Application of GC-IMS in Detection of Food Flavor Substances

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Abstract. Gas chromatography-ion migration spectroscopy (GC-IMS) is an effective method for the separation and sensitive detection of volatile organic compounds (Vocs). This technology combines the advantages of high separation ability of GC and rapid response of IMS, with fast response speed, high sensitivity, convenient operation and low cost. It has been widely used in the fields of drug detection, disease monitoring and environmental protection, especially in the field of food flavor analysis. This review first introduces the working principle of GC-IMS, and then summarizes the application of GC-IMS in the detection of flavor substances in food in recent years. Finally, the future paths in the research and development of GC-IMS are discussed.

1. Introduction
Undoubtedly, food with both color, aroma and taste, which are three important indicators of food quality, are often loved by consumers. As a kind of substance which can stimulate people's sense of smell (fragrance, smell) and taste (sour, sweet, bitter, spicy, salty), flavor substances have a significant effect on food flavor, and even affect the overall evaluation of food. The analysis of flavor substances in food can be divided into sensory analysis and instrumental analysis. Sensory analysis refers to the sensory perception of aroma substances in food. The evaluation results are often subjective and can not be explored at the molecular level. The combination of subjective sensory evaluation and objective instrumental analysis can better explain the relationship between food flavor chemical components and sensory experience, so as to understand the formation mechanism of a certain aroma. The invisible flavor is transformed into a visible fingerprint[1], and the flavor is visible. Gas chromatography-mass spectrometry (GC-MS), gas chromatography-olfactory-mass spectrometry (GC-O-MS) and electronic nose[2]are the most commonly used technical methods to identify volatile aroma compounds in food. Among them, GC-MS is the most commonly used analysis technology of flavor substances. However, due to the complexity of food matrix, complex pretreatment is often needed before analysis, and a long detection time may not be able to meet the rapid detection requirements of multi-component analysis.
GC-O-MS can effectively screen aromatic compounds from complex mixtures, but it requires a lot of repetitive time-consuming work and long detection time, so it is not suitable for situations with heavy workload. GC-IMS can solve these disadvantages with fast detection time, no pre-processing and stable and reliable test results. As a new type of gas phase separation detection technology, GC-IMS combines the high separation ability of GC with the rapid response of IMS, and has been widely used in drug detection, disease surveillance and environmental protection[3-4], especially in food flavor analysis. Here, we focus on the application of GC-IMS in food flavor analysis, and the future paths in the development of GC-IMS are discussed.

2. GC-IMS

FlavourSpec® Flavor Spectrometer, developed by the company of German G.A.S, for example, is mainly composed of host, automatic sampler, headspace sampler and sample table(Figure 1). Among them, the host is consist of a chromatography system chromatographic column separation system, ion generator system and ion migration detection system. The working principle is shown in Figure 2A. The volatile components in the sample were pre-separated by chromatographic column and eluted directly to the IMS ionization chamber for ion migration analysis[5]. The hyphenated technique skillfully combines the high separation of GC with the high sensitivity of IMS, and achieves the analytical effect of mutual superposition of advantages[6]. On the one hand, due to the two-dimensional information of ion drift time, the chemical information obtained from the separation of ion migration spectra is more abundant. On the other hand, the mixed samples are pre-separated in the chromatography, the signal response quality of ion migration spectrum has been greatly improved. The invisible flavor substances were transformed into visible fingerprints by GC-IMS technology. As shown in Figure 2B, one point represents a volatile organic compound, the color of the point represents the content of the substance, the more the darker, the Abscissa represents the substance detected by a sample, and the ordinate indicates the content of the same substance in different samples.

Figure 1. Schematic illustration of GC-IMS analyzer: (A) Host, (B) Automatic sampler, (C) Headspace sampler and (D) Sample table.

Figure 2. Schematic illustration of GC-IMS working principle and fingerprints of different products.

The GC-IMS instrument has the following advantages when detecting flavor substances, such as extremely high sensitivity, no need for enrichment and concentration, good stability and fast response speed. In addition, GC-IMS operates under normal pressure, without a vacuum system, it can work after 20 minutes of start-up, a single detection time is 2~30 minutes, the instrument operation and data processing are simple, and the use of nitrogen or synthetic air, the annual operating cost, the annual operating cost about one thousands dollars. The application fields of GC-IMS are food flavor and related research, for instance, the detection of volatile oil in traditional Chinese medicine preparations; VOCs in water, silt and soil; human metabolites(blood and urine)[7].
3. Application of GC-IMS in the Detection of Food Flavor substances

The application of GC-IMS in the detection of food flavor substances is mainly reflected in the protection of geographically marked products, the study of changes in food quality during storage; the impact of processing methods on food flavor; the optimization of storage conditions and the differentiation of food varieties and quality.

Rice is one of the most important foods in the world. Wang[8] studied the source of rice by LC-MS (Liquid chromatography-mass spectrometer), GC-MS and GC-IMS combined technology, respectively. Combining the advantages and disadvantages of the three methods, it was found that GC-IMS technology has high reliability and can effectively identify rice from different areas. It can be analyzed directly by headspace injection (Figure 3), without enrichment and concentration, without organic solvent extraction, and it is simple and easy, without too much human intervention, automatic analysis, 15 minutes to produce the results.

