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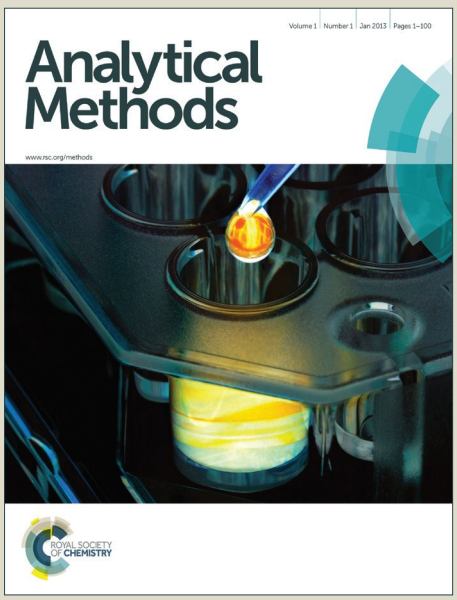

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Analysis of Volatile Compounds in Chinese Laobaigan Liquor using Headspace Solid-phase Microextraction Coupled with GC-MS

Liping Du, Tingting He, Wei Li, Ruoyu Wang, *Dongguang Xiao

A method based on headspace solid-phase microextraction (HS-SPME) coupled with gas chromatography-mass spectrometry (GC-MS) was used for the analysis of volatile compounds in "Hengshui Laobaigan" liquor. Five different fibers were evaluated in terms of the number of volatile compounds, sensitivity and reproducibility. The results showed that 50/30 μm divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS) fiber was most suitable for acquiring a complete profile of volatile compounds in Laobaigan liquor. For specific application, 75 μm carboxen/polydimethylsiloxane (CAR/PDMS) fiber was proper to extract acids, alcohols, pyrazines and aromatic and phenolic compounds because of its high sensitivity, and 50/30 μm DVB/CAR/PDMS fiber was found to have higher sensitivity than others for extracting esters, hydrocarbons and aldehydes and ketones. It is concluded that different fibers should be selected depending on different research object for acquiring accurate and reliable results.

Key words: headspace solid-phase microextraction; gas chromatography-mass spectrometry; extraction fibers; sensitivity; reproducibility; Hengshui Laobaigan

1 Introduction

Chinese liquor is one of the oldest distillates in the world and the most popular among alcoholic beverages in China. It is usually fermented from grains, mainly including sorghum, wheat, rice, sticky rice and corn, etc. After the fermentation, the fresh spirit is distilled out and then aged under controlled conditions. The aged distillate is adjusted to the designated ethanol concentration and blended to ensure the quality of the final product[1]. Chinese liquor contains quite a number of volatile compounds which can greatly influence its flavor and aroma[2]. These volatile compounds belong to different chemical families, mainly including acids, esters, alcohols, aldehydes, ketones, hydrocarbons, pyrazines and phenolic compounds. According to different production processes and aroma characteristics, Chinese liquor can be classified into many types.

Over the past decades, many studies were focused on the volatile compositions in various alcoholic beverages. The commonly used extraction methods for these volatile compounds from the alcoholic beverages included liquid-liquid extraction[3], closed-loop stripping analysis[4], solid-phase extraction[5], stir bar sorptive extraction[6] and solid phase microextraction (SPME)[7, 8]. Due to the simple operation, high sensitivity and little sample loading, SPME extraction method is recognized ideal for analysis of volatile compounds in alcoholic beverage[9]. The fused-silica fiber coated with an appropriate stationary phase outside is the most crucial part of SPME techniques, and it plays an important role on the extraction yield and the quality of the extractive. Different commercial SPME fibers, such as polyacrylate (PA), polydimethylsiloxane (PDMS), carboxen/polydimethylsiloxane (CAR/PDMS) and divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS), had been used to extract the volatile compounds depending on the structure and volatility of the analytes. The performance of these different types of fibers have been systematically compared in the classification of the botanical origin of cinnamon, analysis of the volatiles in various fruit juices, identification of the possible odor-impact volatile organic compounds in cupuassu, etc[10, 11, 12].

In the analysis of the volatiles in wine, Fan[13] analyzed the potentially important aroma compounds in young and aged "Yanghe Daqu" liquors using HS-SPME/GC-O method with DVB/CAR/PDMS fiber, and investigated the effect of extraction time and temperature as well as alcohol concentration on the analysis results. Cheng[14] and co-workers studied the quality grade discrimination of Chinese liquor of strong aroma type by using head space-solid phase microextraction-mass spectrometry (HS-SPME-MS) method also with DVB/CAR/PDMS fiber. They concluded that the HS-SPME-MS technique combined of multivariate analysis methods had high classification accuracy for Chinese liquors of strong aroma type. Because the aroma of liquor is the result of an extremely complex mixture, single SPME fiber is difficult to accurately identify the volatile composition. Martí [15]

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and co-workers studied wine aroma using SPME and GC/O analysis. They compared three fibers (DVB/CAR/PDMS, PDMS and PA) and concluded that HS-SPME with DVB/CAR/PDMS fiber was the most suitable for analyzing odor compounds in wine aroma because of its wide range for odorants extraction. However, few investigations have been performed on the extraction performances of different fibers on the different volatile compounds of Chinese liquor.

