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Application Note

Application of RADIAN ASAP-LiveID Platform in Flavor Type Discrimination of Chinese *Baijiu* and Authentication of Maotai

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Abstract

In this application note, Waters RADIAN ASAP System was employed to discriminate the flavor type of different Chinese *Baijiu*, while the authenticity of Maotai was identified.

Benefits

- Ease of operation – Little to no sample preparation and the and minimum instrument optimization.
- Fast and accurate results – Based on direct analysis and LiveID real-time recognition technology with easy data elucidation, analysis and results of identification can be done and generated in seconds.
- Compact design with excellent performance – the RADIAN ASAP System is designed with robust and reliable single quadrupole mass spectrometry technology in combination with Atmospheric Solids Analysis Probe (ASAP), featuring small footprint, ease of use, and the ability to provide high-quality MS data.

Introduction

Being a traditional fermented beverage of China, Chinese ***Baijiu*** (liquor) as a long history and ranks among the top six distilled spirits in the world together with whiskey, brandy, rum, vodka, and gin. Chinese ***Baijiu*** differs from other distilled spirits in the aspects of brewing ingredients, production process, and flavor components. Chinese ***Baijiu*** is usually made from grains such as sorghum, wheat, rice, maize, etc. through saccharification, fermentation, distillation, aging, and blending. ***Daqu*** fermentation starter offers essential enzymes and microbes for saccharification and fermentation of the starch in the starting materials. The flavor components of Chinese ***Baijiu*** mainly include esters, ethanols, acids, aldehydes, ketones, pyrazines, and some trace components. Most of these components are metabolites produced by the brewing microbes during the fermentation process. There are 12 flavor types of Chinese ***Baijiu*** depending on the production ingredients and process, they are: sauce-flavor, strong-flavor, light-flavor, miscellaneous-flavor, ***feng***-flavor, rice-flavor, medicine-flavor, sesame flavor, ***te***-flavor, ***chi***-flavor, ***laobaigan***-flavor, and ***fuyu***-flavor ***Baijiu***. Where the sauce-flavor, strong-flavor and light-flavor ***Baijiu*** are the three basic flavor types, from which all the other flavor types are derived.[1–2]

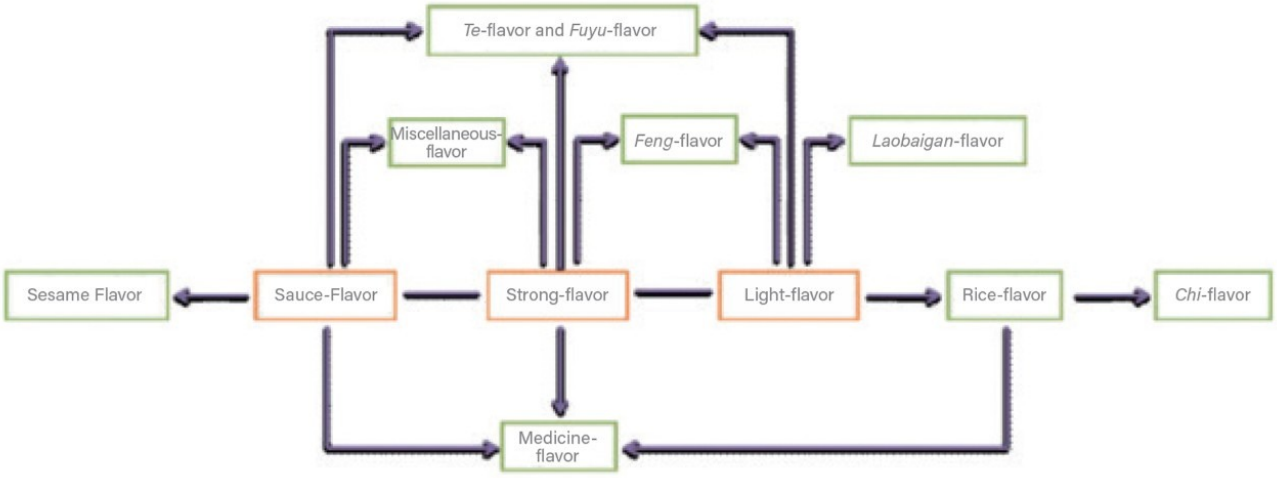

Figure 1. Relationships among Chinese Baijiu of different flavor types.

