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Review

CE and CEC analysis of phytochemicals in herbal medicines

CE and CEC, due to their versatility and high efficiency, have attracted great interest in the analysis of phytochemicals in herbs and their preparations. Previously, we reviewed the analysis of phytochemical bioactive compounds by CE in 2006 (*Electrophoresis* 2006, *27*, 4808–4819) or CEC in 2010 (*Electrophoresis* 2010, *31*, 260–277). This review followed the previous studies and covered the literature published since 2006 for CE and 2009 for CEC (excluding those mentioned in the two previous reviews), which emphasized the development of CE and CEC techniques in phytochemical analysis. In addition, sample preparation and detection were also discussed.

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CE / CEC / Herbal medicines / Phytochemicals DOI 10.1002/elps.201100347

1 Introduction

CE and CEC are powerful analytical techniques that provide fast and efficient separation with low consumption of sample and reagent. A variety of molecules and particles (organic/inorganic, charged/uncharged, micro/macromolecules) can be successfully analyzed by CE and CEC. Due to their versatility and high efficiency, CE and CEC have attracted great interest of analysts in the analysis of phytochemicals in herbs and their preparations, and become alternative methods to the widely used HPLC. Previously, we reviewed the analysis of phytochemical bioactive compounds by CE [1] in 2006 and CEC [2] in 2010. This review will follow the previous studies and covers the literature published since 2006 for CE and 2009 for CEC (excluding those mentioned in the two previous reviews). Though Gotti reviewed CE analysis of phytochemicals recently [3], focussing on the application for different types of compounds, this review emphasized the development of CE and CEC techniques in phytochemical analysis. In addition, sample preparation and detection were also discussed.

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Abbreviations: **C^4D,** capacitively coupled contactless conductivity detection; **CCD,** central composite design; **CL,** chemiluminescence; **ECD,** electrochemical detection; **IS,** internal standard; **LLE,** liquid–liquid extraction; **pCEC,** pressurized CEC; **$Ru(bpy)_3^{2+}$,** Tris-(2,2′-bipyridyl) ruthenium (II)

2 Sample preparation

2.1 Extraction

Generally, extraction should be performed before CE and CEC analysis of phytochemicals in herbal medicines. Therefore, extraction, which could greatly influence the repeatability and accuracy of analysis, is the first crucial step. Ultrasonic extraction was the most frequently used method due to its efficiency and easy manipulation. Indeed, it was employed in about two-thirds (180 out of 271 articles) of cited references (Supporting Information Tables 1–7) [4–271]. Other conventional extraction methods included reflux [6, 14, 15, 21, 45, 74, 84, 87, 97, 117, 121, 123, 131, 134, 157, 162, 164, 169, 171, 172, 176, 179, 182–184, 205, 212, 227, 235, 236, 259], Soxhlet extraction [23, 89, 91, 128, 131, 244], heating extraction [22, 39, 51, 56, 64, 94, 127, 158, 161, 194, 224, 253, 262], and maceration [22, 35, 43, 62, 114, 224]. Pressurized liquid extraction (PLE) or accelerated solvent extraction, with the advantages of short extraction time, low-solvent consumption, high extraction efficiency, and automated sample handling, was utilized for the sample preparation to enhance the extraction efficiency [12, 68, 200,

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Colour Online: See the article online to view Fig. 2 in colour.

211, 237]. In addition, microwave-assisted extraction [100] and far infrared-assisted extraction [109], which could significantly decrease the extraction time to few minutes with high extraction efficiency, have also been employed for the extraction of phenolic compounds from *Eriobotrya japonica* [100] and *Lycium barbarum* [109], respectively.

Organic solvents and deionized water were usually used for the extraction based on physicochemical property of the analytes. Sometimes, proper concentration may be necessary because of high-concentration detection limit of CE and CEC. Then, the residue was redissolved or diluted with running buffer, deionized water, or organic solvents before CE and CEC analysis.

2.2 Preconcentration

Low-concentration sensitivity, due to the small injection volume and short optical path length, is one of the major limitations of CE and CEC. Therefore, many offline or online preconcentration techniques were developed. Liquid–liquid extraction (LLE) [4, 7, 8, 25, 35, 43, 48, 50, 63, 88, 131, 134, 137, 139, 140, 142, 167, 168, 192, 199, 221] and solid-phase extraction (SPE) [69, 88, 94, 103, 141, 148, 152, 189, 205, 215] were commonly used offline preconcentration techniques. A variety of organic solvents and extraction cartridges could be chosen to enrich the trace analytes and remove salts, lipids, pigments, and other potentially interfering compounds. In addition, cloud-point extraction, which is based on the ability of nonionic surfactants in aqueous solution to become turbid and separate into a surfactant-rich phase when heated to the cloud-point temperature, was applied to enrich triptonide from *Tripterygium wilfordii* for MEKC analysis [246]. However, offline preconcentration methods had the disadvantages of time consumption and labor intension.

Online preconcentration is a useful technique that can be performed just by injecting a large volume of sample solution using hydrodynamic or electrokinetic methods without instrument modification, and the analytes can be focused into a minimum volume inside the capillary. Online preconcentration in CE has been reviewed during the past years [272–276]. Field-amplified sample stacking (FASS) [35], field-amplified sample injection (FASI) [5, 7, 8, 24, 34, 37, 116, 145, 187, 196, 220, 244, 247], large-volume sample stacking (LVSS) [52, 112, 201, 241], ITP [110, 112], dynamic pH junction [200], and sweeping [207, 210, 238, 239] were employed for online preconcentration of phytochemicals in CE and CEC. Recently, a new online preconcentration technique called micelle to solvent stacking (MSS) was proposed by Quirino [277]. The focusing effect relies on the reversal in the effective electrophoretic mobility at the boundary zone between the micellar sample matrix and the BGE modified with organic solvent. The technique, by which up to 50-fold improvement in concentration sensitivity could be achieved, has been successfully applied to online preconcentration of alkaloids in CE analysis [45, 197]. Furthermore, the combination of preconcentration techniques, such as field-amplified sample injection – sweeping [198] and anion-selective electrokinetic injection and water plug – sweeping with reverse migrating micelles (ASIW–sweep–RMM) [209], was also reported.

3 Separation

3.1 Optimization of separation

For CE and CEC analysis, composition of BGE or mobile phase and operating conditions should be carefully investigated during the method development. The influence of several parameters, including buffer type and concentration, pH, additives, voltage, and temperature, has been discussed in our previous reviews [1, 2]. Besides, micelle and microemulsion composition for MEKC and MEEKC (Supporting Information Tables 5 and 6) [187–262], as well as sample matrix and injection parameters for online preconcentration [5, 7, 8, 25, 34, 37, 52, 112, 187, 196–198, 207, 209, 220, 238–240, 244, 247] should also be considered.

Various strategies such as univariate design, factorial design, and response surface methodology have been devised to aid the optimization of CE and CEC conditions. Their procedures and applicability were discussed in our previous reviews [1, 2, 278]. Generally, univariate design is the simplest and most commonly used (Supporting Information Tables 1–7) [4–271], but it is time consuming and labor intensive, and most importantly it could not reflect the interaction of investigated factors [278]. Therefore, triangle and tetrahedron optimization methods based on the interaction of different factors were adapted for the selection of BGE in CE fingerprint development [182, 183]. Chemometrics-based techniques such as factorial design [4, 48, 199, 237, 249, 262] and response surface methodology [160, 217] were also employed. Factorial design of 3^2 and 2^3 was used for the optimization of CE analysis of phenolic acids in exotic fruits [48] and butenolides in *Piper malacophyllum* [249], respectively. Orthogonal design, one kind of fractional factorial design, has been employed for the optimization of CE analysis of alkaloids [4], benzoic acid compounds [199], and iridoid glycosides [237] in herbs. Uniform design that allocates experimental point scattering uniformly and regularly in the experimental domain could reduce experimental trials when the number of factors and levels increases. To develop MEKC fingerprint of complex herbal prescription Sheng-Mai-San, a six-factor, three-level orthogonal design was used to screening significant factors based on the preliminary experiments. Concentrations of SDS and borate identified as important factors were further optimized by sequential uniform design. With three sequential steps, peak capacity and separation were evidently improved step by step [262]. Central composite design (CCD), one of the most common designs generally used in response surface modeling, allows the determination of both linear and quadratic models [278]. In order to develop MEKC

fingerprint of *Scutellaria baicalensis*, five parameters that displayed more pronounced effects on the separation, including concentration of borate and phosphate, concentration of SDS, proportion of ACN, and 2-propanol, were optimized by CCD using the resolutions of main copossessing peaks as the responses. Finally, a good separation was achieved based on CCD-aided optimization [217]. Similarly, CZE of eleven active components in Resvis XR® effervescent tablet was also optimized by CCD [160].

3.2 Separation techniques

Different CE modes including CZE (Supporting Information Tables 1–4) [4–186], MEKC and MEEKC (Supporting Information Tables 5 and 6) [181, 187–262], and CEC (Supporting Information Table 7) [225, 263–271] have been employed for the analysis of phytochemicals in herbal medicines. The analytes were alkaloids (Supporting Information Tables 1, 5, and 7) [4–47, 187–197, 263, 264], phenolic compounds such as phenolic acids, flavonoids, coumarins, lignans and quinones (Supporting Information Tables 2, 5, and 7) [48–124, 198–235, 265, 266], terpenoids (Supporting Information Tables 3 and 6 [125–132, 236–246]), steroids, nucleosides and saccharides (Supporting Information Table 3) [133–144], multiple components and fingerprint (Supporting Information Tables 4, 6, and 7) [153–186, 251–262, 268–271]. Besides, natural resources, sample preparation, preconcentration, and analysis optimization, as well as separation condition and detection were also summarized in Supporting Information Tables 1–7 [4–271].

