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Analytical Methods

Sensitive simultaneous determination of three sulfanilamide artificial sweeters by capillary electrophoresis with on-line preconcentration and contactless conductivity detection

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ABSTRACT

A sensitive method followed by capillary electrophoresis with on-line perconcentration and capacitively coupled contactless conductivity detection (CE–C^4D) was evaluated as a novel approach for the determination of three sulfanilamide artificial sweeteners (acesulfame-K, sodium saccharin and sodium cyclamate) in beverages. The on-line preconcentration technique, namely field-amplified sample injection, coupled with CE–C^4D were successfully developed and optimized. The separation was achieved within 10 min under the following conditions: an uncoated fused-silica capillary (45 cm × 50 μm i.d., L_{eff} = 40 cm), 20 mmol L^{-1} HAc as running buffer, separation voltage of −12 kV, electrokinetic injection of −11 kV × 8 s. The detection limits of acesulfame-K, sodium saccharin and sodium cyclamate were 4.4, 6.7 and 8.8 μg L^{-1}, respectively. The relative standard deviation varied in the range of 3.0–5.0%. Results of this study show a great potential method for the fast screening of these artificial sweeteners contents in commercial beverages.

1. Introduction

In modern food industries, acesulfame-K, sodium saccharin and sodium cyclamate are the common artificial sweeteners and non-caloric sweeteners that have been widely used to replace sugars in foods such as soft drinks, juices, jams, candies, and many others. Those non-caloric sweeteners were mostly recommended for people that desire or need to reduce energy or sugar intakes for health reasons, as well as for individuals with diabetes (Santivarangkna, Higl, & Foerst, 2008). In the last two decades, the consumption of these low-calories foods by the worldwide population has dramatically increased. However, sodium saccharin is the oldest artificial sweetener, but it has been the center of controversy during the last few decades due to its possible carcinogenic effects. The strictest restriction is placed on its usage owing to its potential toxicity and its acceptable daily intake (ADI) value formulated by the Would Health Organization (WHO) is the lowest among these three sweeteners (FAO & WHO, 2006; Mathlouthi & Berssan, 1993), in China, 0.15–5.0 g kg^{-1} (GB2760-1996, 1996). Sodium cyclamate is banned in USA, while its usage is permitted in Europe (Mathlouthi & Berssan, 1993) and in China is 7–11 mg kg^{-1} (GB2760-1996, 1996). Acesulfame-K also has been used in many countries. In China, the maximum amount of acesulfame-K in beverages is 300 mg kg^{-1} (GB2760-1996, 1996), but according to the FAO/WHO, the ADI for acesulfame-K is 15 mg kg^{-1} (FAO & WHO, 2006).

Commercial beverages contained considerable amount of acesulfame-K, sodium saccharin and sodium cyclamate for maintaining food quality and characteristics. In order to ensure proper implementation of the existing legislation to guarantee consumer safety, sensitive and rapid analytical methods to monitor the artificial sweetener consumption are required. A number of analytical methods are available for their determination individually or simultaneously in their mixtures. These include: high-performance liquid chromatography (HPLC) (Ferrer & Thurman, 2010; Wasik, Mccourt, & Buchgraber, 2007), ion chromatography (Zhu, Guo, Ye, & James, 2005), flow injection analysis (García-Jiménez, Valencia, & Capitán-Vallvey, 2007), kinetic spectrophotometry (Ni, Xiao, & Kokot, 2009), potentiometric determination (Filho et al., 2003), and capillary electrophoresis (CE) (Bergamo, Fracassi da Silva, & de Jesus, 2011; Frazier, Inns, Dossi, Ames, & Nursten, 2000; Horie et al., 2007; Schnierle, Kappes, & Hauser, 1998) in conjunction with various detectors. Among those reports, HPLC has been the most popular choice for the determination of these artificial sweeteners. However, it encounter some disadvantages, such as the usage of toxic solvents, involvement of complex sample pre-treatments, generation of waste products, and even low sensitivity.

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CE is considered as an efficient and inexpensive analytical technique, and offered an attractive alternative to traditional HPLC methods. As known, Photometric detection in the UV region is the most commonly used detection method, although for some applications it shows inadequate limits of detection because of the low UV absorptivities of the most sweeteners, especially cyclamate. Conductivity detection is a good alternative method for compounds lacking a strong UV-absorbing moiety. Using this detection technique an isotachophoresis method was published for determination of sweeteners in chewing gums and candies (Herrmannová, Krivánková, Bartos, & Vytras, 2006). Capacitively coupled contactless conductivity detection (C^4D) is a relatively new approach for detection on CE. It is universal for all ionic compounds without derivatization or indirect approaches. C^4D features unprecedented ease of the cell arrangement and inherent prevention of the electrode fouling (Coltro et al., 2012; Fracassi da Silva & do Lago, 1998; Kubáň & Hauser, 2013; Zemann, 2003; Zemann, Schnell, Volgger, & Bonn, 1998). An earlier article (Tanyanyiwa, Abad-Villar, & Hauser, 2004) has demonstrated the possibility of using CE–C^4D on a microchip platform for separation and detection of acesulfame-K and cyclamate in model solutions. Recently, Bergamo reported another CE–C^4D method for the analysis of aspartame, cyclamate, saccharin and acesulfame-K in commercial soft drinks samples, and the LODs of cyclamate, saccharin and acesulfame-K were 2.5, 1.5 and 1.4 mg/L, respectively.