At present, flavor type discrimination of Chinese ***Baijiu*** is based on the brewing ingredients and process, and the authentication of Chinese ***Baijiu*** is mainly conducted through organoleptic evaluation. However, the development of mass spectrometry technology and chemometrics provides us with an additional way of flavor

type discrimination and authentication. And these techniques in combination with the ambient ionization, which is a fast, scientifically proven, and real-time technology, can help us to further improve the studies in this area. In this experiment, Waters RADIAN ASAP System was employed to discriminate the flavor type of different Chinese *Baijiu*, while the authenticity of Maotai was identified.

Experimental

Sample Source

The samples were provided by collaborating laboratories and purchased from supermarkets.

Sample Preparation

5 µL of *Baijiu* sample was pipetted into the ASAP sampling capillary to perform direct analysis.

MS Conditions

MS system:	RADIAN ASAP
Ionization parameters:	See Table 1

Parameter	Setting
Ionization mode	ASAP+
Corona current	3 µA
Desolvation gas (N_2) temperature	600 °C
Desolvation gas (N_2) flow rate	3 L/min
Cone voltage	15 V
Acquisition mode	Full scan (Continuum)
Mass range	40–250 Da
Scan speed	2 Hz

Table 1. RADIAN ASAP parameter settings.

LiveID chemometric model

In this experiment, MassLynx MS Software (v4.2) was used to acquire non-target full scan data, and multivariate statistical software LiveID (v2.0) was used for modeling and sample assignment and identification.

RADIAN ASAP System.

Results and Discussion

Discrimination of Different *Baijiu* Flavor Types

Establish the experimental model

The raw MS data of different *Baijiu* samples were acquired, the samples include: strong-flavor *Baijiu* (Wuliangye, Luzhou Laojiao, Yanghe, and Jiannanchun), light-flavor *Baijiu* (Fenjiu, Niulanshan, and Hongxing), sauce-flavor *Baijiu* (Maotai, Langjiu, and Baiyunbian), sesame-flavor *Baijiu* (Jingzhi, Qingzhi, Nongzhi, and Bandaojing), *feng*-flavor *Baijiu* (Xifeng), and *laobaigan*-flavor *Baijiu* (Hengshui Laobagan). The identification and study of *Baijiu* samples of different flavor types were conducted by performing multivariate statistical analysis based on Principal

Component Analysis-Linear Discriminant Analysis (PCA-LDA) and then establishing an identification model based on the LDA results.

