Food Chemistry 129 (2011) 206–212

Contents lists available at ScienceDirect

Food Chemistry

journal homepage: www.elsevier.com/locate/foodchem

Analytical Methods

A novel miniaturised electrophoretic method for determining formaldehyde and acetaldehyde in food using 2-thiobarbituric acid derivatisation

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ARTICLE INFO

Article history:
Received 30 November 2010
Received in revised form 26 March 2011
Accepted 9 April 2011
Available online 16 April 2011

Keywords:
Miniaturised capillary electrophoresis
Electrochemical detection
2-Thiobarbituric acid
Derivatisation
Formaldehyde
Food

ABSTRACT

A novel miniaturised capillary electrophoresis with electrochemical detection (mini-CE-ED) method has been developed for fast determination of formaldehyde (FA) and acetaldehyde (AA) in several food products without preconcentration. Because FA and AA usually exist as uncharged molecules with zero electrophoretic mobility, plus the fact that these two compounds lack of chromophore for sensitive ultraviolet (UV) detection, effective and sensitive determination of FA and AA in real samples is often a challenging task. In this work, an electroactive compound 2-thiobarbituric acid (TBA) was selected as the ideal derivatisation reagent to facilitate the electrochemical determination of FA and AA. Under the optimum conditions, FA-TBA and AA-TBA adducts can be well separated by mini-CE-ED with low detection limit of 9.10×10^{-9} g/mL (13.2 fg) for FA (S/N = 3). The proposed method should find a wide range of analytical applications in food products as an alternative to conventional and microchip CE approaches.

1. Introduction

Low-molecular-weight aliphatic aldehydes have received much attention as air pollutants usually produced by incomplete combustion of fossil fuels, biomass and many organic substances, as well as several photochemical reactions (Kim, Hong, Pal, Jeon, Koo, & Sunwoo, 2008). In addition, several aldehydes such as formaldehyde (FA) and acetaldehyde (AA) are mostly minor compounds in food, and their occurrence can be an indication of quality deterioration (Kim, Pal, Ahn, & Kim, 2009; Kim & Richardson, 1992; Nicoletti, Corrandini, Cogliandro, & Corradini, 1996), overheating (Lee & Nagy, 1988), micro-bacterial fermentation (Woller & Wurdig, 1989) and/or off-flavour (Yan & Yan, 2007). Many aldehydes have been shown to be highly cytotoxic and genotoxic due to the nucleophilic attack to amine and sulphydryl groups of proteins, nucleic acids or related amino acids (Hoberman & George, 1988; Wilson et al., 1991). In fact, several aldehydes are considered toxic or carcinogens by the International Agency for Research on Cancer (IARC) (IARC, 1985). However, some unscrupulous traders driven by economic interests often add the non-food additive FA to the soaking solution to extend the shelf life of waterishlogged food products. Therefore, it is necessary and important to establish sensitive and selective analytical methods for determining aldehydes in view of their importance not only as ubiquitous air pollutants but also as indicators of food quality, biomarkers of cancer and symptoms of alcohol abuse.

Many methods proposed for aldehyde determination are based on spectrophotometric measurements (Guan, 2002; Pal & Kim, 2007), however, which are unspecific, time consuming and require the use of hazardous or toxic chemicals. In recent years, those above methods have been progressively replaced by gas chromatography (GC) and reversed-phase liquid chromatography (RPLC) approaches where aldehydes are determined as their 2,4-dinitrophenylhydrazine (Chen, Li, & Ding, 2009; da Cunha Veloso, da Silva, Santos, & de Andrade, 2001; Pal & Kim, 2008; Saito, Ueta, Ogawa, & Jinno, 2006; Schulte, 2002; Zhu, Guo, & Shi, 2002), triazine-based hydrazines (Kempter & Karst, 2000), oxime (Vesely, Lusk, Basarova, Seabrooks, & Ryder, 2003), ethyl 3-oxobutanoate and ammonia (Burini & Coli, 2004) or fluorescent derivatives (Yang et al., 2003). Therefore, it's necessary to develop a fast and low-cost analytical method plus simple preparation.

