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Development of the mass spectral fingerprint by headspace-solid-phase microextraction-mass spectrometry and chemometric methods for rapid quality control of flavoring essence

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ABSTRACT

Based on non-separative headspace-solid-phase microextraction-mass spectrometry (HS-SPME-MS) method and multivariate statistical analysis, we describe in this paper a reliable and rapid technique capable of controlling the quality and verifying the authenticity of flavoring essences. Two similar types of essences corresponding to formula A and formula B were extracted and concentrated by the HS-SPME method. Subsequently, the constituents adsorbed on SPME fiber were thermally desorbed in the chromatographic injection port and directly transferred to mass spectrometer without prior chromatographic separation. Thus, a unique mass spectral fingerprint of essence was formed. Three multivariate statistical processes were carried out to distinguish the samples and analyze the results. Firstly, similarity analysis based on correlation coefficient was used to evaluate the resemblance of the essences. The results indicated that the correlation coefficients of formula A and B from different batches were more than 0.980 and 0.920, respectively. In addition, principal component analysis (PCA) and partial least square discriminant analysis (PLS-DA) were employed to provide a visual comparison of the two types of flavoring materials. We demonstrated that the PLS-DA method can establish a discrimination rule to predict the “belongingness” of new samples and further screen out the main ionic markers, which might be suitable for recognizing and monitoring the quality of flavoring essences.

1. Introduction

Flavoring essence is a mixture of various kinds of additives and flavors, which is widely added or sprayed on commodities to improve the taste of food, as well as to give them special and stable fragrance. There is no doubt that products with stable taste and smell are more easily accepted by consumers [1]. Hence, the effective quality control of flavoring essence is one of the major concerns for food manufacturers. At present, the commonly used methods for monitoring the quality of flavoring materials in the food industry include physicochemical parameter testing and sensory evaluation. The former is usually performed by detecting the relative density, refractive index or total volatile constituents of essences [2]. And the latter method requires an expert panel to describe flavoring essence via a variety of proprietary vocabularies within a single process, implying inevitable subjectivity between individuals [3]. Both of the two methods could effectively monitor the quality of essence to some extent. However, considering fierce competitions in food industry, both methods are time-consuming and/or costly, which are fatal disadvantages and have a great negative influence on production efficiency and industrial cost of enterprises. Therefore, it is in urgent need of developing a rapid, simple and cost-effective analytical technique to meet the manufacturer's demand for controlling the quality of flavoring essence.

The volatile organic compounds (VOCs) are the major components in flavoring essence, so how to extract more VOCs in essence sample is a prerequisite to control the quality of essence [4,5]. Recently, solid-phase microextraction (SPME) is becoming one of the most popular sample pretreatment techniques in the field of food and fragrance analysis, since it has several unique advantages of solvent-less, high repeatability and easy operation [6,7]. For desorption, separation and detection of the compounds adsorbed on SPME fiber, gas chromatography (GC) and gas chromatography–mass spectrometry (GC–MS) have been considered as preferred choices due to their superiority that the original devices needn't be modified. Nevertheless, what should not be overlooked is that chromatographic technique can only be used in

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laboratory analysis, and it is hard to be applied in the modern and competitive food industry because of the time-consuming processes and the requirement for specialized personnel to interpret the results.

To overcome the limitations of GC–MS method and for fast collection of the aroma information of flavoring essence, recently a new type of non-separative MS method (perhaps better known as MS-electronic nose) based on the direct combination of mass spectrometer and solid-phase microextraction has been booming [8–10]. In non-separative MS method, the chromatographic column of GC–MS instrument is replaced by a fused silica tube, then the volatile portion of a sample is immediately desorbed in the injection port at a high temperature and subsequently injected into the ionization chamber without chromatographic separation procedure. The compounds in the sample are ionized with electron ionization (EI) to obtain a characteristic and representative spectrum which is called the “mass spectral fingerprint”. And each ion fragment of the mass fingerprint can be regarded as a latent chemical descriptor of the sample. When the non-separative MS method is combined with appropriate multivariate statistical analysis (chemometrics), it will have a great potential to identify the samples and monitor their quality. Although many research efforts have been made in the quality control of dairy product (cheese and milk) [11–14], beverage (wine and spirits) [3,15–18], and agricultural products (rice and tomato sauces) [19,20], little attention has been paid to the rapid and effective quality control of flavoring essence, especially employing non-separative method.