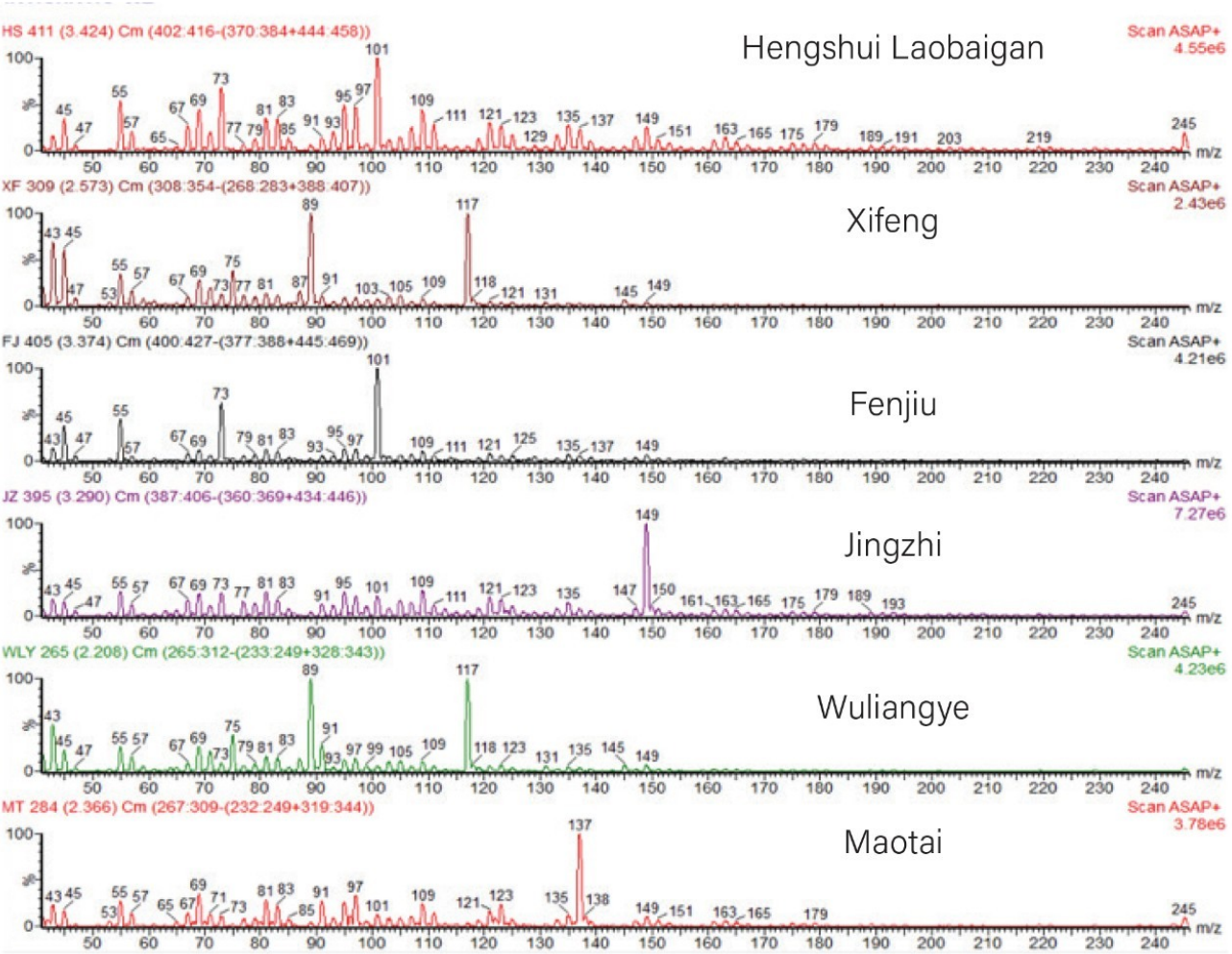

Figure 2. Mass spectra of 6 Baijiu samples of different flavor types (m/z 40–250).

The chemometric model was established based on 20 PCA components and 5 LDA components. As shown in the PCA-LDA clustering scores plot (Figure 3), the qing xiang xing *Baijiu*, nong xiang xing *Baijiu*, jiang xiang xing *Baijiu*, feng xiang xing *Baijiu*, and zhima xiang xing *Baijiu* samples were well separated. However, the laobaigan xiang xing *Baijiu* sample was very close to the qing xiang xing *Baijiu* sample. This is very likely because that the laobaigan xiang xing flavor is derived from the qing xiang xing flavor and they are intrinsically very similar. In addition, one zhima xiang xing *Baijiu* sample was also very close to the qing xiang xing *Baijiu* sample. It was

confirmed to be the *Baijiu* sample from the brand Qingzhi, which is a *Baijiu* of mixed-flavor combining both the qing xiang xing flavor and zhima xiang xing flavor. This further demonstrates that classification based on this model is scientific to some extent.