3.2.1 CZE

CZE has been widely applied to the separation of not only charged compounds (e.g. alkaloids, phenolic acids), but also some neutral molecules such as saccharides and phenolic glycosides, in which the charge can be created by complexation of vicinal hydroxy groups with *cis*-configuration and borate anions (Supporting Information Tables 1–4). Furthermore, NACE using organic solvents, which increase the solubility of less polar compounds and improved the selectivity, instead of water widened the application of CZE. The commonly used organic solvents for NACE include ACN [10–12, 16, 18, 25, 34, 38, 39, 43, 44, 69], methanol [10–12, 16, 25, 29, 33, 34, 38, 39, 43, 44, 47, 52, 69, 71, 179, 180, 186], ethanol [11] and 2-propanol [18]. Generally, organic solvents generate low electric current and Joule heat because of their low conductivity. Therefore, high voltages can be applied within short capillary to improve the analysis speed and/or peak efficiency. In addition, due to high volatility and low surface tension of organic solvents, NACE appears to be ideally suited for online coupling with MS [11, 12, 16, 25, 34, 43]. NACE was mainly applied to the determination of hydrophobic alkaloids [10–12, 16, 18, 25, 29, 33, 34, 38, 39, 43, 44, 47] in herbal medicines, whereas the analysis of phenolic acids [52] and flavonoids [69, 71] was also reported.

Besides buffer type, concentration, pH, and organic modifier, other additives also play an important role in CZE analysis and make it more versatile. A variety of additives were employed to alter EOF and improve selectivity. CD, usually used as chiral selector, was widely used for enantiomeric separation of phytochemical compounds [19, 65, 88, 133, 141] and improving the separation of analytes [17, 51, 70, 80, 89, 102, 131, 146, 147, 153, 159, 163, 164, 176, 185]. Application of various CD derivatives, such as α-CD [89], β-CD [17, 51, 65, 70, 80, 102, 131, 146, 147, 159, 163, 164, 176, 185], dimethyl-β-CD [19], carboxymethyl-β-CD [88], 2,6-di-*O*-methyl-β-CD [89], methyl-β-CD [133], sulfobutylether-β-CD [133], and hydroxypropyl-β-CD [141, 153], were also reported. Ionic liquids (ILs), which are salts in the liquid state at room temperature, have been employed in CE analysis as BGE or additive [5, 24, 70, 90] because they are environmental benign, nonvolatile, nonflammable, thermal stable, and good solvents for many inorganic and organic materials. Cationic surfactants, such as CTAB [149, 153] and tetradecyltrimethyl ammonium bromide (TTAB) [149], could be used to reverse EOF so as to improve the separation of organic acids and shorten migration time. In addition, BSA [20], Cu(II)-L-lysine complex [21], cucurbit[7]uril [145], hydroxypropyl cellulose (HPC) [37], hydroxyethylcellulose (HEC) [110], and PEG [152] were also employed as additives in CZE of phytochemicals.

On the other hand, internal standard (IS) was usually necessary in order to increase the repeatability and accuracy of CE analysis. Therefore, the selection of IS is very important for ensuring the accuracy of quantification. Especially, the stability of IS may influence quantitative analysis unwarily. For CZE analysis of 15 flavonoids in *Epimedium*, rutin was selected as IS at the beginning. However, the quantitative results were much higher than those obtained by HPLC and UPLC due to the degradation of rutin in sample solution. Using stable daidzein as IS, 15 flavonoids could be determined accurately [68]. CZE of phytochemicals in herbal medicines was summarized in Supporting Information Tables 1–4.

3.2.2 MEKC and MEEKC

MEKC and MEEKC introduce micelles or microemulsions into BGE as pseudo-stationary phase, and the separation mechanism contains partitioning of analytes between pseudo-stationary phase and continuous phase, as well as electrophoretic mechanism. Both charged and neutral compounds can be analyzed simultaneously by MEKC or MEEKC. The selectivity can be modulated not only by varying buffer type, concentration, pH, and organic modifier, but also by optimizing composition of micelles and microemulsions.

SDS is the most frequently used surfactant to form micelle in MEKC. Using a BGE consisting of 7.5 mM sodium tetraborate, 60 mM SDS, 4 mM urea, 20% ACN, and 0.5 mM $CaCl_2$, essential oils that were rarely dealt with CE

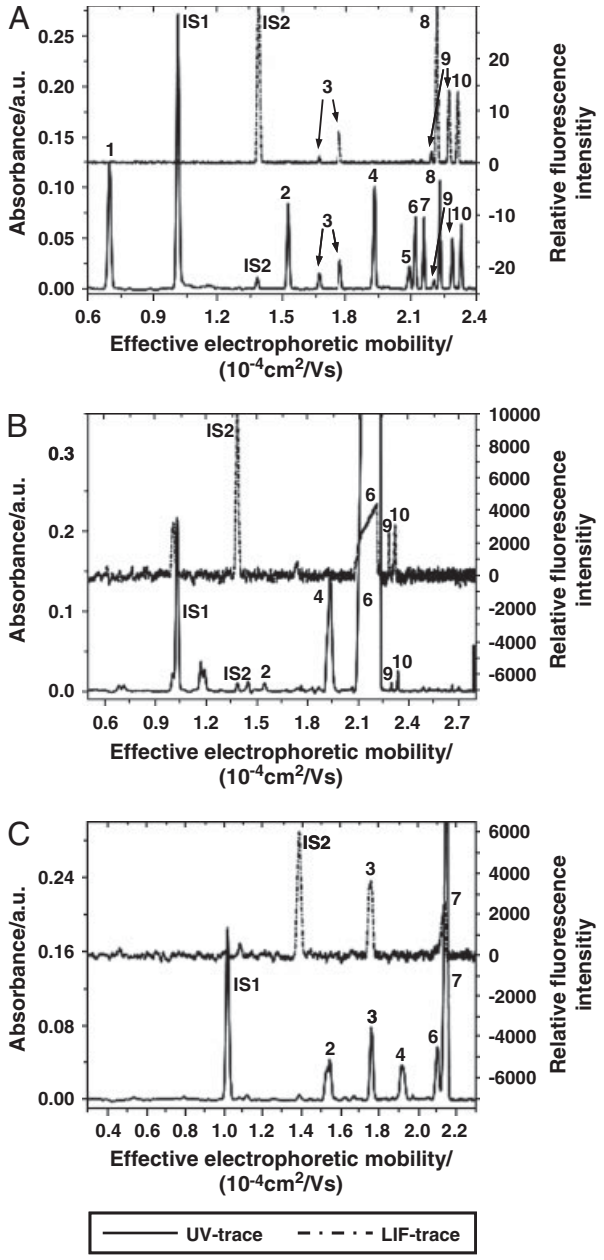

Figure 1. Electropherograms of (A) mixed standards, (B) commercial *Sassafras albidum* oil and (C) commercial *Myristica fragrans* oil (adapted from [250] with permission of Wiley). 1, Piperonal; 2, eugenol; 3, *cis*-/*trans*-isoeugenol; 4, methyleugenol; 5, thymol; 6, safrole; 7, myristicin; 8, asaron; 9, *cis*-/*trans*-isosafrole; 10, anethol; IS1, methyl-4-cyanobenzoate; IS2, acridone.

could be analyzed by MEKC (Fig. 1) [250]. SDS could form reverse micelles when dissolved in nonpolar solvents, in which the polar groups present in surfactant constitute inner core of micelles and the hydrocarbon chains form outer layer. The reverse micelle systems are similar to water-in-oil emulsion systems, and had been used in BGE for reverse MEKC analysis of flavonoids in *Alpinia katsumadai* and Kuaiwei tablet [204]. Besides, sodium cholate (SC) [206, 225], sodium deoxycholate (SDC) [248], Brij-35 [238], Tween-20 [187, 197, 231], polysodium *N*-undecenoxycarbonyl-L-leucinate [188, 189], lauric acid [192, 233], tetradecyltrimethyl ammonium bromide [193], as well as mixed surfactants of SDS and sodium cholate [212, 218] were also used for MEKC analysis of phytochemicals.

Microemulsions are stable, isotropically clear solutions consisting of nanometer-size oil droplets suspended in aqueous buffer, stabilized by a surfactant and a cosurfactant [279]. Cao et al. conducted a series of experiments focusing on MEEKC analysis of phenolic acids and diterpenoids in *Salvia miltiorrhiza* [201, 202, 230, 254], saponins in *Panax notoginseng* [239, 241], and flavonoids in Radix Astragali. [207, 230]. Several microemulsion systems including oil-in-water [201, 207, 230, 239, 241, 254], water-in-oil [254], and ionic liquid-in-water [202] were investigated. The use of nonionic [201, 239] or mixed anionic and cationic surfactants [207], as well as surfactant-coated single-walled carbon nanotubes as additives [230] was also reported. The applications of MEKC and MEEKC in the analysis of phytochemicals in herbal medicines were summarized in Supporting Information Tables 5 and 6.

3.2.3 CEC

CEC is a high-performance liquid-phase separation technique carried out in columns packed with media containing ionizable functionalities, which utilizes flow driven by electroosmosis and enables to achieve significantly improved performance compared with HPLC [280]. It is usually considered as a hybrid technique that possesses properties of both CE and LC, which combines high efficiency of CE (movement of solutes by electrical forces) and high selectivity of LC (chromatographic interactions). Based on the differences of column format, three modes of CEC, i.e. granular packed CEC, monolithic CEC, and open-tubular CEC, are distinguished. All three modes of CEC have been employed for the analysis of phytochemicals [2, 281, 282] (Supporting Information Table 7). Their characteristics have been reviewed [2, 283].

