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Original Article

Determination of underivatized amino acids to evaluate quality of beer by capillary electrophoresis with online sweeping technique

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ABSTRACT

Capillary electrophoresis (CE) with ultraviolet detection was applied to determine underivatized amino acids in beer, based on the coordination interaction of copper ions and amino acids. An online sweeping technique was combined with CE to improve detection sensitivity. Using the United Nations Food Agriculture Organization/World Health Organization model of essential amino acid pattern and flavor of amino acids, the quality and taste in three kinds of beer were evaluated. It was found that Beer2 had higher quality than the other two kinds and the content of phenylalanine, proline, serine, and isoleucine was relatively large in all three kinds of beers with a great influence on beer flavor. Optimal conditions for separation were as follows: 50mM $CuSO_4$ at pH 4.40 as buffer; total length of fused silica capillary, 73 cm; effective length, 65 cm; separation voltage, 22.5 kV; and optimized sweeping condition, 70 seconds. In the appropriate range, linearity ($r^2 > 0.9989$), precision with a relative standard deviation < 8.05% ($n = 5$), limits of detection (0.13–0.25 μg/mL), limit of quantification (0.43–0.83 μg/mL), and recovery (80.5–115.8%) were measured. This method was shown to be applicable to the separation of amino acids in beer and to perform quantitative analysis directly without derivatization for the first time.

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1. Introduction

Amino acids, as the building blocks of proteins [1], are important life substances in nature, and they are essential nutrients in a series of samples, such as foods, beverages, plants, and pharmaceutical drugs. Therefore, they are often used to characterize foods [2] and beverages [3], as well as in quality control tests. Amino acids are also regarded as necessary ingredients in beer, because they play a key role in beer brewing [4], which can affect the taste and quality of beer [5]. There are many kinds of amino acids in beer, but their contents are low. Therefore, establishing a rapid and sensitive method for determination of amino acids in beer is helpful to control the quality and supervise the preparation process of beer.

At present, the analytical methods of determining amino acids in beer are gas chromatography (GC) [6], high-

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performance liquid chromatography (HPLC) [5,7–9], ^{1}HNMR spectroscopy [10], HPLC–mass spectrometry (HPLC–MS) [11–13], GC–MS [7], and capillary electrophoresis (CE) [4,14]. Among these methods, CE has advantages such as high efficiency, good resolution [15], and low consumption of samples and reagents [16], so it is widely used in the analysis of amino acids in beer. However, because most amino acids (except phenylalanine, tryptophan, and tyrosine) do not have strong chromospheres in their structures, they exhibit neither UV absorption nor fluorescence [17]. Consequently, amino acids are always determined by derivatization to increase detection sensitivity [18]. However, the derivative methods have some specific drawbacks, for instance, high requirements of reagents, complex operation process, and long derivatization time [14]. In addition to derivatization, the HPLC–MS and GC–MS methods can directly determine the amino acids in beer, but these techniques are more expensive than HPLC, GC, and CE, and not all laboratories are equipped with the related equipment to perform these analyses. Therefore, using a method of underivatization with commonly available technology is desirable.

Although the UV absorption of amino acids is very weak, they can form complexes $[Cu(AA)n]^{+2}$, where AA is amino acids, by coordination interaction with copper ions. This method was first proposed by Bazzanella and Bächmann [19] in 1998. The N and O atoms on the amino acid are used as coordination atoms [20]. The metal ions that have empty orbits and the ability to accept electrons act as center ions [21]. Under the effect of radiation, charges on the ligand orbitals transfer to copper tracks while producing an absorption band that has a strong molar absorptivity (ε) about 10^4. $[Cu(AA)n]^{+2}$ complexes have the strongest UV absorption under 254 nm [20,22], which greatly improves the sensitivity of determination of amino acids. Determination of amino acids according to the coordination interaction between amino acids and copper ions has been reported previously. Jiang et al [20] used this method to analyze amino acids in human saliva and green tea. In 2012, Xue and Hong-Mei [22] achieved effective separation of amino acids, also based on coordination interaction, in Radix Asparagi. In a similar way, Zhou and Shi [23] determined amino acids in plasma and nutritional supplements. However, there are no studies about using this method to analyze amino acids in beer. As mentioned earlier, beer is rich in amino acids and amino acids have a decisive effect on the fermentation of beer and on its taste and quality. In this study, we accurately and rapidly analyzed amino acids in beer according to the coordination interaction between amino acids and copper ions for the first time.

The effective separation of underivatized amino acids was achieved by coordination interaction between amino acids and copper ions. However, the sensitivity of amino acids sample was reduced, as copper ions with ultraviolet absorption were added to the buffer, and the contents of amino acids in beer were low. Therefore, in this study, the sweeping technique was used to improve the detection sensitivity. Sweeping is an effective online preconcentration technique that utilizes the interaction of analytes with additives that include a pseudostationary phase in electrokinetic chromatography such as sodium dodecyl sulfate and a complex agent in capillary zone electrophoresis to concentrate the analytes into a narrow zone to enhance the detection sensitivity [15,24]. The role of copper ions is similar to additives. Under high voltage conditions, the effective mobilities of amino acids are slower than copper ions; copper ions are regarded as *besom* and concentrate amino acids into narrow bands within the capillary. Thus, the sensitivity of amino acids is greatly enhanced.

In this study, based on the coordination interaction between amino acids and copper ions, the sweeping technique was applied for direct separation of amino acids in beer for the first time. Using United Nations Food Agriculture Organization/World Health Organization's [25] model of essential amino acid pattern and flavor of amino acids, quality and taste in three kinds of beers were evaluated.

2. Materials and methods

2.1. Reagents and solutions

L-Lysine, L-histidine, L-aspartate, L-cysteine, L-tryptophan, L-serine, L-phenylalanine, L-glycine, L-valine, L-alanine, L-leucine, L-isoleucine, L-threonine, L-methionine, L-proline, and L-glutamic acid were purchased from Yuanye Biological Technology Co., Ltd. (Shanghai, China; purity >99.5%). Copper sulfate and sodium acetate were purchased from Shuang Shuang Chemical Reagent Co., Ltd (Yantai, China). The purified water used to prepare various solutions was obtained from the GLP Laboratory of Lanzhou University (Lanzhou, China). Acetic acid (HPLC grade) was purchased from Shandong Yu Wang Pharmaceutical Co., Ltd. (Shandong, China). Three kinds of beers were purchased from a local supermarket (Lanzhou, China).

2.2. Equipment

In this work, the CE was equipped with a K1060 system (KAIAO, Beijing, China) and a UV detector. A workstation with Easychrom-1000 software (Beijing, China) was used for data acquisition and evaluation. The uncoated fused silica capillaries (Hebei, China) were used to finish separation; the dimensions of the capillary were as follows: 50 μm i.d. × 375 μm o.d., 73 cm in total length, with length to the detector of 65 cm. The FE20 pH meter (Mettler Toledo Instrument Co., Ltd, Shanghai, China) was used to measure the pH of the buffer. Lac part analytical balance (Shanghai Ohaus Discovery professional analytical balance, Shanghai, China) was used for weighing the buffer solution.

2.3. Solution and sample preparation

All 16 amino acids (0.00100 g) were dissolved in purified water to obtain a concentration of 1.00 mg/mL; stock solutions were stored at 4°C until use. The stock solutions were then diluted in different concentrations as needed prior to use. Stock buffer solutions of copper sulfate (100mM) were prepared with purified water daily. Beer samples were obtained from a local supermarket (Lan Zhou), degassed, and then subjected to direct sampling. All solutions and samples were filtered using 0.22-μm membranes prior to use.

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