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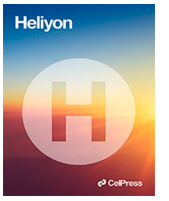

Research article

Qualitative determination of volatile substances in different flavored cigarette paper by using headspace-gas chromatography-ion mobility spectrometry (HS-GC-IMS) combined with chemometrics

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ABSTRACT

In order to investigate the difference of volatile substances among flavored cigarette paper, which are supplied by several manufacturers with different batches, the stability of the complex system of scented cigarette paper was analyzed and evaluated. In this study, Headspace-gas chromatography-ion mobility spectrometry (HS-GC-IMS) was used to detect the aroma compounds of 23 flavored cigarette paper samples. Based on fingerprint analysis, the differences and changes of aroma compounds of different samples were studied in the form of data visualization. Principal component analysis, partial least squares regression analysis, cluster heatmap analysis and artificial neural network analysis were used to evaluate the stability of different cigarette paper. The results show that: A total of 29 volatile substances were identified from different scented cigarette paper. Fingerprint analysis revealed that the volatile substances of different cigarette paper samples were roughly the same, but not the content. The results of chemometrics analysis showed that there were significant differences in the characteristic aroma compounds of cigarette paper from different manufacturers. HS-GC-IMS technology combined with chemometrics method could be applied to determine the difference of volatile substances among different flavored cigarette paper, which theoretically and technically supported the quality stability maintenance and identification of flavored cigarette paper processed in different places.

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1. Introduction

Cigarette paper, a thin sheet paper, is a specially designed for wrapping tobacco, which are characterized by denseness, softness and delicateness, high longitudinal tensile strength, certain air permeability and suitable burning speed [1]. As an important accessory material of cigarettes, cigarette paper directly participates in the combustion [2]. Although the mass of cigarette paper accounts for a small proportion in a cigarette, it has a greater impact on the overall style, chemical composition of smoke, as well as burning performance of cigarettes [3]. Cigarette auxiliary materials, such as cigarette paper, plug-wrap paper, tipping paper and filter tip, were important carriers of cigarette flavoring. Some functional materials with flavoring and sweetening ingredients are added into cigarettes paper during the manufacturing process. When the cigarette is burning, fragrance components of the additives on the cigarette paper are released through volatilizing and pyrolytic cracking, resulting in a certain characteristic fragrance enduing [4, 5]. Recently, flavored cigarette paper has been widely used in the production of upscale cigarettes [6, 7]. Flavored cigarette paper contains various substances, complex components, and low content of aroma components [8, 9]. Up to now, the process of papermaking and flavoring about flavored cigarette paper are basically outsourced. The quality control system of flavored cigarette paper has not been established. Many issues about flavored cigarette paper, such as difficult trace of raw materials, long detection time, and insufficient monitoring, affect the quality stability of cigarette. Moreover, the existing GC/MS methods of the national standard has the shortcomings of specificity and insufficient sensitivity for the detection of trace aroma compounds. Therefore, establishing an accurate, efficient, and convenient method for detecting the aroma components of flavored cigarette paper is an urgent problem for cigarette manufacturers.

Ion Mobility Spectrometry (IMS) technology has good qualitative and semi-quantitative analysis capabilities. Compared with spectroscopy, more qualitative and quantitative information can be achieved [10, 11]. As a tool, it can be used in basic research, stability monitoring and fingerprint analysis of edible flavor and fragrance industry [12, 13]. The headspace-gas chromatography-ion mobility spectrometer (HS-GC-IMS) combines the advantages of gas chromatography with high separation efficiency and ion mobility spectrometer with high sensitivity. There is no any special sample pretreatment and operation is simple. Quick measurement for trace volatile components in solid or liquid samples can be achieved. Through NIST database, HS-GC-IMS can be used for qualitative analysis of substances and visualize it highly [14, 15]. It is suitable for trace analysis and detection of volatile and semi-volatile substances. At present, this technology is mainly used in the detection and analysis of olive oil [16, 17], meat [18, 19], fruit [20] and dairy products [21]. It was rarely used in analysis of electronic cigarettes [22], and has not been used in the analysis of flavored cigarette paper at present.

In this study, 23 different batches of flavored cigarette paper of the same variety produced by 3 different manufacturers were used as the experimental samples. The HS-GC-IMS technology was used to collect and trace analysis of volatile substances in cigarette paper. A fingerprint has been established to compare the differences in the content of volatile substances from different cigarette paper. Principal component analysis, partial least squares regression analysis, cluster heatmap analysis and artificial neural network analysis were used to visually analyze the data, and then evaluate the stability of different samples. In order to provide a new theoretical basis and data support for monitoring the change of aroma components of flavored cigarette paper and traceability identification.

