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Review

# On-line sample preconcentration in capillary electrophoresis Fundamentals and applications

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**Abstract**

On-line preconcentration is one of the aspects of analytical method development using capillary electrophoretic techniques. The choice of the sample matrix alone can significantly alter both method sensitivity and separation efficiency. The recent trend to detect samples in narrower separation vessels also necessitates the need to improve detection sensitivity. The desire to detect very low levels of analytes using limited amounts of sample from biological specimens and the high separation efficiency obtainable using very large injections compared to classical small size injections also adds to this list. Indeed, one of the rich areas of research in the capillary electrophoresis field is on on-line sample preconcentration. More than 400 published research articles gathered from the http://www.webofscience.com from the year 2000 described a form of on-line preconcentration in capillary electrophoresis. This review provides a comprehensive table listing the applications of on-line preconcentration in capillary electrophoresis.
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*Keywords:* Field-enhanced sample stacking; Transient isotachophoresis; Dynamic pH-junction; Sweeping

## Contents



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## 1. Introduction

Capillary electrophoresis (CE) is now a mature technique for analytical separation and it has several advantages over other separation techniques: high efficiency separation, minimum requirements of sample and chemical amounts, almost no need of the use of organic solvents. Although CE is popular among academia, it has not been widely accepted among industry yet as a routine analytical method except for some specific applications such as DNA and protein analysis. One of the disadvantages of CE is generally thought to be poor concentration sensitivity of photometric detectors, which are the most popular among CE detectors. Since the volume or length of the injected sample zone in capillary is very small (nL) or short (mm), it is essential to employ on-capillary detection methods not to deteriorate separation efficiency. On-capillary detection causes a short pathlength of the light, which is nearly equal to the diameter of the capillary (50–100 μm), less than 1/100 of the conventional detection cell used in high-performance liquid chromatography (HPLC). Therefore, the concentration sensitivity of the UV detector in CE is much lower than that in HPLC.

To solve the problem of low concentration sensitivity in CE, several techniques have been developed. One is the use of high sensitivity detectors such as laser-induced fluorescence (LIF), chemiluminescence or electrochemical detectors: LIF and chemiluminescence detectors can increase sensitivity more than 1000-fold than that of the conventional absorbance detector, while electrochemical detectors do not provide very high concentration sensitivity but they can be used with the minimum detection volume as low as tens of fL. The extended pathlength capillary with bubble cell or Z-type cell is available for absorbance detectors to increase sensitivity up to 10-fold. Another is the sample preconcentration before (off-line) or after (on-line) sample injection. The off-line technique or sample pretreatment is popularly employed in combination with the sample extraction in analytical separations such as gas chromatography (GC) or HPLC: liquid–liquid extraction (LLE) or solid-phase extraction (SPE). The concentration efficiency is rather limited up to 100-folds in these sample pretreatments because of difficult handlings of large sample volumes. For example, the analyte is extracted from a 10 mL sample solution and concentrated to 0.1 mL, giving 100-fold concentration. While on-line sample preconcentration can be performed just by injecting a large volume of sample solution without modification of the instrument and the analyte can be focused into a minimum volume inside the capillary. Therefore, on-line sample preconcentration is a useful technique to improve the concentration sensitivity of the detector by taking advantage of small sample volume requirement in CE. The final volume of the sample subject to the CE analysis is usually in the order of nL and off-line handling of these small volumes needs special skills.

On-line sample preconcentration is a very useful technique in CE, where a larger volume of the sample solution compared to the conventional run is introduced into the capillary by pressurized or electrokinetic methods and the analytes in a long sample zone is focused into a narrow zone before separation. The principle of most techniques is based on the velocity change of the analytes between the sample zone and the separation solution zone, while conventional CE separations are performed in a homogeneous free solution and the migration velocity is constant under a constant applied voltage. The change in migration velocity is caused by the change in electric field strength between the sample solution and separation zone or the change in effective charge on the analyte. Some preconcentration techniques such as sweeping are based on the chromatographic principle, that is, the migration velocity is different either the analyte is complexed by the pseudostationary phase or free from the pseudostationary phase. A complexing reagent that forms a complex with the analyte can be also used for sweeping.

The background for several on-line sample preconcentration techniques are discussed in this article but off-line techniques are not described. The preconcentration techniques caused by molecular sieving effect in gel electrophoresis are also not described. Transient isotachophoresis (tITP), field enhanced (although the term "field-amplified" is more popularly used, "field-amplified" is not a suitable philological term for the electric field strength and "field enhanced" is used in this article) sample stacking, dynamic pH junction, and sweeping are described. The in-capillary solid-phase extraction techniques are not discussed but the applications of the techniques are included in this article. It should be mentioned that the concentration of the analyte must be high enough to be detectable by absorbance inside the detector cell even if a diluted sample solution is injected, or the total amount of the analyte injected must be similar to that in conventional CE even by employing on-line sample preconcentration techniques. However, in some examples, the peak width becomes very narrow by on-line preconcentration techniques compared with the conventional CE and the total amount of the analyte injected can be reduced (see later discussion).

On-line sample preconcentration in CE is a topic that attracted much attention last 10 years and several review articles were published even after the year 2000 [1–15]. The article aims to introduce on-line sample preconcentration techniques with an emphasis on the mechanism and advantages and disadvantages of each technique. We also try to tabulate the results from just over 400 papers published on this topic since the year 2000, summarized in a table.

## 2. Background considerations

It may be interesting to compare the column or capillary volume between HPLC and CE: an HPLC column of 15 cm × 4.5 mm I.D. has an inside volume of 1.7 mL and mobile phase volume may be 1.2 mL if we assume mobile phase volume is 70% of the column volume. The detector cell volume is about 5–10 μL for the photometric detector. A typical capillary used in CE is 50 cm × 50 μm I.D., which gives about 1 μL inside volume, while the detector cell volume is typically less than 1 nL. The relative cell volume to the column volume in HPLC seems larger than that of CE but it should be remembered that a separated zone is diluted by the mobile phase by a factor of (retention factor +1) when the analyte is eluted out from the column. The sample volume is few μL in HPLC, while approximately nL in

CE. The relatively low sample volume in CE is required to keep high efficiency separation: an extra column contribution of the sample zone length, $(1/12)l_{inj}^2$, must be kept lower than 10% (preferably less than 5%) of the total variance of the separation, $\sigma_{total}^2$, not to deteriorate the high separation efficiency in CE, where $l_{inj}$ is the sample zone length injected. For $N = 250{,}000$, where $N$ it the plate number, $\sigma_{total}^2$ is 1 mm$^2$ and hence, $l_{inj}$ must be less than 1 mm. This will be discussed again in the following sections.

Two types of sample injection methods are available in CE, pressurized (or hydrodynamic) and electrokinetic. The former is more widely accepted, where the sample volume injected can be precisely estimated and any analytes including neutral ones are introduced keeping the same composition as that of the sample solution. The amount injected can be controlled by changing pressure and time. If the viscosity is significantly different between the sample solution and the running solution or background solution (BGS), the sample volume injected will not linearly proportional to the injection time and any calibration must be employed to know exact amount injected. To inject a large sample volume for on-line sample preconcentration, it takes few minutes. The latter is employed in capillary gel electrophoresis and capillary electrochromatography because the former technique is not applicable. The amount of the analyte injected is related to the electrokinetic velocity, which is a sum of electroosmotic velocity and electrophoretic velocity. The analyte having a shorter migration time will be injected more than that having a longer migration time. It is possible to inject more amounts of analytes in electrokinetic injection by a prolonged injection time than those by pressurized injection when the migration velocity of the analyte is faster than the electroosmotic velocity. It should be noted that even during electrokinetic injection, the electrolysis of water proceeds and the pH of the sample solution may be changed during the prolonged injection, causing change in electrophoretic velocity of the analyte in the sample solution particularly because the sample solution is usually not pH buffered. It should be also mentioned that the depletion of the analyte or exhaustive injection will occur in prolonged injection in the electrokinetic injection. An advantage of the electrokinetic injection is the possible selective injection of analytes because only charged analytes can be successfully injected by this technique. That is, the analytes having higher p$K_a$ than the pH of the sample solution can be efficiently injected at positive polarity and vice versa.

The maximum sample volume that can be injected by pressure is limited less than the capillary volume: even when a highly efficient preconcentration technique is employed, while more than 10% of the effective length (from injection front to the detector) of the capillary must be available for the CE separation. Therefore, concentration efficiency with pressurized sample injection is limited by the capillary length. Although the plate number in CE does not depend on the capillary length, as given by [16]

$$N = (\mu_{ep} + \mu_{eo})V/2D \quad (1)$$

where $\mu_{ep}$ and $\mu_{eo}$ are electrophoretic and electroosmotic mobility, respectively, $V$ applied voltage, $D$ diffusion coefficient of the analyte, the contributions of extra-column effects, sample zone length and detector cell length, to the total plate number becomes critical when a short length capillary is used for separation as in case of on-line sample preconcentration. If we assume $N = 250{,}000$, the analyte zone length at the detector must be 0.4 mm ($4\sigma$) for 5 cm separation length. This simple assumption suggests the sample zone length after preconcentration must be much narrower than that in conventional CE. The conditions are more critical in case of microchip electrophoresis because the channel length is much shorter than the capillary length.

There are many definitions proposed to describe the concentration efficiency. Most papers use the ratio of peak heights obtained by the conventional procedure, for example, 1 or few second-injection, to that obtained under sample preconcentration conditions multiplying the dilution factor. This definition is a little bit arbitrary because even in conventional procedure large volume injection will give higher peaks. Another definition is the ratio of the length of the sample zone to that of the analyte at the detection cell, called the detector-to-injection bandwidth ratio (DIBR) [17]. This definition does not apply to electrokinetic injection because the sample zone length may become narrower during injection. A more practical definition is to compare the limits of detection (LODs) between the conventional and preconcentration procedures.

## 3. On-line sample preconcentration techniques

### 3.1. Field-enhanced sample stacking

The principle of field-enhanced sample stacking is straightforward and the technique is easy to perform by simply optimizing the sample solution and the separation solution or BGS, mainly in concentrations or electrical conductivities of the solutions to constitute different electrical field strengths between the two solutions. The electrophoretic velocity, $v_{ep}$, of the analyte in free solution is described as

$$v_{ep} = \mu_{ep}E = \mu_{ep}\frac{V}{L} \quad (2)$$

where $E$ and $L$ are electric field strength and capillary length. Eq. (2) assumes that the field strength is homogeneous throughout the capillary or the capillary is filled with homogeneous BGS. To perform preconcentration, the discontinuous zones having different electrical conductivities must be constructed along the capillary axis. The ratio of the electrophoretic velocities of the ions, $\gamma$, between the two zones having different conductivities is given

$$\gamma = \frac{v_{ep1}}{v_{ep2}} = \frac{E_1}{E_2} = \frac{\rho_1}{\rho_2} \quad (3)$$

where $\rho$ is resistivity and 1 and 2 indicate two discontinuous zones, for example, sample zone and BGS. If the sample solution is prepared as a high resistivity or a low electrolyte concentration solution and BGS is a low resistivity or a high electrolyte concentration solution, the analytes in the sample solution will

be concentrated at the boundary of the two zones. The concentration of the analyte concentrated by field-enhanced sample stacking, $C_{\text{stacked,}}$ is given by

$$C_{\text{stacked}} = C_{\text{injected}}\gamma \quad (4)$$

where $C_{\text{injected}}$ is the concentration of the analyte in the sample solution injected. The resistivity is inversely proportional to the concentration of the electrolyte. It is easy to realize the value $\gamma$ higher than 1000 but it is not easy to realize high concentration efficiency even with a high $\gamma$ conditions. The velocity of electroosmotic flow (EOF), which is the bulk liquid flow in the capillary generated under most CE conditions either strong or weak, is also proportional to the field strength. However, the bulk liquid flow velocity must be constant throughout the capillary and hence mixing of the two solutions will occur at the boundary, causing broadening of the focused zone. Therefore, it is recommended to employ acidic condition or EOF suppressed condition using coated capillary to obtain a high concentration efficiency or to avoid the mismatch of EOF velocity between the two zones.

Several techniques have been developed by utilizing the field-enhanced sample stacking for sample preconcentration [1,18]. Normal stacking mode (NSM) is the simplest among the techniques but concentration efficiency is not high (ca. 10-fold). The sample solution prepared in low electrical conductivity matrix is introduced as a long plug by pressurized method and a voltage is applied without any additional procedures. The amount of the sample injected must be rather low to keep separation efficiency high. If EOF is suppressed, the concentration efficiency is higher than that with a strong EOF.

To obtain higher concentration efficiency, large volume sample stacking (LVSS) and field-enhanced sample injection (FESI) techniques are available and more than 100-fold concentration is possible. The sample matrix must be removed from the capillary before CE separation in LVSS: two techniques are available for the removal of the sample matrix, with or without polarity switching. LVSS has also been defined in the literature as stacking with matrix removal (SWMR). For the preconcentration of anions under a strong positive (toward cathode) EOF, a negative voltage is first applied to remove the sample matrix and the polarity is switched to positive when the current reaches 90–99% of the actual current (the current observed when whole capillary is filled with BGS only). For the analytes to be concentrated the electrophoretic velocity of the analyte anion in the sample solution must be faster in opposite direction than the velocity of EOF, which condition is generally satisfied because the field strength in the sample solution zone is higher than that in the BGS. For the preconcentration of cations by LVSS, an additive is used to reverse EOF. LVSS without polarity switching is less popular technique and must be performed under low EOF having opposite migration direction to the electrophoretic migration of the analyte. Acidic conditions are usually employed for this purpose. It should be noted that only anions (or cations) can be concentrated and separated in LVSS in a run.

In FESI the sample solution is prepared in a low conductivity matrix and is electrokinetically injected by applying positive or negative voltage depending on the charge of the analyte. A useful theoretical treatment is given by Chien [19] for FESI. The sample solution is prepared in a low conductivity matrix as in other stacking modes and electrokinetically injected; low or reduced EOF conditions are employed. A short water plug is often injected prior to electrokinetic injection to secure field-enhanced sample stacking conditions. The amount of the sample injected can be much larger in FESI than that in LVSS but the amount injected is biased by the electrophoretic mobility. FESI is a powerful sample preconcentration technique and more than 1000-fold increase in sensitivity is possible. It should be noted that the amount of the sample injected is not proportional to the injection time if the injection time is long due to depletion of the analyte in the sample solution. An advantage of FESI is possible selective injections by optimizing the pH of the sample solution; this is particularly useful for selective injection of amphoteric analytes. For example, amphoteric analytes such as peptides can be negatively or positively charged depending on pH and only positive or negative analytes are injected in FESI [20].

Although neutral analytes are not directly concentrated by this technique, the use of the pseudostationary phase as in electrokinetic chromatography (EKC) enables on-line sample preconcentration as in capillary zone electrophoresis (CZE) [21,22], because neutral analytes are apparently charged when they are complexed with the pseudostationary phase. However, the concentration efficiency depends significantly on the retention factor or the ratio of the complexed and free analytes; a weakly interacting analyte have low apparent charge and hence low apparent electrophoretic mobility causing low concentration efficiency. Under suppressed EOF, hydrophobic analytes can be concentrated about 100-fold in MEKC either with pressurized injection [23] or with electrokinetic injection [24].

### 3.2. Transient isotachophoresis

Isotachophoresis (ITP) is a separation mode of CE, where analytes are separated as adjoining successive zones in the order of decreasing electrophoretic mobilities. Therefore, separated analyte peaks give a stepwise electropherogram different from peaks in CZE. The sample solution is introduced between the leading electrolyte solution and the terminating electrolyte solution. The leading electrolyte has higher and the terminating electrolyte has lower electrophoretic mobility than any analyte ions in the sample solution. When the voltage is applied the concentration of each separated zone is automatically adjusted to that determined by the concentration of the ion in the foregoing neighbor zone as given by

$$C_{\text{A}} = \frac{C_{\text{L}}\mu_{\text{A}}(\mu_{\text{L}} + \mu_{\text{Q}})}{\mu_{\text{L}}(\mu_{\text{A}} + \mu_{\text{Q}})} \quad (5)$$

where $\mu_{\text{L}} > \mu_{\text{A}}$ and $C_{\text{A}}$, $C_{\text{L}}$ are concentrations of analyte ion, A, in the adjoining zone to the leading ion, L, zone and $\mu_{\text{A}}$, $\mu_{\text{L}}$, $\mu_{\text{Q}}$ electrophoretic mobility of A, that of L, and that of the counter ion Q (assumed the same ion for A and L), respectively. Eq. (5) suggests that the concentration of A is determined by $C_{\text{L}}$, $\mu_{\text{L}}$ and $\mu_{\text{A}}$. Another ion, for example, the concentration of B in the following B zone is similarly determined by $C_{\text{A}}$. If the

concentration of analyte ion A in the sample solution is much lower than that of the leading electrolyte, it will be concentrated up to that determined according to Eq. (5).

The principle of ITP can be applied to preconcentration in CZE, which is termed as transient ITP (tITP). There are several modifications in tITP to perform sample preconcentration. For example, a BGS having a low electrophoretic mobility like borate is filled inside the capillary and a leading electrolyte (e.g., chloride ion) solution is injected, followed by the sample solution. When the voltage is applied, the ITP separation starts and the analytes are concentrated by the ITP principle if their concentrations are low. The concentrated zones are soon separated further by CZE. The leading electrolyte can be added to the sample solution to obtain the same tITP effect. The choices of BGS and leading or terminating electrolyte are very important to perform tITP successfully. Computer simulation of tITP concentration is reported Schwer et al. [25] and zone behaviors in tITP are schematically described by Beckers and Boček [3].