Capillary electrophoresis (CE) is increasingly recognised as an important analytical separation technique because of its speed, efficiency, reproducibility, ultra-small sample volume, little consumption of solvent and ease of clearing up the contaminants. For example, good results have been achieved for the CE separation of low molecular weight aldehydes in air samples by using UV–Vis (Bai et al., 2010; Pereira, Carrilho, & Tavares, 2002; Pereira, Rezende, & Tavares, 2004; Ruiz-Jimenez & Luque de Castro, 2006) and conductivity (Rocha et al., 2008) detection. CE performed in

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doi:10.1016/j.foodchem.2011.04.025

miniaturised devices (microchips) has also experienced a remarkable growth during the last decade because of its distinct advantages, such as efficient separation, high speed, minimal reagent consumption and small dimensions (Effenhauser, Manz, & Widmer, 1993). Moreover, coupling with electrochemical detection (ED), CE-ED offers many desirable features for portable/disposable CE systems because of high sensitivity, tunable selectivity and compatibility with advanced micromachining technology (Martin, 2006). Dossi's group has applied microchip electrophoresis coupling ED to determine light aldehydes in air (Dossi, Susmel, Toniolo, Pizzariello, & Bontempelli, 2009) and vegetable oil (Dossi, Susmel, Toniolo, Pizzariello, & Bontempelli, 2008) samples. However, microchip fabrication processes were usually costly, time-consuming, labour-intensive and requiring skill-intensive micro-alignment of the electrode to the channel outlet – a setback to the day-to-day repeatability.

In this work, an improved novel miniaturised capillary electrophoresis with electrochemical detection (mini-CE-ED) system was reported which was dependable, low-cost, easy to operate and no need of microfabrication. In fact, the mini-CE-ED system showed better mechanical stability and better durability (Chu, Jiang, Tian, & Ye, 2008; Wu, Wang, Jiang, Chu, Jacques, & Ye, 2008). The research showed the smaller molecular weight, the stronger toxicity (Henson, Charleston, & Virginia, 1959), therefore, FA and AA were selected as the target analytes. Because FA and AA usually exist as uncharged molecules with zero electrophoretic mobility, plus the fact that these two compounds lack of chromophore for sensitive UV detection, effective and sensitive determination of FA and AA in real samples is often a challenging task. In this work, an electroactive compound 2-thiobarbituric acid (TBA) was selected as the ideal derivatisation reagent to facilitate the determination of FA and AA. With a common laboratory chemical derivatisation regent TBA, a new derivatisation approach has been developed. As an electroactive species (You, Yang, & Wang, 2000), TBA can make FA-TBA and AA-TBA adducts also becoming electroactive after derivatisation, thus to facilitate the determination of FA and AA in wines and soaking solution of waterishlogged products based on the mini-CE-ED method.

2. Materials and methods

2.1. Reagents and solutions

All solvents and reagents were of analytical grade. The standard compounds of FA (40%) and AA (40%) were purchased from Sigma (St. Louis, MO, USA), TBA ($\geqslant$98.5%) was purchased from China National Pharmaceutical Group Corporation (Shanghai, China), and they were all used as received. The stock solutions of FA (1.00×10^{-2} g/mL) and AA (1.00×10^{-2} g/mL) were prepared with twice distilled water, TBA (7.25×10^{-3} g/mL) was prepared in ethanol solution (1:1), and all standard solutions were stable for 1 week, when stored in a refrigerator at 4 °C.