As a typical aroma style of Chinese liquor, "Laobaigan" is welcomed by consumers, particularly in the north of China. In the present work, taking "Hengshui Laobaigan" for instance, the sensitivity and repeatability of five different fibers (PDMS/DVB, CAR/PDMS, PDMS, PA and DVB/CAR/PDMS) were compared in extracting the volatile compounds by using HS-SPME method and the suitable fiber for analyzing different types of volatile compounds were selected. It is expected that the results of this research will help to accurately analyze the volatile compounds in Chinese liquor.

2 Materials and Methods

2.1 Sample

The "Hengshui Laobaigan" liquor sample was purchased from a local store. It was bottled on August 21, 2011 and stored at 4 °C before analysis. The sample was diluted with deionized water to a final concentration of 15 % (v/v) ethanol for analysis.

2.2 SPME fiber and conditions

Five SPME fibers were tested and used in this work: 50/30 μm DVB/CAR/PDMS, 65 μm PDMS/DVB, 75 μm CAR/PDMS, 85 μm PA and 100 μm PDMS. All fibers were purchased from Supelco (Bellefonte, PA, USA), and were conditioned by keeping them in the GC injector following the manufacturer's instructions before use.

A total of 8 mL of diluted sample was put into a 20 mL vial and spiked with 3 g of NaCl, and a small magnetic stirrer was added. The vial was tightly capped with a Teflon/silicone septum. The sample was equilibrated for 10 min and extracted for 40 min at 60 °C with continuous stirring. After extraction, the fiber was pulled into the needle sheath and the SPME device was removed from the vial and inserted into the injection port of the GC-MS system (at 250 °C for 5 min) to desorb the analytes.

2.3 GC-MS conditions and analysis

Identification was carried out using an Agilent 7890A GC coupled with an Agilent 5975C mass selective detector (MSD). The sample was analyzed on a CP-Wax column (60 m × 0.25 mm i.d., 0.50 μm film thickness). The injector temperature was 250 °C, and the splitless mode was used. The oven temperature was held at 40 °C for 2 min, raised to 100 °C at a rate of 2 °C/min, increased to 230 °C at a rate of 4 °C/min, and held at 230 °C for 3 min. The column carrier gas was helium at a constant flow rate of 0.8 ml/min. The mass spectrometer was operated in an electron-impact (EI) mode of 70 ev. The mass scan range was 30-500 aum. The temperatures of the interface, ion source and quadrupole were 280 ° C, 230 ° C and 150 ° C, respectively.

The volatile compounds were determined by comparing the MS fragmentation present with the mass spectra present in the National Institute of Standards and Technology (NIST) MS 08 spectral database. The compounds identified by MS were further confirmed by comparing retention times generated for each reference compound analyzed using a commercial hydrocarbon mixture (C8–C40) for determination of the retention indices (RI) in comparison with the retention indices described in the literature[1,13,16].

2.4 Evaluation of sensitivity of the different fibers

Sensitivity was evaluated on the basis of a parameter named "Cumulative area normalization value, CANV"; it was calculated as follow[7]:

$$AV_K = [A_{K(PDMS)} + A_{K(PDMS/DVB)} + A_{K(CAR/PDMS)} + A_{K(PA)} + A_{K(DVB/CAR/PDMS)}]/5$$

$$NA_{K(X)} = A_{K(X)}/AV_K$$

$$CA_{K(X)} = \sum_{n=1}^{K} NAn(X)$$

AV_k: average area of the compound ''k'' determined with all the fibers;
$A_{k(X)}$: absolute area of the compound ''k'' determined with the fiber ''X'';
$NA_{k(X)}$: normalized area of the compound ''k'' determined with the fiber ''X'';
$CA_{k(X)}$: cumulative area of the compound ''k'' determined with the fiber ''X''.

The higher is the sensitivity of the fiber, the higher is the cumulative area with the cumulative number of compound.

2.5 Evaluation of reproducibility of the different fibers

As not all the fibers could extract the whole compounds, only the analytes which can be detected by all the fibers were considered for the reproducibility evaluations.

Relative standard deviations (RSD) were calculated for all compounds which were detectable using each fiber. Their average value and standard deviation were evaluated fiber by fiber.

3 Results and Discussion

3.1 Volatile compounds extracted by different fibers

The identification of volatile compounds extracted by different fibers based on matching the resulting mass spectra to those in the NIST MS 08 Library, and comparing the retention index reported in literatures. The results show in Table 1. It was found that the volatile compounds from "Hengshui Laobaigan" liquor includes acids esters, alcohols, aldehydes, ketones, hydrocarbons, pyrazines and aromatic and phenolic compounds. Among them, the number of esters was the largest, followed by the alcohols and aromatic and phenols compounds. The volatile compounds extracted by the five fibers are apparently different in quantity and variety. 45 analytes including ethyl acetate, 3-methyl-1-butanol, acetic acid and ethyl benzoate were detected by all the fibers.