Shihabi reported that the addition of a water miscible organic solvent such as acetonitrile, acetone, methanol or 2-propanol and salts such as sodium chloride was useful for on-line sample preconcentration and the method was named as transient pseudo-isotachophoresis [26], where the mechanism was assumed that the organic solvent functions as a terminating ion and chloride ion acts as the leading ion when sodium chloride was used. Borate (300 mM, pH 8.4) or β-alanine (300 mM, pH 10.4) was used as BGS.

### 3.3. Dynamic pH junction

It is well understood that the pH of BGS is very important to optimize the separation in CZE. The pH close to the p$K_a$ of the analytes is generally a good choice for the separation because the ionization states are most diverse among the analytes when their p$K_a$ values are close each other. The dynamic pH junction technique utilizes significant changes in ionization states of the analytes or electrophoretic velocities between different pH values. The name dynamic pH junction was named by Britz-McKibbin and Chen [17], although the use of discontinuous buffer system was reported by Aebersold and Morrison previously [27]. For example, a weakly acidic analyte dissolved in an acidic matrix is injected as a long plug and the capillary is filled with an alkaline BGS. When a positive voltage is applied at the injection end, the acidic sample zone is gradually titrated by the hydroxide ion in the alkaline BGS from the cathodic side and the analyte will be ionized in the neutralized zone. The negatively ionized analyte will migrate toward the anode but if it enters into the acidic sample zone, it will be protonated again to neutral and stop the electrophoretic migration. Thus, the weakly acidic analyte can be focused at the neutralization boundary during the neutralization of the sample zone. The concentration mechanism is discussed by comparing experimental and computer simulated results by Kim et al. [28], where electrokinetic dispersion was found to play an important role; that is, the choices of sample matrix and BGS were important as well as that of pH values. Lee et al. discussed the importance or tITP mechanism in dynamic pH junction [29] by experiments and computer simulation. Generally a high concentration buffer of high pH consisting of a low electrophoretic mobility electrolyte is needed as BGE for the concentration of weak acids and a high concentration acidic sample matrix consisting of a high mobility ion. Dynamic pH junction technique can selectively concentrate analytes having a narrow range of p$K_a$ and it is useful for the concentration of weakly acidic or basic analytes.

Wei et al. developed an interesting technique to form the pH gradient inside the capillary by electrolysis of water [30]. A Pt wire was inserted inside the capillary and when the voltage was applied the electrolysis of water occurred and $H^+$ ion was continuously generated at the cathodic end and $OH^-$ ion at the anodic end. These ions titrated the BGS and the sharp pH gradient was formed; high [$H^+$] at the cathodic end of the Pt wire to low [$H^+$] at the cathodic end of the capillary, and high [$OH^-$] at the anodic end of the Pt wire to low [$OH^-$] at the anodic end of the capillary. As the BGS, a low conductivity 15 mM histidine solution (pH 7.0) with 0.2% poly(vinylpyrrolidone) was used to suppress the bubble formation at the end of the Pt wire and EOF. For the separation of anionic analytes, the Pt wire was placed at the injection end of the capillary and negative voltage was applied. For the separation of cationic analytes, the same polarity and same position of the Pt wire were held but reversed EOF condition was employed with an addition of didodecyldimethylammonium bromide. More than several hundredfold concentration factors for anionic analytes and a 30-fold concentration factor for cationic analytes were observed. The concentration mechanism is explained in terms of sweeping of analytes by $OH^-$ ion for anionic analytes and $H^+$ ion for cationic analytes.

### 3.4. Sweeping

Sweeping has been originally developed for the on-line concentration of neutral analytes for micellar electrokinetic chromatography (MEKC) separation [31]. Sweeping can be defined as a phenomenon whereby analytes are picked up and accumulated by the pseudostationary phase (micelles) that penetrates the sample zone. The length of the analyte zone after sweep, $l_{sweep,}$ is given by

$$l_{sweep} = l_{inj}\left[\frac{1}{(1+k)}\right] \quad (6)$$

where $l_{inj}$ and $k$ are the length of the sample solution injected and the retention factor defined by the ratio of the amount of the analyte incorporated into the micelle to that free of the micelle. The concentration of the micelle entering the sample zone is assumed equal to the micellar concentration in the BGS. It is apparent that the analyte having a higher $k$ value is more efficiently concentrated. When the interaction between the analyte and the pseudostationary phase is very strong or $k$ is large the concentration efficiency is very high up to 5000-fold. Eq. (6) gives the length of the sample zone when sweeping completed and not the zone length observed at the detection cell. To make $k$ large, the sample matrix should be prepared without organic solvents or other additives to improve separation such as cyclodextrins. An extremely narrow zone length was observed for analytes having

large $k$ values when the swept zone was measured just at the end of the sweeping process inside a microchip channel with laser-induced fluorescence detection [32]. The narrow zone (less than 30 μm), however, broadened quickly according to the thermal diffusion along the channel. Therefore, when the length from the detection end of the injected sample zone to the detection point was very short and very narrow detection window was employed, a very high concentration efficiency up to 3,900,000-fold was observed [33].

Sweeping phenomenon was experimentally and theoretically studied and it is shown that Eq. (6) is valid also for charged analytes regardless of charge of the analyte and the direction of EOF, provided $k$ is defined as mentioned above [34]. Sweeping is very useful for the concentration of ions as well as neutral analytes because the interaction between ions and micelles are strong if their charges are opposite. For example, several amino compounds can be efficiently concentrated by sodium dodecyl sulfate (SDS) micelle under acidic conditions [35].

It should be mentioned that the conductivity of the sample zone is usually adjusted to be nearly equal to that of the running micellar solution but no micelle is added to the sample solution. Therefore, homogeneous electric field strength is assumed throughout the whole capillary under sweeping conditions different from field-enhanced stacking techniques. Palmer et al. claimed a better preconcentration effect upon addition of a salt in high concentrations into the sample matrix (high-salt) [36,37], while Quirino et al. described the mechanisms of focusing using high salt matrices under acidic conditions [38]. The data obtained since the seminal paper on sweeping in 1998 prescribed the use of sample matrices with conductivity values that are lower, equal to, or higher than that of the BGS. This suggests that an additional mechanism(s) may be affecting the focusing results of sweeping, such mechanisms is the subject of future investigations. Introduction of electrokinetic injection in combination with sweeping made it possible to inject a large volume of samples, although injection volume in conventional sweeping is limited less that the capillary volume [39].

Other pseudostationary phases are equally available for sweeping, for example, microemulsions in microemulsion EKC (MEEKC) or charged cyclodextrins in cyclodextrin EKC [40]. The idea can be extended to another interaction such as complexation reaction between metal ions and ethylenediaminetetraacetic acid (EDTA) [41], *cis*-diols and borate ion [42]. The former is very effective for the concentration of many metal ions which complex with EDTA can be concentrated by in situ complexation and sweeping, where metal ions dissolved in a weakly acidic buffer (e.g., 30 mM acetate buffer, pH 5.0 but the conductivity of the solution is adjusted to nearly equal to that of BGS, which contains, for example, 1 mM EDTA in the same acetate buffer) are used and more than 100-fold increase in sensitivity is obtained.

### 3.5. Combination of different preconcentration techniques

Although each on-line concentration technique is useful, the combination of two techniques is more efficient in increasing detection sensitivity. The first combination technique involved FESI and sweeping, this combination generated almost million-fold increase in sensitivity [43], because FESI enabled the injection of charged analytes only from a dilute sample solution for a prolonged duration of time and the analytes were injected with simultaneous concentrations. Although the technique was applied to the concentration of basic compounds with SDS micelle as the pseudostationary phase under acidic conditions, acidic analytes also can be concentrated with a cationic surfactant such as cetyltrimethylammonium chloride (CTAC) using a coated capillary to suppress EOF [44]. The similar technique named electrokinetic supercharging (EKS) in combination with tITP was published by Hirokawa et al. [45], where the first step is FESI and the second step is tITP. A leading electrolyte zone was injected before FESI and after a long time period of FESI a terminating electrolyte zone was injected and a CZE separation was performed with approximately 3000-fold concentration. If the analytes are a mixture of neutral and weakly acidic analytes, it may be possible to concentrate both analytes by sweeping under acidic conditions keeping the analyte neutral. However, weakly acidic analytes can be successfully concentrated by dynamic pH junction and if SDS is added to BGS, neutral analytes also can be simultaneously concentrated by sweeping [46].

## 4. Applications of on-line sample preconcentration in capillary electrophoresis

The applications of CE technologies in conjunction with on-line preconcentration will be explored here, classified in their relevance to several categories:

(1) Biological, either basic biological research or more biomedical/clinical research of applied technology/therapy.
(2) Environmental, in terms of the characterization of the native components of environmental samples, for example, cationic/anionic contents, or exogenously derived elements in environmental samples, such as chemical contaminants.
(3) Food analysis, for nutritional assessment, determining the presence and amount of nutritional components in food/beverages, as well as food safety inspection for antibiotics or pest-control chemical residues.
(4) Pharmaceutical products, referring to the quality control for production, quantifying the desired components or verifying the absence of contaminants, as well as in research and development, and determining the presence of desired bioactive components in animal or human samples, as well as phytochemical analysis.
(5) Toxicological/Forensic, related in some extent to the previous categories, looks for and determines the amounts of analytes in human samples, as well as psychotropic drugs, toxic compounds, or/and their derivatives.

Table 1 describes a list of applications of on-line preconcentration techniques in capillary electrophoresis. A few examples from each application category will be mentioned here. Many different names and abbreviations are used for similar techniques but the names used in original papers are used in this table as they are. These abbreviations are explained following the table,

Table 1
Applications of on-line sample preconcentration in capillary electrophoresis

| Sample target | Sample matrix | Separation mode | Limit of detection | Concentration factor | Application | Ref. |
|---|---|---|---|---|---|---|
| 2,5-Dimethoxy-4-ethylthiophenethylamine (2C-T-2) | Murine urine samples | CZE-MEKC; LVSEP-CZE; Sweeping-MEKC | CZE-MEKC: 4.5–5.0 μg/mL; LVSEP-CZE: 19.2 ng/mL; Sweeping-MEKC: 9.1 ng/mL | | Biological | [47] |
| 2-Naphthalenesulfonic acid, L-tryptophan | Biological matrices | PEO-CE | 2-Naphthalenesulfonic acid: 8 pM; L-tryptophan: 70 pM | | Biological | [48] |
| 3-Nitrotyrosine | Rat urine | LVSS-CE | 0.08 μM | | Biological | [49] |
| 4-Nonylphenol, 4-*tert*-octylphenol, bisphenol A, and 4-*tert*-butylphenol | Biological matrices | SPE-RMM-MEKC | 4-Nonylphenol: 0.089 mg/L; 4-*tert*-octylphenol: 0.030 mg/L; bisphenol A: 0.0091 mg/L; 4-*tert*-butylphenol: 0.033 mg/L | | Biological | [50] |
| Adrenocorticotropic steroid hormones (cortisol, cortisone, corticosterone, 11-dehydrocorticosterone, 17-hydroxyprogesterone, 11-deoxycortisol, and progesterone) | Biological matrices | RMM-MEKC | 3 ng/mL | | Biological | [51] |
| Alexa fluor 488, BODIPY | *Proof of concept* | tITP-CE | | $6.4 \times 10^4$ | Biological | [52] |
| Amines | Biological matrices | RPRP-HCFASS-CE | $10^{-13}$ M | | Biological | [53] |
| Amino acids | Cerebrospinal fluid | PEO-CE | 4 nM | | Biological | [54] |
| Amino acids | Cerebrospinal fluid | PEO-Sweep-MEKC | 0.30–2.76 nM | 50–800-fold sensitivity enhancement | Biological | [55] |
| Amino acids | Pharmaceutical samples | LVSS-CZE | 1000-fold increase in detection sensitivty relative to conventional CE | | Biological | [56] |
| Amino acids | Amniotic fluid | CZE | Arg: 1.5 μM; Asp: 6.7 μM | | Biological | [57] |
| Amino acids | Biological matrices | CD-CZE | CBI-DL-serine: 0.20 nM; CBI-DL-glutamate: 0.30 nM | | Biological | [58] |
| Amino acids | Biological matrices | tITP-CZE | | 150,000-fold | Biological | [59] |
| Amino acids | Biological matrices | tITP-CZE | Asp: 5200; Trp: 2800, Phe: 3100 times improvement in sensitivity, compared with normal CE separation | | Biological | [60] |
| Amino acids | Murine brain microdialyste, murine serum, human saliva | ABS-CE | Murine brain: Glu:0.26–0.83 μM, Asp: 0.24–0.64 μM; murine serum: Glu: 37–40 μM, Asp: 8.4–10 μM; human saliva: Glu: 5.8 μM, Asp: 1.0–4.1 μM | | Biological | [61] |
| Amino acids (glycine, glutamine, glutamate, and γ-aminobutyric acid) | Cerebrospinal fluid | PEO-CE | 10–30 nM | | Biological | [62] |
| Amino acids (tryptophan) | Biological matrices | SPE-CE | | ∼300-fold | Biological | [63] |
| Anilines | Biological matrices | Dynamic pH-junction CE | 1.9-3.7 ppb | | Biological | [64] |

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|---|---|---|---|---|---|---|
| Aromatic amino acids (tyrosine, phenylalanine, dihydroxyphenylalanine, tryptophan, 3-nitrotyrosine, 3-chlorotyrosine, *ortho*-tyrosine, *meta*-tyrosine, 3-hydroxyphenylacetic acid) | Biological matrices | FASS-LVSS-CE | 2.5–10 nM | | Biological | [65] |
| Aromatic carboxylic acids, dansyl amino acids, and naphthalene-disulfonic acids | Biological matrices | ASEI-MEKC | | 1000–6000-fold | Biological | [44] |
| Biogenic amines (histamine, methylhistamine, and serotonin) | Biological matrices | CZE | 0.1 μM level | | Biological | [66] |
| Biomolecules (lipoproteins) | Biological matrices | MFMP-ACE | 82-fold increase in sensitivity | | Biological | [67] |
| BODIPY | *Proof of concept* | SPE-CEC (ODS column) | 70 fM | | Biological | [68] |
| Catecholamines (epinephrine) | Biological matrices | VDIF-pH junction-CE | $4 \times 10^{-8}$ M | | Biological | [17] |
| Catecholamines, purines, nucleosides, nucleotides, amino acids, steroids, and coenzymes | *Bacillus subtilis* cell extracts | Dynamic pH junction-sweeping CE | | >3 orders of magnitude increase | Biological | [46] |
| Charged proteins | Biological matrices | Mobility-based selective preconcentration-CE | | ~60–200-fold | Biological | [69] |
| Chlorophenols, chlorophenoxy acids | Biological matrices | LVSS-Sweep-MEKC | 10–40-fold improvement of sensitivity relative to standard injection | | Biological | [70] |
| Cisplatin | Human serum | tITP-MEKC | 2 μg/L | | Biological | [71] |
| Corticosterone | Murine plasma | Sweep-MEKC | 5 ng/mL | | Biological | [72] |
| Dichlorprop, mecoprop enantiomers | Drinking, surface waters | SPE-Stacking-CE | 0.1 μg/L | | Biological | [73] |
| DNA | Biological matrices | SPE-MCE | | 500-fold | Biological | [74] |
| DNA | Biological matrices | FASS-FASI-AuNP-MGE | 5.7 amol/50 μL | 23,000-fold for 400 bp; 25,500-fold for 2000 bp DNA fragments | Biological | [75] |
| DNA | Biological matrices | Ultra-high voltage EC | | 5-fold | Biological | [76] |
| DNA | Biological matrices | EKS-MCGE | 0.22 mg/L | | Biological | [77] |
| DNA | Hepatitis B virus genome | tITP-CZE | 0.0021 pg/μL | | Biological | [78] |
| DNA (φX174 RF DNA–*Hae*III digest) | Biological matrices | PEO-CE | 0.171 ng/m | | Biological | [79] |
| DNA adducts | Human breast tissue extract | CE | $3 \times 10^{-8}$ M | | Biological | [80] |
| DNA fragments | Biological matrices | PEO-CE | >400-fold improvements in the sensitivity relative to that by conventional injections | | Biological | [81] |
| DNA fragments | Biological matrices | PEO-CE | | 27-fold | Biological | [82] |
| DNA fragments | Biological matrices | tITP-CZE | 0.2 mg/L of each DNA fragment | | Biological | [83] |
| DNA fragments | Biological matrices | Dynamic pH junction-CE | 0.2 mg/L | | Biological | [84] |
| DNA fragments | Nuclear extracts | PEO-CE | 0.015 μg/mL | | Biological | [85] |