Monoliths are currently popular stationary phases for electrochromatography and are being rapidly developed. There are several reviews [280, 284–286], and a plethora of articles about the preparation and use of monolithic materials in separation science and particularly in CEC. Besides widely used for enantioseparations, monolithic stationary phases have also been employed for phytochemical analysis (Supporting Information Table 7). CEC for quantitative analysis of bioactive naphthoquinones in *Eleutherine americana* was developed and compared with MEKC and HPLC [225]. The results showed that both CEC and MEKC were well comparable to those obtained by HPLC. But CEC on a polymeric methacrylate-based monolith with strong cationic properties could successfully separate two enantiomers, eleutherin, and isoeleutherin, whereas MEKC failed.

Generally, flow of mobile phase or buffer in conventional CEC is driven through a capillary column by an

electric field. However, high applied voltage across the column in ''pure'' CEC format often causes Joule heating, which leads to bubble formation that can result in dryout of the column and disruption of the current [287]. It is also difficult to achieve quantitative sample introduction using ''dip in'' method, electrokinetic, and hydrodynamic modes [288]. In addition, a complete separation of all herbal compounds under isocratic conditions was usually not possible because of the wide hydrophobicity of phytochemicals, and gradient elution mode was also used as an online sample concentration method to improve the detection sensitivity [289]. Therefore, pressurized CEC (pCEC), or electrokinetic high-performance liquid chromatography (eHPLC), with EOF combining hydraulic pressure as its driving force has gained more attention [290–292]. In this novel separation technique, both solvent gradient elution and quantitative injection in pCEC can be conveniently realized as in HPLC. A much higher theoretical plate number was obtained using pCEC rather than μHPLC and HPLC. In addition, the retention time of flavone compounds (quercetin, isorhamnetin, and kaempferol) separated by pCEC was nearly only half of that in HPLC under similar pressure [293]. Due to the advantages of pCEC, its application in phytochemical analysis has being steadily increased (Supporting Information Table 7). In addition, CEC has been developed for the analysis of glycoconjugates [294], and herbal extract as one of the 2-D chromatography [295]. Electrochromatography was also used for the preparation of tea polyphenols and caffeine [296]. Supporting Information Table 7 summarizes the CEC analysis of phytochemicals.

3.2.4 2-D separation

For complex samples, 2-D CE separation techniques can provide higher separation power and peak capacity, which has attracted analytical chemists' great interest in recent years. A new sweeping with electrokinetic injection preconcentration scheme coupled with a heart-cutting 2-D MEKC-CZE separation was developed for the analysis of *Leonurus japonicus* [297]. As shown in Fig. 2, the sample was separated in first dimension by MEKC, and then only flavonoid fraction (fraction b) of the first-dimensional separation was transferred into the second-dimensional capillary by pressure and separated by CZE. The sample was well cleaned up by the first-dimension MEKC and the interfering components were not detected [297]. A continuous 2-D open-tubular ion exchange-RP monolithic column CEC system was also constructed for the analysis of *Gastrodia elata* [298]. The first-dimensional separation by open-tubular ion exchange column could significantly increase the analysis speed, whereas the second dimension using monolithic column could provide high peak capacity to fulfill the requirement of complex sample analysis [298].

The combination of LC with CE or CEC has also been reported, mostly in offline mode. Cortex Phellodendri

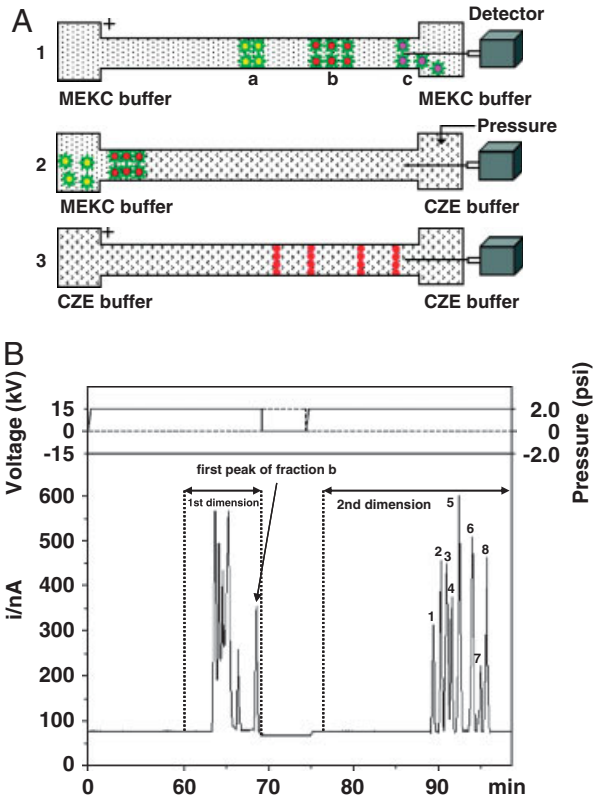

Figure 2. Scheme of hearting cutting 2-D MEKC-CZE separation (A) and (B) electropherogram of flavonoids in the *L. japonicus* (adapted from Ref. [297] with permission of American Chemical Society). Step 1: MEKC separation of sample in the first dimension; Step 2: elimination of interfering fractions and return of the fraction of interest (fraction b) to the inlet end of the capillary; Step 3: CZE separation of the purified sample in the second dimension. The pink circle, yellow circle, and red circle represent the components in *L. japonicus* sample; the star represents the SDS micelle. 1, Phlorizin; 2, kaempferol; 3, hesperetin; 4, apigenin; 5, rutin; 6, hyperoside; 7, quercitrin; 8, quercetin.

extract had been analyzed by micro strong cation exchange LC and RP pressurized capillary electrochromatography (μ-SCXLC/RP-pCEC). The results showed that 2-D chromatographic system had higher resolution and larger peak capacity compared with 1-D LC [295]. Similarly, 2-D LC-CE had also been employed for the analysis of phenolic compounds in olive oil [299] and green tea [300].

4 Detection

4.1 UV–vis detection

As a standard detector of many commercial instruments, UV–vis absorption is currently the most popular detection for CE and CEC of phytochemicals due to its nearly universal detection nature (Supporting Information Tables 1–7). Even for non-UV absorbing analytes such as saccharides, it can be performed after derivatization of analytes

[137–144, 147]. However, the major deficiency of UV–vis detection is the limited sensitivity due to the short optical path length. One strategy to improve sensitivity is to use extended path length flow cells, such as bubble cell [301, 302] and Z-shaped cell [302]. But they are seldom reported in CE and CEC of phytochemicals [61, 258].

4.2 LIF

LIF is one of the most sensitive detections in CE. It allows extremely sensitive detection of fluorescently labeled compounds. However, only few compounds have native fluorescence, and hence derivatization with a suitable fluorogenic or fluorescent reagent to produce a fluorescent adduct is necessary. To develop CE-LIF methods for the analysis of ephedrine and pseudo-ephedrine in *Ephedra* herb and its preparations, derivatization was carried out precapillary [190] or in-capillary [191]. Unfortunately, the species that could be derivatizated are limited, thus indirect LIF may be an alternative. CE with indirect LIF was developed for the determination of six coumarins and flavonoids in *Sophora japonica* and *Sarcandra glabra*. The analytes were detected by displacement of a certain fluorophore, fluorescein sodium, which is added to BGE and excited when passing through the detection window to yield a steady fluorescence background signal [86].

4.3 Chemiluminescence detection

Chemiluminescence (CL) is a highly sensitive detection method that is based on the production of electromagnetic radiation (UV, visible, or infrared) by a chemical reaction. CL has been satisfactorily used for the analysis of a variety of species that can participate in CL process directly or indirectly. Luminol CL reaction is one of the most commonly used methods in CE-CL system. It is based on the reaction of luminol or its derivative with oxidant in alkaline medium in the presence of a catalyst, and emits light in the wavelength range of 425–435 nm [303]. Luminol CL detection has been used for the analysis of antioxidants in *Astragalus* [125] and injection of puerarin [77]. ECL is a sort of CL, in that a light emission is produced by a electrochemical reaction, and a Tris-(2,2′-bipyridyl) ruthenium (II) ($Ru(bpy)_3^{2+}$) reaction was usually involved. $Ru(bpy)_3^{2+}$-based ECL detection was mainly concerned with the determination of alkaloids containing tertiary amine group [17, 24, 26, 27, 30, 32, 36] because tertiary amine has high enhancement effect on $Ru(bpy)_3^{2+}$ ECL [304].

4.4 Electrochemical detection

Electrochemical detection (ECD) is an attractive alternative to optical detection which is ideal for small dimensions of capillaries used in CE and it would not be limited by the short optical path length. The analytes that had no UV–vis absorption or fluoresce could be detected using ECD without derivatization. Usually, there are three modes of ECD, i.e. amperometry, conductimetry, and potentiometry. Among them, the first two modes were used more frequently for phytochemical analysis.

Amperometric detection (AD) is the most extensively reported ECD coupled with CE, which is accomplished by applying a constant potential to working electrode and measuring the current as a function of time. The applied potential facilitates redox reactions of analytes, whereas current output is proportional to the concentration of analytes [305]. Usually, an end-column wall-jet configuration without decoupling is employed using the capillaries of typically 25 μm id (instead of 75 or 50 μm capillaries used in optical detection). However, only electroactive compounds could be detected by amperometric detection, and hence it was usually applied to the detection of phenolic compounds such as flavonoids and phenolic acids in herbal medicines to improve the sensitivity [49, 55, 65, 67, 81, 82, 85, 92, 95–101, 108, 109, 113, 115, 118, 119, 121, 123, 124, 134, 154, 157, 216].

Conductometric detection measures the conductivity between two inert electrodes. The presence of analytes in BGE would cause a detectable change in conducted current [306]. It is not selective and therefore well suited as a universal detection. Conductometric detection can be performed in contact and contactless form. The contactless form, especially capacitively coupled contactless conductivity detection (C^4D), has been obtained more and more attention in recent years. For C^4D, there is no direct contact between measuring electrodes and solution, and hence interference of separation field with detector electronics and corrosion or fouling of the electrodes can be eliminated [307]. C^4D was approximately seven times and two times more sensitive compared with indirect and direct UV detection, respectively [79].

