein, formononetin, kushenol B, exiguaflavanone D, genistin, daidzin sophora-iso-flavanone D, kushenol M, 6-methoxytaxifolin, genistein 7-*O*-malonylglucoside, daidzein 7-*O*-malonylglucoside, naringenin 7-*O*-glucoside and taxifolin 3-rhamnoside. To achieve that, they employed a fused-silica capillary of 50 μm i.d. and 84 cm of effective length, a 50 mM ammonium hydrogencarbonate (pH 9.0), a voltage of 28 kV. Samples were injected for 10 s and the wavelength chose in UV–vis was 200 nm. One of the most significant results obtained in this work was the presence of one compound in traditional soybean that was not found in the transgenic one.

There are other publications analysing soy and other legumes used in different applications. For example, Micke et al. [230] used MEKC to identify isoflavones in soy germ pharmaceutical capsules, and Mellenthin and Galensa [231] resorted to CZE to analyse polyphenols of soy, lupin and pea for determining the presence of proteins of those legumes in meat products.

4.7. Others

As commented before, we have decided to include a section entitled "Other matrices" which will enclose information about cocoa beans and bee products.

4.7.1. Cocoa beans and products

Cocoa beans, the seeds from *Theobroma cacao*, are a rich source of polyphenols, in particular flavan-3-ols (or catechins) and procyanidins, representing about 10% of the whole bean's dry weight and its derivative chocolate, especially dark chocolate [232]. Geographic and climatic factors can affect the content of flavonoids in cocoa beans, as well as changes in their quantities are occurring during the chocolate and/or cocoa manufacture. Different electroseparation techniques have been used for the analysis of phenolic compounds in cocoa beans and its products.

A patented MEKC method [233] was applied in the separation of cocoa procyanidin oligomers. The buffer consisted of 200 mM boric acid and 50 mM SDS (pH 8.5 adjusted with sodium hydroxide), and the uncoated fused-silica capillary maintained at 25 °C was 50 cm length × 75 μm i.d. Analytes were separated in 12 min and detected by DAD at 200 nm.

Modified MEKC methods, using SDS as a principal component of the running buffer, were developed for the determination of catechins and xanthines in cocoa extracts [234,235]. The separations were obtained on fused-silica capillaries of 50 μm i.d. with a total length of 38.5 cm, used in the "short-end" mode (8.5 cm of effective length). The applied voltage was maintained at 15 kV (anodic detection), the temperature at 30 °C and compounds were detected at 220 nm. Owing to the reported poor stability of catechins in alkaline solutions, MEKC under acidic conditions was preferred. As a result, the EOF was significantly suppressed, resulting in a fast migration of the SDS micelles into the anode and making necessary the use of additives into the buffer to modulate selectivity. In a first study [234], three different systems for the separation of (+)-catechin, (−)-epicatechin, caffeine, and theobromine in four different commercial chocolate types (black and milk) and two cocoa powder samples were optimised. 3-[(3-cholamidopropyl)dimethylammonio]-1-propansulfonate and taurodeoxycholic acid sodium salt were individually supplemented to the SDS solution to obtain binary mixed micelles with varied hydrophobicity. A further cyclodextrin-modified MEKC approach was developed by addition of hydroxypropyl-β-cyclodextrin (HP-β-CD) to the SDS-based buffer. This system resulted more suitable to analyse the cocoa samples than those based on micelles. Under the optimum conditions (50 mM Britton–Robinson buffer at pH 2.5, 90 mM SDS, 10 mM HP-β-CD), the method was applied to improve the extraction procedure, choosing water under sonica-

tion for 10 min at 60 °C; then it was validated and used for the quantitative determinations.

