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Original Article

Identification of cow milk in goat milk by nonlinear chemical fingerprint technique

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ABSTRACT

The objective of this paper was to develop a nonlinear chemical fingerprint technique for identifying and detecting adulteration of goat milk with cow milk. In this study, by taking the Belousov-Zhabotinsky oscillatory chemical reaction using acetone and substrates in goat milk or cow milk as main dissipative substances, when the same dosage of goat milk and cow milk was introduced to the "$H^+ + Mn^{2+} + BrO_3^- +$ acetone" oscillating system respectively, nonlinear chemical fingerprints were obtained for goat milk and cow milk from the same origin. The results showed that inductive time value and the content of cow milk in goat milk had a linear relationship in the range of 0–100% and the corresponding regression coefficient was 0.9991. A detection limit of 0.0107 g/g was obtained, and the content of cow milk in mixed milk was calculated. The proposed method in this study was simple, economical and effective. In addition, the method did not need the pretreatment and separation of samples for identifying and evaluating cow milk adulteration in goat milk.

1. Introduction

Goat milk is a kind of highly nutritious food because it possesses unique properties which distinguish it from cow milk. Recently, goat milk plays an increasingly important role in the human diet, and it suits not only for infants but also for adults, especially for nursing mothers [1]. Furthermore, goat milk has become popular as an infant diet because the fat globules of goat milk are smaller than those of cow milk and goat milk has higher percentage of short-and medium-chain (C_6-C_{14}) fatty acids in comparison with cow milk, which is probably main reason for the easy digestion of goat milk [2–4]. However, for higher profit, increasing demand for goat milk might result in the adulteration by cheaper cow milk, which has become a serious quality problem. Due to the similarity of goat milk and cow milk in appearance and composition, it is difficult to

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differentiate goat milk and cow milk [5]. This situation also presents a risk for people afflicted with cow milk allergies, when they consume adulterated goat milk [6,7]. Thus, analytical methods with high selectivity to identify and evaluate adulteration in goat milk are required.

Currently, chemical fingerprint analysis has been applied as an effective method for milk and dairy products quality control. These fingerprinting methods include HPLC [5], capillary electrophoresis [8], isoelectric focusing [9,10], enzyme-linked immunosorbent assay [11], PCR technology [6,12], pulse polarography method [13], liquid chromatography tandem mass spectrometry [14] and so on. Most of these methods exhibit high sensitivity and can meet the requirements for identifying and evaluating adulteration of milk and dairy products. However, these techniques described above are mainly used to identify and distinguish adulteration of milk and dairy products by detecting various chemical compositions of milk, such as the detection of specific protein components by HPLC [15]. Moreover, these methods usually require complex preprocessing, such as separation and purification. So the research on the effective method for directly showing the throng character of chemical components in cow milk and goat milk has become one of the primary tasks which the analysts are facing. In addition, it would be beneficial to develop simple and cost effective methods based on different principles from different aspects for distinguishing and evaluating samples, and the techniques may be complementary with each other.

The discovery of Belousov–Zhabotinskii (B–Z) oscillatory reaction (Belousov and Zhabotinsky were the names of the two Russian scientists, who were the first ones to study the reaction) began the times to investigate nonlinear chemical reaction systems [16], and the research on the application of nonlinear chemical reaction had aroused increasing attention. Chemical oscillation based on Belousov–Zhabotinskii (B–Z) reaction was a common phenomenon in nonlinear chemistry. The phenomena of the reaction are complex, involving chemical oscillation, chemical turbulence, chemical patterns and chemical waves [16]. The reaction mechanism and applications of chemical oscillation in single component detection had been investigated extensively and thoroughly by domestic and foreign scholars [16–19]. While the research to apply it in fingerprint analysis for characterizing throng characteristic of the components in foods was rare abroad, and also started rather late in China. Such as authenticity identification and quality evaluation of soya sauce had been reported by nonlinear electrochemical fingerprint and system similarity [20]. According to the literatures [21,22], because of the differences in the types and the content of their components, different samples had different influences on an identical nonlinear chemical reaction, which caused that the shapes of the relevant potential-time (E–t) curves were different from each other. The E–t curve is very helpful for the rapid identification and evaluation of cow milk in goat milk because it contains abundant qualitative and quantitative information. In this work, we introduced goat milk with or without artificially added cow milk to "$H^+ + Mn^{2+} + BrO_3^- +$ acetone" oscillating system, and cow milk adulteration in goat milk was identified and evaluated by a nonlinear chemical fingerprint technique.

Thus, the objective of this study was to evaluate the feasibility to apply nonlinear chemical fingerprint technique to detect and identify cow milk adulteration in goat milk. The content of cow milk in mixed milk was calculated by the least square method, and the mechanism of the method was introduced using H^+, Mn^{2+}, BrO_3^-, acetone and glucose as the reaction substrates. The method developed in this study has the advantages of low operational cost and no pretreatment for identifying and evaluating cow milk adulteration in goat milk.

2. Materials and methods

2.1. Materials

All chemicals used were of analytical grade. Sulfuric acid (1.0 mol L^{-1}), acetone (1.0 mol L^{-1}), sodium bromate (0.8 mol L^{-1}) and manganese sulfate (0.08 mol L^{-1}) were used. Solutions were kept at a constant temperature (50.0 °C) until used. Double distilled water was used throughout the experiments. In addition, acetic acid (5%), dichloromethane (200 μL) and formic acid (0.2%) were used.

2.2. Milk samples

Raw goat milk and cow milk were collected from local farms. Then, milk samples were freeze dried milk powder. A series of adulteration samples were made of raw cow milk and raw goat milk in volume ratios 0, 5%, 10%, 20%, 40%, 60%, 80%, and 100% v/v.

2.3. Main apparatus

A nonlinear chemical fingerprint instrument (Model MZ-1B) developed by Central South University and Xiangtan Ltd. (Hunan, China) was used. A Type 217 calomel electrode was used as reference electrode and a Type 213 platinum electrode was used as working electrode (both were purchased from Shanghai Precision & Scientific Instrument Co., China). All studies were conducted using the experimental set-up which was illustrated in the literature [21]. In addition, an ion trap mass spectrometer (Thermo Finnigan, San Jose, USA) was used.

2.4. Procedure

The following procedure was used in all experiments. The nonlinear chemical reaction mixture was prepared by mixing 25.00 mL of sulfuric acid, 10.00 mL of acetone, 12.00 mL of manganese sulfate, 10.00 ml of double distilled water and appropriate dosage of cow milk or goat milk sample. All components of reaction mixture were added into the reactor. The reactor cover with two injection holes, the electrodes and a thermometer was closed. The instrument was then turned on, with temperature and stirring rate adjusting to 50.0 °C and 800 r/min, respectively. After stirring for 5.0 min, 5.00 mL of sodium bromate solution was injected into the reactor. Electric potential-time (E–t) curve was immediately obtained and finished as soon as the potential oscillation disappeared.