4.5 MS detection

Hyphenation of CE and MS is a powerful technique for chemical identification and confirmation. The analytes are transferred from liquid phase of CE to gas phase for MS via interfaces and many online interfaces involving sheath liquid, sheathless, and liquid junction have been developed. Although sheath liquid may reduce the sensitivity due to dilution effect and additional background noise, almost all CE-MS applications of phytochemicals in recent years adapted this interface [9, 11, 12, 16, 25, 34, 43, 66, 103, 106, 111, 114, 117, 136, 158, 188, 189, 233] because it allowed the postcolumn addition of chemicals to improve ESI characteristics and ionization efficiency.

On the other hand, volatile electrolyte buffer is essential for CE-MS to reduce background noise and not to suppress ionization efficiency of analytes in ESI. Therefore, the most

widely used BGEs for CE-MS are free acetic acid [11, 16, 34, 43], formic acid [11, 136], and their ammonium salts [9, 11, 12, 16, 25, 34, 43, 106, 111, 114, 158]. However, for some compounds such as flavonoids, these BGEs could not provide sufficient separation. Hence, boric acid–ammonia buffer system was also used [66, 103, 117]. Though the use of nonvolatile surfactant (e.g. SDS) is usually restricted to MS, some new types of surfactants such as polysodium *N*-undecenoxycarbonyl-L-leucinate (poly-L-SUCL) [188, 189] and lauric acid [233], which are compatible with ESI-MS, were introduced for MEKC-MS analysis.

5 Concluding remarks

Nowadays, CE and CEC have definitively established a strong position in phytochemical analysis of herbal medicines due to their high efficiency and great resolution. Many efforts on preconcentration and more sensitive detection had been made in order to improve sensitivity, which is one of the major drawbacks of CE and CEC. Various separation modes made CE and CEC to be powerful tools for phytochemical analysis.

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6 References

[1] Li, P., Li, S. P., Wang, Y. T., *Electrophoresis* 2006, *27*, 4808–4819.

[2] Yang, F. Q., Zhao, J., Li, S. P., *Electrophoresis* 2010, *31*, 260–277.

[3] Gotti, R., *J. Pharm. Biomed. Anal.* 2011, *55*, 775–801.

[4] Liu, H., Wen, Y., Luan, F., Gao, Y., *Anal. Chim. Acta* 2009, *638*, 88–93.

[5] Hu, X., Cui, S., Liu, J. Q., *Chromatographia* 2010, *72*, 993–997.

[6] Song, J. Z., Han, Q. B., Qiao, C. F., But, P. P. H., Xu, H. X., *Phytochem. Anal.* 2010, *21*, 137–143.

[7] Li, J. M., Jiang, Y., *Chin. J. Chin. Mater. Med.* 2008, *33*, 1684–1687.

[8] Li, C., Jiang, Y., *Chin. J. Chin. Mater. Med.* 2010, *35*, 3287–3290.

[9] Arráez-Román, D., Zurek, G., Bäßmann, C., Segura-Carretero, A., Gutiérrez, A. F., *Electrophoresis* 2008, *29*, 2112–2116.

[10] Wang, S., Zhang, Z., He, L., Li, H., *Anal. Lett.* 2010, *43*, 1534–1542.

[11] Buchberger, W., Gstö Ttenmayr, D., Himmelsbach, M., *Electrophoresis* 2010, *31*, 1208–1213.

[12] Chen, J., Zhao, H., Wang, X., Lee, F. S. C., Yang, H., Zheng, L., *Electrophoresis* 2008, *29*, 2135–2147.

[13] Gao, X., Li, F., Qiao, Y., *Chin. J. Chin. Mater. Med.* 2010, *35*, 158–161.

[14] Li, W., Song, F. R., Liu, Z. Q., Liu, S. Y., *Chemical. Res. Chin. Univ.* 2008, *24*, 162–166.

[15] Li, W., Song, F. R., Liu, Z. Q., Liu, S. Y., *Acta Pharm. Sin.* 2008, *43*, 191–194.

[16] Sturm, S., Seger, C., Stuppner, H., *J. Chromatogr. A* 2007, *1159*, 42–50.

[17] Li, J., Chun, Y., Ju, H., *Electroanalysis* 2007, *19*, 1569–1574.

[18] Yuan, B., Zheng, C., Teng, H., You, T., *J. Chromatogr. A* 2010, *1217*, 171–174.

[19] Jiang, T. F., Lv, Z. H., Wang, Y. H., *J. Anal. Chem.* 2007, *62*, 85–89.

[20] Ye, N., Gu, X., Luo, G., *J. Chromatogr. Sci.* 2007, *45*, 246–250.

[21] Li, F., Ding, Z., Cao, Q. E., *Electrophoresis* 2008, *29*, 658–664.

[22] Jing, H., Guo, H., Wang, Z., Wang, M., Zhang, B., *Chin. J. Chin. Mater. Med.* 2009, *34*, 980–983.

[23] Huang, B. M., Yao, C. W., Wang, Z. G., Mo, J. Y., *Acta Sci. Nat. Univ. Sunyatseni* 2008, *47*, 71–73.

[24] Gao, Y., Xu, Y., Han, B., Li, J., Xiang, Q., *Talanta* 2009, *80*, 448–453.

[25] Ganzera, M., Krüger, A., Wink, M., *J. Pharm. Biomed. Anal.* 2010, *53*, 1231–1235.

[26] Deng, B., Xie, F., Li, L., Shi, A., Liu, Y., Yin, H., *J. Sep. Sci.* 2010, *33*, 2356–2360.

[27] Deng, B., Ye, L., Yin, H., Liu, Y., Hu, S., Li, B., *J. Chromatogr. B* 2011, *879*, 927–932.

[28] Fakhari, A. R., Nojavan, S., Ebrahimi, S. N., Evenhuis, C. J., *J. Sep. Sci.* 2010, *33*, 2153–2159.

[29] Chen, Q., Li, P., Zhang, Z., Li, K., Liu, J., Li, Q., *J. Sep. Sci.* 2008, *31*, 2211–2218.

[30] Ren, X., Ma, Y., Zhou, M., Huo, S., Yao, J., Chen, H., *Chin. J. Chromatogr.* 2008, *26*, 223–227.

[31] Patnala, S., Kanfer, I., *J. Pharm. Biomed. Anal.* 2008, *48*, 440–446.

[32] Zhou, M., Ma, Y. J., Ren, X. N., Zhou, X. Y., Li, L., Chen, H., *Anal. Chim. Acta* 2007, *587*, 104–109.

[33] Zhu, Y., Chen, Q., Zeng, A., Li, P., *Chromatographia* 2010, *71*, 447–454.

[34] Wang, S., Qu, H., Cheng, Y., *Electrophoresis* 2007, *28*, 1399–1406.

[35] Fan, X., Tian, J., Li, X., Sun, H., *Chem. Bull.* 2008, *71*, 453–456.

[36] Yin, J., Xu, Y., Li, J., Wang, E., *Talanta* 2008, *75*, 38–42.

[37] Hou, X., Deng, D., Wu, X., Lv, Y., Zhang, J., *J. Chromatogr. A* 2010, *1217*, 5622–5627.

[38] Chen, Q., Li, P., Cheng, F., Li, B., Wu, S., He, J., *Chromatographia* 2009, *69*, 1443–1446.

[39] Li, Y. H., Zhang, Z., Lu, W., He, L. C., *Acad. J. Xi'an Jiaotong Univ.* 2010, *22*, 7–13.

[40] Zhang, X. M., Liu, X. P., Li, H., *J. Chin. Med. Mater.* 2007, *30*, 97–99.

[41] Zhang, G. Q., Lü, L., Zhao, L., *Acad. J. Second Mil. Med. Univ.* 2008, *29*, 108–110.

[42] Tong, Z. Q., Gao, J. Y., Chen, B. Y., *Chin. Tradit. Herb. Drugs* 2010, *41*, 725–727.

[43] Sturm, S., Shinneri, J., Greger, H., Stuppner, H., *Electrophoresis* 2008, *29*, 2079–2087.

[44] Li, Y. Q., Chen, X. G., Qi, Y. X., Li, K., Jia, B. X., Liu, C. H., Cao, M. L., *Chin. J. Chin. Mater. Med.* 2007, *32*, 1992–1995.

[45] Yin, X. F., Li, Z., Zhang, S. H., Wu, C. X., Wang, C., Wang, Z., *Chin. Chem. Lett.* 2011, *22*, 330–333.

[46] Li, M., Zhou, J., Gu, X., Wang, Y., Huang, Y. J., Yan, C., *J. Sep. Sci.* 2009, *32*, 267–274.

[47] Wang, Y. W., Yu, K., Cheng, Y. Y., *Chin. Pharm. J.* 2007, *42*, 935–937.

[48] Fukuji, T. S., Tonin, F. G., Tavares, M. F. M., *J. Pharm. Biomed. Anal.* 2010, *51*, 430–438.

[49] Chu, Q. C., Zhang, D. L., Zhang, H. T., Ye, J. N., *Chin. Chem. Lett.* 2010, *21*, 217–220.

[50] Li, F., Cao, Q. E., Ding, Z., *J. Chromatogr. Sci.* 2007, *45*, 354–359.

[51] Wang, X., Zheng, W., Xie, G., Qiu, M., Jia, W., *Chin. J. Chin. Mater. Med.* 2009, *34*, 189–192.

[52] Li, L. J., Feng, J., Cheng, H., Chen, Q. F., Zhong, Z. H., Kong, H. X., Wu, J. L., *Chin. J. Anal. Chem.* 2007, *35*, 401–404.