Table 1 (*Continued*)

| Sample target | Sample matrix | Separation mode | Limit of detection | Concentration factor | Application | Ref. |
|---|---|---|---|---|---|---|
| DNA fragments | PCR buffer | | | | | |
| DNA oligonucleotides | Biological matrices | Sweep-CZE | | 112-fold sensitivity enhancement for the oligonucleotides relative to that run in a running buffer without DTAB | Biological | [87] |
| DNA oligonucleotides w/adducts | Biological matrices | PAEKI-CZE | 0.04–0.08 μM for ds oligonucleotides | 300–800-fold | Biological | [88] |
| dsDNA | Biological matrices | PEO-BCE | | 170-fold | Biological | [89] |
| dsDNA fragments | PCR buffer | pH-mediated sample stacking-CE | 9 fg/μL | | Biological | [90] |
| dsDNA markers V (pBR 322/*Hae*III digest) and VI (pBR 328/*Bgl*I digest and pBR 328/*Hin*fI digest) (∼3–2176 bp) | Biological matrices | PEO-CE | 2.0 ng/mL | | Biological | [91] |
| Ecdysteroids (20-hydroxyecdysone, ajugasterone C, polypodine B and ponasterone A) | Biological samples | Stacking-MEKC | LOD improved ∼1 order of magnitude relative to conventional methods | | Biological | [92] |
| Enantiomers of 2,4-dinitrophenyl labeled norleucine (DNP-Nleu); tryptophan enantiomers | Human urine | tITP-CZE | 200 nmol/L | | Biological | [93] |
| Estrogen and estrogen binding proteins | Biological matrices | SHDI-EKC | | 200–300-fold | Biological | [94] |
| Ethyl glucuronide, lactate and acetate | Human serum, diluted | SSS-CZE | EtG: $3.8 \times 10^{-7}$ M, lactate: $2.60 \times 10^{-6}$ M and EtG acetate: $2.18 \times 10^{-6}$ M | | Biological | [95] |
| Flavin denvatives (riboflavin, flavin mononucleotide (FMN) and flavin–adenine dinucleotide (FAD)) | Human body fluids, Beverages | MCE | 0.15–1.0 μg/L | | Biological | [96] |
| Flavin derivatives, riboflavin, flavin mononucleotide (FMN), and flavin adenine dinucleotide (FAD) | *Bacillus subtilis* cell extracts | Dynamic pH junction-sweeping CE | 4.0 pM | | Biological | [97] |
| Flavin derivatives, riboflavin, flavin mononucleotide (FMN), and flavin adenine dinucleotide (FAD) | *Bacillus subtilis* cell extracts | Dynamic pH junction-sweeping CE | 4.0 pM | 1200-fold improvement in sensitivty relative to standard injection | Biological | [98] |
| Flavins (riboflavin) | Biological matrices | Dynamic pH junction-MEKC | 3–7 ppb | | Biological | [99] |
| Fluorescein | Biological matrices | MCE | | 300-fold | Biological | [100] |
| Fluorescein and bodipy | *Proof of concept* | tITP-CE | 100 aM | | Biological | [101] |
| Fluorescein and bodipy | *Proof of concept* | FASS-MCE | | 1100-fold | Biological | [102] |
| Gabapentin | Human plasma | CZE | 60 nM | | Biological | [103] |
| Glucoconjugated and hydroxylated porphyrins and chlorins (e.g., *m*-THPP, TPP(glu)2) | Human serum | NACE | 10–30 nM | | Biological | [104] |
| Glutathione | Biological matrices | FASI-CD-MEKC | | 10–20-fold | Biological | [105] |

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|---|---|---|---|---|---|---|
| Glutathione (GSH); oxidized-form glutathione (GSSG) | Human plasma | tITP-CZE | GSH: $6.3 \pm 0.8$ μmol/L; GSSG: $8.8 \pm 0.5$ μmol/L | | Biological | [106] |
| Glycoprotein-derived oligosaccharides | Biological matrices (glycoproteins) | 2D-PAGE-MEKC | | 60–360× | Biological | [107] |
| Heavy metal cations ($Fe^{2+}$, $Ni^{2+}$, $Zn^{2+}$) | Human urine | tITP-CZE | $Fe^{2+}$, 0.3 ppb; $Ni^{2+}$, 0.16 ppb;and $Zn^{2+}$, 0.8 ppb | | Biological | [108] |
| Heavy metal cations ($Fe^{2+}$, $Ni^{2+}$, $Zn^{2+}$) | Human urine | tITP-CZE | $Fe^{2+}$, 0.7 ppb, $Ni^{2+}$, 0.4 ppb; $Zn^{2+}$, 1.2 ppb | | Biological | [109] |
| Histamine | Biological matrices | FASI-CZE | $1.25 \times 10^{-11}$ M | | Biological | [110] |
| Human serum albumin (HSA) and its immunocomplex with a monoclonal antibody | Human serum | tITP-MCE | 7.5 pM | | Biological | [111] |
| Low-abundance proteins | Proteomes | LVSEP-CE | μg/mL | >100-fold | Biological | [112] |
| Major milk proteins (e.g., β-lac B) | Skimmed bovine milk | CABCE | A few mg/L | 30–200× | Biological | [113] |
| Melatonin and its precursors/metabolites (L)-tryptophan ((L)-TRP), 5-methoxyindoleacetic acid (5-MIAA), 6-hydroxymelatonin (6-HMT), MT, serotonin (SER) and 5-methoxytryptamine (5-MTRA)) | Human serum, diluted | RMM-MEKC | L-Trp: 21 ng/mL; 5-MIAA: 26 ng/mL; 6-HMT: 100 ng/mL | | Biological | [114] |
| Melatonin and other pineal hormones | Biological matrices | MEKC | 9.7–41.8 nmol/L | | Biological | [115] |
| Metal-binding proteins | Biological matrices | tITP-CZE | 50–160 fmol | | Biological | [116] |
| Mixed cultures of microorganisms *Escherichia coli*, *Candida albicans*, *Enterococcus faecalis*, and *Staphylococcus epidermidis* | Biological matrices | CZE | 1–10 injected cells | | Biological | [117] |
| Muramic acid (MA) and diaminopimelic acid (DAP) enantiomers | Complex biological samples | Dynamic pH junction-CE | 100-fold enhancement in concentration sensitivity compared to conventional off-line derivatization procedures | | Biological | [118] |
| Naphthalene-2,3-dicarboxaldehyde (NDA)-derivatized dopamine | Biological matrices | MEKC; Sweeping-MEKC | MEKC: $2.0 \times 10^{-7}$ M; sweeping-MEKC: $4.0 \times 10^{-9}$ M | | Biological | [119] |
| Neuropeptide Y | Murine nuclear extract | Competitive immunoassay-CE | 850 pM | | Biological | [120] |
| Neuropeptides (somatostatin, vasopressin, neurotensin, thyrotropin-releasing hormone) | Human plasma | ACN-stacking/CZE | 20 ng/mL | | Biological | [121] |
| Nitrate/nitrite | Human serum, deproteinated | CZE | Nitrite: 4.1 μM and nitrate 2.0 μM | | Biological | [122] |
| Nitrate/nitrite | Human serum, diluted | MCE | Nitrite: 24 μM and nitrate 12 μM | | Biological | [123] |
| Nitrate/nitrite | Human serum, saliva | tITP-CZE | Nitrite: 2.6 μM and nitrate 1.5 μM | | Biological | [124] |
| Nitrate/nitrite | Murine brain and liver tissue extracts from LPS-treated animals | tITP-CZE | sub-μM | | Biological | [125] |

Table 1 *Continued*

| Sample target | Sample matrix | Separation mode | Limit of detection | Concentration factor | Application | Ref. |
|---|---|---|---|---|---|---|
| Nitrate/nitrite | Neuronal tissues | tITP-SPME-CZE | Nitrite: 8.9 nM (0.41 ppb); Nitrate: 3.54 nM (0.22 ppb) | | Biological | [126] |
| Nucelotides | Biological matrices | PAEKI-CZE | 0.04–0.07 ng/mL | 5000-fold enrichment | Biological | [127] |
| Nucleotides | Cell extracts | VDIF-CE | $4.0 \times 10^{-8}$ M | 50-fold | Biological | [128] |
| Organic acids | Cerebrospinal fluid | CZE | 2–8 μg/mL | | Biological | [129] |
| Peptides | Biological matrices | Dynamic pH junction-CE | 550–1000-fold sensitivity enhancement | | Biological | [131] |
| Peptides | Biological matrices | Dynamic pH-junction-CE | | 124-fold improvement in concentration sensitivity | Biological | [132] |
| Peptides | Biological matrices | CE | 500 aM | | Biological | [133] |
| Peptides | Biological matrices | CE | | 100–200-fold | Biological | [134] |
| Peptides | Biological matrices | CE | 20 pg | | Biological | [135] |
| Peptides | Biological matrices | SPE-CE | | 3–4 orders of magnitude | Biological | [136] |
| Peptides | Biological matrices | FASI-CE | Detection sensitivity increase >3000-fold | | Biological | [137] |
| Peptides | Biological matrices | CE | 8–32 nM. | | Biological | [138] |
| Peptides (bradykinin, L-enkelphalin) | Biological matrices | LVSS-CE | Bradykinin: 7 pM; L-enkelphalin: 3 pM | | Biological | [139] |
| Peptides (enkephalin) | Cerebrospinal fluid | Tee-split interface SPE-CE | 5 ng/mL | | Biological | [140] |
| Peptides (enkephalin) | Cerebrospinal fluid | MI-CE | 5–10 ng/mL | | Biological | [141] |
| Peptides (enkephalin) | Cerebrospinal fluid | SPE-CE | 1.5–3 ng/mL | | Biological | [142] |
| Peptides (enkephalin) | Cerebrospinal fluid | Tee-split interface SEC-CE | 100 ng/mL | | Biological | [143] |
| Peptides (enkephalins and albumin) | Biological matrices | SEC-CZE | 0.8 μg/mL | | Biological | [144] |
| Peptides/proteins | Biological matrices | FESI-CE | Low nM levels (fmol/μL) | | Biological | [20] |
| Phenol derivatives | Biological matrices | SEI-Sweep-MEKC | | >100-fold | Biological | [145] |
| Phenolic compounds (derivatives of benzoic and cinnamic acids) | Biological matrices | CZE | 2.3–3.3 μM | | Biological | [146] |
| Phosphoamino acids | Biological matrices | Dynamic pH junction-CE | 0.1 μM | | Biological | [147] |
| Phosphopeptides | Biological matrices | CZE | | 600-fold | Biological | [148] |
| Phosphopeptides | Tryptic digests of α- and β-casein | CE | Low pmole levels | | Biological | [149] |
| Plant hormones (gibberellic acid, abscisic acid, indole-3-acetic acid, 1-naphthaleneacetic acid, 2,4-dichlorophenoxyacetic acid, kinetin-6-furfurylaminopurine and *N*-6-benzyladenine. | Tobacco flowers | LVSS-BCE | 0.306 ng/L | 10–600-fold | Biological | [150] |
| Porphyrins (zinc-protoporphyrin, protoporphyrin, and coproporphyrin (CP) I and III) | Biological matrices | ACN-stacking-CZE | 0.8 ng/mL (1.1 nmol/L of CPIII or CPI) | ∼1000-fold | Biological | [151] |
| Protein | *Staphylococcus* proteome | FESI-CE | Species-specific protein patterns for 6 *Staphyloccal* species | | Biological | [152] |

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|---|---|---|---|---|---|---|
| Protein (ovalbumin) | Biological matrices | CZE | 0.1 nM | >1–2 orders of magnitude relative to conventional electrophoretic/chromatographic-based proteome technologies | Biological | [130] |
| Proteins | Biological matrices | EKSI-MCE | | Local and spatially averaged concentration are increased by 4 and 2 orders of magnitude, respectively | Biological | [153] |
| Proteins | Mixture of test proteins and cadmium | LVSS-CE | | 6-fold | Biological | [181] |
| Proteins (lysozyme and ribonuclease A) | Biological matrices | IEF-CZE | | 100-fold | Biological | [154] |
| Proteins (α-lactalbumin) | Biological matrices | PEO-CE | 0.48 nM | | Biological | [155] |
| Proteins (bovine carbonic anhydrase, α-lactalbumin, and β-lactoglobulins A and B) | Biological matrices | CZE | nM range | <40-fold | Biological | [156] |
| Proteins (bovine serum albumin) | Biological matrices | CE | | 550-fold | Biological | [157] |
| Proteins (carbonic anhydrase) | Biological matrices | PEO-CZE | 31 pM | | Biological | [160] |
| Proteins (cytochrome *c*, lysozyme, ribonuclease, and chymotrypsinogen) | Biological matrices | CE | | Cytochrome *c*, lysozyme, ribonuclease, and chymotrypsinogen were 65, 155, 705, and 800-fold, respectively | Biological | [158] |
| Proteins (cytochrome *c*, ribonuclease A, and carbonic anhydrase II) | Biological matrices | 2D-IEF-tITP-CE | | 50–100× | Biological | [159] |
| Proteins (lysozyme) | Biological matrices | CE | 1.2 nM | | Biological | [161] |
| Proteins (lysozyme, myoglobin, carbonic anhydrase, and α-lactalbumin) | Biological matrices | pH-junction-CE | Lysozyme: 1.9 nM; myoglobin: 3.2 nM; carbonic anhydrase: 11.3 nM; α-lactalbumin: 6.5 nM | | Biological | [162] |
| Proteins (myoglobin) | Biological matrices | Dynamic pH-junction-CE | | ∼1700-fold preconcentration | Biological | [163] |
| Proteins (myoglobin) | Biological matrices | tITP-dynamic pH junction-CE | | 65-fold | Biological | [164] |
| Proteins (ovalbumin) | Biological matrices | FASI-CE | 100 fM | | Biological | [165] |
| Proteins, amino acids (myoglobin, aspargine) | Biological matrices | Dynamic pH-junction-CE | | $3 \times 10^3$ for myoglobin, $7 \times 10^3$ for asparagine | Biological | [166] |
| Proteins, peptides | Protein digests | tITP-CZE | $<10^{-8}$ M | | Biological | [167] |
| Purine metabolites | Human urine | Dynamic pH junction-CE | 80 nM | | Biological | [168] |
| Purines (adenosine, hypoxanthine, and inosine) | Biological matrices | CE | Adenosine: 2.2 μM; hypoxanthine: 3.6 μM; inosine: 1.4 μM | | Biological | [169] |

Table 1 (*Continued*)

| Sample target | Sample matrix | Separation mode | Limit of detection | Concentration factor | Application | Ref. |
|---|---|---|---|---|---|---|
| Purines (mercaptopurine monohydrate, 6-methylmercaptopurine, thioguanine, thioguanosine, and thioxanthine) | Biological matrices | LVSS-CE w/polarity switching | 44–90-fold improvement of sensitivity | | Biological | [170] |
| Pyridine and adenine nucleotide metabolites | *Bacillus subtilis* cell extracts | Sweeping-CE | 20 nM | | Biological | [171] |
| Pyrimidine bases (uracil) | Biological matrices | CD-CZE | 0.8–1.8 μg/mL; 0.05 μg/mL | | Biological | [172] |
| Quinine | Biological matrices | Sweep-MEKC | 12.5 ppb; | 5800–10000-fold | Biological | [173] |
| Racemic vesamicol | Human serum | SPE-CD-CE | 0.5 μg/mL | | Biological | [174] |
| Rhodamine B | Biological matrices | Sweep-MCMEKC | | 450-fold | Biological | [32] |
| Sanguinarine | Biological matrices (e.g., rat hepatocytes, human gingival fibroblasts, feed, porcine faeces, body fluids and tissues) | SPE-SSS-CZE | 3 nM | | Biological | [175] |
| SDS–protein complexes (phosphorylase b, albumin, ovalbumin, carbonic anhydrase, trypsin inhibitor, and α-lactalbumin) | Biological matrices | EKS-MCGE | 0.27 μg/mL | | Biological | [176] |
| Seleno amino acids (selenomethionine, selenoethionine, and selenocystine) | Biological matrices | EKSI-Sweep-MEKC | μmole/L | 80× enrichment | Biological | [177] |
| Seleno amino acids (selenomethionine, selenoethionine, and selenocystine) | Biological matrices | tITP-MCE | μmole/L | | Biological | [178] |
| Staphylococcal enterotoxin B | Bovine serum albumin, casein, and milk sample matrixes | MACE | 28.5 fg/mL | | Biological | [179] |
| Tertiary amines | Biological matrices | FASS-pH junction-CE | TEA: 24 nM; TPA: 20 nM; TBA: 32 nM | | Biological | [180] |
| Thymidylate, thymidine 5′-diphosphate | Biological matrices | CE | TMP: 2.6 μM; TDP: 3.8 μM | | Biological | [182] |
| Tryptophan derivatives (5-hydroxy L-tryptophan, 5-methyl L-tryptophan, 1-methyl L-tryptophan and L-tryptophan) | Amino acid mixture solutions | HLL-Sweep-CE | 10 nmol/L | | Biological | [183] |
| Unsaturated disaccharides of hyaluronic acid (di-HA) and chondroitin sulfate (di-CS) | Biological matrices | LPME-sweeping-MEKC | di-HA: 1.0–400.0; di-CS: 0.2–1.0 μg/mL | | Biological | [184] |
| Urinary 8-hydroxydeoxyguanosine (80HdG) | Human urine | SPE-Dynamic pH-junction-CE | 20 nmol/L | | Biological | [185] |
| Weakly acidic organic compounds | Biological matrices | LVSEP-SPE-NACE | 10–100 nM | | Biological | [186] |
| Xanthine and purine metabolites | Human urine | Dynamic pH junction-CE | Xanathine: 40 nM | | Biological | [187] |
| 2,4-Dichlorophenol and 2,4,5-trichlorophenol | Environmental water samples | SPE-CE | 2,4-Dichlorophenol and 2,4,5-trichlorophenol: 25 and 17 pg/mL, respectively. | | Environmental | [188] |

