INVESTIGATION OF BAIJIU AROMA TYPES AND REGIONAL ORIGIN

BY GC×GC-TOFMS IN CONVENTIONAL AND REVERSED COLUMN CONFIGURATION

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Introduction

The manufacturing process of Baijiu is very complex compared to other strong alcohols with the mixed microbial cultures, unique saccharification and spontaneous fermentation and lack of rectification. It imparts the liquor with its distinctive aroma and further enhances the richness and complexity of volatile compounds. The routine one-dimensional gas chromatography is incapable of separating the complex volatiles of Baijiu satisfactorily. Therefore, comprehensive two-dimensional gas chromatography is suggested for analyzing Baijiu volatiles. As polar columns are usually preferred for resolving polar compounds present in alcoholic beverages, the reversed column setup application was tested in our study. The conventional column setup as a traditional configuration was also included in the investigation. The orthogonality, aroma types classification and regional origin classification were explored.

Materials and methods

Baijiu samples (65) were purchased from Chinese liquor stores. The information regarding the aroma types and regional origin included in our study was displayed in ***Figure 1***. The main analytical strategies and results comparison approaches were demonstrated in ***Figure 2***.

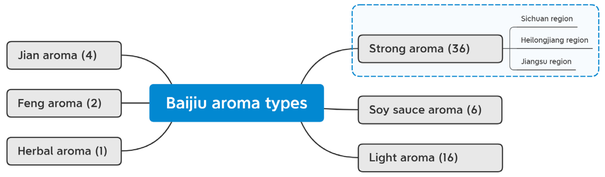

Figure 1. *Baijiu samples information involved in the study*

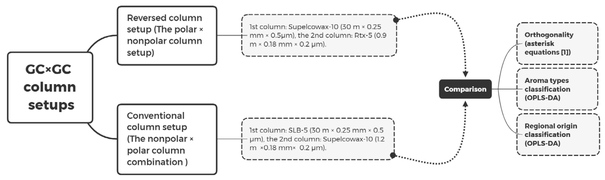

Figure 2. *The main analytical methods and strategies*

Results

Orthogonality comparison

To completely use the potential of multi-dimensional chromatography to achieve the maximum separation power possible, it is essential that the separation mechanisms used in each dimension be independent of each other – the two dimensions should be orthogonal.

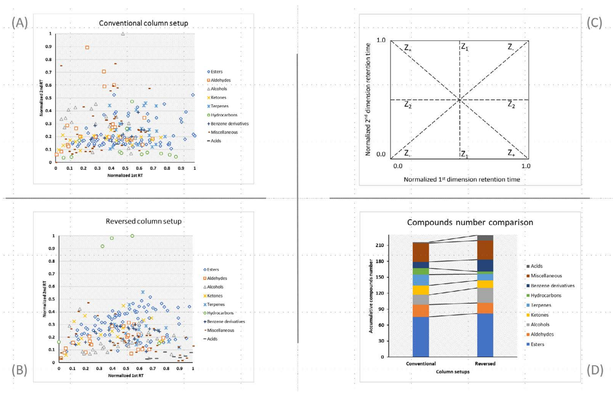

Figure 3. *(A) GC×GC separations of Baijiu samples from conventional column setup, (B) GC×GC separations of Baijiu samples from reversed column setup, (C) Graphical illustration of parameters from asterisk equation [1], (D) Compounds number comparison between different chemical groups from conventional (216 compounds in total) and reversed column setup (229 compounds in total).*

The orthogonality measuring method was adopted from the paper of Camenzuli and Schoenmakers [1], in which they introduced a set of asterisk equations enable to not only measure the orthogonality but also provide facilitated comparison of different multi-dimensional methods between systems and samples by providing more information about the location of the peaks within the separation space (***Figure 3***. (C)). Our study with the analysis of Baijiu samples the reversed column setup (A_o=45.13%) presents a better separation power than the conventional one (A_o=43.92%).

Classification of aroma type

Considering the great variety present in our Baijiu samples, a strategy for lowering the 'noise' presented in the dataset was adopted by integrating the orthogonal signal correction (OSC) filter. Orthogonal partial least squares discriminant analysis (OPLS-DA) is applied to discriminate 6 Baijiu aroma groups. Models from the conventional and reversed setups both presented an excellent predictive power in the classification of the Soy sauce, Light, Herbal and Feng aromas, however, regarding Jian and Strong aroma, the model based on the conventional setup showed better discrimination performance (***Figure 4***.), which was confirmed by both internal and external validation.