[53] Liu, X., Zhang, J., Chen, X., *J. Chromatogr. B* 2007, *852*, 325–332.

[54] Qiao, C., Zhao, L., Jiang, S., Song, P., *J. Liq. Chromatogr. Relat. Technol.* 2007, *30*, 2819–2833.

[55] Zhang, L., Dong, S., Yang, Z., Wang, Q., He, P., Fang, Y., *J. Pharm. Biomed. Anal.* 2008, *48*, 198–200.

[56] Cui, Y., Ll, Y., Shi, W., Yang, M., Zhao, X., Xia, Z., *Chin. J. Chromatogr.* 2007, *25*, 686–689.

[57] Başkan, S., Öztekin, N., Erim, F. B., *Food Chem.* 2007, *101*, 1748–1752.

[58] Li, Y. L., Zheng, P., Yan, Y., Yang, F., *J. South. Med. Univ.* 2009, *29*, 551–552.

[59] Liu, Y., Li, W., Ling, X., Lai, X., Li, Y., Zhang, Q., Zhao, Y., *Chromatographia* 2008, *67*, 819–823.

[60] Zheng, C. Y., Liu, S. M., Li, H. T., Shi, Z. H., Ping, W. X., *Chin. Pharm. J.* 2008, *43*, 783–785, 800.

[61] Kočevar, N., Glavač, I., Injac, R., Kreft, S., *J. Pharm. Biomed. Anal.* 2008, *46*, 609–614.

[62] Ren, Z. Y., Zhang, Y., Shi, Y. P., *Talanta* 2009, *78*, 959–963.

[63] Liu, X. H., Zhang, Y. C., Li, J. S., Wang, M., Wang, L. J., *Chin. Pharm. J.* 2010, *45*, 464–467.

[64] Gavrilin, M. V., Senchenko, S. P., *Pharm. Chem. J.* 2009, *43*, 582–584.

[65] Zhang, S., Dong, S., Chi, L., He, P., Wang, Q., Fang, Y., *Talanta* 2008, *76*, 780–784.

[66] Sawalha, S. M. S., Arráez-Román, D., Segura-Carretero, A., Fernández-Gutiérrez, A., *Food Chem.* 2009, *116*, 567–574.

[67] Gong, W., Cao, Y., Wang, Y., *Chromatographia* 2007, *66*, 767–771.

[68] Chen, X. J., Tu, P. F., Jiang, Y., Wang, Y. T., Li, S. P., *J. Sep. Sci.* 2009, *32*, 275–281.

[69] Lu, Y., Wu, H., Tian, Y., Cheng, Y., Qi, R., Wu, Y., Zhang, S., *Anal. Lett.* 2010, *43*, 2381–2389.

[70] Lu, Y., Li, Y., Li, H., *J. Chem. Soc. Pak.* 2008, *30*, 829–835.

[71] Kac, J., Zakrajšek, J., Mlinaric, A., Kreft, S., Filipiè, M., *Electrophoresis* 2007, *28*, 965–969.

[72] Zhang, Y., Zhao, L., Shi, Y. P., *J. Chromatogr. Sci.* 2007, *45*, 600–604.

[73] Luo, M., Lu, H., Ma, H., Zhao, L., Liu, X., Jiang, S., *J. Pharm. Biomed. Anal.* 2007, *44*, 881–886.

[74] Jing, R. J., Jiang, X. Y., Hou, S. R., Li, X. J., Yuan, Z. B., *Chin. J. Anal. Chem.* 2007, *35*, 1187–1190.

[75] Yi, A. Q., Chen, Y. M., Zheng, C. X., *J. Beijing For. Univ.* 2010, *32*, 9–12.

[76] Wang, Y. G., Sun, X. G., Wei, F. H., *J. South. Med. Univ.* 2008, *28*, 1407–1408.

[77] Han, S., *J. Chromatogr. B* 2009, *877*, 1591–1594.

[78] Tian, J., Qin, W., *Anal. Sci.* 2009, *25*, 1119–1123.

[79] Bachmann, S., Huck, C. W., Bakry, R., Bonn, G. K., *Electrophoresis* 2007, *28*, 799–805.

[80] Zhang, Q. F., Cheung, H. Y., *Food Chem.* 2010, *119*, 907–912.

[81] Xu, J., Zhang, H., Chen, G., *Talanta* 2007, *73*, 932–937.

[82] Chen, Z., Zhang, L., Chen, G., *Electrophoresis* 2009, *30*, 3419–3426.

[83] Zhang, Q., Zhang, X. S., Dai, Y., *Chin. Pharm. J.* 2009, *44*, 1269–1272.

[84] Zhou, B., Wu, Z., Li, X., Zhang, J., Hu, X., *Phytochem. Anal.* 2008, *19*, 86–89.

[85] Zhou, X. g., Sun, J. y., Zhu, D. r., Yuan, B. q., You, T. y., *Chem. Res. Chin. Univ.* 2008, *24*, 148–153.

[86] Wang, W., Tang, J., Wang, S., Zhou, L., Hu, Z., *J. Chromatogr. A* 2007, *1148*, 108–114.

[87] Chen, J., Chen, L., Zhang, H. L., Shi, Y. P., *J. AOAC Int.* 2010, *93*, 1410–1415.

[88] Müller, U., Mrestani, Y., Neubert, R., Dräger, B., *Electrophoresis* 2008, *29*, 3582–3587.

[89] Koyama, J., Morita, I., Kobayashi, N., *J. Chromatogr. A* 2007, *1145*, 183–189.

[90] Tian, K., Wang, Y., Chen, Y., Chen, X., Hu, Z., *Talanta* 2007, *72*, 587–593.

[91] Kuo, C. H., Lee, C. W., Lai, Y. C., Lee, S. S., *J. Pharm. Biomed. Anal.* 2008, *47*, 195–200.

[92] Yao, X., Zhang, J., Chen, G., *J. Plant Sci.* 2007, *2*, 273–282.

[93] Nair, V. D. P., Kanfer, I., *Phytochem. Anal.* 2007, *18*, 475–483.

[94] Karamać, M., *Eur. J. Lipid Sci. Technol.* 2009, *111*, 1063–1071.

[95] Zhou, X., Zheng, C., Huang, J., You, T., *Anal. Sci.* 2007, *23*, 705–711.

[96] Yao, X., Chen, G., *Anal. Bioanal. Chem.* 2007, *388*, 475–481.

[97] Jin, S., Li, P., Dong, S., Wang, Q., Fang, Y., *Chin. J. Chromatogr.* 2009, *27*, 229–232.

[98] Zhang, Y. Y., Li, Z. C., Zhu, J. K., Yang, Z. Y., Wang, Q. J., He, P. G., Fang, Y. Z., *Chin. Chem. Lett.* 2010, *21*, 1231–1234.

[99] Geng, C. H., Lin, M., Wang, W. Y., Ye, J. N., *J. Anal. Chem.* 2008, *63*, 75–81.

[100] Chen, Z., Zhang, L., Chen, G., *J. Chromatogr. A* 2008, *1193*, 178–181.

[101] Zeng, Y., Tang, Z., Wang, Q., He, P., Fang, Y., *J. Chromatogr. Sci.* 2007, *45*, 610–615.

[102] Citová, I., Ganzera, M., Stuppner, H., Solich, P., *J. Sep. Sci.* 2008, *31*, 195–200.

[103] Segura-Carretero, A., Puertas-Mejía, M. A., Cortacero-Ramírez, S., Beltrán, R., Alonso-Villaverde, C., Joven, J., Dinelli, G., Fernández-Gutiérrez, A., *Electrophoresis* 2008, *29*, 2852–2861.

[104] Helmja, K., Vaher, M., Püssa, T., Kamsol, K., Orav, A., Kaljurand, M., *J. Chromatogr. A* 2007, *1155*, 222–229.

[105] Jáč, P., Polášek, M., Batista, A. I. V., Kaderová, L., *Electrophoresis* 2008, *29*, 843–851.

[106] Gómez-Caravaca, A. M., Verardo, V., Segura-Carretero, A., Caboni, M. F., Fernández-Gutiérrez, A., *J. Chromatogr. A* 2008, *1209*, 238–245.

[107] Li, C., Liu, J. X., Zhao, L., Di, D. L., Meng, M., Jiang, S. X., *J. Pharm. Biomed. Anal.* 2008, *48*, 749–753.

[108] Chu, Q. C., Jiang, L. M., Ye, J. N., *J. Anal. Chem.* 2010, *65*, 103–108.

[109] Duan, H., Chen, Y., Chen, G., *J. Chromatogr. A* 2010, *1217*, 4511–4516.

[110] Šafra, J., Pospíšilová, M., Honegr, J., Spilková, J., *J. Chromatogr. A* 2007, *1171*, 124–132.

[111] Arráez-Román, D., Sawalha, S., Segura-Carretero, A., Menendez, J., Fernández-Gutiérrez, A., *Agro Food Ind. Hi-Tech* 2008, *19*, 18–22.

[112] Honegr, J., Šafra, J., Polášek, M., Pospíšilová, M., *Chromatographia* 2010, *72*, 885–891.

[113] Chu, Q., Tian, X., Jiang, L., Ye, J., *J. Agric. Food. Chem.* 2007, *55*, 8864–8869.

[114] Arráez-Román, D., Zurek, G., Bäßmann, C., Almaraz-Abarca, N., Quirantes, R., Segura-Carretero, A., Fernández-Gutiérrez, A., *Anal. Bioanal. Chem.* 2007, *389*, 1909–1917.

[115] Jin, S., Guo, X., Zhang, Y., Li, P., He, P., Wang, Q., Fang, Y., *Chin. J. Chem.* 2009, *27*, 773–776.

[116] Hu, X., Cui, S., Chen, X., Hu, Z., *Chromatographia* 2009, *70*, 1733–1736.