Comparison of the performance of the five fibers tested shows that, in general, DVB/CAR/PDMS enables detection of a wider range of compounds than other fibers, e.g. Isoamyl acetate, pentanoic acid ethyl ester, nonanal and tetradecane were not detected by the other fibers. 62 volatile compounds were extracted by DVB/CAR/PDMS, while the number of volatile compounds detected by PDMS/DVB, CAR/PDMS, PA and PDMS were 57, 59, 53 and 57, respectively. Previous studies showed that DVB/CAR/PDMS is the most appropriate due to its extraction ability over an expanded range of compounds[17, 18, 19].

Table 1 Composition of volatile compounds of Chinese Laobaigan liquor by five fibers

Conpounds	RI	Basis of identification	DVB/CAR/PDMS Peak area	NAK(X)	PDMS/DVB Peak area	NAK(X)	CAR/PDMS Peak area	NAK(X)	PA Peak area	NAK(X)	PDMS Peak area	NAK(X)
Acids												
Acetic acid	1456	MS,RI	1,616,358	0.22	5,711,494	0.78	14,408,336	1.98	6,886,035	0.94	7,822,432	1.07
Hexanoic acid	1851	MS,RI	2,138,311	0.57	3,466,062	0.92	5,355,317	1.42	6,163,817	1.63	1,782,113	0.47
Octanoic acid	2072	MS,RI	4,329,279	0.59	6,690,409	0.91	9,995,882	1.37	11,028,110	1.51	4,565,950	0.62
Decanoic acid	2291	MS,RI	2,384,332	0.32	11,390,851	1.54	10,205,546	1.38	8,516,604	1.15	4,470,939	0.6
			Total	1.7		4.15		6.14		5.23		2.77
Esters												
Ethyl acetate	894	MS,RI	249,395,903	1.01	220,213,322	0.89	317,138,489	1.29	179,421,529	0.73	266,084,395	1.08
Isoamyl acetate	1102	MS,RI	56,098,445	5	ND	0	ND	0	ND	0	ND	0
Pentanoic acid ethyl ester	1108	MS,RI	11,805,916	5	ND	0	ND	0	ND	0	ND	0
Hexanoic acid ethyl ester	1218	MS,RI	159,211,632	2.55	33,192,904	0.53	39,143,389	0.63	23,021,217	0.37	58,184,520	0.93
Hexanoic acid propyl ester	1306	MS,RI	1,235,405	2.84	ND	0	403,710	0.93	ND	0	535,938	1.23
Heptanoic acid ethyl ester	1320	MS,RI	15,093,937	2.64	2,591,199	0.45	4,936,665	0.86	1,505,595	0.26	4,473,375	0.78
Ethyl 2-hydroxypropanoic acid	1332	MS,RI	71,630,166	0.31	234,048,522	1.02	294,166,609	1.28	266,641,119	1.16	284,013,105	1.23
Octanoic acid ethyl ester	1428	MS,RI	565,270,105	2.36	128,405,265	0.54	268,853,837	1.12	69,364,466	0.29	163,384,546	0.68
Ethanol, 2-(1-methylethoxy)-, acetate	1432	MS,RI	736,773	0.74	1,340,819	1.34	1,616,435	1.62	1,292,152	1.3	ND	0
Isopentyl hexanoate	1449	MS,RI	5,166,785	2.96	ND	0	ND	0	ND	0	3,572,616	2.04
Nonanoic acid ethyl ester	1525	MS,RI	30,405,544	1.85	10,668,125	0.65	22,506,466	1.37	4,803,723	0.29	13,763,777	0.84
2-Hydroxy-4-methyl pentanoic Acid ethyl ester	1535	MS,RI	10,572,314	0.48	20,550,959	0.93	26,326,557	1.2	28,476,413	1.29	24,040,402	1.09
Isoamyl lactate	1563	MS,RI	5,620,352	0.59	8,303,047	0.87	13,077,150	1.38	11,726,661	1.23	8,820,584	0.93