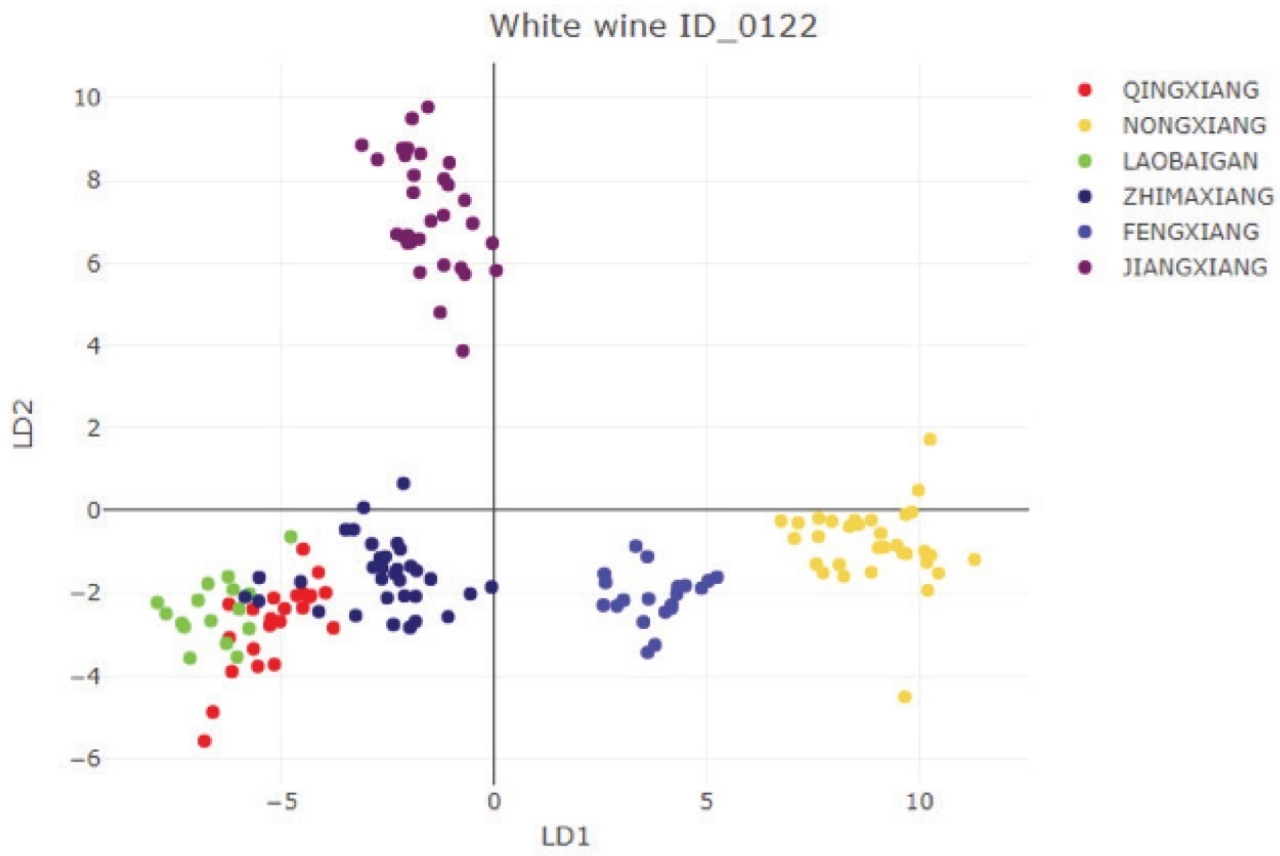

Figure 3. The two-dimensional PCA-LDA model plot of Baijiu samples of different flavor types.

Cross validation of the PCA-LDA classification model of the 6 *Baijiu* flavor types was performed with the method of "Leave 20% Out". It can be seen from the validation results shown in Figure 4, the correctness score was as high as 93.59%.

Validation report

Download as .csv

Description	:
Created	: 1/22/2021, 10:21:04 AM

Model details

Name	: White wine ID_0122
Type	: PCA-LDA
Outlier threshold	: 15 (standard deviations)
PCA components	: 20
LDA discriminants	: 5
Mass range	: 65 - 250 (m/z)
Bin size	: 1 (m/z)

Validation parameters

Validation type	: 5 fold

Results summary

	Spectra	Passes	Failures	Outliers	Correctness score
Total	156	146	6	4	93.59%

Figure 4. Cross validation results of the classification model of Baijiu flavor type based on RADIAN ASAP data.

After construction of the classification model of *Baijiu* flavor type, the flavor type of several *Baijiu* samples (Luzhou Daqu, Niulanshan, Xijiu, and Xuanjiu) purchased from the supermarkets was determined. LiveID Software generated the identification results in a near instantaneous way (Figure 5), and the results were exactly correct.