In a subsequent study [235], (+)-catechin, (−)-epicatechin and theobromine from different cocoa beans and commercial black chocolate were quantified using an enantioselective CD-MEKC method in order to evaluate the possible epimerisation of epicatechin during chocolate manufacture. The method conditions were similar to those described previously from the same authors, changing the buffer composition (12 mM of HP-β-CD instead of 10) and the extraction protocol (29% ethanol under sonication for 15 min at 65 °C). The analysis of cocoa beans showed remarkable differences in (+)-catechin and (−)-epicatechin contents depending on the provenience and maturation degree of the beans. (−)-Catechin was not detected in any of the analysed samples. Interestingly, in black chocolate very small amounts of the native (+)-catechin were found, whereas a clear peak of (−)-catechin was detected. This results confirmed the hypothesis of an epimerisation at the C-2 position of (−)-epicatechin probably occurring during heat processing and storage of the beans.

Kofink et al. [236] obtained a similar conclusion regarding (−)-epicatechin epimerisation during chocolate production; (−)-epicatechin and small amounts of (+)-catechin were detected in unfermented, dried, unroasted cocoa beans, while increased levels of (−)-catechin were found in roasted cocoa beans and in commercial cocoa products. The high temperature during the bean roasting process and particularly the alkalisation of the cocoa powder were the main factors inducing the epimerisation reaction. The enantioselective separation was achieved by CCE-UV detection using 100 mM borate buffer (pH 8.5) with 12 mM (2-hydroxypropyl)-γ-cyclodextrin as chiral selector, an applied voltage of 18 kV and a fused-silica capillary (50 cm effective length × 75 μm i.d) maintained at 20 °C.

Ohashi et al. [237] did not analysed the phenolic compounds coming from cocoa, but those added as flavouring material. In particular, the vanillin and ethylvanillin included in three types of cocoa drinks and their metabolites 2-methoxyphenol and 2-ethoxyphenol after the addition of the bacterium *Bacillus firmus* were determined by CE-DAD. Those metabolites were responsible of off-flavours in the cocoa drinks. The running buffer system comprised 50 mM phosphate buffer and 2 mM cetyltrimethylammonium hydroxide at pH 10.0 with 10% acetonitrile and sorbic acid as the internal standard. Samples were simply diluted before their analysis.

4.7.2. Bee products

Honeybee products have been employed since ancient times with both domestic and medical purposes, being subjected to extensive clinical studies during the last few decades. The phytochemical composition of hive products depends on their floral origin and thus on the geographic and climatic characteristics at the site of collection. Such composition differences are likely to affect the biological and clinical properties of bee products. Major hive products are honey, propolis, royal jelly, bee pollen, bee bread and beeswax. Among them, only the phenolic profiles of honey, propolis and pollen have been studied by CE methods.

To make honey, bees gather the nectar from various flowers, ingest and regurgitate it several times before being stored in the comb. Then, considerable amounts of water are evaporated, raising honey's sugar concentration and preventing its fermentation. Monofloral honeys are appreciated by consumers, and their price is often related to this floral origin. The analysing methodology to prove the origin of monofloral honeys is not fully established. However, the study of phenolic compounds has resulted in a useful tool for the determination of honey's botanical and geographical origins [238–240].

Delgado et al. [238] made the first attempt to provide an alternative methodology based on CE for the characterisation of honey flavonoids, comparing the separation obtained by MEKC with that achieved by HPLC. Fourteen different flavonoids isolated from honey were analysed by MEKC with UV–vis detection. However, it was difficult to find specific experimental conditions to separate all flavonoids in a single run, optimising three different electrophoretic methods, depending on the flavonoid markers sought in honey. These authors achieved the complete separation of 13 flavonoids from honey in a single run [239] (12 of them also included in the preceding work) by adding 10% methanol as organic modifier to the MEKC running buffer, which consisted of 200 mM sodium borate and 50 mM SDS (pH 8.0). The optimised method was applied to study honey samples with different botanical (lavender, rosemary, orange tree and heather) and geographical (Spain, Mexico and Canada) sources to asses the use of flavonoids as possible markers for honey origins. Citrus honey was characterised by the accumulation of hesperetin, lavender by luteolin, rosemary by 8-methoxykaempferol and heather by some unidentified flavonoids. Regarding geographical origin, no significant differences were found on the honey flavonoid pattern.