2. Experimental

2.1. Materials, reagents and instruments

8 batches of flavored cigarette paper samples produced by A paper mill (numbered FXJYZ10-01#∼08#); 10 batches of flavored cigarette paper samples produced by B paper mill (numbered FXJYZ11-01#∼10#); 5 batches of flavored cigarette paper produced by C paper mill (numbered FXJYZ14-01#∼05#).

Carrier gas N_2: Purity>99.999%, commercially available.
Electronic analytical balance: Model JE203G, METTLER, Switzerland.
Screw-top headspace bottle: model 22.5 × 75.5mm, precision brown 20 mL, China HAMAG company.
GC-IMS flavor analyzer: FlavourSpec type (with CTC automatic headspace sampler, Laboratory Analytical Viewer (LAV) analysis software and Library Search qualitative software), Germany G.A.S. company.

2.2. Sample preparation

Accurately weigh 0.500 g (accurate to 0.00 1 g) of flavored cigarette paper sample at room temperature, place it in a 20 mL precision brown screw-top headspace bottle, incubate at 90 °C for 20 min, and then inject the sample. Each sample is subjected to 3 parallel tests at the same time.

2.3. HS-GC-IMS analytical conditions

The incubation time of the headspace bottle containing the sample is 20 min; the incubation temperature is 90 °C; the injection volume is 200 μl; the injection needle temperature is 95 °C; the incubation speed is 500 rpm.

Analysis time: 30 min, column type WAX, column length 30 m, inner diameter ID-0.53 mm, film thickness FT-1 μm, column temperature 60 °C.

Gas chromatographic gradient program: 0–2 min, carrier gas flow rate 2 mL/min; 2–20 min, carrier gas flow rate 10 mL/min; 20–30 min, carrier gas flow rate 100 mL/min. The drift gas flow rate is 150 mL/min.

The length of the drift tube is 98 mm; the linear voltage in the tube is 500 V/cm; the temperature of the drift tube is 45 °C; the carrier gas/drift gas is N_2; the drift gas flow rate is 150 mL/min; radiation source: β-ray (tritium, 3H); ionization mode:Positive ions.

2.4. GC-QTOF/MS analytical conditions

Gas chromatographic conditions: inlet temperature 250 °C; Programmed heating: temperature 40 °C, keep 1 min; The temperature rose to 150 °C/min at 5 °C/min for 1 min, and rose to 300 °C at 30 °C/min for 2 min. Carrier gas: He gas; Injection method: no shunt injection.

Mass spectrum conditions: ion source EI, electron energy 70 eV, transmission line temperature 250 °C, ion source temperature 230 °C, mass range 30–600 m/z. Ion Source Gas1:50; Ion Source Gas2:50, Curtain Gas: 35; Temperature: 500 °C, Ion Spray Voltage Floating: 5500 V–4500 V.

2.5. Data analysis

GC-IMS Library Search V2.2.1 was used for qualitative analysis, and the built-in National Institute of Standards and Technology (NIST) database was used for qualitative analysis of volatile substances in the samples. GC-IMS data were processed and viewed with GC-IMS Library Search and Laboratory Analytical Viewer (LAV) software. The database employed chromatographic retention index and compound ion mobility rate (cm^2/Vs) to qualitatively identify compounds. The Reporter, PCA and Gallery plug-ins of LAV were used to compare the 2D- and 3D-spectrogram and fingerprint differences of identified volatiles among different samples. ModelLab Matman general chemometrics solution software (Chemmind Technologies, Beijing, China) has been adopted. Principal Component Analysis (PCA), Partial least Squares Regression (PLS), clustering heat map analysis and artificial Neural Network (ANN) analysis were performed on the data.

3. Results and discussion

3.1. 2D- and 3D-topographic plots analysis of volatile substances in flavored cigarette paper

23 different cigarette paper samples had been selected for the rapid analysis of gas chromatography-ion mobility spectrometry (GC-IMS). Eight representative samples were selected for visual comparative analysis of the results. Figure 1 showed the GC-IMS three-dimensional comparison spectrum of the aroma components of different cigarette paper samples analyzed by LAV software. It could be visually observed from Figure 1 that the types of volatile organic compounds among different samples were relatively close. In order to facilitate the comparison and analysis among samples, the 3D-topographic plots of each sample was changed to a two-dimensional contour map as shown in Figure 2 for difference comparison. In Figure 2, the abscissa represented the migration time of the aromatic substance relative to the reaction ion peak during IMS separation, the ordinate represents the retention time of the aromatic substance during GC separation, the red vertical line at abscissa 1.0 was the reaction ion peak (RIP) peak, and each point on both sides of RIP peak represented an aromatic substance. Different color mean different content, with red and white representing high and low respectively. The darker color indicated the higher content of the compound. The results showed that the normalized migration time