[117] Arráez-Román, D., Fu, S., Sawalha, S. M. S., Segura-Carretero, A., Fernández-Gutiérrez, A., *Electrophoresis* 2010, *31*, 2289–2296.

[118] Zhou, G., Guan, Y., Chen, H., Ye, J., *J. Chromatogr. A* 2007, *1142*, 236–239.

[119] Chen, Z., Zhang, J., Chen, G., *J. Chromatogr. B* 2008, *863*, 101–106.

[120] Yue, M. E., Li, Y., Shi, Y. P., *Biomed. Chromatogr.* 2007, *21*, 376–381.

[121] Yang, G., Zhang, L., Chen, G., *Chromatographia* 2010, *71*, 143–147.

[122] Jiang, T. F., Wang, Y. H., Lv, Z. H., Yue, M. E., *J. Pharm. Biomed. Anal.* 2007, *43*, 854–858.

[123] Tang, Z., Zeng, Y., Zhou, Y., He, P., Fang, Y., Zang, S., *J. Liq. Chromatogr. Relat. Technol.* 2007, *30*, 59–71.

[124] Wang, W., Geng, C., Zhang, Y., Shi, X., Ye, J., *Chromatographia* 2007, *66*, 697–701.

[125] Xia, Z. N., Pang, Y., Zheng, G. C., *Chin. J. Anal. Chem.* 2008, *36*, 1646–1650.

[126] Ding, N., Yang, Q., Huang, S. S., Fan, L. Y., Zhang, W., Zhong, J. J., Cao, C. X., *J. Pharm. Biomed. Anal.* 2010, *53*, 1224–1230.

[127] Chen, H., Ding, X., Wang, M., Chen, X., *J. Chromatogr. Sci.* 2010, *48*, 866–870.

[128] Jiang, T. F., Wang, Y. H., Lv, Z. H., Yue, M. E., *Chromatographia* 2007, *65*, 101–104.

[129] Xuan, P., Chen, X., Sun, Q., Liang, J. B., Chen, F., *Microchim. Acta* 2009, *165*, 35–38.

[130] Tian, Y., Lu, Y., Xie, J., Cheng, Y., Qi, R., Wu, Y., Zhang, S., *Anal. Methods* 2009, *1*, 203–207.

[131] Yang, P., Li, Y., Liu, X., Jiang, S., *J. Pharm. Biomed. Anal.* 2007, *43*, 1331–1334.

[132] Li, J., Huang, X., Lai, D., Sun, W., *Chromatographia* 2008, *67*, 989–993.

[133] Majid, E., Male, K. B., Tzeng, Y. M., Omamogho, J. O., Glennon, J. D., Luong, J. H. T., *Electrophoresis* 2009, *30*, 1967–1975.

[134] Huang, B., Yao, C., Mo, J., Du, S., Bian, Q., Wang, Z., *Acta Sci. Nat. Univ. Sunyatseni* 2010, *49*, 65–67, 71.

[135] Li, J., Feng, C. Q., Ni, X. M., Zhang, W. S., *Chin. Pharm. J.* 2008, *43*, 1105–1107.

[136] Yang, F. Q., Ge, L., Yong, J. W. H., Tan, S. N., Li, S. P., *J. Pharm. Biomed. Anal.* 2009, *50*, 307–314.

[137] Chen, R., Liu, Z., Zhao, J., Meng, F., Zhang, M., Ge, W., *Food Chem.* 2011, *127*, 434–440.

[138] Yang, X., Zhao, Y., Zhou, Y., Lv, Y., Mao, J., Zhao, P., *Biol. Pharm. Bull.* 2007, *30*, 1884–1890.

[139] Yang, X., Zhao, Y., Ruan, Y., Yang, Y., *Biol. Pharm. Bull.* 2008, *31*, 1860–1865.

[140] Zhang, H. Y., Ling, J. Y., Lv, P., Zhang, C. K., Duan, G. L., *Fudan Univ. J. Med. Sci.* 2007, *34*, 446–448.

[141] Kuo, C. Y., Liao, K. S., Liu, Y. C., Yang, W. B., *Molecules* 2011, *16*, 1682–1694.

[142] Xia, Y. G., Wang, Q. H., Liang, J., Yang, B. Y., Li, G. Y., Kuang, H. X., *Phytochem. Anal.* 2011, *22*, 103–111.

[143] Yang, X., Zhao, Y., Yang, Y., Ruan, Y., *J. Agric. Food. Chem.* 2008, *56*, 6905–6909.

[144] Xia, L., Sun, Z. W., Li, G. L., Suo, Y. R., You, J. M., *Eur. Food Res. Technol.* 2010, *230*, 715–722.

[145] Wei, F., Feng, Y. Q., *Talanta* 2008, *74*, 619–624.

[146] Dahab, A. A., Smith, N. W., Marlin, N., *Chromatographia* 2009, *70*, 467–473.

[147] Bai, X. W., Song, C. H., You, J. M., Sun, Z. W., Fu, Y. Y., Li, G. L., *Chromatographia* 2010, *71*, 1125–1129.

[148] Palíková, I., Heinrich, J., Bednáø, P., Marhol, P., Køen, V., Cvak, L., Valentová, K., Rùzčièka, F., Holá, V., Koláø, M., Šimánek, V., Ulrichová, J., *J. Agric. Food. Chem.* 2008, *56*, 11883–11889.

[149] Muensritharam, L., Tolieng, V., Chaichantipyuth, C., Petsom, A., Nhujak, T., *J. Pharm. Biomed. Anal.* 2008, *46*, 577–582.

[150] Kornysova, O., Stanius, Z., Obelevicius, K., Ragazinskiene, O., Skrzydlewska, E., Maruska, A., *Adv. Med. Sci.* 2009, *54*, 41–46.

[151] Li, M., Fan, L. Y., Zhang, W., Sun, J., Cao, C. X., *J. Pharm. Biomed. Anal.* 2007, *43*, 387–392.

[152] Zandberg, W. F., Mohan, S., Kumarasamy, J., Pinto, B. M., *Anal. Chem.* 2010, *82*, 5323–5330.

[153] Law, W. S., Zhao, J. H., Hauser, P. C., Yau Li, S. F., *J. Sep. Sci.* 2007, *30*, 3247–3254.

[154] Wu, T., Guan, Y., Ye, J., *Food Chem.* 2007, *100*, 1573–1579.

[155] Cevallos-Cevallos, J. M., Rouseff, R., Reyes-De-Corcuera, J. I., *Electrophoresis* 2009, *30*, 1240–1247.

[156] Gorbatsova, J., Lõugas, T., Vokk, R., Kaljurand, M., *Electrophoresis* 2007, *28*, 4136–4142.

[157] Tang, Z., Zeng, Y., Zang, S., He, P., Fang, Y., *Am. Biotechnol. Lab.* 2009, *27*, 23–26.

[158] Quirantes-Piné, R., Arráez-Román, D., Segura-Carretero, A., Fernández-Gutiérrez, A., *J. Sep. Sci.* 2010, *33*, 2818–2827.

[159] Cheung, H. Y., Zhang, Q. F., *J. Chromatogr. A* 2008, *1213*, 231–238.

[160] Orlandini, S., Giannini, I., Pinzauti, S., Furlanetto, S., *Talanta* 2008, *74*, 570–577.

[161] Chen, J., Zhu, H., Chu, V. M., Jang, Y. S., Son, J. Y., Kim, Y. H., Son, C. G., Seol, I. C., Kang, J. S., *J. Pharm. Biomed. Anal.* 2011, *55*, 206–210.

[162] Li, Q., Jiang, X., *Chromatographia* 2008, *68*, 421–424.

[163] Zhang, Q. F., Li, S. C., Lai, W. P., Cheung, H. Y., *Food Chem.* 2009, *113*, 684–691.

[164] Zhang, Q. F., Zhang, Z. R., Cheung, H. Y., *Food Chem.* 2009, *115*, 297–303.

[165] Liu, Y., Jiang, Y., Sun, J., *Chin. J. Chin. Mater. Med.* 2008, *33*, 133–135.

[166] Orav, A., Viitak, A., Vaher, M., *Procedia Chem.* 2010, *2*, 152–160.

[167] Shi, L., Zhu, H., Wang, J. X., Ma, Z., Liu, Y. W., *Chin. Tradit. Herb. Drugs* 2008, *39*, 1726–1729.

[168] Wang, M., Zhang, Y. C., Liu, X. H., Song, J. P., Wang, L. J.,.*J. Chin. Med. Mater.* 2010, *33*, 201–204.

[169] Luo, G. M., Tan, X. H., Xu, L. F., Yang, Y. Q., Yang, S. L., *Chin. J. Chin. Mater. Med.* 2008, *33*, 2362–2364.

[170] Ye, B., Song, L. Y., Yu, R. M., *J. Chin. Med. Mater.* 2007, *30*, 28–30.

[171] Zha, X. Q., Luo, J. P., Wei, P., *S. Afr. J. Bot.* 2009, *75*, 276–282.

[172] Salinas-Hernández, P., López-Bermúdez, F. J., Rodríguez-Barrientos, D., Ramírez-Silva, M. T., Romero-Romo, M. A., Morales-Anzures, F., Rojas-Hernández, A., *J. Sep. Sci.* 2008, *31*, 741–745.

[173] Cui, Y., Zhang, L., Kong, D., Zhu, H., Kong, Z., *Chin. J. Chin. Mater. Med.* 2010, *35*, 2440–2443.

[174] Miao, W. J., Yang, L., Wu, D. R., Zhang, P., Chen, C., Ye, L. M., *Chin. Tradit. Herb. Drugs* 2007, *38*, 1171–1174.

[175] Chen, B., Li, J. H., Zang, P., Yu, Y. B., Tian, R. H., Yan, Y. C., Chi, Y. M., Zhang, L. D., Yan, Y. L., *Spectrosc. Spect. Anal.* 2010, *30*, 2124–2128.