A more extensive study about the use of phenolic compounds as floral markers for honeys was carried out using CZE with UV detection at 280 nm [240]. A total of 26 phenolic compounds, including 16 phenolic acids and 10 flavonoids, together with hydroxymethylfurfural were analysed in 11 monofloral honey samples (heather, lavender, acacia, rape, sunflower, rosemary, citrus, rhododendron, thyme, chestnut-tree and calluna). The analysis were carried out on a fused-silica capillary (50 cm × 50 μm) at 30 °C using 100 mM sodium borate buffer with 20% methanol (pH 9.5), within 18 min. Phenolic profiles of the analysed honeys showed significant differences. Total phenolic acid content or the relative amount of one individual phenolic acid derivative could be related to the floral origin of the honey. The higher contents of phenolic acid derivatives were found in heather honey whereas citrus and rosemary honeys were characterised for having small amounts. On the other hand, heather honey had a considerable amount of phenylethyl-caffeate, while lavender honey contained *m*-coumaric acid as the principal phenolic compound. In some cases, a single phenolic compound was detected in only one unifloral honey type, and could be considered as a potential floral marker. Thus, thyme honey was characterised by the presence of rosmarinic acid, heather honey by ellagic acid, citrus honey by hesperetin, and lavender honey by naringenin.

Gómez-Caravaca et al. [241] studied the polyphenolic profile of six different honeys using as well CZE with UV detection. Standard solutions of 22 phenolic compounds previously found in honey were prepared and spiked individually in the honey extracts. Good resolution in a satisfactory time was achieved with the developed CZE method. Nonetheless, only five phenolic compounds were identified in the studied samples, of which two coeluted, enabling the quantification of only three of them. Due to the problems found with the UV detection, the use of MS was recommended and, in fact, used in another work for the identification of phenolic compounds in rosemary honey [242]. CZE and ESI-MS parameters (i.e. running buffer composition and pH, applied voltage, sheath liquid composition and flow rate, drying gas flow rate and temperature, and nebulisation gas pressure) were optimised. This methodology allowed the identification of 13 flavonoids in rosemary honey, being one of them the flavonol kaempferol, potential floral marker for rosemary honey.

Propolis, or bee glue, is a dark-coloured resinous substance collected by honeybees from leaf buds and cracks in the bark of various tree species and enriched with salivary and enzymatic secretions. Bees use propolis to seal holes in their hives, make stronger the borders of the comb or make the entrance weather-proof. It is also

used as an "embalming" substance to cover the killed invaders that can not be transported out of the hive. The modes of operation used for the determination of phenolic compounds in raw propolis and commercial propolis preparations have been CZE [243–245], MEKC [49,246,247] and a combination of both [248,249] coupled to DAD, with the exception of a work employing CZE-MS [250]. Besides the well-known advantages of CE over HPLC for the characterisation of compounds (analysis time, solvent consumption, sample quantity), CE allowed the analysis of propolis samples without any pre-cleaning, since contaminants can be removed from the capillary by rinsing with the appropriate solvents after each analysis.

Chi et al. [243] developed the first CE method to determine the composition of a propolis sample collected in China. The electrophoretic conditions were optimised using 12 phenolic standards occurring in propolis. To achieve a good separation, 0.7 mM β-ciclodextrin was added to the buffer solution consisting of 25 mM sodium dihydrogenphosphate and 25 mM sodium tretraborate at pH 10.1. Caffeic, 3,4-dimethylcaffeic and isoferulic acids and quercetin were identified and quantified in the ethanolic extracts of the real propolis sample.

Cao et al. [244] developed a CZE method that could separate ferulic and caffeic acids, rutin, apigenin, luteolin and quercetin within 12 min with no need of incorporating additives to the buffer. The effects of several factors such as acidity and concentration of the background electrolite, separation voltage, injection time and UV wavelength were investigated, being the optimum values borax buffer with pH 9.2 and 50 mM, 23 kV, 12 s and 262 nm, respectively. The six active constituents were determined in raw propolis and propolis capsules from China. Capsules were indeed more concentrated than raw propolis, except for caffeic acid that was not detected. Rutin content increased notably more than the rest of the ingredients.