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|---|---|---|---|---|---|---|
| Alkylphosphonic acids (methyl-, ethyl-, and propylphosphonic acids) | Environmental samples | HSS-MEKC | MPA, EPA, and PPA were MPA: 0.13 μM (12 ppb), EPA: 0.13 μM (14 ppb) PPA: 0.14 μM (17 ppb) | | Environmental | [189] |
| Aluminum concentration (aluminum ion Al(III)) | Soil sample | FASS-CE | Minimum detectable Al concentration can be increased 12 times | | Environmental | [190] |
| Anionic metal cyclohexane-1,2-diaminetetraacetic acid (CDTA) complexes (Cu(II), Co(II). Zn(II), Mn(II), and Pb(II)) | Environmental samples | MEKC | $0.6 \times 10^{-6}$ M to $1.8 \times 10^{-6}$ M) | | Environmental | [191] |
| Anions | Environmental samples | IE-EF-CE | 1 μg/L | | Environmental | [192] |
| Anions ($Cl^-$, $NO_2^-$, $SO_4^{2-}$, $NO_3^-$, $HCO_3^-$) | Snow | CZE | 0.03 mg/L $Cl^-$, 0.1 mg/L $NO_2^-$, 0.07 mg/L $SO_4^{2-}$ 0.08 mg/L $NO_3^-$, 0.05 mg/L $F^-$, and 0.2 mg/L | | Environmental | [193] |
| Cations (Co, Ni, Zn, Mn) | Environmental samples | CZE | Increase in detection sensitivty 40x | | Environmental | [194] |
| Cations (Cu(II) and Co(II)) | Environmental water samples | CPE-CE | Co(II) and Cu(II) were 0.12 and 0.26 μg/L, respectively | 15.9-fold for Co(II); 16.3-fold for Cu(II) | Environmental | [195] |
| Cations (Cu(II), Ni(II), Co(II), and Fe(III)) | Tap water | CE | 2–10 μg/L | | Environmental | [196] |
| Aromatic amines and alkyl phthalates | Environmental samples | SEI-Sweep-MEKC | 100-fold increase in the concentration sensitivity relative to conventional MEKC-APCl-MS | | Environmental | [197] |
| Aromatic amines of environmental relevance | Environmental samples | CSEI-Sweep-MEKC | ppt-levels | | Environmental | [35] |
| Arsenic and selenium species (arsenite [As(III)], arsenate [As(V)], monomethylarsonic acid (MMA), dimethylarsinic acid (DMA), selenate [Se(VI)], selenite [Se(TV)], selenocystine (SeC), selenomethionine (SeM), and selenocystamine (SeCM)) | Environmental water samples | HSDC-CE | 0.049–2.38 mg/L | | Environmental | [198] |
| Arsenic compounds (arsenite, arsenate, dimethylarsenic acid, and monomethylarsenic acid) | Environmental water samples | CE | 5.0–9.3 μg/L | 37–50-fold | Environmental | [199] |
| Arsenic compounds (roxarsone, or 3-nitro-4-hydroxyphenylarsonic acid) | Animal feed | Dynamic pH-junction-CE | LOD reduced 100–800-fold | | Environmental | [200] |
| Arsenic species (arsenate (As(V)), monomethylarsonate (MMA), and dimethylarsinate (DMA)) | Environmental samples | LV-FASI-CZE | 0.026 mg/L for As(III), 0.023 mg/L for As(V), 0.043 mg/L for MMA, and 0.018 mg/L for DMA | 34–100-fold | Environmental | [201] |

Table 1 (*Continued*)

| Sample target | Sample matrix | Separation mode | Limit of detection | Concentration factor | Application | Ref. |
|---|---|---|---|---|---|---|
| Arsenic species (arsenite, arsenate, monomethylarsonic acid (MMA), dimethylarsinic acid (DMA), 4-hydroxy-3-nitrophenylarsonic acid (Roxarsone), *p*-aminophenylarsonic acid (*p*-ASA), 4-nitrophenylarsonic acid (4-NPAA), and phenylarsonic acid (PAA)) | Environmental water samples | LVSS-HSC-CZE | 5.61, 9.15, 11.1, and 17.1 μg/L for As(III), DMA, MMA, and AsM, respectively | | Environmental | [202] |
| Arsenic species (arsenite, arsenate, monomethylarsonic acid, dimethylarsonic acid, *p*-aminophenylarsonic acid, 4-hydroxy-3-nitrobenzenearsonic acid, 4-nitrophenylarsonic acid, phenylarsonic acid, and phenylarsine oxide) | Environmental water samples | CE | Arsenite 1.62 mg/L, arsenate: 6.22 mg/L, monomethylarsonic acid: 1.45 mg/L, dimethylarsonic acid: 1.83 mg/L, *p*-aminophenylarsonic acid: 0.34 mg/L, 4-hydroxy-3-nitrobenzenearsonic acid: 0.40 mg/L, 4-nitrophenylarsonic acid: 0.40 mg/L, phenylarsonic acid: 0.18 mg/L, and phenylarsine oxide: 0.30 mg/L | | Environmental | [203] |
| Benzene and hexylbenzene | Environmental samples | FASS-CE | Detection sensitivity benzene and hexylbenzene is improved by a factor of 4 and 8, respectively | | Environmental | [204] |
| Bromate ion | Drinking water | EKSI-CZE | 0.1 μg/L | | Environmental | [205] |
| Bromide, Potassium | Environmental water sample (saline groundwaters) | CZE | $Br^-$: 0.1 mg/L; $K^+$: 0.5 mg/L | | Environmental | [206] |
| Cationic impurities ($Na^+$, $Li^+$, and methylimidazolium (Ml(+)) | Butylmethylimidazolium (BMI+)-based lLs | tITP-CZE | MI(+): 10 ppb; $Li^+$: 1 ppb | | Environmental | [207] |
| Cations | Mixture containing alkali metals, alkaline earths, transition metals and lanthanides | CZE | <0.5 μM | | Environmental | [208] |
| Ceftiofur | Environmental water samples | SPE-CZE | 3 μg/L | | Environmental | [209] |
| Ceftiofur | Environmental water samples | SPE-LVSS-CE | 10 ng/L | | Environmental | [210] |
| Chromium (Cr(III) and Cr(VI)) | Environmental samples | SE-CE | Cr(III): 1.8 μ g/L; Cr(VI): 1.9 μg/L | | Environmental | [211] |
| Chromium(III) | Environmental water samples | MCE | $1.6 \times 10^{-16}$ mol/L | | Environmental | [212] |
| Copper(II) | Environmental samples | FASI-CE | $4 \times 10^{-12}$ M | | Environmental | [213] |
| Divalent metal ions | Factory wastewater | CSEI-Sweep-CZE | range of $(1.8–23.4) \times 10^{-8}$ M | | Environmental | [41] |
| Dyes extracted from wool, cotton, viscose, polyamide, and silk fibres | Environmental samples | tITP-MEKC | | 190–640-fold | Environmental | [214] |
| EDTA | Drinking water | LVSEP-CE | 0.2 μg/L | | Environmental | [215] |
| Enantiomers | Environmental samples | FASI-CE w/water plug | $10^{-9}$ M | | Environmental | [216] |
| Estrogens (estrone, β-estradiol, and ethynylestradiol) | Environmental water samples | tITP-CZE | 0.16–0.30 nM | | Environmental | [217] |
| Glufosinate enantiomers | Environmental water samples | SPE-γ-CD-CZE | $2.0 \times 10^{-9}$ M | | Environmental | [218] |
| Glyphosate | Environmental water samples | CE | 0.06 μg/mL | | Environmental | [219] |
| Haloacetic acid | Environmental samples | LVSS-CZE | 97–120-fold sensitivity enhancement | | Environmental | [220] |

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|---|---|---|---|---|---|---|
| Halogenated phenolic and bisphenolic compounds | Environmental water samples | LVSEP-CE, LVSEP-NACE | LVSEP-CE and LVSEP-NACE improved peak heights by 5–26 and 16–330 folds, respectively | | Environmental | [221] |
| Heavy metal anions ($Fe^{2+}$ and $Fe^{3+}$) | Environmental samples | CE | <0.1 μM | 50-fold relative to conventional hydrodynamic injection. | Environmental | [222] |
| Heavy metal cations (Cd(II), Pb(II), Cu(II), Ni(II), and Zn(II)) | Molten snow | tITP-CZE | 40–120 μg/L | | Environmental | [223] |
| Heavy metal ions (Zn(II)) | Tap water | CE | 5 nM (Zn(II)) to 30 nM (Cu(II)) | | Environmental | [224] |
| Heavy metal ions (Zn(II), Co(II), Cu(II), and Ni(II)) | Environmental samples | FASI-CE | 5 nM | >3 orders of magnitude relative to non-stacking CE | Environmental | [225] |
| Herbicides (chlorinated acid herbicides) | Environmental water samples | SPE-FASS-CZE | 0.269–20.3 ppt | 5000–10,000-fold | Environmental | [226] |
| Herbicides (chlorophenoxy acid herbicides) | Drinking water | SPE-CE | $1–4 \times 10^{-2}$ ng/mL | | Environmental | [227] |
| Herbicides (diclosulam, cloransulam-methyl, flumetsulam, metosulam, and florasulam)) | Mineral/stagnant waters | SPE-ACN-stacking-CE | 131 and 342 ng/L | | Environmental | [228] |
| Herbicides (metribuzin, lenacil, ethofumesate, atrazine, terbutryn, isoproturon, chlorotoluron and linuron, and five of their principal degradation products; namely, deethylatrazine, 2-hydroxyatrazine, deethyl-2-hydroxyatrazine, deisopropylatrazine and 3-chloro-4-methylphenylurea)) | Environmental samples | SPE-SDS-DOSS mixed-micellar MEKC | ppb range | | Environmental | [229] |
| Herbicides (paraquat, diquat, difenzoquat) | Drinking water | CSEI-Sweep-MEKC | <1 μg/L | | Environmental | [230] |
| Herbicides (paraquat, diquat, difenzoquat) | Drinking water | SPE-CZE | <2.2 μg/L | | Environmental | [231] |
| Herbicides (paraquat, diquat, difenzoquat) | Drinking water | Stacking-CE | ~30–150 μg/L | | Environmental | [232] |
| Herbicides (*s*-triazine herbicides) | Environmental samples | FASS-RMM-CZE | 9–15 ng/mL | | Environmental | [234] |
| Herbicides (triazines) | Environmental samples | LVSS-CE | | 500-fold | Environmental | [235] |
| Herbicides (triazines) | Environmental water samples | SPE-REPSM-MEKC | 3.3–8.5 μg/L | 4–10-fold | Environmental | [236] |
| Herbicides (triazolopyrimidine herbicides: flumetsulam, florasulam, cloransulam-methyl, diclosulam, and metosulam) | Soil sample | SPE-FASI-CE | 13.0–31.5 μg/L | | Environmental | [237] |
| Hydride-forming elements (As(III) to As(V)) | Environmental samples | ALOV-AFS | 0.02 ng/mL As | 8.8-fold | Environmental | [238] |
| Inorganic anions | Cigarette samples | ASEI-CZE | 6–14 ng/L | | Environmental | [239] |
| Inorganic anions ($(Cl^-$, $I^-$, $Br^-$, $NO_2^-$, $NO_3^-$, and $SCN^-)$) | Seawater | CZE | 1–3 μmol/L | | Environmental | [240] |
| Inorganic anions ($Br^-$, $I^-$, $NO_3^-$, $CrO_4^{2-}$, and $MoO_4^{2-}$) | Ice | PAEKI-CZE | 2.2–11.6 ppb | | Environmental | [241] |

Table 1 (*Continued*)

| Sample target | Sample matrix | Separation mode | Limit of detection | Concentration factor | Application | Ref. |
|---|---|---|---|---|---|---|
| Inorganic anions (bromide, nitrate, iodide, iodate, bromate, thiocyanate, and chromate) | Seawater | tITP-CZE | 75 pM (9.5 ng/L) | | Environmental | [242] |
| Inorganic anions (chloride, nitrate, and sulfate) | Environmental water samples | FI-CE | <125 μg/L | | Environmental | [243] |
| Inorganic mercury (Hg(II)) and methylmercury (MeHg(I)) | Environmental water samples | FI-CE | 0.1 and 0.2 μg/mL (as Hg) for Hg(II) and MeHg(I) | | Environmental | [244] |
| Iodide | Artificial seawater | tITP-CE | 0.2 μg/L | | Environmental | [245] |
| Iodide | Artificial seawater | tITP-CE | 0.6 μg/L | | Environmental | [246] |
| Iodide | Seawater | tITP-CE | 0.4 μg/L | | Environmental | [247] |
| Iodide/iodate | Seawater | tITP-CE | Iodide: 0.23 μg/L (2 nM); Iodate 10 μg/L (57 nM) | | Environmental | [248] |
| Iodide/iodate | Seawater | tITP-CZE | Iodide: 4.0 μg/L; iodate: 5.0 μg/L | | Environmental | [249] |
| Light-absorbing anions | Environmental samples | CZE | 0.02–0.1 μg/mL | | Environmental | [250] |
| Linear alkylbenzenesulfonates | Laundry/dishwashing detergents | LVSS-CZE | | 100-fold | Environmental | [251] |
| Mercury species (inorganic $Hg^{2+}$, methyl-, ethyl-, and phenylmercury | Environmental samples | CZE | 1.7 μg/L | | Environmental | [252] |
| Mercury species (inorganic $Hg^{2+}$, methyl-, ethyl-, and phenylmercury) | Environmental samples | SPE-CE | 2.9–6.9 ng/mL | 25–150-fold | Environmental | [253] |
| Methylmercury | Environmental samples | EKSI-NACE | 18 ng/mL | | Environmental | [254] |
| NaCl | NaCl standard solution | tITP-CZE | 0.3 pM | 500-fold improvement | Environmental | [255] |
| Naphthalene and benzenesulfonates | Environmental water samples | LVSS-CZE | 5–10 μg/L | | Environmental | [256] |
| Naphthalene, fluorene, pyrene, anthracene, phenanthrene, and chrysene | Airbornes particulates | CD-MEKC | 10–20-fold increase in sensitivity relative to sweeping | | Environmental | [257] |
| Naphthalenesulfonate compounds | Environmental samples | MEKC | 0.96–0.47 ppb | | Environmental | [258] |
| Naphthalenesulfonate compounds | Environmental water samples | CE | 4 μg/L | 100-fold | Environmental | [259] |
| Naphthalenesulfonate compounds | Environmental water samples (industrial effluent, river water) | SPE-CZE | 1.0 μg/L in 200 mL | | Environmental | [260] |
| Neutral compounds (butyrophenone, valerophenone, and acetophenone) | Environmental water samples | LLsME-MEKC | 0.05, 0.05, and 0.1 mg/L for butyrophenone: 0.05 mg/L; valerophenone: 0.05 mg/L; acetophenone: 0.1 mg/L | 63–151-fold | Environmental | [261] |
| Niobium(V), tantalum(V) | Environmental samples | MCL-CE | Nb(V): 9.1 μg/L; Ta(V): 25.2 μg/L | | Environmental | [262] |
| Nitrate | Seawater | SSS-CZE | 35 μg/L | | Environmental | [263] |
| Nitrite/nitrate | Artificial seawater | tITP-CE | Nitrite: 15 μg/L; nitrate: 7.0 μg/L | | Environmental | [264] |
| Nitrite/nitrate | Artificial seawater | tITP-CZE | Nitrite: 2.7 μg/L; nitrate: 3.0 μg/L | | Environmental | [265] |
| Nitrite/nitrate | Artificial seawater | tITP-CE | Nitrite: 2.7 μg/L; nitrate: 3.0 μg/L | | Environmental | [266] |
| Nitroaromatic explosives | Seawater | HSS-MEKC | <100 μg/L | | Environmental | [267] |
| Nonsteroidal anti-inflammatory drugs (NSAIDS) | Environmental water samples | LVSEP-ASEI-CE | LVSEP, LVSEP-ASEI, and FAEP improved the sensitivity of the peak area by 100-, 1200-, and 1800-fold, respectively | | Environmental | [268] |