[176] Sun, G., Yang, H., Deng, X., Sun, Y., *Chin. J. Chromatogr.* 2007, *25*, 96–100.

[177] Zhao, L., Xiang, B., Tan, X., *J. Chromatogr. Sci.* 2010, *48*, 417–420.

[178] Zhang, H., Chen, H., *Anal. Methods* 2011, *3*, 745–750.

[179] Hu, K., Zhao, S. L.,.*Chin. J. Anal. Chem.* 2007, *35*, 857–860.

[180] Li, J. S., Liu, X. H., Cai, B. C., Fu, X. S.,.*J. Chin. Med. Mater.* 2010, *33*, 349–352.

[181] k, H., Ge, L., Chen, H., Jing, C., Shi, Z., *Chin. J. Chromatogr.* 2009, *27*, 489–493.

[182] Sun, G., Song, Y., *Chin. J. Chromatogr.* 2009, *27*, 494–498.

[183] Sun, G., Song, W., Lin, T., *Chin. J. Chromatogr.* 2008, *26*, 232–236.

[184] Sun, G., Shi, C., *J. Chromatogr. Sci.* 2008, *46*, 454–460.

[185] Zhang, Q. F., Cheung, H. Y., *Phytochem. Anal.* 2011, *22*, 18–25.

[186] Hu, K., Zhao, S., Ye, F., Lu, X., *Chromatographia* 2008, *68*, 475–479.

[187] Liu, L., Chen, X., Hu, Z., *Microchimica Acta* 2007, *159*, 125–131.

[188] Hou, J., Zheng, J., Rizvi, S. A. A., Shamsi, S. A., *Electrophoresis* 2007, *28*, 1352–1363.

[189] Hou, J., Zheng, J., Shamsi, S. A., *Electrophoresis* 2007, *28*, 1426–1434.

[190] Wang, W. P., Wang, S. M., Luo, Z., Hu, Z. D., *Chin. J. Anal. Chem.* 2007, *35*, 382–385.

[191] Zhou, L., Zhou, X., Luo, Z., Wang, W., Yan, N., Hu, Z., *J. Chromatogr. A* 2008, *1190*, 383–389.

[192] Qi, X., Wang, S., Wu, B., Qu, H., *Chromatographia* 2009, *70*, 281–285.

[193] Zhu, J., Zhang, H., Qi, S., Chen, X., Hu, Z., *Chromatographia* 2011, *73*, 535–540.

[194] Hsiao, H. Y., Cheng, T. J., Yang, G. M., Huang, I. J., Chen, R. L. C., *Phytochem. Anal.* 2008, *19*, 136–140.

[195] Reid, R. G., Durham, D. G., Boyle, S. P., Low, A. S., Wangboonskul, J., *Anal. Chim. Acta* 2007, *605*, 20–27.

[196] Yu, L., Xu, X., Huang, L., Lin, J., Chen, G., *J. Chromatogr. A* 2008, *1198–1199*, 220–225.

[197] Liu, L., Deng, X., Chen, X., *J. Chromatogr. A* 2010, *1217*, 175–178.

[198] Li, L. J., Cai, Z., Li, S. G., Wu, F. M., Li, H. Y., Cheng, C. D., Cheng, H., Wu, J. L.,.*Chin. J. Anal. Chem.* 2008, *36*, 1261–1264.

[199] Gao, S. Y., Li, H., Wang, L., Yang, L. N., *J. Chin. Chem. Soc.* 2010, *57*, 1374–1380.

[200] Petr, J., Vítková, K., Ranc, V., Znaleziona, J., Maier, V., Knob, R., Ševèík, J., *J. Agric. Food Chem.* 2008, *56*, 3940–3944.

[201] Cao, J., Qi, L. W., Liu, E. H., Zhang, W. d., Li, P., *J. Pharm. Biomed. Anal.* 2009, *49*, 475–480.

[202] Cao, J., Qu, H., Cheng, Y., *Electrophoresis* 2010, *31*, 3492–3498.

[203] Liu, L., Chen, X., Hu, Z., *Talanta* 2007, *71*, 155–159.

[204] Wang, S., Zhou, L., He, W., Hu, Z., *J. Pharm. Biomed. Anal.* 2007, *43*, 1557–1561.

[205] Kalinova, J., Dadakova, E., *Plant Food Hum. Nutr.* 2009, *64*, 68–74.

[206] Song, Y., Li, P., Wang, D., Cheng, Y. Y., *Planta Med.* 2008, *74*, 84–89.

[207] Cao, J., Dun, W. L., *Talanta* 2011, *84*, 155–159.

[208] Zehrmann, N., Zidorn, C., Ganzera, M., *J. Pharm. Biomed. Anal.* 2010, *51*, 1165–1168.

[209] Zhu, J., Yu, K., Chen, X., Hu, Z., *J. Chromatogr. A* 2007, *1166*, 191–200.

[210] Zhu, J., Qi, S., Zhang, H., Chen, X., Hu, Z., *J. Chromatogr. A* 2008, *1192*, 319–322.

[211] Chang, Y. Q., Tan, S. N., Yong, J. W. H., Ge, L., *J. Sep. Sci.* 2011, *34*, 462–468.

[212] Herrero-Martínez, J. M., Oumada, F. Z., Rosés, M., Bosch, E., Ràfols, C., *J. Sep. Sci.* 2007, *30*, 2493–2500.

[213] Jiang, L., Fang, G., Zhang, Y., Cao, G., Wang, S., *J. Agric. Food Chem.* 2008, *56*, 11571–11577.

[214] Zhang, Y., Chen, J., Ma, X. M., Shi, Y. P., *J. Pharm. Biomed. Anal.* 2007, *45*, 742–746.

[215] Vrchotová, N., Šerá, B., Dadáková, E., *J. Indian Chem. Soc.* 2010, *87*, 1267–1272.

[216] Yu, L. S., Xu, X. Q., Huang, L., Ling, J. M., Chen, G. N., *Electrophoresis* 2008, *29*, 726–733.

[217] Yu, K., Gong, Y., Lin, Z., Cheng, Y., *J. Pharm. Biomed. Anal.* 2007, *43*, 540–548.

[218] Dong, Y., Leu, Y. L., Chien, K. Y., Yu, J. S., *Anal. Lett.* 2009, *42*, 1444–1457.

[219] Zhang, Y., Chen, J., Zhao, L., Shi, Y. P., *Biomed. Chromatogr.* 2007, *21*, 987–992.

[220] Jiang, T. F., Lv, Z. H., Wang, Y. H., Yue, M. E., *Biomed. Chromatogr.* 2010, *24*, 581–587.

[221] Liu, M., Kong, D., Yang, W., Wang, Q., Zhang, L., *Chin. J. Chin. Mater. Med.* 2010, *35*, 1840–1844.

[222] Zhang, H., Zhu, J., Qi, S., Chen, X., Hu, Z., *Biomed. Chromatogr.* 2007, *21*, 1083–1087.

[223] Lü, W., Chen, Y., Zhang, Y., Ding, X., Chen, H., Liu, M., *J. Chromatogr. B* 2007, *860*, 127–133.

[224] Stege, P. W., Sombra, L. L., Davicino, R. C., Olsina, R. A., *Phytochem. Anal.* 2011, *22*, 74–79.

[225] Ganzera, M., Nischang, I., Siegl, C., Senzenberger, B., Svec, F., Stuppner, H., *Electrophoresis* 2009, *30*, 3757–3763.

[226] Wang, L., Li, D., Bao, C., You, J., Wang, Z., Shi, Y., Zhang, H., *Ultrason. Sonochem.* 2008, *15*, 738–746.

[227] Ba◦kan, S., Daut-Özdemir, A., Günaydin, K., Erim, F. B., *Talanta* 2007, *71*, 747–750.

[228] Zheng, C. Y., Liu, S. M., Li, H. T., Niu, W. Y., Ping, W. X., *Chin. Pharm. J.* 2007, *42*, 1248–1251.

[229] Ganzera, M., Egger, C., Zidorn, C., Stuppner, H., *Anal. Chim. Acta* 2008, *614*, 196–200.

[230] Cao, J., Qu, H., Cheng, Y., *Electrophoresis* 2010, *31*, 1689–1696.

[231] Wang, X. K., He, Y. Z., Qian, L. L., *Talanta* 2007, *74*, 1–6.

[232] Verardo, V., Bendini, A., Cerretani, L., Malaguti, D., Cozzolino, E., Caboni, M. F., *J. Food Qual.* 2009, *32*, 262–281.

[233] Zeng, Y., Wei, X., Xu, Y., *Chem. Bull.* 2010, *73*, 814–818.

[234] Mi, X., Zhu, R., *Chin. J. Chromatogr.* 2010, *28*, 209–214.

[235] Li, Y. L., Ding, C. X., Wang, H. L., Suo, Y. R., You, J. M., Chen, G. C., *J. Anal. Chem.* 2008, *63*, 574–579.

[236] Wang, R., Wang, S. M., Liang, S. W., Xu, G. W., Weng, Q. F., *J. Chin. Med. Mater.* 2007, *30*, 946–950.

[237] Li, W. L., Chen, J. H., Yin, Y. F., Wu, F. Q., Yang, B. J., Yang, H. H., Wang, X. R., *Chin. Pharm. J.* 2007, *42*, 1736–1740.

[238] Cao, J., Li, B., Chang, Y. X., Li, P., *Electrophoresis* 2009, *30*, 1372–1379.

[239] Cao, J., Yi, L., Li, P., Chang, Y. x., *J. Chromatogr. A* 2009, *1216*, 5608–5613.

[240] Ye, S., Wang, S. F., Qu, H. B., Cheng, Y. Y., *Chin. J. Anal. Chem.* 2007, *35*, 115–118.