A broad study of the levels of phenolic compounds in other pharmaceutical products containing propolis was accomplished using as well CZE-UV by Volpi [245]. With a buffer constituted by 30 mM of sodium tetraborate (pH 9) and applying 15 kV, 15 phenolic standards were separated on a uncoated fused-silica capillary 70 cm (50 cm effective length) × 50 μm i.d. within 40 min, although not all could be identified in the samples. Commercial propolis preparations were in the form of ethanolic, aqueous-ethanolic, and aqueous-glycolic extracts used to prepare oral sprays, tablets, and syrups. The aqueous-ethanolic preparation mainly contained caffeic acid, galangin, quercetin and chrysin, whilst the ethanolic extract was mostly composed of resveratrol, chrysin and caffeic acid, with 12.4% and 6% of nonidentified compounds, respectively. On the contrary, the aqueous-glycolic propolis preparation contained 11% of caffeic acid and approx. 85% of nonidentified compounds.

There is only one report using CZE-ESI-MS for the identification of propolis antioxidant compounds [250]. Therefore, the separation parameters and the MS conditions were carefully optimised using directly the ethanolic extract of raw propolis. Due to volatility requirements, the most commonly used buffers or additives for CZE-DAD were not suitable. Separation was achieved in a 90 cm × 50 μm i.d. bare fused-silica capillary with a running buffer of 80 mM ammonium acetate/NH_3 (pH 10.5) at 30 kV. 11 flavonoids previously reported in propolis were identified by comparing both migration times and MS data of the peaks in the propolis extract with those of pure standards, when available. Identification was confirmed by the data provided by a TOF mass spectrometer, which enabled formula generation for each mass.

The usefulness of both CZE and MEKC–DAD for the profiling of phenolic compounds in 10 raw propolis samples was demonstrated by Hilhorst et al. [248]. First, the samples were extracted with water to isolate the more polar constituents, such as phenolic acids. The extracts were subsequently analysed by CZE with borate buffer at pH 7.0 and 9.3, and MEKC (borate, pH 9.3, 10% acetonitrile), using 50 mM SDS as surfactant. The selectivity of both systems differed considerably but the information obtained was similar. The dry residues from the water extraction were extracted with ethanol/water (70:30, v/v) and analysed by MEKC only, to enable the identification of the more hydrophobic constituents of propolis. In this way, pinocembrin, chrysin and galangin could be identified in all the samples. On the basis of the recorded CZE and MECK electropherograms, samples could be clearly divided into two different groups, probably due to their different origin.

In the later work, CZE and MEKC methods were developed independently and the obtained results compared, being able to identify a different number of compounds in the water extracts using CZE or MECK. In the following investigation [249], the MEKC method was supplemented to separate two phenolics, quercetin and myricetin, that could not be separated by CZE. Therefore, the combination of CZE, utilizing 100 mM borate buffer (pH 9.5) containing 5% methanol under a voltage of 18 kV, and MEKC, utilizing 0.03 M sodium borate (pH 8.5) containing 50 mM SDS under a voltage of −15 kV, allowed the separation of 15 flavonoids, of which 12 were detected in raw propolis and 11 in the commercial propolis products. The total contents of the identified flavonoids in raw and commercial propolis ranged from 254 to 19147 mg/kg and from 1228 to 7985 mg/kg, respectively, suggesting that both origin and processing were important factors affecting the flavonoid content.

MEKC itself has also being employed in the determination of several compounds in propolis. After the systematic optimisation of the analytical conditions of the borax buffer concentration (30 mM) and pH (9.0), surfactant concentration (12 mM), organic modifier (5% ethanol), applied voltage (14 kV), and injection time (8 s), Lu et al. [247] established a MEKC method for the determination of hesperetin, cinnamic and nicotinic acids in a propolis oral liquid preparation. The method was validated in terms of linearity, reproducibility and detection limits.