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|---|---|---|---|---|---|---|
| Nonsteroidal anti-inflammatory drugs (NSAIDS) | Environmental water samples | LVSS-CE | Sensitivity was enhanced by 80–100-fold | | Environmental | [269] |
| Nonsteroidal anti-inflammatory drugs (NSAIDS) | Environmental water samples | REPSM-MEEKC | Sensitivity enhanced up to 40-fold | | Environmental | [270] |
| Nonsteroidal anti-inflammatory drugs (NSAIDS) (ibuprofen, fenoprofen, naproxen, ketoprofen, and diclofenac sodium) | Mineral waters | SRMM-MEKC; SRMM-ASEI-MEKC; FESI-RMM-MEKC | SRMM-MEKC, SRMM-ASEI-MEKC; FESI-RMM-MEKC: sensitivity was improved up to 154-, 263-, and 63-fold, respectively | | Environmental | [271] |
| Ochratoxin A | Household dust | SPE-CE | 0.2 ng/L | | Environmental | [272] |
| Organic anions | Environmental samples | SPE-CZE | Ranging between 1.5 and 12 nM for the organic anions studied | | Environmental | [273] |
| Parabens (methyl, ethyl, propyl, and butyl *p*-hydroxybenzoate) | Cosmetic products | SEI-RMM-LVSS-MEKC | $3.0 \times 10^{-7}$ M | | Environmental | [274] |
| Perfluorocarboxylic acids | Environmental samples | CE | C6-PFCA: 2 μg/mL; C12-PFCA: 33 μg/mL | | Environmental | [275] |
| Pesticides (aldicarb, carbofuran, isoproturon, chlorotoluron, metolachlor, mecoprop, dichlorprop, MCPA, 2,4-D, methoxychlor, TIDE, DDT, dieldrin, and DDE) | Drinking water | SPE-FASS-CZE | 0.04–0.46 ng/mL | 30-fold | Environmental | [276] |
| Pesticides (amitrole (AMT), carbendazim (MBC), 2-aminobenzimidazole (ABI), thiabendazole (TBZ) and 1,2-diaminobenzene (DAB)) | Environmental samples | CE | ppm levels | | Environmental | [277] |
| Pesticides and metabolites | Environmental water samples | FASS-SM-EKC | $10^{-7}$ to $10^{-9}$ M | | Environmental | [278] |
| Phenol pollutants | Environmental samples | FI-CZE | 2000-fold enhancement of detection sensitivity | | Environmental | [279] |
| Phenolic acids | Environmental samples | LVSS-CZE | 0.01–0.025 μg/mL | | Environmental | [280] |
| Phenols (*p*-nitrophenol, phenol, and resorcinol) | Environmental samples | CZE | 40 μg/mL for a Kapel'-103R instrument and 0.05–0.1 μg/mL for a Hewlett-Packard $HP^{3D}$ CE | | Environmental | [281] |
| Phenoxy acid herbicides | Environmental samples | FAEP-CE | | >3000× | Environmental | [233] |
| Phenoxy acid herbicides | Environmental samples | FASI-CE | 100 pg/mL | | Environmental | [282] |
| Phenylurea herbicides (monuron, isoproturon, diuron) | Tap, pond water | RMM-MEKC | 1 ppb | 500-fold | Environmental | [283] |
| Phosphate | Seawater | tITP-CZE | 32 μg/L | | Environmental | [284] |
| Polyclic aromatic hydrocarbons | Environmental water samples | SE/HLL-CE (Triplex concentration system) | 3.60 ppt | $10^7$-fold concentration | Environmental | [285] |
| Polycyclic aromatic hydrocarbons (PAHs) (Benzo[*a*]pyrene and pyrene) | Environmental samples | CE-RS | Bap and Py were Bap: $1.6 \times 10^{-9}$; Py: $4.8 \times 10^{-9}$ mol/L | 8335-fold | Environmental | [286] |
| Propranolol and metoprolol | Environmental samples | CSEI-CE | | ∼5000 times relative to normal EKSI | Environmental | [287] |
| Propranolol and metoprolol | High-salt samples | FASIAS-CE | Propranolol and metoprolol was $10^{-4}$ and $7 \times 10^{-4}$ mg/L, | | Environmental | [288] |

Table 1 (*Continued*)

| Sample target | Sample matrix | Separation mode | Limit of detection | Concentration factor | Application | Ref. |
|---|---|---|---|---|---|---|
| Rare earth ions | Environmental samples | EKS-CZE | 0.1 μM | 20,000-fold | Environmental | [45] |
| Rare earth ions | Environmental samples | tITP-CZE | 0.1 μM | 20,000-fold | Environmental | [289] |
| Short-chain organic acids | Natural rubber latex | LVSS-CZE | | >17 | Environmental | [290] |
| Strontium, lithium | Seawater | tITP-CZE | 1.3 mg/L Sr(II) and 0.12 mg/L $Li^+$ | | Environmental | [291] |
| Tetrabromobisphenol A | Environmental water samples | LVSEP-NACE | Improved sensitivity of the peak height by 90–300-fold | | Environmental | [292] |
| Tetracycline antibiotics (tetracycline, oxytetracycline, and doxycycline) | Environmental water sample (surface water samples) | SPE-CE | 2 g/L | | Environmental | [293] |
| Thiol/cyanide hydrolysis products of chemical warfare agents *O*-ethyl *S*-2-diisopropylaminoethyl methylphosphonothiolate (VX), *O*-isobutyl *S*-2-diethylaminoethyl methylphosphonothiolate (R-VX), and tabun (GA) (2-dimethylaminoethanethiol, 2-diethyl-aminoethanethiol, and cyanide) | Environmental samples | CE | 9.3 μg/L for cyanide, 1.8 μg/L for 2-diethylaminoethanethiol, 35 μg/L for 2-dimethylaminoethanethiol, 15 μg/L for 2-mercaptoethanol, and 89 μg/L for 1-pentanethiol | | Environmental | [294] |
| Trace metal | Environmental samples | tITP-CZE | $0.4–4.2 \times 10^{-7}$ M | | Environmental | [295] |
| Trace metal impurities | Nickel and iron salts | CZE | $10^{-7}$ M | | Environmental | [296] |
| Trace phenolic compounds | Environmental water samples | FASI-FASS-MCE | 100–150 pM | 5200-fold | Environmental | [297] |
| Trace transition metals ($Cd^{2+}$, $Zn^{2+}$) | Environmental water samples | tITP-CZE | 0.1–0.5 μg/L | | Environmental | [298] |
| Uncharged pesticides (naphthalene acetamide, carbaryl, 1-naphthol, thiabendazole, and carbendazime) | Environmental samples | MEKC | Carbaryl: 0.22 μg/mL; 1-naphthol 1.13 μg/mL | | Environmental | [299] |
| Vanadium | Fertilizer | CE | 19 ppb | | Environmental | [300] |
| Weakly acidic organic compounds, chlorinated phenols, aromatic amino acids | Environmental samples | LVSEP-CE | Sensitivity enhancement factors as large as 170 | | Environmental | [301] |
| Acidic phenolic compounds (caffeic acid, 3,4-dihydrobenzoic acid, gallic acid, *p*-hydroxybenzoic acid) | Food samples | ASEI-Sweep-MEEKC | 3 ng/L | 96,000–238,000-fold increase in detection sensitivty relative to normal MEEKC | Food analysis | [302] |
| Acrylamide | Food samples | FASI-CZE | 3 ng/L | | Food analysis | [303] |
| Biogenic amines (histamine, tryptamine, phenylethylamine, tyramine, agmatine, ethanolamine, serotonin, cadaverine, and putrescine) | Red wine sample | FASS-CE | 0.02 mg/L for ethanolamine to 0.91 mg/L for serotonin | | Food analysis | [304] |
| Cytokinin nucleotides | Coconut water | SPE-CZE | 0.06–0.19 μM | | Food analysis | [305] |
| Cytokinins | Coconut water | ACN-stacking CE | 0.05–0.18 μM | | Food analysis | [306] |
| Food colorants | Soft drinks, jellies, and milk beverages | LVSS-CE | 0.1–0.5 μg/mL | | Food analysis | [307] |
| Fungicides (carbendazim, metalaxyl, captan, procymidone, folpet, captafol, vinclozolin, and iprodione) | Fruit juices | HSS-MEKC | μg/L | | Food analysis | [308] |
| Fungicides (thiabendazole, procymidone) | Fruits and vegetables | SPE-LVSS-CE | 1.6–16.0 μg/kg | | Food analysis | [309] |

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|---|---|---|---|---|---|---|
| Heavy metal anions ($Cd^{2+}$, $Cu^{2+}$, $Zn^{2+}$) | Fish liver metallothioneins | LVSS-CZE | | 13-fold | Food analysis | [310] |
| Herbicides (triazolopyrimidine sulfoanilide herbicides: cloransulam-methyl, metosulam, flumetsulam, florasulam, and diclosulam) | Soy Milk | SPE-CE | 74 μg/L | | Food analysis | [311] |
| Pesticides (carbendazim (benzimidazole), simazine, atrazine, propazine and ametryn (triazine), diuron and linuron (urea), carbaryl and propoxur (carbamate)) | Drinking water, vegetables | SRMM-Sweep-MEKC | 2–46 μg/L | 3–18-fold | Food analysis | [312] |
| Pesticides (cyprodinil, cyromazine, pyrifenox, pirimicarb, and pyrimethanil) | Water, apple/orange juice | SPME-FESI-CE | 2.5 μg/L in water and 3.1 μg/L in juices | | Food analysis | [313] |
| Quinolone antibiotics (ciprofloxacin, enrofloxacin, and flumequine) | Porcine plasma samples | tITP-CZE | Ciproflacin: 70 μg/L; Enrofloxacin: 85 μg/L; Flumequine: 50 μg/L | | Food analysis | [314] |
| Quinolone antiobiotics (ciprofloxacin, ofloxacin, and enrofloxacin) | Porcine tissue | CE | Ciprofloxacin: 0.007 mg/L; ofloxacin: 0.016 mg/L; enrofloxacin: 0.020 mg/L | | Food analysis | [315] |
| Riboflavin | Beer | Sweeping-MEKC | MEKC, stacking-MEKC and dynamic pH junction techniques, the detection limits were found to be 480, 20, and 1 ng/mL respectively | | Food analysis | [316] |
| Riboflavin | Beer | Stacking-MEKC | 20 ng/mL | | Food analysis | [317] |
| Sodium tripolyphosphate | Food samples | tITP-CZE | 0–80 mg $P_2O_5$/L | | Food analysis | [318] |
| Sulfonamides (sulfapyridine, sulfamethazine, sulfamerazine, sulfamether, sulfadiazine, sulfadimethoxine, sulfamethoxazole, sulfachlorpyridazine, and sulfamethizole) | Meat, ground water | SPE-CZE | 2.59–22.95 μg/L | | Food analysis | [319] |
| *trans*-Resveratrol | Red wine sample | Sweep-MEKC | 1500-fold improvement in detection sensitivity in comparison with normal-MEKC mode | | Food analysis | [320] |
| Alkaloids | *Sophora flavescens ait* sample | FASI-CE | Concentration sensitivity was about 3–4 orders of magnitude higher than in hydrodynamic injection | | Pharmaceutical | [321] |
| Alkaloids (berberine, coptisine, and palmatine) | *Coptidis rhizoma* sample | EKSI-FASS-CE | ~5 ng/mL | | Pharmaceutical | [322] |
| Alkaloids (berberine, coptisine, and palmatine) | *Coptidis rhizoma* sample | Sweeping-MEKC | Berberine, coptisine and palmatine were found to be 2.5 ppb (ng/mL) | | Pharmaceutical | [323] |

Table 1 (*Continued*)

| Sample target | Sample matrix | Separation mode | Limit of detection | Concentration factor | Application | Ref. |
|---|---|---|---|---|---|---|
| Benzoin, mephenytion, and propatenene | Standards (*Proof of concept*) | tITP-CZE | | Benzoin, 134-fold; mephenytion, 219-fold; propatenene, 1600-fold | Pharmaceutical | [324] |
| Carbamazepine | Pharmaceutical tables, human serum | Sweep-MEKC | 0.10 μg/mL | | Pharmaceutical | [325] |
| D-Amphetamine, diphenhydramine | Anti-motion sickness capsules | CZE | D-Amphetamine and diphenhydramine were 10.0 and 5.5 ng/mL | | Pharmaceutical | [326] |
| Ethynyl estradiol | Female contraceptive pill extract | Dynamic pH junction-sweeping CE | | 100-fold | Pharmaceutical | [327] |
| Fangchinoline, tetrandrine | Herbal medicine | FI-MEKC | 6.8–8.9-fold improvement in concentration sensitivity relative to conventional CE methods | | Pharmaceutical | [328] |
| Fangchinoline, tetrandrine | *Radix stephaniae tetrandrae* and its medicinal preparations | NACE | Fangchinoline: 0.30 ng/mL; tetrandrine:0.34 ng/mL | | Pharmaceutical | [329] |
| Flavonoids | *Epimedium brevicornum* maxim extracts | FESI-RMM-MEKC | 40–360-fold improvement in the detection sensitivity | | Pharmaceutical | [330] |
| Flavonoids (hyperoside, isoquercitrin, quercitrin, quercetin, and rutin) | Methanolic extracts of *Hypericum perforatum* leaves/flowers | tITP-CZE | Quercetin-3-0-glycosides was 100 ng/mL | | Pharmaceutical | [331] |
| Inorganic anions ($Cl^-$, $NO_2^-$, $NO_3^-$, $SO_4^{2-}$, $F^-$, $HPO_4^{2-}$) | Cigarette samples | ASEI-CE | 6.2 ng/L | | Pharmaceutical | [332] |
| Lovastatin | Chinese medicine monascus capsule | tMCRBM-CZE | 0.73 g/mL | | Pharmaceutical | [333] |
| Paracetamol (Par), pseudoephedrine hydrochloride (Pse), dextromethorphan hydrobromide (Dex) and chlorphenamine hydrogen maleate (Chl) | Pharmaceutical samples | FI-CE | 0.22 μg/mL, 0.29 μg/mL, 0.42 μg/mL and 0.70 μg/mL for Par, Pse, Dex, and Chl, respectively | | Pharmaceutical | [334] |
| Pharmaceuticals (eletripan, dofetilide, doxazosin, sildenafil, UK-103,320, UK-202,581, and CP-122,288) | Ringer's solution | FASS-CZE | 10–27-fold sensitivity enhancement | | Pharmaceutical | [335] |
| Phenolic compounds (salicylic acid, cinnamic acid, ferulic acid and vanillic acid) | Biological samples | NACE | Salicylic acid: 0.069, cinnamic acid; 0.051; ferulic acid 0.107; vanillic acid 0.089 | | Pharmaceutical | [336] |
| Phenolic compounds (several cinnamic acid derivatives and flavonoids) | Methanolic extracts of *Sambucus* flowers and *Crataegus* leaves and flowers | tITP-CZE | 20–50 ng/mL and 100 ng/mL for the acids and flavonoids, respectively | | Pharmaceutical | [337] |
| Pyrrolizidine alkaloids (PAs) of senkirkine, senecionine, retrorsine, and seneciphylline | Chinese herbal medicine (kuan donghua) | Dynamic pH-junction-Sweeping | LOD as low as 30 ppb for the PAs | 23.8–90.0-fold | Pharmaceutical | [338] |
| Quinolizidine alkaloids (sophoridine, matrine, sophocarpine, and oxymatrine) | Roots of *Sophora flavaescens ait* and *S. tonkinensis Gagnep* | FASS-EMI-NACE | 0.0210–0.0446 ng/mL | | Pharmaceutical | [339] |
| Saponins | *Panax notoginseng* extract | FESI-RMM-MEKC | 1.7–6.3 μg/mL | | Pharmaceutical | [340] |
| SSRIs (sertraline, fluoxetine, and fluvoxamine) | Aqueus mixture of analytes | SPE-CZE | | >500-fold | Pharmaceutical | [341] |
| Strychnos alkaloids (strychnine and brucine) | *Strychnos nux-vomica* L | FESI-CE | 1.0 ng/mL for strychnine and 1.4 ng/mL for brucine | | Pharmaceutical | [342] |

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|---|---|---|---|---|---|---|
| Terbinafine | Commercial spray/tablets | CZE | 1.73 μmol/L | | Pharmaceutical | [343] |
| 5-Hydroxytryptamine (5-HT) and 5-hydroxyindole-3-acetic acid (5-HIAA) | Human urine | CE | 5-HT: 0.27 nM; 5-HIAA: 0.31 nM | | Toxicological/forensic | [344] |
| 3,4-Methylenedioxymethamphetamine (3,4-MDMA) | Biological samples | LTB-NACE | $5.0 \times 10^{-9}$ M | | Toxicological/forensic | [345] |
| 8-Oxoguanine (8oxoG) and 8-hydroxydeoxyguanosine (8OHdG) | Cerebral cortex microdialysate samples | CE w/pH-mediated anion stacking | 0.5 nM | | Toxicological/forensic | [346] |
| Acyclovir | Human plasma | MEKC | 6.67 ng/mL | | Toxicological/forensic | [347] |
| Amino alcohols | Human urine | LPME-CE | 0.08–0.5 μg/mL | 72–110-fold | Toxicological/forensic | [348] |
| Amiodarone, desethylamiodarone | Human serum | EKSI-FASS-CE | 6.46 ng/mL | | Toxicological/forensic | [349] |
| Amitriptyline (Ami); nortriptyline (Nor) | Human plasma | FASI-CE | Ami and Nor were 2.0 ng/mL (6.3 and 6.7 nM, respectively) | | Toxicological/forensic | [350] |
| Amphetamine and derivatives (amphetamine, methamphetamine, and methylenedioxy-methamphetamine) | Biological matrices | Sweeping-MEKC | 6 to 8 pg/mL (ppt), | | Toxicological/forensic | [351] |
| Amphetamine and derivatives (amphetamine, methamphetamine and methylenedioxy-methamphetamine) | Human hair | CSEI-MEKC | <50 pg/mL using CSEI-MEKC | | Toxicological/forensic | [352] |
| Amphetamines and derivatives (amphetamine, methamphetamine, 3,4-methylenedioxyamphetamine, and 3,4,-methylenedioxymethamphetamine) | Human hair | FASS-CZE | <0.06 μg/L | | Toxicological/forensic | [353] |
| Amphetamines and derivatives (amphetamine, methamphetamine, 3,4-methylenedioxyamphetamine, and 3,4,-methylenedioxymethamphetamine) | Human urine | SPME-CZE | 25–34 μg/L | | Toxicological/forensic | [354] |
| Anabolic steroids (methyltestosterone, methandrostenolone, and testosterone) | Human serum | LVSS-CD-CEC | Methyltestosteron: $2.79 \times 10^{-7}$ mol/L; testosterone: $3.47 \times 10^{-7}$ mol/L; methandrostenolone: $3.56 \times 10^{-7}$ mol/L (for | | Toxicological/forensic | [355] |
| Anthracycline antibiotics (doxorubicin, daunorubicin) | Aqueous mixture of analytes | MEKC | nM | | Toxicological/forensic | [356] |
| Anthracycline antibiotics (doxorubicin, daunorubicin) | Human plasma | SSS-CZE | nmole/L | | Toxicological/forensic | [357] |
| Antibiotic (tobramycin) | Human serum | FASS-CE | 50 μg/L | | Toxicological/forensic | [358] |
| Antibiotics (kanamycin) | Human serum | SPE-CE | 2 μg/mL | | Toxicological/forensic | [359] |
| Antibiotics (marbofloxacin) | Porcine plasma samples | tITP-CZE | 20 μg/kg | 75-times more sensitive than conventional CE | Toxicological/forensic | [360] |
| Antibiotics (rapamycin) | Human whole blood | PAEKI-CZE | low μg/L levels | | Toxicological/forensic | [361] |