Brown rice is a kind of rice grain which still retains the cortex and embryo after shelling. It not only contains more nutrients such as protein, vitamins and minerals, but also contains dietary fiber, oryzanol, glutathione and other functional factors to promote human health. Wang[9] used brown rice at different times and different storage methods as the research object through GC-IMS technology, collected and analyzed the volatile organic compounds produced during brown rice storage, and quickly judged the storage period and freshness of brown rice. The japonica brown rice used in the study was packed in woven bags of 25 kg each. The bagged brown rice was placed in a cascading manner and stored in a PVC film grooved tube sealed on five sides. Brown rice samples were divided into two groups A and B according to different packaging methods. Group A was packed with modified atmosphere by filling N₂(≥98%), B group was ordinary gas packaging. The storage period was 18 months, and samples were taken every 0, 6, 12 and 18 months to analyze the change process of brown rice flavor substances during the storage period. Through the fingerprint, it was found that nitrogen packaging had little effect on the flavor substances of brown rice, except isooctanol and acetone. The flavor of brown rice changed obviously with the extension of storage time. This study can establish a database to distinguish the storage time of brown rice based on PCA analysis (Fig. 4), which can be used to quickly judge the storage time of brown rice. It can also optimize the storage mode of brown rice and reduce the cost as much as possible under the premise of ensuring flavor. According to this case, it can be found that nitrogen packaging has little effect on the flavor substances of brown rice, and the cost of nitrogen packaging is high, so we can use ordinary packaging, there is no need to use nitrogen packaging, can reduce the cost.

Figure 3. Headspace injection experiment process of GC-IMS analyzer[8].

Figure 4. PCA analysis chart of brown rice during different storage conditions[9].

Guo[10] established the fingerprints of volatile organic compounds in fresh kumquat, vacuum impregnated kumquat preserves and atmospheric pressure impregnated kumquat preserves by GC-IMS, and studied the effects of two different processing methods on the volatile substances of kumquat.
preserves. Contrast and analyze the flavors of kumquat compote when the two dipping methods have different drying time. The results showed that the content of flavor substances such as 2-hexene-1-alcohol will gradually increase as the drying time is extended by vacuum impregnation; atmospheric pressure impregnation, unique flavor substances, such as furfural, benzaldehyde, etc., will not appear until two hours after benzaldehyde drying and the content is constant. It is not difficult to draw conclusions that GC-IMS can be used to optimize the processing technology by Vocs detection, and the best processing scheme can be worked out to reduce the cost under the condition of ensuring flavor.

Li[11] studied and compared the effects of four fermentation methods on the changes of flavor substances and sensory evaluation in raspberry wines through GC-IMS. During sensory evaluation, the flavor of spontaneous fermentation(RU) is very similar to that of single S. cerevisiae inoculation(RS), which is related to high concentrations of methyl 2-methyl butyrate, hexyl acetate, 1-butanol and acetone. However, the flavor of sequential inoculation(RT) was completely different from that of co-fermentation(RC) mode. RT characterized by fruity type, is related to high concentrations of ethyl formate, isobutyl acetate, ethyl butyrate, isoamyl acetate, ethyl caproate, etc. That of RC fruit wine is related to ethyl isobutyrate, ethyl 2-hexanoate, 1-propanol and 2-methyl-1-propanol and belongs to the floral type. Overall, GC-IMS technology can be used to identify the changes of characteristic volatile components in different flavor raspberry wines, and it is more suitable for the screening of bacteria. It is an important means to realize the precise regulation and control of fermentation process.

Figure 5. Average values of sensory evaluation scores of raspberry wines resulting from different fermentations[12].

Sea cucumber peptide powder can improve anemia, supplement nutrition, improve immunity, heart failure, hypertension, tracheitis and so on. Therefore, it is a healthy food for many people, and its quality and flavor are also the focus of many people's attention. Wang[12] studied the volatile compounds of sea cucumber peptide powder under different storage conditions. Through the maps of three groups of comparative experiments, it was found that moisture absorption could affect the composition of volatile substances in sea cucumber peptide powder, compared with the influence of microorganisms. The effect of moisture absorption is greater. Similarly, Li[13] analyzed the frozen fish meat under the influence of different bacteria (A bacteria, P bacteria, S bacteria) and found six substances that could mark freshness/decay.

4. Conclusions and Perspectives
Using GC-IMS technology to detect the flavor fingerprint of specific food is a rapidly developing agricultural food detection technology. With the advantages of fast detection, simple operation and portable equipment, GC-IMS is a convenient and rapid tool for chemical analysis of food flavor. It is widely used in food classification, identification of food freshness, quality control of production process and characterization of main aroma and odor compounds in food. Compared with GC-MS the most popular flavor analysis tool, the most prominent feature of GC-IMS is its high separation efficiency. Secondly, GC-MS analysis usually takes dozens of minutes to get results, while the qualitative analysis of data depends on programs such as the calculation of retention index and the use
of chromatographic library. Third, GC-MS needs vacuum conditions, and GC-IMS works at atmospheric pressure, which provides more possibilities for the development of the instrument, such as portability, high throughput, low cost and easy operation.

It is worth noting that GC-MS is still the instrument gold standard for food flavor analysis, and GC-IMS can not replace GC-MS at present. This is because IMS, as a GC detector, has its limitations in accurate quantitative analysis, and the response of IMS is nonlinear, which means that it is also a challenge to provide concentrations at ppbv and pptv levels. In addition, the current GC-IMS database is incomplete, but with the development of technology, a complete GC-IMS database will be established to achieve fast, sensitive, and automatic characterization. In addition, further improved GC-IMS technology can increase the resolution. At the same time, the four-dimensional analysis of information, including two sets of retention time, drift time and ionic strength data, makes it possible to analyze very complex substances in food matrices. In the future, the diversity of food flavors requires the further development of GC-IMS technology to improve its special functions and explore new application areas.

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