Screening determination of food additives using capillary electrophoresis coupled with contactless conductivity detection: A case study in Vietnam

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ABSTRACT

In this study, a simple and inexpensive method for food analysis is discussed. The approach is based on capillary electrophoresis (CE) instruments with capacitively coupled contactless conductivity detection (C^4D). Following the pilot deployment of in-house fabricated CE-C^4D instruments in Vietnam, a number of food additives in different food matrices, including i) oxalate and citrate in instant noodles, beer and tea drinks, ii) acidulants in beverage, coffee, alcohol and vinegar samples, and iii) artificial sweeteners in jelly and drink samples, were determined using this method. Good agreement between results obtained with CE-C^4D-instruments and those from the confirmation method (HPLC-PDA) was achieved.

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1. Introduction

In order to guarantee the safety and good quality of foods, food control is of extreme importance during and after food production in order to assure the safe consumption of foods in compliance with the current and incoming legislation. The food control activities are especially critical in developing countries in general and in Vietnam in particular where food contamination occurs very often whilst the food regulations have not been well established. The scare of food poisoning/contamination has recently hit Vietnam whose markets are flooded with foods containing harmful chemicals. With an alarming surge in cancer rate, many of the cancer cases being linked to toxic or badly treated food, food contamination has become a national problem in Vietnam. In this context, there is an urgent need for robust, efficient and cost-effective analytical methodologies that can be widely used even in the local and decentralized areas and allow screening and/or tracing food contaminants with little requirement of expertise and budget. So far, food analysis has mostly been carried out in central institutes, notably at the National Institute for Food Control (NIFC). Well established methods, for example gas chromatography (GC), high-performance liquid chromatography (HPLC) and ion exchange chromatography (IC) in combination with optical (i.e. photodiode array (PDA) or laser induced fluorescence (LIF)) or mass spectrometry (MS) detection have been frequently used for this purpose. However, their high costs for sample analyses and instrumental maintenance, as well as the requirement for skillful and experienced operators render their employment for screening analysis unsuitable to many

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(decentralized) food control centers where only modest financial resources and limited expertise are available. Very often, food samples suspected to contain (overdosed) harmful chemicals are sent to NIFC and there is a delay of at least some days until the analyses are completed. This poses a significant delay for the authority to reach a conclusion. Some quick tests, which are commercially available in the market, however are only limited to some certain chemicals and aim to qualitative identification rather than quantitative determination. The aforementioned issues lead to the desire for a more approachable and affordable alternative for food analysis.

Among different analytical separation techniques used for food analysis, capillary electrophoresis (CE) has been established as a versatile and high-performance tool that provides fast and efficient separations with low consumption of samples, solvents and reagents. This technique relies on the electro-migration of the concerned species through a capillary under an electrical field. The use of CE techniques in food control has been reviewed several times (Acunha, Ibáñez, García-Cañas, Simó, & Cifuentes, 2016; Castro-Puyana, García-Cañas, Simó, & Cifuentes, 2012; García-Cañas, Simó, Castro-Puyana, & Cifuentes, 2014; Herrero, García-Cañas, Simo, & Cifuentes, 2010). Bench-top CE instruments coupled with optical or MS detectors were employed in most of the cases. Nevertheless, the high cost of commercial CE-UV/LIF/MS instruments is still a factor that prevents the widespread use of this electro migration technique in Vietnam. The miniaturized version of CE, *i.e.* microchip electrophoresis has also been used repeatedly for food analyses. Recent applications of microchip electrophoresis in this domain can be found in different reviews (Coltro et al., 2015; Escarpa et al., 2015; Ferey & Delaunay, 2016; Martín, Vilela, & Escarpa, 2012). Although CE and microchip electrophoresis share the same principle of electrokinetic separation, they require much different instrumental setups, methodology development and possess different degrees of robustness and maturity. From our point of view, the suitable option that offers low-cost instrumentation and unsophisticated operation is the employment of a system based on CE with capacitively coupled contactless conductivity detection (C^4D). In this case, ionic species separated by CE are detected based on the difference of their electrical conductivities from that of the background electrolyte (BGE). Fundamental aspects of C^4D can be found in (Brito-Neto, da Silva, Blanes, & do Lago, 2005a,b; Coltro et al., 2012; Kubáň & Hauser, 2004a,b, 2009; Mai & Hauser, 2012; Zemann, 2003). Interesting applications of CE-C^4D for food control can be gleaned from some recent reviews (de Oliveira et al., 2016; Elbashir & Aboul-Enein, 2014; Kuban & Hauser, 2014; Kubáň & Hauser, 2016). Some notable examples include the analysis of saccharides in various matrices, the identification and quantification of monoethyl carbonate in beer, distilled beverage and a carbonated soft drink, the identification of oligosaccharides, the analysis of underivatized fatty acids, and simultaneous determination of biogenic amines in water and hard liquor samples. Very recently, Coelho and Jesus communicated a CE-C^4D method for determination of erythritol, maltitol, xylitol and sorbitol in sugar-free chocolates (Coelho & de Jesus, 2016). Pavlicek and Tuma gave an account of the use of CE-C^4D for determination of stevioside and rebaudioside A in foods and beverages (Pavlíček & Tůma, 2016). Liu et al. employed CE-C^4D coupled with electromembrane extraction for determination of diamine plastic restricted substances (Liu et al., 2016). For CE-C^4D both the separation and detection of ions are based on electronic principles and the method only requires low-pressure fluidic components. This technique therefore offers many advantageous features, notably portable instrumentation for mobile deployment (Greguš, Foret, & Kuban, 2016; Lewis et al., 2013; Schepdael, 2016), high configuration flexibility with multi-channel setups for high throughputs