Online preconcentration can be regarded as one of the major developments in CE specifically to overcome the sensitivity limitations (Breadmore et al., 2013; Chen, Lü, Chen, & Teng, 2012; Chien, 1991; Simpson, Quirino, & Terabe, 2008). Among these preconcentration techniques, including sweeping, stacking, focusing, dynamic pH junction and extraction, field-amplified sample injection (FASI) is the simplest method with enrichment factors of several 100-fold or higher (Chien, 1991; Zhang & Thormann, 1996). Due to its simplicity and ease of applicability, FASI is regards as a most attractive method even though the sensitivity is not the highest one.

CE–C^4D, coupled with on-line preconcentration technique, has been demonstrated a simple, rapid, accurate, high sensitive and cost-effective analytical method with many advantages compared with the normal CE-UV system (Coltro et al., 2012; Ji, Chen, Zhang, Li, & Xie, 2014; Kubáň & Hauser, 2013). To the best of our knowledge, no paper regarding the highly sensitive detection of three sulfanilamide artificial sweeteners (acesulfame-K, sodium saccharin and sodium cyclamate) in commercial beverages by FASI–CE–C^4D is published.

The aim of this work is to establish a sensitive, simple, cost effective and highly specific analytical method for simultaneous determination of acesulfame-K, sodium saccharin, and sodium cyclamate in beverages by FASI–CE–C^4D. The performance of the method was evaluated with regard to the ability to generate accurate and precise qualitative and quantitative data in the relevant concentration range. These indicated its valuable potential application for the simple, sensitive analysis of trace-amount sulfanilamide artificial sweeteners in food samples.

2. Materials and methods

2.1. Reagents and materials

Acesulfame-K, sodium saccharin and sodium cyclamate were bought from J&K Chemical Co. (Beijing, China). Acetic acid was purchased from Guangzhou Chemical Reagent Co. (Guangzhou, China). All reagents were analytical grade unless otherwise indicated. All solutions were prepared with ultra-pure water (18 MΩ-cm) and stored in a refrigerator at 4 °C when not in use. 20 mmol L^{-1} HAc was used as the running buffer, i.e. background electrolyte (BGE), throughout this work. BGE was prepared fresh during the experiments. Individual standard solution (100 mg L^{-1}) of each sweetener was prepared by dissolving the corresponding solid reagents in deionized water. Lower concentration of working standard solution used in the analysis was prepared by dilution of the respective stock solutions with deionized water, as required.

2.2. Preparation of real samples

Real beverage samples were collected from the local supermarkets. Three different bands of Chinese chrysanthemum beverage samples with the batch number (CCB01, CCB02, and CCB03) were treated. The commercial beverage sample was degassed in an ultrasonic bath during 10 min, in order to remove the carbon dioxide gas that might be present in the beverage. Then, it was diluted with deionized water as required. The artificial sweetener in liquid form required only a dilution with deionized water before injection in the CE–C^4D system.

2.3. Instrumentation and procedure

The CE–C^4D equipment mainly includes CES2008-C^4D/CD-1B, fused-silica capillary and personal computer (Lenovo, China). The CES2008-C^4D/CD-1B was manufactured by School of Chemistry and Chemical Engineering, Sun Yat-sen University, China. The C^4D parameters were the same as the previous report (Wei, Li, Yang, Jiang, & Xie, 2011). The CE–C^4D instrument control and data collection were performed using the computer. The fused silica capillary was obtained from Hebei Ruifeng Instrumental Co. (Handan, China). The dimension of the capillary was 50 μm i.d., 375 μm o.d., 40 cm effective length, and 45 cm total length, respectively.

2.3.1. FASI–CE–C^4D procedure

Before the analysis, capillary was flushed with 0.1 M NaOH, water, 0.1 M HNO_3, water and the BGE for 3 min, respectively. After each run, the capillary was only rinsed with the BGE for 3 min. Unless noted, samples were injected electrokinetically with a voltage of −11.0 kV for 8 s. The separation voltage was set to

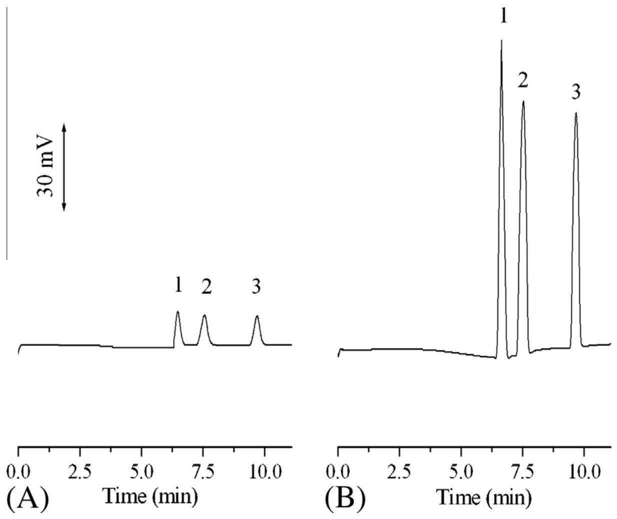

Fig. 1. Comparison of FASI method with the conventional gravity sample injection. (A) conventional gravity injection, 5.0 mg L^{-1} mixture of acesulfame-K, sodium saccharin and sodium cyclamate, 20 cm × 8 s; (B) FASI procedure, 0.10 mg L^{-1} mixture, electrokinetic injection of −11 kV × 8 s. Other conditions: 20 mM HAc as the running buffer; separation voltage of −12 kV; uncoated fused-silica capillary (45 cm × 50 μm i.d., L_{eff} = 40 cm). Peak identification: 1, acesulfame-K; 2, sodium saccharin; 3, sodium cyclamate.