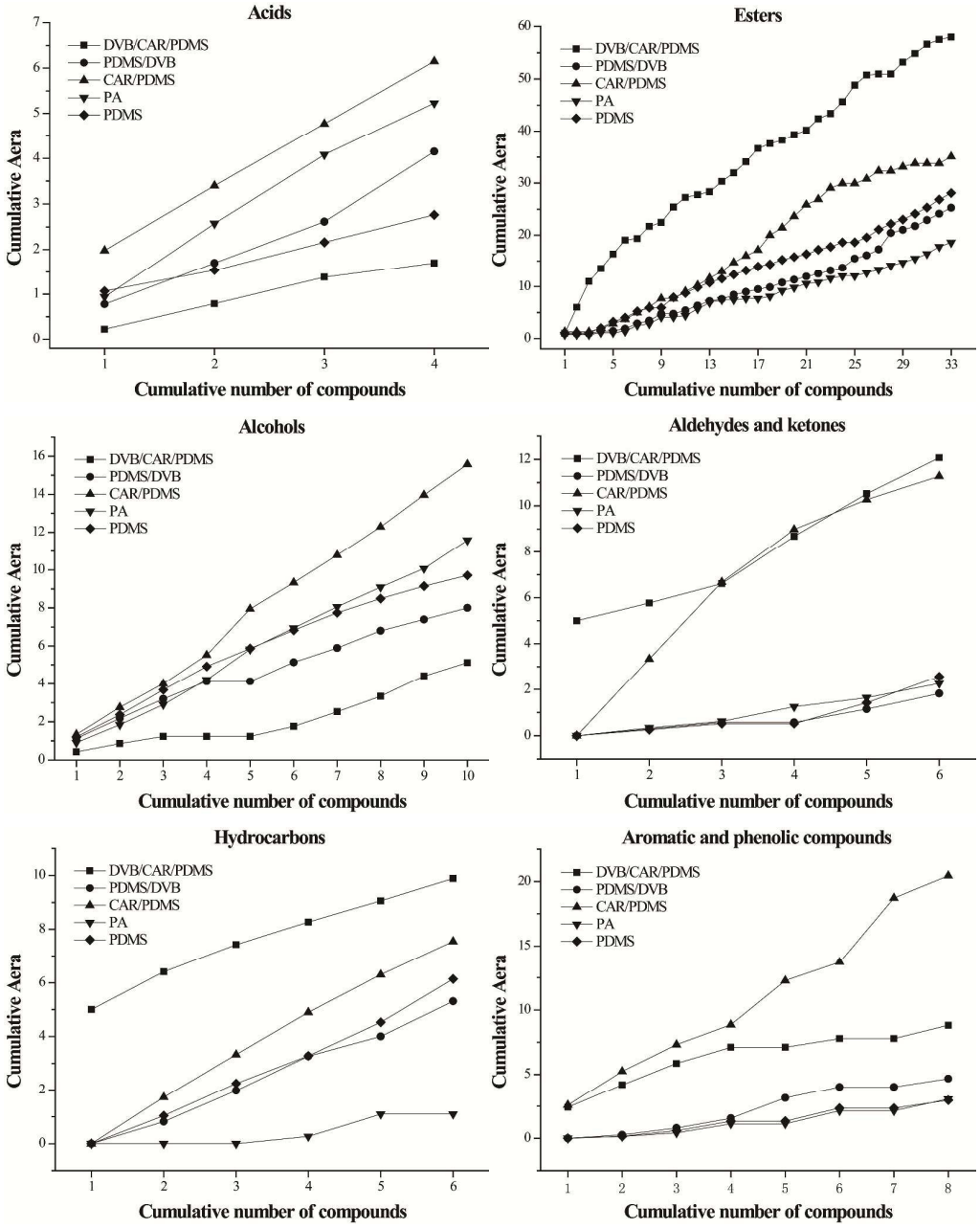
3-Nonenoic acid ethyl ester	1573	MS,RI	7,298,301	1.99	1,406,335	0.38	4,850,657	1.32	2,022,782	0.55	2,785,252	0.76
Hexanoic acid hexyl ester	1601	MS,RI	1,397,232	1.63	739,901	0.86	1,467,139	1.71	ND	0	691,845	0.81
Decanoic acid ethyl ester	1635	MS,RI	808,112,849	2.12	200,463,138	0.53	498,610,423	1.31	98,509,972	0.26	300,452,328	0.79
Octanoic acid 3-methylbutyl ester	1650	MS,RI	5,564,863	2.58	1,176,732	0.55	2,392,821	1.11	ND	0	1,633,527	0.76
Benzoic acid ethyl ester	1653	MS,RI	24,243,892	0.94	9,793,051	0.38	74,357,586	2.88	10,247,783	0.4	10,539,135	0.41
Butanedioic acid diethyl ester	1664	MS,RI	19,103,474	0.71	24,628,579	0.91	38,438,764	1.42	28,749,289	1.07	24,048,408	0.89
Benzeneacetic acid ethyl ester	1770	MS,RI	6,523,461	1.04	3,513,306	0.56	13,763,554	2.2	3,999,730	0.64	3,507,656	0.56
Acetic acid 2-phenylethyl ester	1801	MS,RI	4,756,497	0.83	3,506,989	0.62	12,847,641	2.25	4,209,218	0.74	3,179,452	0.56
Dodecanoic acid ethyl ester	1832	MS,RI	103,421,020	2.25	25,377,388	0.55	47,935,185	1.04	14,682,448	0.32	38,227,979	0.83
Benzenepropanoic acid ethyl ester	1874	MS,RI	7,084,272	0.97	4,587,823	0.63	15,714,786	2.14	5,240,073	0.71	4,053,720	0.55
Tetradecanoic acid ethyl ester	2040	MS,RI	17,012,515	2.23	3,876,925	0.51	6,719,849	0.88	3,792,220	0.5	6,747,573	0.88
Pentadecanoic acid ethyl ester	2094	MS,RI	4,364,049	3.21	2,442,232	1.79	ND	0	ND	0	ND	0
Ethyl 13-methyl-tetradecanoate	2110	MS,RI	5,053,698	1.94	1,617,577	0.62	2,250,003	0.87	1,677,150	0.64	2,406,776	0.93
Hexadecanoic acid methyl ester	2209	MS,RI	561,426	0.18	3,575,035	1.15	4,747,720	1.53	1,803,387	0.58	4,797,282	1.55
Isopropyl palmitate	2234	MS,RI	ND	0	6,801,405	3.16	ND	0	1,715,433	0.8	2,259,474	1.05
Hexadecanoic acid ethyl ester	2248	MS,RI	25,649,553	2.22	6,841,726	0.59	9,345,510	0.81	6,266,724	0.54	9,730,470	0.84
Ethyl 9-hexadecenoate	2275	MS,RI	4,782,688	1.68	2,086,357	0.73	1,863,694	0.65	2,359,584	0.83	3,165,451	1.11
Ethyl oleate	2474	MS,RI	6,576,829	1.72	4,430,876	1.16	ND	0	3,597,918	0.94	4,567,816	1.19
Linoleic acid ethyl ester	2523	MS,RI	6,902,982	0.93	9,025,434	1.22	ND	0	9,853,714	1.33	11,329,613	1.53
1,2-Benzenedicarboxylic acid, bis(2-methylpropyl) ester	2546	MS,RI	2,635,772	0.47	6,517,118	1.17	7,226,648	1.3	4,497,908	0.81	6,977,311	1.25
			Total	57.96		25.29		35.09		18.57		28.08
Alcohols												
2-Methylpropanol	1090	MS,RI	35,632,801	0.42	96,320,425	1.13	113,800,214	1.34	77,178,881	0.91	300,452,328	1.2