Propolis and other complex food samples were analysed by a mixed MEKC–DAD method developed for the separation of 10 flavonoid aglycones [49]. The micellar system composed of 25 mM SDS and 25 mM sodium cholate buffered at pH 7 provided the separation of all the analytes in less than 20 min. In raw propolis, chrysin and galangin were the flavonoids with the highest concentration, identifying naringenin, quercetin, and kaempferol as well.

Fontana et al. [246] described a MEKC method for profiling flavonoids and phenolcarboxilic acids from propolis collected in different Brazilian provinces. The authors did not state clearly in the text which compounds were identified in the samples, however they recommended the use of CZE if the profiling of phenolics in propolis, when it is limited only to phenolcarboxilic acids analysis.

Bee pollen is the male seed of a flower blossom collected by honey bees on their legs as they move from flower to flower, mixed with their digestive enzymes and some nectar, accumulating many flavonoids and phenolic acids [251]. In the hive, pollen is used as a protein source for the brood-rearing. To our knowledge, three studies have been carried out in relation to the phenolic content of pollen using CE.

Yang et al. [252] developed a MEKC-UV methodology to determine two flavonoids, isorhamnetin-3-O-neohesperidoside and typheneoside, in pollen typhae (pollen of several species of the genus Typhaceae, an important traditional Chinese medicine). Later on, the use of CZE coupled to ED [253] and MS detection [251] allowed the identification of 13 phenolic acids and flavonoids and 10 flavonoids, respectively, in various pollen samples. The CZE-ED method was validated in terms of repeatability, linearity, and accuracy and subsequently used for the analysis of the phenolic content of honeybee-collected pollen from natural and broken pine, buckwheat, corn, rape, papaver, camellia, basswood, Chinese gooseberry and mixed plant sources. The pollen samples were rich in pheno-

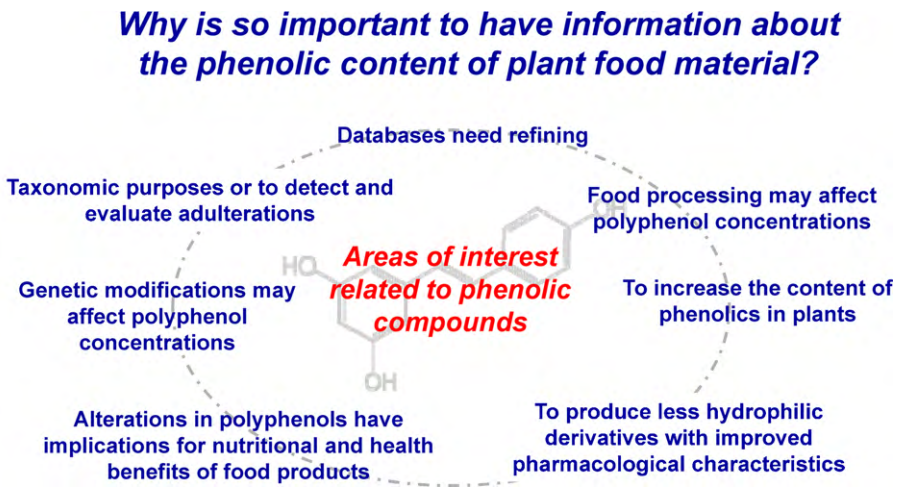

Fig. 4. Why is so important to have information about the phenolic content of plant food material? Usefulness of generated data about polyphenolic content in plant food matrices.

lic compoundss, particularly chrysin, rutin, baicalein, kaempferol, apigenin, vanillic acid and luteolin. Rape, Chinese gooseberry and papaver pollens contained the highest levels of the assayed compounds. The authors stated that the data presented was insufficient to identify unknown samples based on their phenolic profiles, needing additional samples and statistical methods to indicate possible floral markers for pollen.