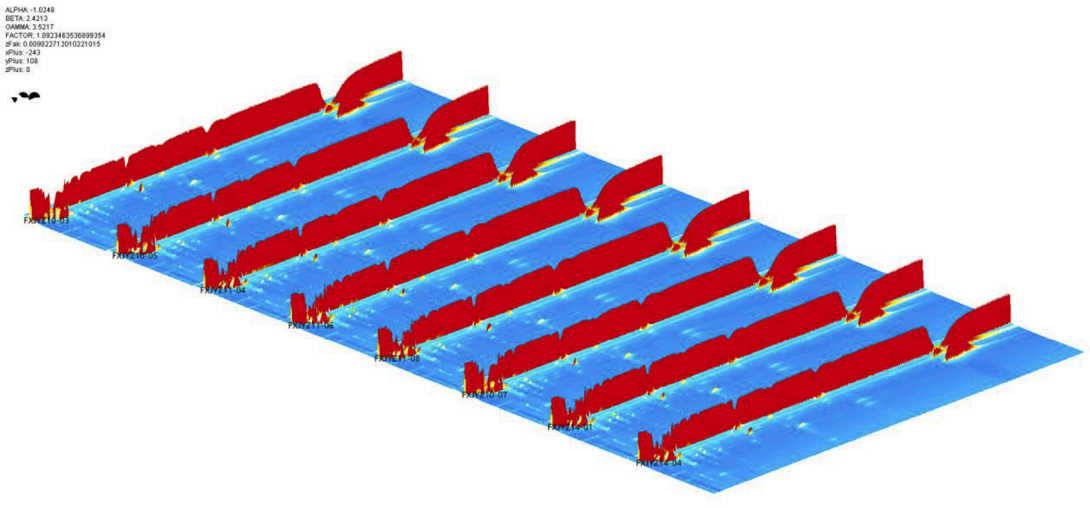

Figure 1. 3D-topographic plots of samples among different flavored cigarette paper.

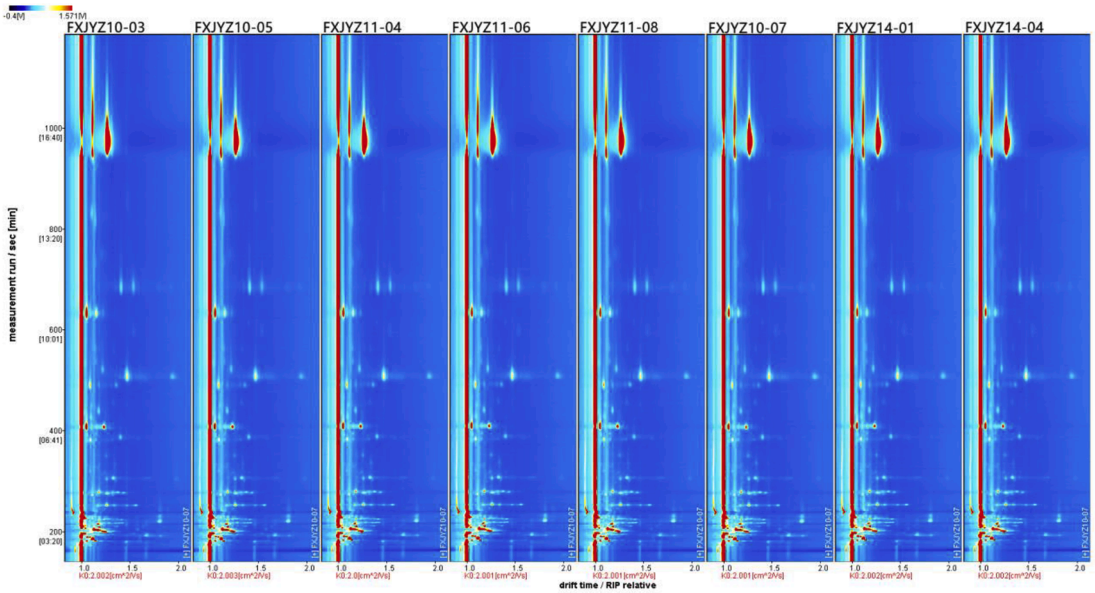

Figure 2. 2D-topographic plots of samples among different flavored cigarette paper.

was 4.48 m, most of the organic matter had completed effective migration in 200–1000 s, and the content of volatile substances in different samples varied. In order to more obviously compare the difference in the content of volatile substances among different samples, the difference comparison mode was adopted, and Figure 3 was obtained. The spectrum of sample FXJYZ10-03 was selected as the reference, and the spectrums of the other 7 samples were deducted as the reference. If the volatile organic compounds of the two samples were consistent, the deducted background would fade to white, and the red indicated that the concentration of the substance was higher than that of the reference sample, and the blue indicated that the concentration of the substance was lower than that of the reference sample. It could be seen from Figure 3 that different volatile substances in the 8 cigarette paper samples demonstrated different GC-IMS spectral characteristic information. The samples FXJYZ10-05, FXJYZ10-07 and the reference sample FXJYZ10-03 from the same factory A were generally similar. The three samples FXJYZ11-06, FXJYZ11-04, and FXJYZ11-08 from factory B demonstrated similar types and contents of volatile substances, compared with the reference sample FXJYZ10-03, significant difference in the color of the volatile substances at retention time around 200s. The volatile substances of the samples FXJYZ14-01 and FXJYZ14-04 from factory C were similar to the three samples of the factory B, and the volatile substances compared with the reference sample FXJYZ10-03 are also different at retention time around 200s.