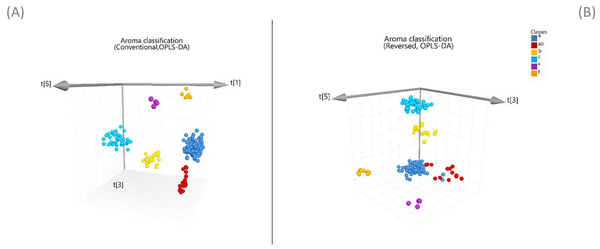

Figure 4. *a: Strong aroma, ab: Jian aroma, b: Soy sauce aroma, c: Light aroma, x: Herbal aroma, f: Feng aroma. OPLS-DA model based on conventional setup (A): R^2Y=0.875, Q^2=0.861; OPLS-DA model based on reversed setup (B): R^2Y=0.851, Q^2=0.827. R^2Y: Total explained fraction of the variation of Y block (aroma types), Q^2: Total fraction of the variation of Y block (aroma types) that can be predicted.*

Classification of regional origin

For the regional classification, both models based on conventional and reversed setups presented perfect model fitness and predictive ability to classify the Strong aroma Baijiu originating from the Sichuan, Heilongjiang, and Jiangsu regions (***Figure 5***.). Besides, two validation methods were applied in our study and all the predictive abilities evaluated by the internal validation were further confirmed by the external validation.

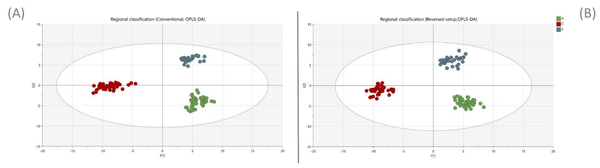

Figure 5. *A: Sichuan, C: Heilongjiang, S: Jiangsu, OPLS-DA model based on conventional setup (A): R^2Y=0.961, Q^2=0.951; OPLS-DA model based on reversed setup (B): R^2Y=0.961, Q^2=0.941. R^2Y: Total explained fraction of the variation of Y block (regional origins), Q^2: Total fraction of the variation of Y block (regional origins) that can be predicted.*

Conclusion

- A better classification for the Strong and Jian aroma types of Baijiu was achieved by the model built from conventional column setup. For the regional classification, both models from conventional and reversed setups showed perfect model fitness and predictive ability to classify the Strong aroma Baijiu originating from the Sichuan, Heilongjiang, and Jiangsu regions.

- Comparing these results with our previous works on the same subject using one-dimensional gas chromatography with simultaneous injection into two columns [2] and classification performed using quasi electronic noses (SPME-MS, fast GC-based E-nose)[3], SPME-GC×GC-TOFMS showed the benefits of using high number of peaks obtained by GC×GC for subsequent statistical analysis: Approach [2] enabled quantification of 62 compounds, however, data obtained allowed for only partial separation of different aromas and it was not possible to separate the Baijiu from different regions. Approach [3] using the same classifier (OPLS-DA), indicated that the aroma classification models built from SPME-MS and GC based E-nose both met difficulties in the separation among Strong, Jian and Feng aroma groups. This problem was greatly improved by applying GC×GC-TOFMS configuring conventional column setup. The regional classification model based on SPME-MS achieved a complete classification with total correct classification rate 100%, as same as in this investigation. Still, referring to the fast GC based E-nose, the misclassification occurred among Sichuan, Heilongjiang and Jiangsu regions, the model achieved a total correct regional classification rate was 93.94% [3].

- To summarize, of all investigated approaches, SPME-GC×GC-TOFMS proved to be of highest potential for aroma and regional classification of Baijiu.

FOOTNOTES: The content of this poster has been published: X. He, H.H. Jeleń, Comprehensive two-dimensional gas chromatography–time of flight mass spectrometry (GC×GC-TOFMS) in conventional and reversed column configuration for the investigation of Baijiu aroma types and regional origin, Journal of Chromatography A. 1636 (2021) 461774. https://doi.org/10.1016/j.chroma.2020.461774

[1] M. Camenzuli, P.J. Schoenmakers, A new measure of orthogonality for multi-dimensional chromatography, Anal. Chim. Acta. 838 (2014) 93–101. https://doi.org/10.1016/j.aca.2014.05.048.

[2] X. He, A. Gaca, H.H. Jeleń, Determination of volatile compounds in Baijiu using simultaneous chromatographic analysis on two columns, Journal of the Institute of Brewing. 126 (2020) 206–212. https://doi.org/10.1002/jib.603

[3] X. He, H. Yangming, E. Górska-Horczyczak, A. Wierzbicka, H.H. Jeleń, Rapid analysis of Baijiu volatile compounds fingerprint for their aroma and regional origin authenticity assessment, Food Chem. 337 (2021). https://doi.org/10.1016/j.foodchem.2020.128002.

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