The present study was aimed to develop a simple, rapid and reliable technique based on the non-separative MS and multivariate analysis to control the quality of essence. The volatile constituents in flavoring essences from different batches and varieties were extracted and detected by using headspace-solid-phase microextraction-mass spectrometer (HS-SPME-MS) technique. In addition, the separative method (HS-SPME-GC–MS) was used as an auxiliary approach to better interpret the information collected from the HS-SPME-MS measurement. Then different chemometrics methods (similarity analysis, PCA and PLS-DA) were attempted to classify samples, assess the adulterated samples or find out possible makers for quality control of flavoring essences. The overall measurement scheme is depicted in Fig. 1.

2. Materials and methods

2.1. Materials

Two similar varieties (a total of 52 flavoring essences), which were frequently confused by manufacturers, were used to test the applicability of the non-separative method. Since the chemical ingredient of essence is one of the top secrets in food industries, we defined the two similar essences involved in this study as formula A and formula B, respectively. A total number of 52 flavoring samples (including formula A and B, each for 26 samples) were supplied from diverse batches by China Tobacco Yunnan Industrial Corporation, and they were flagged as A1–A26 and B1–B26, respectively. The fifty-two samples were regarded as the qualified products via the physicochemical parameter testing and sensory evaluation. The essences of A11 and B15 were randomly selected and used to fabricate the adulterated samples by mixing

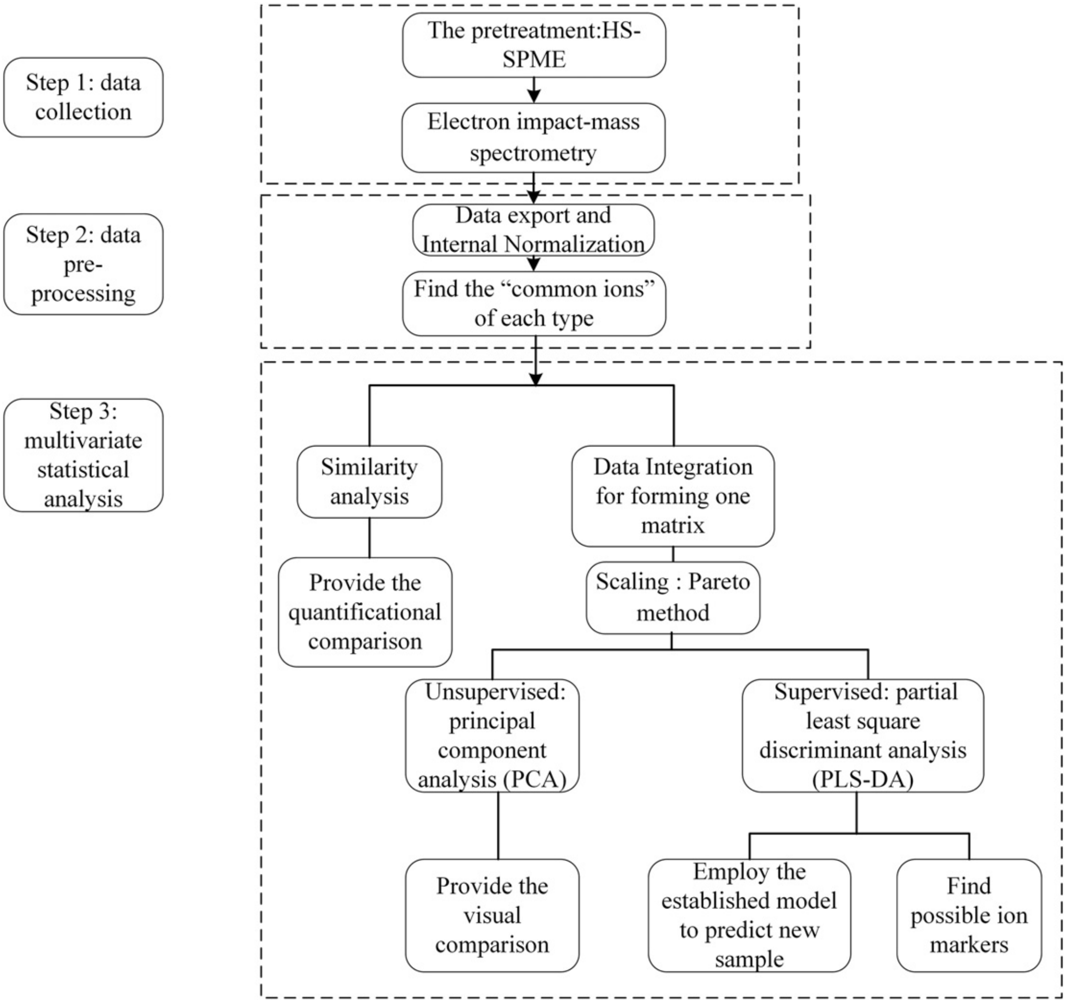

Fig. 1. Schematic overview of the measurement protocol in this study.