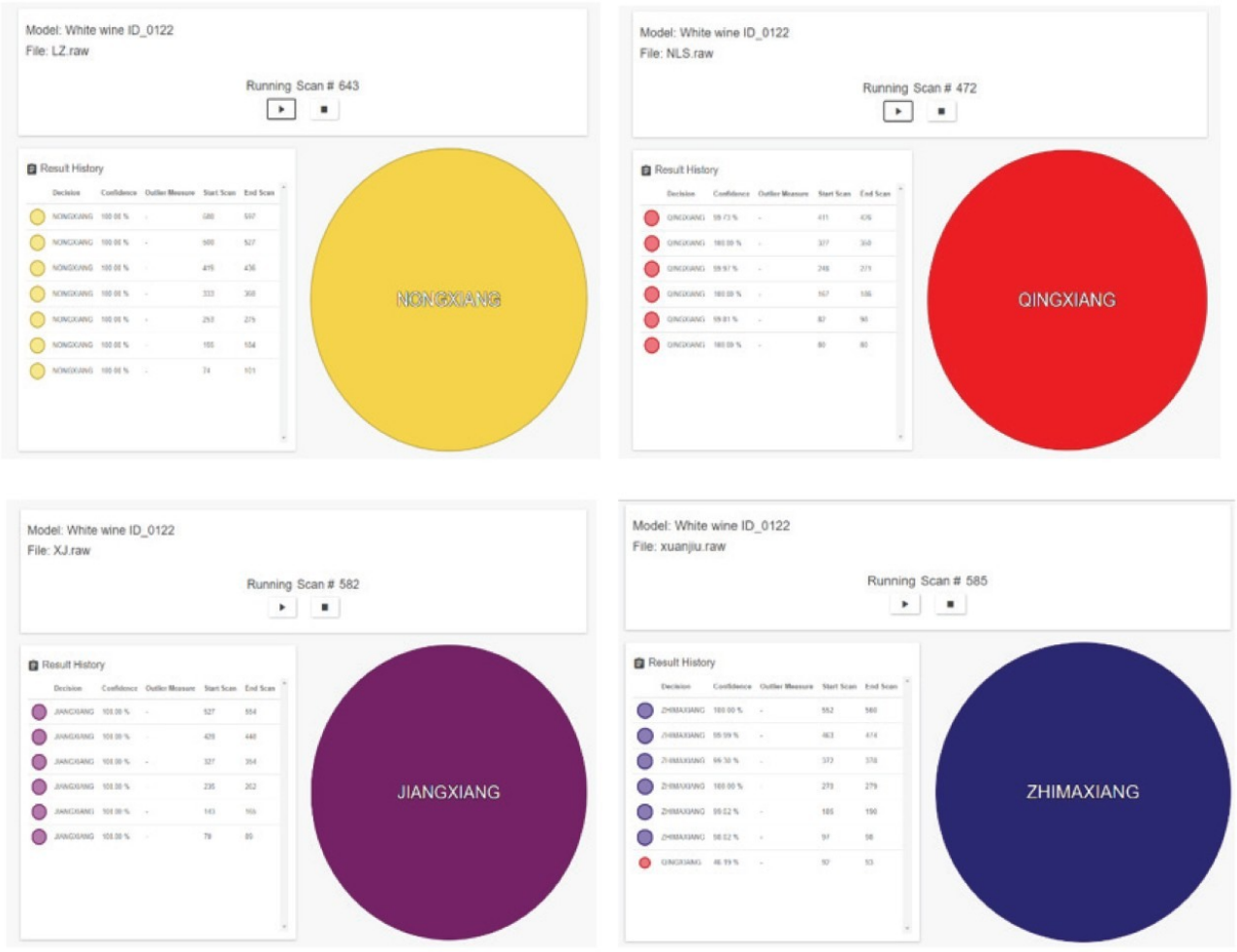

Figure 5. Identification results of the Baijiu samples purchased from supermarkets using the classification model.

Authentication of Maotai

Because of its extremely high market value and collection value, Maotai is currently the most counterfeited product in Chinese *Baijiu* market. In this experiment, an identification model for Maotai was constructed and used to perform Maotai authentication tests on different *Baijiu* samples purchased from the market. The results showed that all non-Maotai *Baijiu* samples were recognized as Outliers.

Figure 6. Results of Maotai authentication tests on different Baijiu samples using the identification model (partial results).

The mass spectral information of the sample acquired by the RADIAN ASAP System was analyzed. It has been reported that more and higher concentration of pyrazines present in jiang xiang xing *Baijiu* compared with *Baijiu* of other flavors types. These pyrazines mainly include tetramethylpyrazine (*m/z* 137), trimethylpyrazine (*m/z* 123), dimethylpyrazine (*m/z* 109), and methylpyrazine (*m/z* 95), while the tetramethylpyrazine (*m/z* 137) concentration in Maotai is the highest.[3–5] By comparing the mass spectra in Figure 2 (6 *Baijiu* samples of different flavor types) with those in Figure 7 (3 *Baijiu* samples of jiang xiang xing flavor), we found the results highly consistent with what has been reported in the above studies. The contents of these four pyrazines in the three *Baijiu* samples of jiang xiang xing flavor were significantly higher than those in other *Baijiu* samples. And the content of tetramethylpyrazine (*m/z* 137) in Maotai sample was significantly higher than in the other two *Baijiu* samples of jiang xiang xing flavor. In addition, Baiyunbian *Baijiu* is nong jiang jian xiang xing *Baijiu* which has a mixed flavor combining both nong xiang xing flavor and jiang xiang xing flavor, and its mass spectrum also showed the characteristics of both nong xiang xing *Baijiu* and jiang xiang xing *Baijiu*.