1-Butanol	1135	MS,RI	1,830,878	0.44	4,399,165	1.05	5,948,282	1.42	3,875,298	0.93	4,883,341	1.17
3-Methybutanol	1203	MS,RI	174,138,229	0.37	484,926,133	1.02	589,321,019	1.24	500,028,183	1.06	300,452,328	1.31
1-Pentanol	1249	MS,RI	ND	0	1,672,288	0.93	2,722,863	1.52	2,346,240	1.31	2,225,541	1.24
3-Methylpentanol	1325	MS,RI	ND	0	ND	0	1,154,014	2.43	769,358	1.62	446,655	0.94
1-Hexanol	1350	MS,RI	3,621,801	0.53	6,931,463	1.01	9,489,049	1.38	7,615,782	1.11	6,671,682	0.97
1-Octanol	1556	MS,RI	2,374,628	0.76	2,330,430	0.75	4,527,385	1.45	3,508,234	1.12	2,854,222	0.92
1-Nonanol	1658	MS,RI	4,089,874	0.82	4,500,212	0.91	7,446,178	1.5	5,133,492	1.03	3,668,262	0.74
1-Decanol	1758	MS,RI	2,272,074	1.07	1,252,921	0.59	3,570,034	1.68	2,107,137	0.99	1,404,682	0.66
Phenylethyl alcohol	1911	MS,RI	6,221,230	0.71	5,275,619	0.61	14,143,772	1.62	13,034,396	1.5	4,916,708	0.56
			Total	5.12		8		15.59		11.58		9.71
Aldehydes and ketones												
Nonanal	1381	MS,RI	4,790,522	5	ND	0	ND	0	ND	0	ND	0
Furfural	1445	MS,RI	14,182,545	0.77	5,282,989	0.29	61,786,582	3.34	6,311,497	0.34	4,869,283	0.26
Benzaldehyde	1508	MS,RI	7,296,458	0.84	2,390,186	0.28	28,861,550	3.34	2,431,721	0.28	2,276,765	0.26
2-Undecanone	1590	MS,RI	3,483,656	2.07	ND	0	3,866,997	2.3	1,061,995	0.63	ND	0
2-Tridecanone	1798	MS,RI	2,236,259	1.84	701,606	0.58	1,568,959	1.29	479,709	0.39	1,097,908	0.9
6,10,14-Trimethyl-2-pentadecanone	2121	MS,RI	2,152,340	1.55	933,199	0.67	1,412,564	1.01	869,172	0.62	1,596,125	1.15
			Total	12.06		1.81		11.28		2.27		2.57
Hydrocarbons												
Tetradecane	1393	MS,RI	2,610,866	5	ND	0	ND	0	ND	0	ND	0
Pentadecane	1492	MS,RI	2,103,350	1.41	1,228,596	0.82	2,578,959	1.73	ND	0	1,547,125	1.04
Hexadecane	1595	MS,RI	2,247,380	1.02	2,551,853	1.16	3,506,129	1.6	ND	0	2,658,147	1.21
Heptadecane	1687	MS,RI	2,132,175	0.84	3,270,486	1.29	3,983,400	1.57	681,367	0.27	2,603,366	1.03
(2,2-Diethoxyethyl)-benzene	1702	MS,RI	1,854,849	0.79	1,700,424	0.73	3,273,465	1.4	1,953,912	0.83	2,938,829	1.25
Octadecane	1785	MS,RI	1,392,676	0.83	2,191,353	1.31	2,086,914	1.25	ND	0	2,695,846	1.61