A CE-ESI-TOF-MS method [251] allowed the identification of several phenolic compounds, mainly flavonoids and glucoside derivatives, in the honeybee-collected pollen from *Ranunculus petiolaris* HKB, a medicinal plant that grows in Durango, Mexico. The separation parameters as well as the MS conditions were systematically investigated. The employed conditions were as follows: 95 cm × 50 μm i.d. fused-silica capillary; 80 mM ammonium acetate buffer (pH 10.5); 30 kV voltage; sheath liquid, 2-propanol/water 60:40 (v/v) plus 0.1% (v/v) triethylamine at 6 μL/min; ESI 4 L/min at 130 °C of drying gas and 0.3 bar of nebulizing gas pressure; *m*/*z* 50–800 MS scan at a spectral rate of 1 Hz in the negative ion mode. Optimisation was carried out using the real sample. The identification of compounds was done without the use of standards due to the mass accuracy and isotopic pattern provided by TOF-MS, which allowed the determination of the elemental composition of the detected compounds.

5. Usefulness of generated data

After having a look at the previous sections of the current review, it seems quite clear that the determination of phenolic compounds is awaking a lot of interest from researchers, indeed phrases like the following one can be read quite often nowadays: "Widely distributed in the plant kingdom and abundant in our diet, plant phenols are today among the most talked about classes of phytochemicals". To answer the question of "why are phenolic compounds so interesting?" we can summarise several issues which have been studied in-depth during the last decade [254]:

- The levels and chemical structure of antioxidant phenols in different plant foods, aromatic plants and various plant materials.
- The probable role of plant phenols in the prevention of various diseases associated with oxidative stress, such as cardiovascular and neurodegenerative diseases and cancer.
- The ability of plant phenols to modulate the activity of enzymes, a biological action not yet understood.
- The ability of certain classes of plant phenols such as flavonoids (also called polyphenols) to bind to proteins.
- The stabilization of edible oils, protection from formation of off-flavours and stabilization of flavours.
- The anti-microbial activity.
- The bitter-tasting and the pungency of phenols.
- The preparation of food supplements.

From our point of view, the development and validation of methodologies for the determination of polyphenols are required. These methods could give us comprehensive information about the composition of the sample under study.

Having detailed information about the phenolic compounds which are present in an extract from plant food material, we could understand better the properties of that extract. All the compounds present in a particular sample will be responsible of its characteristics (antioxidant activity, anticancer activity, etc); therefore, it is not enough to have an idea about the major components of the sample, but about all the minor components as well.

Producing detailed data about the phenolic composition of a sample could help to refine the existing databases. Reliable data on the nutrient composition of foods consumed by people are critical in many areas – health assessment, the formulation of appropriate institutional and therapeutic diets, nutrition education, food and nutrition training, epidemiological research on relationships between diet and disease, plant breeding, nutrition labeling, food regulations, consumer protection, and agricultural goods and products, as well as for a variety of applications in trade, research, development, and assistance.

It is well-know that phenolic compounds appear to offer promising chances as chemical "markers" in biosystematic studies of plants. Essentially, the generally agreed requirements for a chemical character to be in use in taxonomy are as follows: chemical complexity and structural variation, physiological stability, widespread distribution and easy and rapid detection, and phenolic compounds match up well to these criteria.

All these areas of interest and the ones included in Fig. 4 try to point out the importance of the determination of this kind of analytes. CE methods can obviously help a lot in these areas giving complementary information to that achieved by other analytical platforms, such as HPLC or GC coupled to different detectors, and NMR, among others.

6. New trends and perspectives

Despite the very interesting results achieved so far about the antioxidant phenolic compounds from plant food material by cap-

illary electroseparation methods, there is no doubt about the fact that more potent CE methods will be developed in the near future giving answer to the necessity of the analyst to face complicated problems. It is expected that nanotechnology will play a main role in the evolution of CE, improving its results in terms of analysis time, selectivity, sensitivity, etc. Indeed, in the last 10 years CE has already undergone several transformations related to miniaturisation and undoubtedly, nowadays the use of minidevices is significantly increasing.

In that respect, Wang et al. [255] developed a pressurised CEC method with gradient elution to analyse different flavonoids in several corn samples; Polášek et al. [256] demonstrated that the addition of molybdate to the CE background electrolyte affect the selectivity of separation of polyhydric phenols; and Dong and et al. [257] used CZE with an electrode modified with vitamin B_{12}.