2.2. Sample preparation and derivatisation

All of food samples were purchased from local supermarkets or retailers in Shanghai (China) including wines (Chinese white liquor, red wine, white wine, yellow wine, rice wine and beer) and waterishlogged products (tripe, pork skin, sea cucumber, jelly fish and squid). Each sample of wines and soaking solutions of waterishlogged products were filtered through 0.22 μm nylon filters prior to derivatisation. An appropriate amount of filtrate was derivatised by adding 165 μL derivatisation reagent TBA (7.25×10^{-3} g/mL), 250 μL hydrochloric acid (2.90 mol/L) and some deionised water to a total volume of 1 mL in a 5 mL flask. The flask was capped and shaken slowly under the effect of magnetic stir, and the reaction proceeded for 60 min at room temperature.

2.3. Fabrication of the mini-CE-ED system

The home-made mini-CE-ED system was used in this work (as shown in Fig. 1), and the principles and details were reported previously (Wu et al., 2008). A ±5 kV direct current power supply (Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai, China) provided a separation voltage between the ends of the capillary column. The inlet end of the capillary column was held at a positive potential and the outlet end was maintained at ground. The separations were performed in a fused-silica capillary column (19.5 cm × 25 μm i.d. × 360 μm o.d., Polymicro Technologies, Phoenix, AZ, USA). A three-electrode electrochemical cell consisting of a lab-made 300 μm diameter carbon disc working electrode (Fig. 1a), a platinum auxiliary electrode (Fig. 1b) and a saturated calomel electrode (SCE) reference electrode (Fig. 1c), was used in combination with a BAS LC-3D amperometric detector (Biochemical System, West Lafayette, IN, USA). After being coated with insulated varnish film, the carbon lead available in the market with a 300 μm diameter can be directly used as the carbon disc working electrode (Fig. 1a). Before use, the disc surface of the carbon electrode was polished with emery sand paper, sonicated in deionised water, and then positioned carefully in the opposite side of the capillary column outlet through the guiding metal tube (Fig. 1i) which was fabricated for the alignment of the working electrode and capillary column. The other end of the carbon electrode was connected to copper lead by soldering tin used as connecting line to the detector. Data acquisition and analysis were preformed using HW-2000 software package, Version 2.21 (Shanghai Qianpu Software Co., Ltd., China). The conversion expression between voltage (mV) unit of the instrumental readout and current (nA) unit of AD instrument is "1 mV = 0.0496 nA".

2.4. Electrophoresis procedure

The capillary column was rinsed before use by 0.1 mol L^{-1} NaOH and deionised water for 5 min each, and then flushed with the running buffer of 80 mmol/L H_3BO_3–$Na_2B_4O_7$ buffer (pH 9.0) by applying 2500 V for 15 min. The detection cell (Fig. 1d) was filled with the same running buffer. The sample solution was introduced into the separation channel by applying a voltage of 2500 V between the sample vial (Fig. 1h) and the grounded detection cell (Fig. 1d) for 4 s. Subsequently, the inlet of capillary column and the high-voltage leading wire were immersed into the running buffer vial (Fig. 1h) and the separation voltage was applied between the high-voltage and grounding wires for separation. The whole system was assembled in an air-conditioned room at 20 °C in order

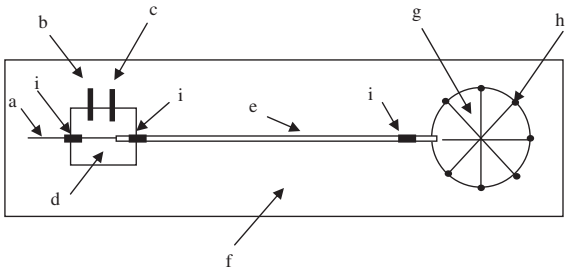

Fig. 1. Top view of the schematic diagram of mini-CE-ED system. (a) Working electrode; (b) Pt auxiliary electrode; (c) saturated calomel electrode (SCE) reference electrode; (d) detection cell; (e) 25 μm i.d. fused silica capillary column; (f) plexiglass plate; (g) turning plexiglass disc; (h) plastic vial for running buffer or sample solution and (i) metal tube.