			Total	9.9		5.31		7.54		1.1		6.14
Aromatic and phenolic compounds												
Styrene	1235	MS,RI	12,730,421	2.41	ND	0	13,664,920	2.59	ND	0	ND	0
Naphthalene	1724	MS,RI	9,944,258	1.78	1,474,461	0.26	14,797,731	2.65	807,125	0.14	900,453	0.16
2-Methyl naphthalene	1838	MS,RI	3,765,924	1.67	1,216,175	0.54	4,705,363	2.08	643,024	0.28	973,492	0.43
2,6-Dimethyl naphthalene	1952	MS,RI	1,879,324	1.25	1,149,801	0.76	2,323,683	1.54	1,061,128	0.7	1,127,198	0.75
1,2,3-Trimethoxybenzene	1956	MS,RI	ND	0	640,103	1.58	1,383,880	3.42	ND	0	ND	0
Phenol	2004	MS,RI	492,111	0.67	651,583	0.88	1,059,166	1.44	742,751	1.01	737,165	1
1,2,4-Trimethoxybenzene	2082	MS,RI	ND	0	ND	0	1,299,729	5	ND	0	ND	0
Phenol,2,4-bis(1,1-dimethyleth yl)-	2306	MS,RI	12,473,375	1.04	7,870,678	0.66	20,753,344	1.73	11,143,569	0.93	7,581,218	0.63
			Total	8.81		4.69		20.45		3.07		2.97
Pyrazines												
Trimethylpyrazine	1410	MS,RI	ND	0	ND	0	665,185	3.5	284,321	1.5	ND	0
			Total	0		0		3.5		1.5		0
Total				95.56		49.26		99.6		43.32		52.26

3.2 Comparison of sensitivity of different fibers

Sensitivity of different fibers was evaluated in relation to cumulative areas of the analytes. All volatile compounds detected were divided into 7 groups: acids, esters, alcohols, aldehydes and ketones, hydrocarbons, pyrazines and aromatic and phenolic compounds, and the results are reported in Fig. 1.



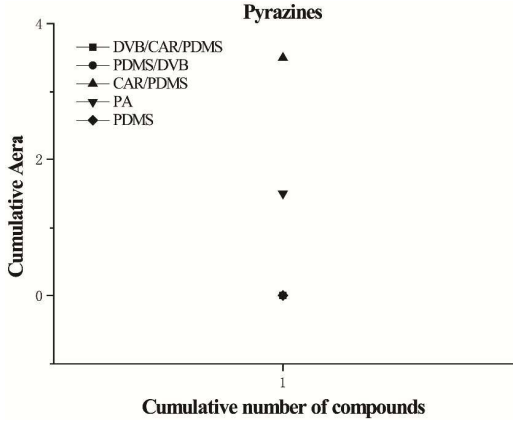


Fig. 1 Cumulative Vs Cumulative number of compounds: The sensitivity of four fibers for different categories of volatile compounds

These diagrams show that the chromatographic response of the different fibers depending on the cumulative number of compound. With the same cumulative number of compound, the wider was the cumulative area, the higher was the fiber sensitivity. The CAR/PDMS fiber has the highest CANV for acids compounds, which was followed by PA (Fig. 1). To esters, the other fibers show a strongly lower sensitivity than DVB/CAR/PDMS (Fig. 1). In the case of alcohols, before the cumulative number of compound reaches 4, the CANV of different fibers except DVB/CAR/PDMS were almost the same. Then the CANV of CAR/PDMS was rapidly rising up (Fig. 1). For aldehydes and ketones, the higher response of DVB/CAR/PDMS turns out to be detectable, for the cumulative number of compound up to 3; beyond this value, the CAR/PDMS shows the best performances, but the CANV of DVB/CAR/PDMS was getting wider (Fig. 1). Again, DVB/CAR/PDMS has the highest sensitivity for extraction of hydrocarbons, followed by the CAR/PDMS, and PDMS and PDMS/DVB were similar (Fig. 1). For the extraction of aromatic and phenolic compounds, higher amount are extracted with a CAR/PDMS fiber. Other fibers result in lower amount (Fig. 1). There was only one of pyrazines were detected, and CAR/PDMS was the highest (Fig. 1). As shown in Fig. 1, for extraction of acids, alcohols, pyrazines and aromatic and phenolic compounds, the sensitivities of CAR/PDMS were highest. And DVB/CAR/PDMS fiber was found to have higher sensitivities than others to extracted esters, aldehydes and ketones, hydrocarbons and aromatic and phenolic compounds. It is shown in the **Table 1** that the CANVs of all volatile compounds extracted by DVB/CAR/PDMS, PDMS/DVB, CAR/PDMS, PA and PDMS were 95.05, 49.61, 99.01, 43.36 and 52.79, respectively.