(Duong, Nguyen, Mai, Saiz, & Pham, 2016; Koenka, Mai, Hauser, & Saiz, 2016; Thanh Duc; Mai et al., 2016; Sáiz, Koenka, Mai, Hauser, & García-Ruiz, 2014) and construction of low cost versions (Duong et al., 2015; Nguyen et al., 2015). Nevertheless, the advantageous features of CE-C^4D have not yet been fully exploited for food analysis. Food control applications implemented with CE-UV detection or CE-MS still much outnumbered those carried out with CE-C^4D (Acunha et al., 2016; Castro-Puyana et al., 2012; García-Cañas et al., 2014; Herrero et al., 2010).

Herein, the employment of CE-C^4D for analyses of various compounds in different food matrices in Vietnam, including i) oxalate and citrate in instant noodles, beer and tea drinks, ii) acidulants in beverage, coffee, alcohol and vinegar samples, and iii) artificial sweeteners in jelly and drink samples, is reported. This study is a follow-up of our pioneering work in the topic of food control in Vietnam with the use of CE-C^4D for the determination of beta-agonists in pig feed samples (Nguyen et al., 2014). Some considerations on the effects of sample matrix treatment on the analytical performance using CE-C^4D are discussed. Cross checking data using confirmation methods with HPLC-PDA were also provided to prove the reliability of the analytical data obtained with CE-C^4D.

2. Experimental

2.1. Chemicals and materials

All chemicals were of analytical or reagent grade and purchased from Fluka (Buchs, Switzerland) or Merck (Darmstadt, Germany). Individual stock solutions (10 mmol/L) of formic acid, acetic acid, propionic acid, butyric acid, oxalic acid, citrate sodium, and tartaric acid were used for the preparation of standards of carboxylate-based species. Those of artificial sweeteners were prepared from stock solutions (1000 mg/L) of acesulfame potassium, aspartame, cyclamate sodium and saccharine. Chemicals used for preparation of CE-C^4D buffers include: Tris(hydroxymethyl)aminomethane (Tris), arginine (Arg), acetic acid, histidine (His), 18-crown-6, cetyltrimethylammonium bromide (CTAB), 2-(N-morpholino) ethanesulfonic acid (MES), 3-(N-Morpholino)propanesulfonic acid (MOPS), N-Cyclohexyl-2-aminoethanesulfonic acid (CHES) and 3-(cyclohexylamino)-1-propanesulfonic acid (CAPS).

Fused silica capillaries of 50–75 μm ID and 365 μm OD were obtained from BGB Analytik AG (Böckten, Switzerland). Before use, the fused silica capillaries were pre-conditioned with 1 M NaOH for 10 min and deionized water for 10 min prior to flushing with the buffer. The capillaries were then used continuously for successive analyses. Deionized water purified using a system from Water Pro (Labconco, Kansas City, MO, USA) was used for the preparation of all solutions and for sample dilution if required. Background electrolyte (BGE) solutions were prepared by addition of the pre-selected acid (Ace, MES, CHES, MOPS or CAPS) into a basic solution containing either His, Arg or Tris at desired concentrations. pH values of solutions were controlled with an HI 2215 Hanna Instruments pH meter (Woonsocket, RI, USA).

2.2. Instrumentation

In-house-made portable CE instruments with manual or semi-automated operation were used for all food analyses. Details on the construction and operation of these CE prototypes can be found in (Kubáň, Nguyen, Macka, Haddad, & Hauser, 2007; Torres, Hauser, Furrer, Brandl, & Mueller, 2013) for the version with manual siphoning injection and in (Nguyen et al., 2014) for the semi-automated single-channel setup. The salient features of these instruments are given in Table 1. Detection was carried out with