CE microchips constitute the first group or generation of μ-TAS (micrototal analysis systems) or lab-on-a-chip in the miniaturisation scene of food analysis [258]. This type of analytical technologies can be coupled to different detection systems [259], such as ED, laser induced fluorescence (LIF), MS, UV, surface plasmon resonance (SPR) sensor or chemical luminiscence (CL) [260].

This new methodology has been applied in several areas, like bioanalytical and clinical analyses, and environmental and food applications among others [258]. It allows the separation and detection of DNA, proteins and peptides, amino acids, nitroaromatics, carbohydrates, hydrazines and antioxidants (catechols and phenols) [261]. Several authors has developed CE-microchip methods to identify phenolic compounds in food samples, such as green tea [262], wine [263], pears and apples [264] and a commercial food sample (Country Gravy Mix) [265].

Novel nanomaterials with unique mechanical, geometrical, chemical and/or electronic properties will enlarge the potential of this technology for CE analysis, including microchip-CE, on-column concentration and clean-up applications.

Apart from the use of minidevices, microchips and novel nanomaterials, the use of MS as detection system is becoming mandatory. The number of applications of CE-MS in the analysis of phenolic compounds from plant food material is constantly increasing, showing the potential of this coupling and the different performance of the developed methods depending on the ionisation source and the mass analyser used. ESI is still one of the most versatile ionisation methods and is the natural method of choice for the detection of ions separated by CE. The trend is to use more and more sophisticated analysers, being triple-quadrupole (QQQ), TOF, quadrupole-time of flight (Q-TOF), fourier transform ion cyclotron resonance (FT-ICR), orbitrap (OT) and ion trap-orbitrap (IT-OT) those more powerful regarding the m/z range that can be covered, the mass accuracy and the achievable resolution. It is expected that new technological advances, as well as novel instrument configurations would make this technique more robust and useful for plant matrices analysis.

One of the most important limitations of CE is its sensitivity, which could be overcome using two different approaches: improving the on-line preconcentration strategies or using new CE interfaces. Both sheath liquid and sheathless interfaces have been proven to enable the coupling of CE with ESI-MS. For several reasons, the first category has been the most popular to date, however it is commonly acknowledged that such interfaces have much lower sensitivity than sheathless one. From our point of view, it is very likely that new and improved sheathless interfaces will be developed soon.

The fact of being nowadays in the omics era is relevant and has some influence in the food analysis as well. Terms such as genomics, transcriptomics, proteomics and metabolomics are quite used in science; however, another term should be defined, since it is getting more attention by the scientific community: Foodomics. It can be defined as a discipline that studies the Food and Nutrition domains through the application of omics technologies [266]. Thus, Foodomics would cover, for instance, the metabolomic study of foods toward compounds profiling, or new investigations on food functions via nutrigenomics or nutrigenetics approaches. In other words, it means that the application of omics technologies can be very helpful to carry out the comprehensive characterisation of food and even to understand the possible role of that foodstuff in the human health. Using this approach to study, for instance, plant food material, will result in a plethora of data that can be overwhelming in its abundance. For meaningful interpretation, the appropriate statistical tools must be employed to manipulate the large raw data sets in order to provide a useful, understandable, and workable format. Different multidimensional and multivariate statistical analyses and pattern recognition programs have been developed to distill the large amounts of data in an effort to interpret the complex information achieved from the measurements. Improvements are also expected in this field in the near future.

Meaningful interpretations of omic data are often limited by poor spatial and temporal resolution of the acquired data sets, and one way to remedy this is to limit the complexity of the samples being studied. An alternative approach is to implement multidimensional systems that may be classified in various ways. For example, based on the type of displacement used, such systems are either simultaneous or sequential. The latter is achieved using two or more separation processes, which occur in different media, under different conditions (for example LC-GC). Such processes may be conducted either on-line or off-line, and we expect that CE will be more used in this kind of bidimensional systems.

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