3.3 Comparison of reproducibility of different fibers

45 volatile compounds were detected by all the fibers tested, and the RSD values confirmed for each compound are reported in Table 2.

Table 2 Reproducibility evaluation: relative standard deviations obtained with five fiber coatings by means of SPME-GC–MS analysis

		RSD (%)				
		50/30 µm	65 µm	75 µm	85 µm	100 µm
		DVB/CAR/PDMS	PDMS/DVB	CAR/PDMS	PA	PDMS
1	Ethyl acetate	7.9	10.6	22.9	11.9	26.7
2	2-Methylpropanol	28.4	34.9	29.5	12.7	49.4
3	1-Butanol	21.9	37.4	37.9	11.4	61.3
4	3-Methybutanol	15.1	39.4	30.4	12.8	52.4
5	Hexanoic acid ethyl ester	5.3	4.0	6.1	3.7	16.1
6	Heptanoic acid ethyl ester	6.9	27.5	28.8	13.5	22.5
7	Ethyl 2-hydroxypropanoic acid	26.1	29.4	24.8	10.0	55.6
8	1-Hexanol	8.4	32.1	18.7	8.7	77.3
9	Octanoic acid ethyl ester	7.7	22.5	16.5	3.2	12.5
10	Furfural	9.2	28.6	1.3	7.4	45.9

11	Acetic acid	16.0	28.5	44.8	23.5	84.1
12	Benzaldehyde	5.6	17.6	42.9	3.5	27.9
13	Nonanoic acid ethyl ester	24.7	21.9	16.2	16.0	26.9
14	2-Hydroxy-4-methyl pentanoic acid ethyl ester	20.7	24.7	13.2	9.1	44.0
15	1-Octanol	23.7	25.0	13.4	9.3	36.4
16	Isoamyl lactate	42.4	21.9	8.3	10.7	40.9
17	3-Nonenoic acid ethyl ester	8.5	26.7	30.6	15.9	23.1
18	Decanoic acid ethyl ester	11.8	14.2	14.8	9.7	34.7
19	Benzoic acid ethyl ester	4.1	24.7	7.9	3.0	19.7
20	1-Nonanol	12.4	84.2	15.4	12.8	28.7
21	Butanedioic acid diethyl ester	23.8	17.3	3.9	11.7	29.5
22	Heptadecane	31.0	37.0	23.0	12.8	40.3
23	(2,2-Diethoxyethyl)-benzene	17.0	19.0	11.3	8.7	10.6
24	Naphthalene	9.1	20.2	11.0	5.5	27.9
25	1-Decanol	12.2	23.9	12.7	16.4	16.6
26	Benzeneacetic acid ethyl ester	10.3	22.1	7.4	9.4	17.2
27	2-Tridecanone	11.6	22.0	20.9	19.4	25.8
28	Acetic acid 2-phenylethyl ester	10.0	18.6	11.5	8.8	15.8
29	Dodecanoic acid ethyl ester	13.4	36.4	20.9	33.5	35.7
30	2-Methyl naphthalene	8.2	9.4	19.2	7.1	36.9
31	Hexanoic acid	41.3	14.4	8.1	14.6	13.2
32	Benzenepropanoic acid ethyl ester	18.1	19.1	18.8	11.6	8.8
33	Phenylethyl alcohol	18.6	14.6	6.7	14.9	22.2
34	2,6-Dimethyl naphthalene	23.3	17.4	23.1	15.2	38.1
35	Phenol	11.8	10.2	12.3	14.7	35.1
36	Tetradecanoic acid ethyl ester	13.1	25.6	35.4	19.0	30.6
37	Octanoic acid	5.9	17.4	15.4	11.8	21.2
38	Ethyl 13-methyl-tetradecanoate	9.3	30.5	38.2	21.9	27.3
39	6,10,14-Trimethyl-2-pentadecanone	31.3	10.4	28.3	21.3	37.7
40	Hexadecanoic acid methyl ester	22.8	46.7	47.6	27.5	74.3
41	Hexadecanoic acid ethyl ester	23.9	30.7	50.0	23.2	33.1
42	Ethyl 9-hexadecenoate	25.3	31.1	49.8	24.4	34.7
43	Decanoic acid	19.0	27.9	19.8	6.4	32.9
44	Phenol, 2,4-bis(1,1-dimethylethyl)-	27.2	7.3	29.6	19.1	19.7
45	1,2-Benzenedicarboxylic acid, bis(2-methylpropyl) ester	13.5	24.9	35.9	38.6	44.3

The distribution of all the RSD values mainly ranged from 4.1% to 42.4% for DVB/CAR/PDMS, from 4.0% to 84.2% for PDMS/DVB, from 1.3% to 50% for CAR/PDMS, from 3.0% to 38.6% for PA and from 8.8% to 84.1% for PDMS.