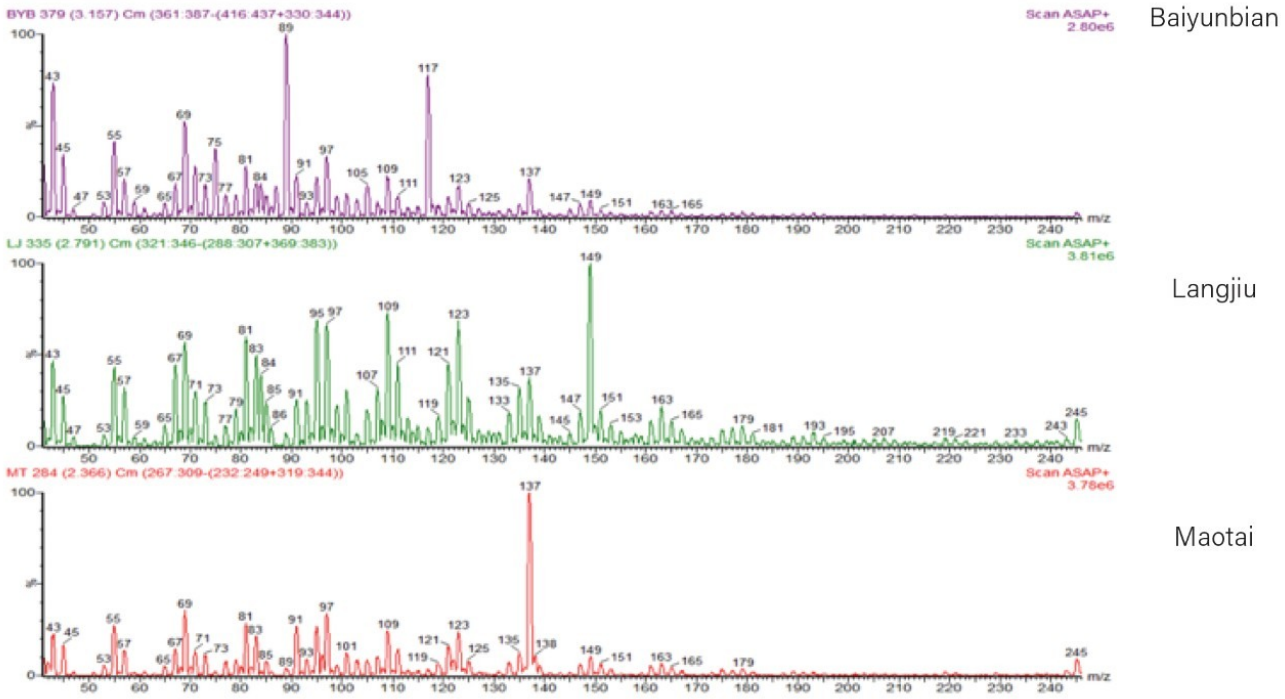

Figure 7. Mass spectra of 3 Baijiu samples of jiang xiang xing flavor.

Conclusion

The RADIAN ASAP System features a simple and flexible design as well as ease of use and fast speed to results, enabling mass detection without the need for any sample preparation or chromatographic separation. By combining the system with LiveID Software, model identification can be done in a near instantaneous way. It is ideal for chemical reaction monitoring, raw material quality control, and food authentication.

In this experiment, the RADIAN ASAP-LiveID System was used to successfully discriminate different flavor types of *Baijiu*, which provides scientific rationale for the characteristics of different *Baijiu* flavor types. In addition, an identification model enabling quick authentication of Maotai was constructed. According to the mass spectrum information acquired by the system, pyrazines, the flavor components commonly found in jiang xiang xing *Baijiu*, were also detected. Based on the data information, we have gained a more straightforward understanding of the

differences in contents of the pyrazines among *Baijiu* of different flavor types, as well as between Maotai and other *Baijiu*. This provides a fast way of food authentication for the regulatory authorities and a new idea of food research and quality control for academic institutions and related industries.

References

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