Table 1 (*Continued*)

| Sample target | Sample matrix | Separation mode | Limit of detection | Concentration factor | Application | Ref. |
|---|---|---|---|---|---|---|
| Antibiotics (trimethoprim and sulfamethoxazole) | Biological matrices | Dynamic pH-junction | | 2.9–4.7-fold relative to conventional capillary electrophoresis methods | Toxicological/forensic | [362] |
| Arsenic species (ASO(2)(2-), ASO(4)(2-), and dimethylarsinic acid, DMA)) | Biological matrices | FASI-CZE | <1 μmol/L | | Toxicological/forensic | [363] |
| Barbiturates (barbital and phenobarbital) | Human urine | Sweeping-MEKC | Barbital:0.27 μg/mL; andphenobarbital: 0.26 μg/mL | | Toxicological/forensic | [364] |
| Biguanides (proguanil, 4-chlorophenylbiguanide and cycloguanil) | Human plasma, urine | Sweeping-MEKC | Limits of detection obtained by sweeping are improved over FASI for plasma but not for urine and the limits of detection are higher than those reported for LC, for these compounds | | Toxicological/forensic | [365] |
| Carbamazepine | Human serum | MEKC | 0.10 μg/mL | | Toxicological/forensic | [366] |
| Cationic constituents (e.g., metal cations, biogenic amines, amino acids) | Human sweat | tITP-CZE | 3.2–5.8 μM for alkali and alkaline-earth cations (hydrostatic injection); 0.27–0.79 μM for other target analytes (hydrodynamicc injection) | | Toxicological/forensic | [367] |
| Cationic low-molecular mass compounds | Human plasma, urine | tITP-CEC | Low nmol/L range | | Toxicological/forensic | [368] |
| Cationic pharmaceuticals | Biological matrices | pH-mediated acid stacking-CE | Two-fold decrease in LOD | 60-fold | Toxicological/forensic | [369] |
| Cefazolin | Human plasma; ringers solution | SE-CE | Plasma: 1.0 μg/mL; Ringers: 2.0 μg/mL | | Toxicological/forensic | [370] |
| Cimaterol, clenbuterol, salbutamol | Biological matrices | FASI-CE | <2.0 ng/mL | 30–40-fold | Toxicological/forensic | [371] |
| Ciprofoxacin | Biological matrices | CE | 0.01 mg/L | | Toxicological/forensic | [372] |
| Clenbuterol, salbutamol | Biological matrices | tITP-CZE | $10^{-6}$ mol/L | | Toxicological/forensic | [373] |
| Clozapine, clozapine *N*-oxide, and desmethylclozapine | Human plasma | FASS-CE | CZP, DMC, and CNO were 5, 5, and 10 ng/mL, respectively | | Toxicological/forensic | [374] |
| Cocaine, thebaine | Water-immiscible solvent samples | OLBE-FASI-CZE | Range of 2–10 ng/mL | | Toxicological/forensic | [375] |
| Coumarin metabolites (7-hydroxycournarin (7-OHC), 4-hydroxycoumarin (4-OHC) and 2-hydroxyphenylacetic acid (HPAA)) | PBS | pH-mediated stacking-CE | 7-Hydroxycournarin: 0.1 μM; 4-hydroxycoumarin: 0.5 μM; 2-hydroxyphenylacetic acid: 0.3 μM | | Toxicological/forensic | [376] |
| Disopyramide | Human urine | CE | $2.5 \times 10^{-8}$ mol/L | | Toxicological/forensic | [377] |
| Ephedra-alkaloids (ephedrine, pseudoephedrine, methylephedrine, methylpseudoephedrine, norephedrine, and norpseudoephedrine | Herbal drug extracts, animal sera | CSEI-Sweep-MEKC | $10^{-3}$ μg/mL | 104-fold | Toxicological/forensic | [86] |
| Ephedrine derivatives | Human urine, serum | OLBE-FASI-CME-CE | 0.15–0.25 ng/mL | | Toxicological/forensic | [378] |

| | | | | | |
|---|---|---|---|---|---|
| Ephedrine, pseudoephedrine | Biological matrices | FASS-CZE | 0.67 and 0.73 μ g/mL for ephedrine (E) and pseudoephedrine (PE), respectively | Toxicological/forensic | [379] |
| Ephedrine, pseudoephedrine | Human plasma, urine | FESI-CZE | 5.3 ng/mL and 8.0 ng/mL in human plasma and urine, respectively | Toxicological/forensic | [380] |
| Escitalopram | Human urine | Sol-gel-CZE | 10 pg/mL | Toxicological/forensic | [381] |
| Ethyl glucuronide | Human serum | CE | 0.1 μg/mL | Toxicological/forensic | [382] |
| Flunitrazepam & its major metabolites (7-aminoflunitrazepam and *N*-desmethylflunitrazepam) | Human urine samples | Sweep-MEKC | 3.4, 5.6, and 12.0 ng/mL for flunitrazepam, 7-aminoflunitrazepam, and *N*-desmethylflunitrazepam, respectively | Toxicological/forensic | [383] |
| Fluoresceins (fluorescein-5-isothiocyanate, fluorescein disodium, and 5-carboxyfluorescein) | Biological matrices | FASI-MCE | LOD was improved by 94-, 108-, and 160-fold for fluorescein-5-isothiocyanate, fluorescein disodium, and 5-carboxyfluorescein, respectively, relative to a traditional pinched injection | Toxicological/forensic | [384] |
| Fluoride | Dental composites | FASI-CE | 20 ng/mL | Toxicological/forensic | [385] |
| Glutathione and glutathione disulfide | Human liver microdialysates | pH-mediated base stacking-CE | Glutathione: 0.75 μM and glutathione disulfide: 0.25 μM | Toxicological/forensic | [386] |
| Heroin metabolites | Human urine | CD-CZE | ng/mL | Toxicological/forensic | [387] |
| Heterocyclic aromatic amines | Human urine | FASI-CE | 0.3 ng/mL | Toxicological/forensic | [388] |
| Heterocyclic aromatic amines | Human urine | HDSI-CE | 18–360 ng/g | Toxicological/forensic | [389] |
| Heterocyclic aromatic amines | Human urine | muSPE-CE | 750–810 fmol | Toxicological/forensic | [390] |
| Illicit drugs | Banknotes | FASS-CE | 50 nM for heroin and 60 nM for cocaine w | Toxicological/forensic | [391] |
| Illicit drugs (methamphetamine, ketamine, morphine, codeine) | Human hair | CSEI-Sweep-MEKC | 50 pg/mg hair for MA and K, 100 pg/mg hair for C and 200 pg/mg hair for M | Toxicological/forensic | [392] |
| Illicit drugs (methamphetamine, ketamine, morphine, codeine) | Human urine | CSEI-Sweep-MEKC | 15 ng/mL for M and C, and 5 ng/mL for MA and K | Toxicological/forensic | [393] |
| Illicit synthetic drugs | Human bodily fluid sample | CE | 0.1–6 μg/L | Toxicological/forensic | [394] |
| Inorganic anions (iodide, bromide, nitrate) | Human urine, serum | tITP-CZE | Iodide 1.4 μg/L | Toxicological/forensic | [395] |
| Isoxyzolylpenicillins (oxacillin, cloxacillin, and dicloxacillin) | Human serum | LVSEP-CE | 2.0 μg/L | Toxicological/forensic | [396] |
| Itraconazole and hydroxyitraconazole | Human serum, plasma | MEKC | 0.01 μg/mL | Toxicological/forensic | [397] |
| Ketamine and its major metabolites (norketamine, ketamine-D-4) | Human bodily fluid sample | RMM-Sweep-MEKC | 2.8, 3.4, and 3.3 ng/mL for ketamine, norketamine, and ketamine-D-4, respectively | Toxicological/forensic | [398] |
| Lithium | Human whole blood samples | tITP-MCE | 0.1 mmol/L | Toxicological/forensic | [399] |
| Lovastatin | Human urine | tMCRBM-CE | 8.8 ng/mL | Toxicological/forensic | [400] |
| Lysergic acid diethylamine (LSD) | Murine blood | CSEI-Sweep-MEKC | 120 and 30 ng/mL | Toxicological/forensic | [401] |

Table 1 (*Continued*)

| Sample target | Sample matrix | Separation mode | Limit of detection | Concentration factor | Application | Ref. |
|---|---|---|---|---|---|---|
| Methacrylic acid | Dental composites | FASI-CE | 50 ppb | | Toxicological/forensic | [402] |
| Methamphetamine and derivatives (methamphetamine; amphetamine, and *p*-hydroxymethamphetamine) | Human urine | ACN-stacking-MEKC | 20 ng/mL for methamphetamine, and 15 ng/mL for amphetamine and *p*-hydroxymethamphetamine | | Toxicological/forensic | [403] |
| Methotrexate and its metabolites | Human plasma | SPE-LVSS-CE | improvement of sensitivity of around a 100-fold | | Toxicological/forensic | [404] |
| Monoamines | Human urine | FASS-CE | $6.0 \times 10^{-10}$ mol/L | | Toxicological/forensic | [405] |
| Morphines (MOR, MOR-3-glucuronide, 6-monoacetylmorphine, codeine, codeine-6-glucuronide, dihydrocodeine, methadone and 2-ethylidene-1,5-dimethyl-3,3-diphenylpyrrolidine) | Human urine | FASS-CE | 100–200 ng/mL | | Toxicological/forensic | [406] |
| *n*-Alkane diamines, lysine, diaminopimelic acid, and isoniazid | Biological matrices | MCE | LOD of isoniazid was improved in the magnitude of 11 times compared with the one of free isoniazid | | Toxicological/forensic | [407] |
| Naphthalene-2,3-dicarboxaldehyde (NDA)-labeled dopamine | Human urine | Sweep-MEKC | MEKC: $9.1 \times 10^{-7}$; sweeping-MEKC: $1.2 \times 10^{-8}$ M; methanol plug assisted sweeping MEKC: $4.7 \times 10^{-9}$ M | | Toxicological/forensic | [408] |
| Nateglinide | Animal plasma | Sweep-MEKC | 0.2–7 mg/L | 100-fold | Toxicological/forensic | [409] |
| Nicotine and metabolites | Human urine | SPE-CZE | ng/mL | | Toxicological/forensic | [410] |
| Nitrophenols | Biological matrices | SPE-FI-CE | 2-NP, 4-NP and 2,4-DNP: 0.3 μg/L, 0.6 μg/L, and 0.7 μg/L | | Toxicological/forensic | [411] |
| Nonsteroidal anti-inflammatory drugs (NSAIDS) | Human urine | SPE-CEC | 0.096 μm for indoprofen, 0.110 μm for ketoprofen, 0.012 μm for naproxen, 0.023 μm for ibuprofen, 0.110 μm for fenoprofen, 0.140 μm for flurbiprofen, and 0.120 μm for suprofen | | Toxicological/forensic | [412] |
| Nonsteroidal anti-inflammatory drugs (NSAIDS) | Human urine, serum | SPE-CE | 0.88–1.71 μg/mL | | Toxicological/forensic | [413] |
| Ochratoxin A | Human serum | ACE | 0.5 ng/mL | | Toxicological/forensic | [414] |
| Ochratoxin A | Human serum | ACE | 0.55 ng/mL | | Toxicological/forensic | [415] |
| Opiate drugs | Hair samples | Dynamic pH junction injection-CE | ng/mL - pg/mL | | Toxicological/forensic | [416] |
| Opiates (heroin, 6-monoacetylmorphine, morphine, codeine, papaverine, and narcotine) | Human urine | CZE | 6.6–19.5 ng/mL | | Toxicological/forensic | [417] |
| Opioids | Human urine | FASS-CE | >1000-fold sensitivity enhancement | | Toxicological/forensic | [418] |
| Oxalate | Human urine | CZE | $8 \times 10^{-8}$ mol/L; Samples containing Cl- LOD: $3.5 \times 10^{-3}$ mol/L | | Toxicological/forensic | [419] |

| | | | | | | |
|---|---|---|---|---|---|---|
| Oxprenolol, atenolol, timolol, propranolol, metoprolol, and acebutolol | Human urine | tITP-CE | <5 μg/mL | | Toxicological/forensic | [420] |
| Penicillins | Human serum | REPSM-MEEKC | Decreased the detection limits by about 40-fold | | Toxicological/forensic | [421] |
| Phenethylamine designer drugs, (2,5-dimethoxy-4-ethylthio-phenethylamine (2C-T-2), 2,5-dimethoxy-4-(*n*)-propylthiophenethylamine (2C-T-7), 4-chloro-2,5-dimethoxyphenethylamine (2C-C), 4-bromo-2,5-dimethoxy-phenethylamine (2C-B), 2,5-dimethoxy-4-iodo-phenethylamine (2C-I)) | Aqueus mixture of analytes | Sweep-MEKC | $10^{-7}$ M | | Toxicological/forensic | [422] |
| Phenolic compounds (dopamine, epinephrine, catechol, and 4-aminophenol) | Biological matrices | CE | 140 and 105 nM for dopamine and epinephrine, respectively. | | Toxicological/forensic | [423] |
| Phenothiazines (thiazinamium methylsulfate, promazine hydrochloride, chlorpromazine hydrochloride, thioridazine hydrochloride, and promethazine hydrochloride) | Human urine | SPE-FASI-CZE | from 2 to 5 ng/mL | | Toxicological/forensic | [424] |
| Procyclidine | Human urine | CZE | $10^{-9}$ mol/L | | Toxicological/forensic | [425] |
| Propranolol enantiomers | Human urine | SPE-CE | 0.01 μg/mL | | Toxicological/forensic | [426] |
| Reserpine | Human urine | FASI-MEKC | $7.0 \times 10^{-8}$ mol/L | | Toxicological/forensic | [427] |
| Sildenafil citrate and metabolites | Human serum | MEKCPS | ~17 ng/mL | | Toxicological/forensic | [428] |
| Steroids | Biological matrices | SEI-MEKC | | 60–600-fold increase in detection sensitivity | Toxicological/forensic | [429] |
| Strychnos alkaloids (strychnine and brucine) | Biological matrices | FESI-PMME-MEKC | Strychnine and brucine were 0.05 and 0.07 μg/mL, respectively | <100-fold improvement in concentration sensitivity relative to convention MEKC | Toxicological/forensic | [430] |
| Strychnos alkaloids (strychnine and brucine) | Human urine | LPME-MEKC | Strychnine and brucine were 1 and 2 ng/mL, respectively | | Toxicological/forensic | [431] |
| Strychnos alkaloids (strychnine and brucine) | Human urine | Sweeping-MEKC | Strychnine and brucine were 1 ng/mL and 2 ng/mL | | Toxicological/forensic | [432] |
| Sulindac | Human urine | muSPE-CE | 2.9 ng/mL | >260 | Toxicological/forensic | [433] |
| Sulindac, sulindac sulfide (SI) and sulindac sulfone (SO) | Human plasma | FASI-CE | 0.1 μM for SU and SO, and 0.3 μM for SI | | Toxicological/forensic | [434] |
| Triadimenol | Biological matrices | CD-MEKC | 0.8–3.8 ppm | 10-fold increase | Toxicological/forensic | [435] |

Table 1 (*Continued*)

| Sample target | Sample matrix | Separation mode | Limit of detection | Concentration factor | Application | Ref. |
|---|---|---|---|---|---|---|
| Tricyclic antidepressants | Human serum | ACN-stacking-SPE-CZE | 5 ng/mL | | Toxicological/forensic | [436] |
| Urinary 8-hydroxydeoxyguanosine (80HdG) | Human urine | CZE | 4.3 nM | | Toxicological/forensic | [437] |
| Valproate | Human serum | tITP-MCE | 0.3–0.7 μmol/L | | Toxicological/forensic | [438] |
| Zotepine and norzotepine | Human plasma | tITP-CZE | Zotepine and norzotepine in plasma were 2 and 1 ng/mL, respectively | | Toxicological/forensic | [439] |