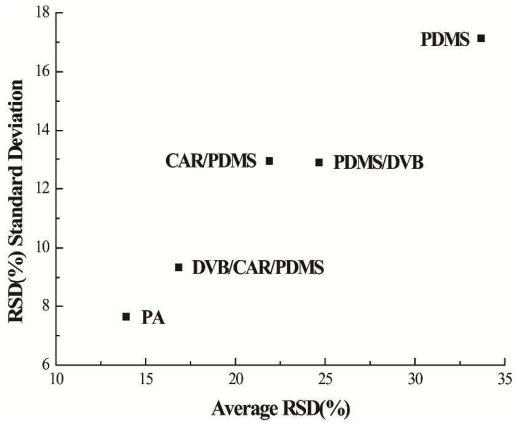


Fig. 2 Reproducibility of the tested fibers of peak area: average vs. standard deviation of RSD of all compounds.

In order to check the reproducibility of the different fibers, the average value and standard deviation were taken into consideration. Those values, shown in Fig. 2, indicated that how the value of RSD changes with different analytes extracted by the same fiber. It is revealed that RSD of PA shows the best reproducibility attribute to the lowest average value and standard deviation, while PDMS is the worst one. Furthermore, DVB/CAR/PDMS, PDMS/DVB and CAR/PDMS are in the middle position among all the fibers for the average RSD, and DVB/CAR/PDMS shows lower standard deviation.

Compared with other similar methods as shown in Table 3, the method used in this work has given comprehensive study and analysis of the volatile compounds in the "Hengshui Laobaigan"liquor, and the fibers suitable for extracting different types of compounds have been determined. Most of the studies listed in the table provided suitable fibers for limited types of compounds. For example, DVB/CAR/PDMS fiber showed good performance for esters extraction and was used for comprehensive analysis of the volatile compounds in whisky, wine and apple wine. And CAR/PDMS fiber was proved suitable for pyrazine extraction, which was consistent with our research. However, PDMS fiber exhibited good extraction performance for hexanol in the analysis of flavor volatiles in apple wine, which was inconsistent with our conclusion. This may due to the different composition and content in different wines, competitive adsorption will occur between different components, which may affect the selection of the fiber.

Table 3 The comparison of analytical performance for the similar methods

Research subjects	The comparison of the fiber coatings	Conclusions	References
Whisky	100 μm PDMS, 85 μm PA, 50/30 μm DVB/CAR/PDMS	The 100 μm PDMS and 50/30 μm DVB/CAR/PDMS fibers showed a higher enrichment capacity than 85 μm PA. The best fibers for SPME were 100 μm PDMS and 50/30 μm DVB/CAR/PDMS.	R6
Liquor	100 μm PDMS, 65 μm PDMS/DVB, 75 μm CAR/PDMS	75 μm CAR/PDMS fiber was suitable for extraction the pyrazines of cupuassu liquor	R12
Wine	85 μm PA, 100 μm PDMS, 65 μm PDMS/DVB, 75 μm CAR/PDMS, 65 μm CW/PDMS, 50/30 μm DVB/CAR/PDMS	65 μm PDMS/DVB showed good performances for esters, while 85 μm PA can be used for more polar compounds such as acids and alcohols. DVB/CAR/PDMS was suitable to analysis the whole composition of an Italian Chardonnay wine.	R7
	100 μmPDMS, 65 μm PDMS/DVB, 50/30 μm	50/30 μm DVB/CAR/PDMS was chose to analysis the volatile compounds in Semillon wines.	R19

	DVB/CAR/PDMS		
Apple wine	85 μm PA, 100 μm PDMS, 75 μm CAR/PDMS	75 μm CAR/ PDMS fiber was suitable for the extraction of the most alchols, ethyl lactate and diethyl succinate; 100 μm PDMS fiber was suitable for extracting hexanol and other esters except ethyl lactate, diethyl succinate.	R20
Chinese Laobaigan liquor	85 μm PA, 100 μm DMS, 65 μm PDMS/DVB, 75 μm CAR/PDMS, 50/30 μm DVB/CAR/PDMS	75 μm CAR/ PDMS was suitable for the extraction of acids, alcohols, pyrazines and aromatic and phenolic compounds. And 50/30 μm DVB/CAR/PDMS fiber was suitable for the extraction of esters, aldehydes and ketones, hydrocarbons and aromatic and phenolic compounds. In the end, 50/30 μm DVB/CAR/PDMS fiber was chose to analysis the volatile compounds in Laobaigan liquor.	In this paper

4 Conclusions

In conclusion, by considering the number of volatile compounds, sensitivity and reproducibility, 50/30 μm DVB/CAR/PDMS fiber was the most suitable in acquiring a complete profile in "Hengshui Laobaigan" liquor volatile compounds. However, for specific application, the choice of a suitable solid-phase depends on the class of compounds be analyzed. For extraction of acids, alcohols, pyrazines and aromatic and phenolic compounds, the sensitivities of 75 μm CAR/PDMS were the highest. And 50/30 μm DVB/CAR/PDMS fiber was found to have higher sensitivities than others for extracting esters, aldehydes and ketones, hydrocarbons and aromatic and phenolic compounds. It is concluded that different fibers should be selected depending on different research object for acquiring accurate and reliable results.

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