[241] Cao, J., Qi, L. W., Chen, J., Li, P., *Electrophoresis* 2008, *29*, 4422–4430.

[242] Du, H., Chen, X., *J. Braz. Chem. Soc.* 2009, *20*, 1268–1274.

[243] Du, H., Chen, X. Q., *J. Iran Chem. Soc.* 2009, *6*, 334–340.

[244] Jiang, T. F., Lva, Z. H., Wanga, Y. H., Yueb, M. E., Peng, J. H., *J. Anal. Chem.* 2010, *65*, 945–950.

[245] Öztekin, N., Başkan, S., Evrim Kepekçi, S., Erim, F. B., Topçu, G., *J. Pharm. Biomed. Anal.* 2010, *51*, 439–442.

[246] Wu, Y. W., Jiang, Y. Y., Xiao, T. X., Zhang, H. L., *J. Sep. Sci.* 2008, *31*, 865–871.

[247] Shi, S., Li, W., Liao, Y., Cai, Z., Liu, H., *J. Chromatogr. A* 2007, *1167*, 120–124.

[248] Chen, J., Li, Z. W., Qi, W., Liu, Z. R., Li, B. G., *Chin. J. Chin. Mater. Med.* 2007, *32*, 1412–1415.

[249] de Oliveira, A., Silva, C. A., Silva, A. M., Tavares, M. F. M., Kato, M. J., *Phytochem. Anal.* 2010, *21*, 428–433.

[250] Huhn, C., Pütz, M., Holthausen, I., Pyell, U., *Electrophoresis* 2008, *29*, 526–537.

[251] Ding, C., Wang, L., Zhao, X., Li, Y., Wang, H., You, J., Suo, Y., *J. Liq. Chromatogr. Relat. Technol.* 2007, *30*, 3069–3083.

[252] Zhao, X., Wang, Y., Sun, Y., *J. Pharm. Biomed. Anal.* 2007, *44*, 1183–1186.

[253] Wang, H., Wang, X., You, J., Suo, Y., Zhao, X., Li, Y., Ding, C., *J. Liq. Chromatogr. Relat. Technol.* 2007, *30*, 363–376.

[254] Cao, J., Chen, J., Yi, L., Li, P., Qi, L. W., *Electrophoresis* 2008, *29*, 2310–2320.

[255] Addolorata Saracino, M., Mercolini, L., Musenga, A., Bugamelli, F., Raggi, M. A., *J. Sep. Sci.* 2008, *31*, 1851–1859.

[256] Li, J. S., Song, J. P., Liu, X. H., Zhang, Y. C., Cai, B. C., Yin, D., *Chin. Tradit. Herb. Drugs* 2010, *41*, 1981–1985.

[257] Cao, Y., Gong, W., Li, N., Yin, C., Wang, Y., *Anal. Bioanal. Chem.* 2008, *392*, 1003–1010.

[258] Obradoviè, M., Krajšek, S. S., Dermastia, M., Kreft, S., *Phytochem. Anal.* 2007, *18*, 123–132.

[259] Lei, Y., Ping, G., Lin, Y., Xuemei, J., Zhining, X., *Chin. J. Chromatogr.* 2007, *25*, 337–340.

[260] Shi, K. Y., Zou, X. B., Xia, Z. N., *Chin. Pharm. J.* 2009, *44*, 571–575.

[261] Liu, X., Li, J., Zhang, Y., Cai, B., Yin, D., *Chin. J. Chin. Mater. Med.* 2009, *34*, 3034–3038.

[262] Fan, X. M., Ji, Y. B., Zhu, D. N., *Chromatographia* 2010, *71*, 667–677.

[263] Yang, B., Zhang, X., Zhang, R., *Braz. J. Pharmacogn.* 2011, *21*, 16–23.

[264] Zhou, S., Tan, J., Chen, Q., Lin, X., Lü, H., Xie, Z., *J. Chromatogr. A* 2010, *1217*, 8346–8351.

[265] Chen, Z., Cai, Y., Cheng, J., Zhang, L., *J. Chromatogr. B* 2010, *878*, 2375–2378.

[266] Wang, J., Chen, D., Chen, Z., Fan, G., Wu, Y., *J. Sep. Sci.* 2010, *33*, 1099–1108.

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

[268] Wang, J., Chen, Z., Wu, Y., Fan, G., *Chin. J. Chromatogr.* 2010, *28*, 240–246.

[269] Wang, J., Tanret, I., Mangelings, D., Fan, G., Wu, Y., Heyden, Y. V., *J. Chromatogr. Sci.* 2010, *48*, 428–435.

[270] Pieters, S., Tistaert, C., Alaerts, G., Bodzioch, K., Mangelings, D., Dejaegher, B., Rivire, C., Nguyen Hoai, N., Chau Van, M., Quetin-Leclerq, J., Vander Heyden, Y., *Talanta* 2011, *83*, 1188–1197.

[271] Wu, Y., Wang, Y., Gu, X., Yan, C., *Sci. China B Chem.* 2009, *39*, 767–773.

[272] Breadmore, M. C., *Electrophoresis* 2007, *28*, 254–281.

[273] Simpson S. L., Jr., Quirino, J. P., Terabe, S., *J. Chromatogr. A* 2008, *1184*, 504–541.

[274] Breadmore, M. C., Thabano, J. R. E., Dawod, M., Kazarian, A. A., Quirino, J. P., Guijt, R. M., *Electrophoresis* 2009, *30*, 230–248.

[275] Breadmore, M. C., Dawod, M., Quirino, J. P., *Electrophoresis* 2011, *32*, 127–148.

[276] Aranas, A. T., Guidote Jr A. M., Quirino, J. P., *Anal. Bioanal. Chem.* 2009, *394*, 175–185.

[277] Quirino, J. P., *J. Chromatogr. A* 2009, *1216*, 294–299.

[278] Li, S. P., Chen, X. J., Yang, F. Q., in: Hanrahan, G., Gomez, F. A. (Eds.), *Chemometric Methods in Capillary Electrophoresis*, Wiley, New Jersey 2010, pp. 227–242.

[279] Ryan, R., McEvoy, E., Sheila, D., Power, J., Altria, K., *Electrophoresis* 2011, *32*, 184–201.

[280] Svec, F., *Electrophoresis* 2009, *30*, S68–S82.

[281] Huo, Y., Kok, W. T., *Electrophoresis* 2008, *29*, 80–83.

[282] Ganzera, M., Nischang, I., *Curr. Org. Chem.* 2010, *14*, 1769–1780.

[283] Mikšík, I., Sedláková, P., *J. Sep. Sci.* 2007, *30*, 1686–1703.

[284] Eeltink, S., Svec, F., *Electrophoresis* 2007, *28*, 137–147.

[285] Svec, F., *J. Chromatogr. A* 2010, *1217*, 902–924.

[286] Karenga, S., El Rassi, Z., *Electrophoresis* 2011, *32*, 90–104.

[287] Zhang, K., Gao, R., Jiang, Z., Yao, C., Zhang, Z., Wang, Q., Yan, C., *J. Sep. Sci.* 2003, *26*, 1389–1394.

[288] Yao, C., Gao, R., Yan, C., *J. Sep. Sci.* 2003, *26*, 37–42.

[289] Wang, S., Jia, L., Chen, D., *J. Sep. Sci.* 2009, *32*, 388–393.

[290] Yan, C., Schaufelberger, D., Erni, F., *J. Chromatogr. A* 1994, *670*, 15–23.

[291] Eimer, T., Unger, K. K., Tsuda, T., *Fresenius J. Anal. Chem.* 1995, *352*, 649–653.

[292] Wu, J. T., Huang, P., Li, M. X., Lubman, D. M., *Anal. Chem.* 1997, *69*, 2908–2913.

[293] Wu, Y., Wang, Y., Zhao, Z., Wu, K., Yan, C., *Am. Lab.* 2010, *42*, 38–41.

[294] Zhong, H., El Rassi, Z., *J. Sep. Sci.* 2009, *32*, 1642–1653.

[295] Wu, Y., Wang, Y., Gu, X., Zhang, L., Yan, C., *Chin. J. Chromatogr.* 2010, *28*, 226–230.

[296] Feng, L., Zhao, F., *Chromatographia* 2009, *69*, 1325–1332.

[297] Zhang, Z., Du, X., Li, X., *Anal. Chem.* 2011, *83*, 1291–1299.

[298] Zhu, Y. X., Zhang, L. Y., Lei, W., Zhang, W. B., *Chem. J. Chin. Univ.* 2011, *32*, 44–49.

[299] García-Villalba, R., Carrasco-Pancorbo, A., Vázquez-Martín, A., Oliveras-Ferraros, C., Menéndez, J. A., Segura-Carretero, A., Fernández-Gutiérrez, A., *Electrophoresis* 2009, *30*, 2688–2701.

[300] Česla, P., Fischer, J., Jandera, P., *Electrophoresis* 2010, *31*, 2200–2210.

[301] Mrestani, Y., Claussen, S., Neubert, R. H. H., *Chromatographia* 2004, *59*, 759–762.

[302] El-Hady, D. A., El-Maali, N. A., *Talanta* 2008, *76*, 138–145.

[303] Huang, X., Ren, J., *Trends Analyt. Chem.* 2006, *25*, 155–166.

[304] Yin, X. B., Wang, E., *Anal. Chim. Acta* 2005, *533*, 113–120.

[305] Vandaveer Iv, W. R., Pasas-Farmer, S. A., Fischer, D. J., Frankenfeld, C. N., Lunte, S. M., *Electrophoresis* 2004, *25*, 3528–3549.

[306] Holland, L. A., Lunte, S. M., *Anal. Commun.* 1998, *35*, 1H–4H.

[307] Matysik, F. M., *Microchim. Acta* 2008, *160*, 1–4.