[a]2-D-IEF, Two-dimensional isoelectric focusing; 2-D-LC, two-dimensional liquid chromatography; 2D-PAGE, two-dimensional polyacrylamide gel electrophoresis; ABS, acid barrage stacking; ACE, affinity capillary electrophoresis; AN, acetonitrile; ASEI, anion-specific exclusion injection or anion selective exhaustive injection; AuNP, gold nanoparticles; BCE, bubble-cell capillary electrophoresis; CABCE, carrier ampholye-based capillary electrophoresis; CD, cyclodextrin modified; CEC, capillary electrochromatography; CME, centrifuge microextraction; CPE, cloud point extraction; CSEI, cation selective exhaustive injection; DOS, dioctyl sulfosuccinate; EC, electrochromatography; EKS, electrokinetic supercharging; EKSI, electrokinetic sample injection; ELISA, enzyme-linked immunosorbent assay; ESI, electrospray ionization; FAEP, field-amplified sample injection and water removal using the EOF pump; FASI, field-amplified sample injection; FASIAS, field-amplified sample injection with acid stacking; FASS, field-amplified sample stacking; FI, flow injection; EKI, electrokinetic injection; FMOC, 9-fluorenylmethoxycarbonyl; HCFASS, head-column field-amplified sample stacking; HLL, homogenous liquid–liquid extraction; HSS, high-salt stacking; HDSI, hydrodynamic sample injection; HSC, high-sensitivity cell; HSDC, high sensitivity detection cell; IE-CEC, ion-exchange capillary electrochromatography; IE-EF-CE, ion-exchange-based eluent-free capillary electrophoresis; LC, liquid chromatography; LLE, liquid–liquid extraction; LLsME, liquid–liquid semimicroextraction; LTB-NACE, low-temperature and ambient temperature nonaqueous capillary electrophoresis; LPME, liquid-phase microextraction; LV-FASI, large volume field-amplified sample injection; LVSEP, large-volume sample stacking injection using the electroosmotic flow pump; LVSS, large-volume sample stacking; LPME, liquid-phase microextraction; MACE, microchip affinity capillary electrophoresis; MBE, moving boundary electrophoresis; MCE, microchip electrophoresis; MCL, metallochromic ligands; MCMEKC, microchip micellar electrokinetic chromatography; MCRB, moving chemical reaction boundary; MEKCPS, micellar electrokinetic chromatography with polarity switching; MGE, microchip gel electrophoresis; MI, microinjection; MFMPs, multifunctional magnetic particles; muSPE, micro solid-phase extraction; NACE, non-aqueous capillary electrophoresis; OLBE-FASI, on-line back-extraction field-amplified sample extraction; PAEKI, pressure-assisted electrokinetic injection; PC-HFME, polymer-coated hollow fiber microextraction; PEO, polyethylene oxide; PEG, polyethylene glycol; LVSEP, large volume stacking with an electroosmotic pump; REPSM, reversed electrode polarity sample stacking; RPRP, reversed-phase, reversed-polarity; RM-MEKC, reverse migration MEKC; RMM, reverse migrating micelle; RPLC, reversed-phase liquid chromatography, SC-CE, short-column CE; SEC, size-exclusion chromatography; SEI, selective exhaustive injection; SHDI, semihydrodynamic injection; SPE, solid-phase extraction; SPME, solid-phase microextraction; SRMM, stacking with reverse migrating micelles; SSS, sample self-stacking; SWMR, stacking with matrix removal; tMCRBM, transient moving chemical reaction boundary method; TOF, time-of-flight; VDIF, velocity-difference-induced focusing.

though readers are advised to consult the individual references to suit their needs.

### 4.1. Biological applications

Within the realm of biological applications, the complexity of components entailed in life necessitates a similar variety of methods and technologies for their concentration and detection. Biological components vary in nature, consisting of simple cationic/anionic entities, amino acids, peptides, proteins, nucleic acids or even whole cells. For these biological components, we will start with the most simple in nature, the inorganic ions. Heavy metal cations, such as iron, nickel and zinc, have been separated from human urine samples, with sweeping allowing LODs in the range of 0.2–1.2 ppb for the same cations [108,109]. Common inorganic anions such as nitrite and nitrate have been the focus of a number of studies, with biological matrices being no different. Nitrate and nitrite have been recovered from human fluid samples using MCE, CZE and tITP, allowing recoveries of 12–24 μM, 2.0–4.1 μM and 1.5–2.6 μM, respectively [123,122,124].

A variety of biomolecules of varying complexities have been preconcentrated and separated from a great many biological matrices. For example, dynamic pH-junction-sweeping-CE on *Bacillus subtilis* extracts to recover amines and other biomolecules with over 3 orders of magnitude increase in recovery relative to conventional CE [46]. LVSS-sweep-CE was applied to murine, porcine and human tissues to quantify sanguinarine at LODs of 3 nM [175]. Plant signaling compounds such as gibberellic acid and abscisic acid were isolated from tobacco flower extracts using LVSS-MEKC, allowing enrichment factors up to 600-fold, relative to standard MEKC [150]. Melatonin and related compounds have been isolated using reversed-migration-MEKC and normal-migration-MEKC, with LODs of 21–100 ng/mL in the former, and as low as 9.7 nmol/L in the latter [114,115].

A class of compounds critical to biological function of certain organisms, as well as to a number of pathophysiological diagnostic tests, are that of anabolic and catabolic intermediates. Ethyl glucuronide, lactate and acetate, elements in glucose metabolism and markers for cellular damage were isolated from diluted human serum using sample self stacking CZE, yielding LODs ranging from 0.38 to 26 μM [95]. Peptide and amino acid metabolism and biosynthesis has been the focus of a number of studies. Hsieh et al. looked at amino acid derivatives with polyethylene oxide modified CE, finding L-tryptophan at 70 pM [48]; tryptophan derivatives were recovered from mixed amino acid solutions using sweeping-CE, with detection limits as low as 10 nmol/L [183]. Nucleotide intermediates have been isolated by a number of means. Wang et al used LVSS-CE with polarity switching to isolate purines, allowing a 44–90-fold improvement in sensitivity relative to standard CE [170]. Pyridine and adenine metabolites were recovered from *B. subtilis* extracts using CZE, allowing an LOD of 20 nM [171]. Using CE, thymidine mono- and diphosphates were found at LODs of 2.6 and 3.8 μM, respectively [182].

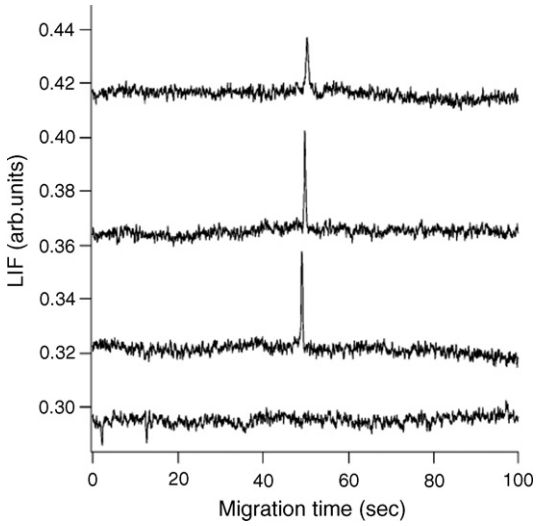


Fig. 1. Three successive analyses of 100 fM ovalbumin by CE in coated channels with 120-s preconcentration steps and 5 mM Tris–borate sample buffer. Mean peak height $\pm 1\sigma$ was $0.031 \pm 0.008$. Traces are offset for clarity; bottom trace shows analysis of pure buffer. Separation conditions: separation buffer, 50 mM Tris–borate, pH 8.9; separation length, 2.2 cm; field strength, ~340 V/cm; PDMA-coated channels (from Ref. [165] with permission).

Amino acids are a varied and complex family of structures, requiring a similarly complex array of detection techniques. Most simply, CZE was applied to amniotic fluid samples, with LODs for arginine and aspartic acid of 1.5 and 6.7 μM, respectively [57]. The in-column derivatization, stacking, and separation of amino acids with a polyethylene oxide plug to stack the derivatized amino acids was applied to cerebrospinal fluid (CSF) to allow detection at 4 nM [54]. PEO-sweeping-MEKC was used to find amino acids in CSF at LODs as low as 0.3 nM, a 50–800-fold enhancement in sensitivity relative to standard methods [55]. tITP-CZE was utilized in other biological matrices, allowing LODs with 2800–5200-fold improvements in sensitivity, compared to normal CE [60]; others have applied tITP-CZE to amino acid concentration, with up to 150,000-fold concentration factor [59].

Peptides, proteins and nucleic acids constitute the major active and structural components in contemporary organisms, thus constituting a wide target for CE technologies to focus upon. Peptides in biological matrices have been separated using CE and MEKC, with differing stacking preconcentration, allowing LODs as low as 500 aM, and enhancement factors of 600-fold [133,148]. Proteins have been similarly targeted, with sub-nM LODs and enhancement factors approaching 800-fold for some samples [155,156,158]. Using microchip affinity capillary electrophoresis (MACE), Staphylococcal enterotoxin B was extracted from bovine serum albumin (BSA), with detection limits at fg/mL levels [179]; others used FASI-CE to detect 100 fM samples of ovalbumin protein [165] (see Fig. 1). Solid-phase extraction microchip capillary electrophoresis was applied to biological matrices to yield enhancement factors in DNA separation of 500-fold [74]. pH-mediated sample stacking-CE was used to concentrate dsDNA following PCR, with detection limits at 9 fg/μL [90]. Microchip gel electrophoresis (MGE) with a hydroxypropyl cellulose matrix modified with gold nanopar-

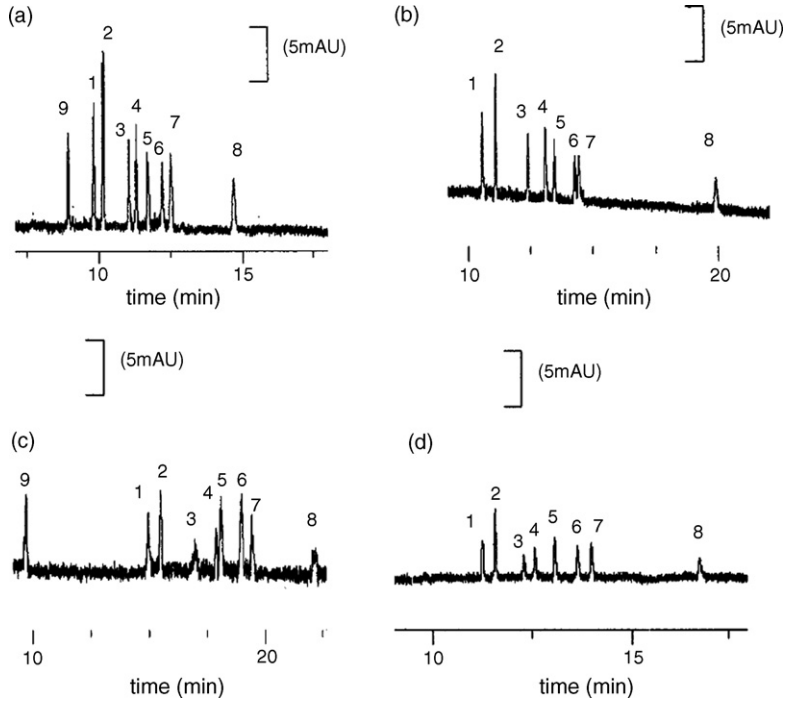


Fig. 2. Comparison of FAEP with FASI and LVSAP individually: (a) FAEP, 50 ng/mL, water plug 100 mbar × 0.5 min, sample injection −10 kV × 1.2 min; (b) FASI, 50 ng/mL, water plug 50 mbar × 0.2 min, sample injection −10 kV × 0.2 min; (c) LVSAP, 50 ng/mL, hydrodynamic sample injection 500 mbar × 2.0 min; (d) common CZE, 10 ppm, hydrodynamic sample injection, 50 mbar × 0.1 min, ∼1% of the total length of capillary. Buffer: pH 3.20, boric and phosphoric acid. 0.1% HEC. Voltage: −30 kV. Peaks: 1 = picloram; 2 = 2,4-DCBA; 3 = 4-CPAA; 4 = 2,4-D; 5 = 2,4,5-T; 6 = dichloroprop; 7 = fenoprop; 8 = mecoprop; 9 = impurity (from Ref. [233] with permission).

ticles was applied to DNA, allowing LODs of 5.7 amol/50 μL, and concentration factors up to 25,500-fold [75].

A particularly incredible application of capillary electrophoresis is the separation of the largest 'biomolecule', whole cells, in this case mixed cultures of bacteria and fungi, with detection limits of 1–10 cells [117].

### 4.2. Environmental

On-line preconcentration in CE has enjoyed much success to the analysis of many types of environmental samples, mainly inorganic pollutants, toxicants, organometallic compounds, and organic compounds typically encountered in industrial manufacturing. A variety of arsenic species were the focus of a number of studies – LVSS-HSC-CZE allowed LODs as low as 5.6–17.1 μg/L, while LV-FASI-CZE brought concentration factors of 34–100-fold, relative to conventional CZE [202,201]. Rare earth ions were recovered from earth samples using EKS-CZE, allowing enhancement factors of 20,000-fold [45,89]. Herbicides in environmental and drinking water and soil were analyzed using different focusing techniques, sample stacking, tITP, or CSEI-sweep separated by CE or MEKC, with LODs as low as the ppt-level and up to 10,000-fold enhancement factors [226–237] (see Fig. 2). Using CSEI-sweep-MEKC, aromatic amines in environmental samples were detected at ppt-levels [35] (see Fig. 3). In the diverse domain of seawater analysis, a number of sample stacking and injection techniques used with CZE allowed concentration and detection of anions in seawater as low as nM levels [245–249]. Other environmental water

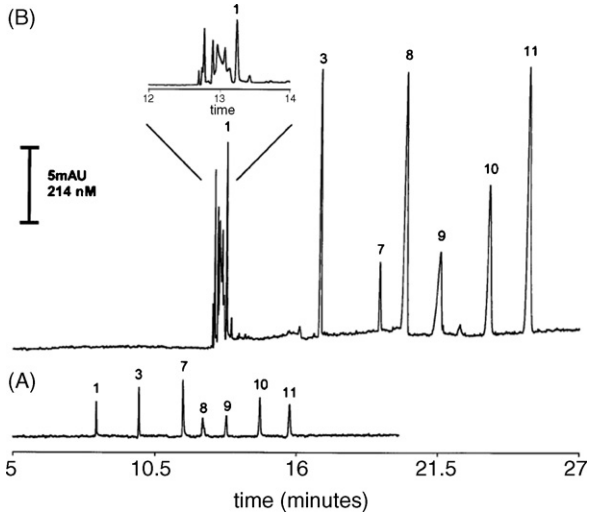


Fig. 3. CSEI-sweep-MEKC analysis of seven aromatic amines. Conditions: nonmicellar BGS, 100 mM phosphoric acid/5 mM triethanolamine/50 mM urea/20% acetonitrile (pH ∼2); micellar BGS, 50 mM SDS/50 mM phosphoric acid/5 mM triethanolamine/50 mM urea/20% acetonitrile (pH ∼2); high conductivity buffer (HCB) 100 mM phosphoric acid; S, aromatic amines in water; sample concentration, (A) 7.9–61.8 ppm, (B) 1/10,000 dilution of (A); conditioning solution before injection, (A) micellar BGS, (B) nonmicellar BGS; injection scheme, (A) 0.7 mm pressure injection of S, (B) ∼13.2 cm pressure injection of HCB, then 3 mm pressure injection of water, followed by 20 kV electrokinetic injection of S for 400 s; sweeping and MEKC voltage, −20 kV with the micellar BGS at both ends of the capillary. Identification of peaks: (1) *N*-1-naphthyethylenediamine, (2) 3,4-dichloroaniline, (3) 3,5-dimethylaniline, (4) 2,4-dichloroaniline, (5) 2,3-dichloroaniline, (6) 2,5-dichloroaniline, (7) 3-chloroaniline, (8) 1-phenylethylamine, (9) *N*-ethylaniline, (10) 2-methylaniline, (11) 4-methoxyaniline, (12) 2-nitroaniline, (13) 4-nitroaniline (from Ref. [35] with permission).

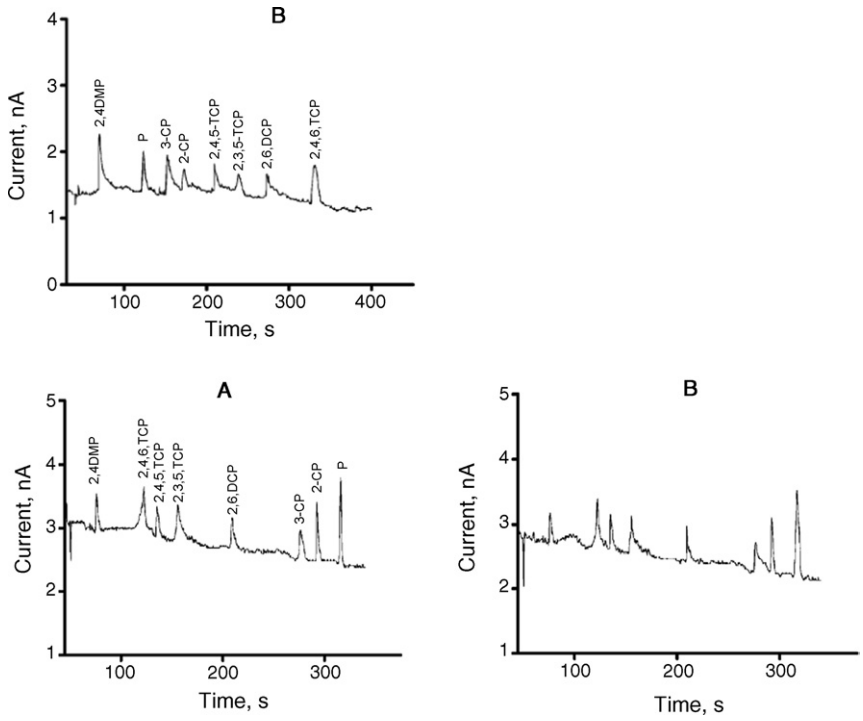


Fig. 4. (*Upper*) MCZE-EC analysis of eight phenolic compounds containing a 15 μM solution of each compound at a modified electrode. Separation field strength, +200 V/cm, sample injection, 3 s at +200 V/cm, DP, +1.0 V vs. Ag/AgCl. (*Lower*) (A) Electropherograms for eight phenolic compounds obtained by the FASI step (A) and by both FASS and FASI steps (B). MEKC-EC conditions: Sample concentration (A) 15 nM and (B) 2.5 nM for each compound. Separation buffer, 10 mM $H_3PO_4$ + 10 mM SDS + 1 M urea (pH 2.1); detection buffer, 10 mM PBS (pH 7.0); separation field strength, −250 V/cm; injection time, 3 s at −200 V/cm; and DP, +1.0 V vs. Ag/AgCl (from Ref. [297] with permission).

samples were analyzed for trace phenolic compounds using sample stacking techniques in MCE, with LODs of 100–150 pM, and concentration factors 5200-fold relative to typical injections [297] (see Fig. 4).

### 4.3. Food analysis

The disparate areas of nutrition and food safety share in common the obvious element of their matrix, food, and/or bever-

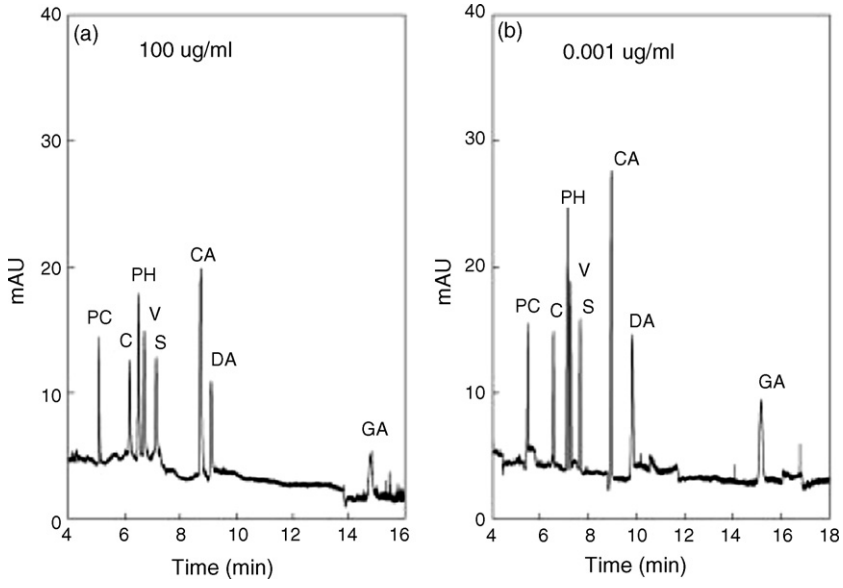


Fig. 5. Comparison of ASEI-sweeping MEEKC and conventional MEEKC with normal hydrodynamic injection. Peak identification, CA, caffeic acid; DA, 3,4-dihydroxybenzoic acid; GA, gallic acid; PH, p-hydroxybenzoic acid. (a) Normal hydrodynamic injection, 0.32 mm (50 mbar, 1 s) (b) ASEI-sweeping MEEKC, 1.9 cm pressure injection of acid plug, then 1.9 cm pressure injection of water plug, followed by −18 kV electrokinetic injection of sample for 300 s. Sample concentration: (a) 100 μg/mL and (b) 0.001 μg/mL of each analyte was prepared in 55 mM borate–boric acid (pH 8.0). Capillalry, 48.5 cm (40.0 cm to the detector) × 50 μm I.D.; applied voltage, −20 kV; temperature, 35 °C; detector wavelength, 200 nm (from Ref. [302] with permission).

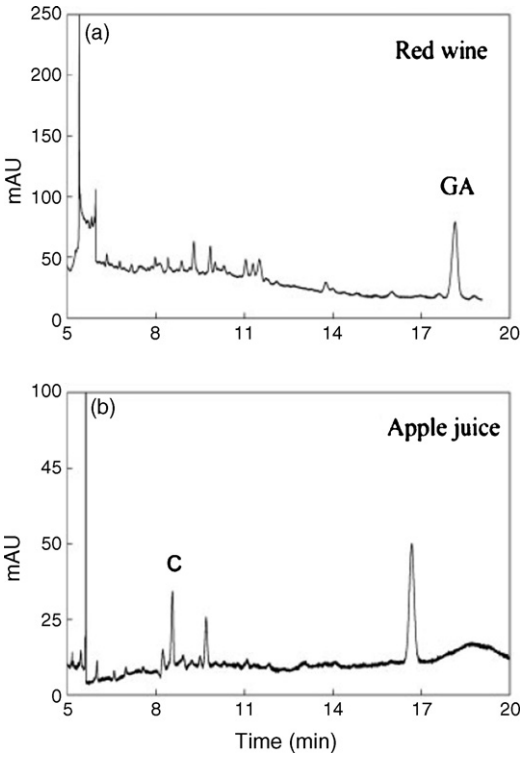


Fig. 6. Electropherograms of food samples determined by ASEI-sweeping MEEKC. Food samples were directly analyzed after 100-fold dilution with 55 mM borate–boric acid buffer (pH 8.0), and no other sample pretreatment was used. Injection scheme: 1.9 cm pressure injection of acid plug, then 1.9 cm pressure injection of water plug, followed by 218 kV electrokinetic injection of sample for 300 s. Other conditions are the same as in Fig. 5 (from Ref. [302] with permission).

age. Contaminants such as heavy metals, pesticides, and others were found in food samples using MEKC and CZE, alongside differing sample preconcentration techniques allowed LODs ranging from mg/L to ng/L (see Figs. 5 and 6) [302–315]. Food colorants in a number of food products such as soft drinks and jellies were quantified using LVSS-CE to μg/mL levels [307].

Knowing the nutritional content of consumables is of significant, if not such immediately critical importance as the verified exclusion of contaminants. Both make abundant use of sample preconcentration methodologies, allowing more authoritative and precise determination of desired qualities of consumables. The nutritional content of riboflavin in humanity's most ancient nutritional beverage creation, beer, has been analyzed using sweeping-CZE with differing stacking preconcentration, allowing LODs on the order of ng/mL [316,317]. Mankind's next greatest hope for the extension of lifespan, resveratrol, found in red wine samples, was the target of sweeping-MEKC, yielding a 1500-fold improvement in detection sensitivity, relative to standard MEKC (see Fig. 7) [320]. Slightly less extraordinary in applications of immortality, biogenic amines in red wine samples were deduced at mg/L levels using sample stacking CE [304]. Cytokinins in coconut water were measured to μM levels using ACN-stacking-CE, as well as SPE-CZE [305,306].

### 4.4. Pharmaceuticals

Much like the preceding application of capillary electrophoretic separation and analysis of food, pharmaceuticals have need for composition identification and quality control. In the perpetual search for the next great drug treatment, the entirety of nature is a potential sample matrix for agents with activity against man's afflictions. CE and MEKC with a different sample stacking preconcentration and sample injection method have been applied to a variety of plant extracts, allowing the isolation of desired compounds to the ng/mL level, and up to 360-fold improvements in detection sensitivities relative to conventional methods [321–323,330,331]. Pharmaceuticals, once produced, have further need for CE, in quality control for inclusion of desired components, as well as the exclusion of contaminants. In the case of the former, LODs as low as parts per billion and ng/L, and enhancement factors of over 500-fold (see Fig. 8) [338,341]. As for harmful or otherwise untoward components, ASEI-CE was used to detect ng/L levels of inorganic cations in cigarette samples, not perhaps the most dangerous component therein, but nonetheless demonstrative of capacity for such analytes and matrices [332].

### 4.5. Toxicological/forensic

Our latter category is novel to the extent to which encompasses those previous, as well as the interesting variety of sample matrices. One such novel matrix is the application of FASS-CE to paper currency to detect illicit drugs at nM levels, a method of great use to the US Drug Enforcement Agency and other law enforcement institutions [391]. More pedestrian, but no less useful in illicit drug detection are those in drug testing of urine, serum, and hair samples. Proportionate to the variety of illicit drugs, as well as the means by which drug abusers attempt to conceal their use, detection of analytes in biological matrices necessitates a range of testing modalities. This was accomplished by a number of sample injection and stacking steps in tandem with CE, MCE, or MEKC, with LODs as low as ng/mL in urine and plasma samples, and pg/mL in hair samples [392–397].

A similar application of drug testing technologies, though with much greater media mention, is in the detection of anabolic steroids in human samples. Given the public outcry in recent years, a range of detection schema are in place, applying selective exhaustive injection MEKC to realize a 600-fold increase in detection sensitivity relative to conventional methods; LVSS-CD-CEC was applied to human serum to detect steroids at sub-μmole/L levels [355,429]. Law enforcement has no solitary claim to this methodology however, and indeed medicine has much broader range of use. Doctors need to detect legal drugs in biological samples to assess treatment efficacy, and use much the same technology as do law enforcement, and similar LODs of nM [347,360–362,421,431–434]. Clinical sample component analysis is applied to serum, urine and tissue samples to assess biological constituents, such as cations, hormones and proteins, allowing ng/mL to pg/mL levels of detection [365,367]. Even dentistry have use for CE preconcentration, utilizing FASI-

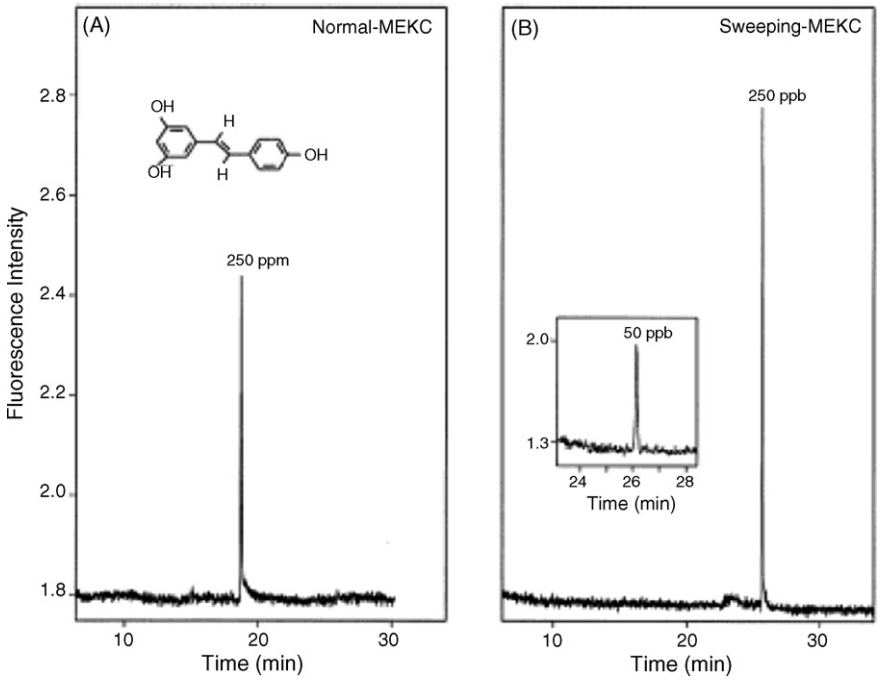


Fig. 7. Electropherograms of *trans*-resveratrol obtained by (A) the normal MEKC mode (250 ppm) and (B) by the sweeping-MEKC mode (250 ppb). The inset in (B) shows the electropherogram at the lowest concentration of 50 ppb (S/N = 3, LOD ~5 ppb). CE conditions: (A) phosphate buffer (30 mM), SDS (150 mM) in a methanol–water solution (25:75); applied voltage −25 kV; current ~ −8 mA; injection length ~0.5 mm; capillary length 93/97 cm. (B) Injection length, ~46 cm; detection conditions: $\lambda_{ex}/\lambda_{em} = 313 \pm 8$ nm/$400 \pm 16$ nm; UV cut filter 320 nm; PMT 700 V; room temperature (from Ref. [320] with permission).

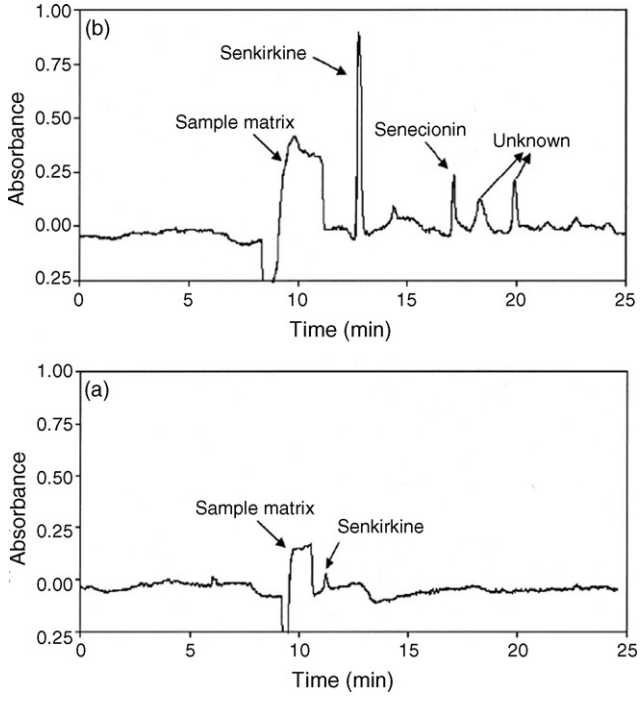


Fig. 8. Electropherograms of *kuan donghua* with normal MEKC and dynamic pH-junction-sweeping. (A) MEKC, sample was diluted ten times with 50% methanol in water; sample injection, 10 s at 20.7 mbar. (B) Dynamic pH-junction-sweeping, sample solution was diluted ten times with 10 mM phosphate with 20% methanol at pH 4.0; sample injection, 265 s at 20.7 mbar. (A) and (B) BGE, 20 mM borate, 30 mM SDS and 20% methanol at pH 9.1; separation voltage 20 kV; detection, 220 nm (from Ref. [338] with permission).

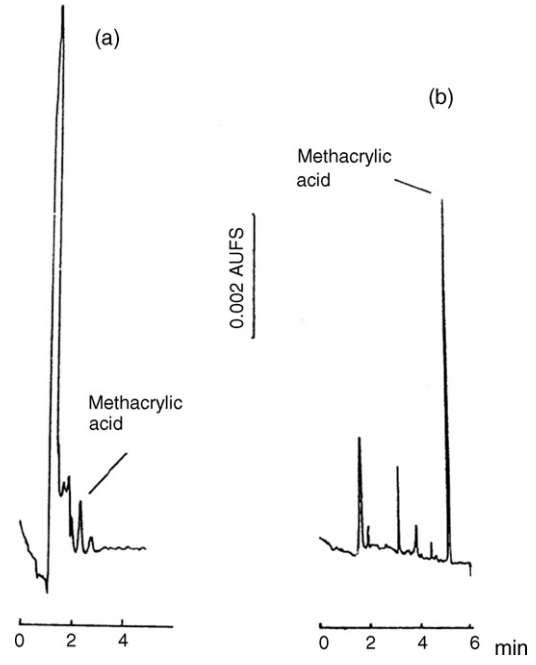


Fig. 9. Electropherograms of water-immersed solution of dental composites. Column, fused-silica capillary (64 cm × 50 μm I.D., 52 cm effective separation length); voltage +30 kV; detection wavelength 215 nm; BGE 20 mM $Na_2B_4O_7$ solution (pH 9.5). (a) Hydrodynamic injection, 50 mbar × 1.0 min; (b) FASI injection, 500 mbar × 0.5 min by hydrodynamic loading, followed by FASI at −15 kV until the electric current reached 95% of that of the pure BGE before sample loading (from Ref. [402] with permission).

CE to assess dental composites for fluoride content, as well as methacrylic acid, with LODs in the ng/mL and ppb-levels, respectively [385,402] (see Fig. 9).

## 5. Conclusion

A significant number of on-line preconcentration strategies have been reported since the year 2000. These strategies include both variants of known focusing principles (e.g., ITP and sample stacking), and more recently, combinations of these focusing principles (e.g., field-enhanced sample injection and sweeping). Several to million-fold enhancements in peak sensitivities had been reported without significant deterioration in separation efficiency, in many cases, there are improvements in plate numbers causing very sharp peaks. As reported here, the possibility to detect at lower levels by CE provides new tools with which to analyze many real world samples; also CE complements other mainstay analytical techniques like HPLC. On-line preconcentration also allows for the analysis of samples in even smaller channels as seen in developments in microchip electrophoresis. Chemical analysis in the chip format has continued to grow and no doubt further applications of on-line preconcentration techniques are expected in the future. The fundamental understanding of focusing principles had also advanced in parallel with the applications development. Real world chemical systems are often unique and thus provide the medium to observe phenomena that would not have been routinely encountered in simple CE systems. The development of dynamic pH junction and acetonitrile stacking in fact resulted from studies that involved the analysis of real world samples. Clearly, there exist possibilities for new focusing principles to emerge as CE is applied to chemical and biological analysis.

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