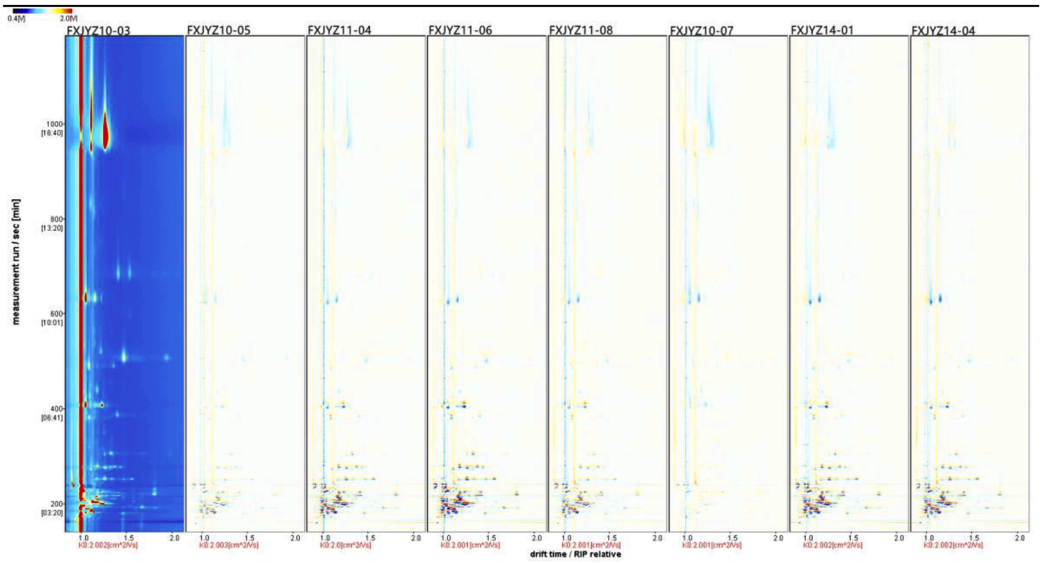

Figure 3. GC-IMS spectrogram referenced by sample FXJYZ10-03 (difference images).

3.2. Qualitative determination of volatile substances in flavored cigarette paper by GC-IMS

For further exploring the volatile substances among 23 different flavored paper samples, the volatile substances were identified by using NIST database in GC-IMS Library Search. As shown in Figure 4, each point marked with a number represented a defined substance. The qualitative determination results of volatile substances had been shown in Table 1. The numbers in Figure 4 corresponded to the volatile substances in Table 1. A total of 72 kinds of common volatile substances were detected in different cigarette paper, and 29 kinds of monomers and dimers of substances could be identified. The above 29 compounds were separated and analyzed statistically. The results showed that majority of volatile substances were alcohols and ketones(7 types of each). Alcohols play a moistening role in the process of cigarette smoking, while it also improves the aroma of tobacco, making the mainstream cigarette smoke delicate and soft, and rich in concentration. Ketones has a strong influence on cigarette taste, aroma and satisfaction, which coordinating cigarette aroma, covering up miscellaneous gas and giving cigarettes different characteristics of aroma [23, 24]. In addition, scented cigarette paper also contained 5 aldehydes, 4 esters, 1 acids, 5 dimers. These substances were the main sources of aroma characteristics of flavored cigarette paper, and the difference in their content had important influence on the flavor characteristics of flavored cigarette paper, also was a core index of internal quality control of flavored cigarette paper. Among them, butyl acetate had a pleasant fruity smell. Methyl furoate has strong fruit and baking aroma, which is coordinated with smoke aroma with enhancement on fullness for smoke and cover up miscellaneous gases [25]. Benzaldehyde has a mixture of almond, cherry and nut. Octyl aldehyde had a light, fresh, sweet and clear smell of sweet orange peel [26]. Nonanal is known as geranium aldehyde, naturally existing in rose oil, citrus oil, white lemon oil and Perilla oil, with a similar rose and citrus-like aroma [27]. 1-Hexanol has a fruity and attractive aroma and was used in the preparation of coconut and berry flavors. β-damascenone produces a cool, pleasant green fragrance and strong rose fragrance,

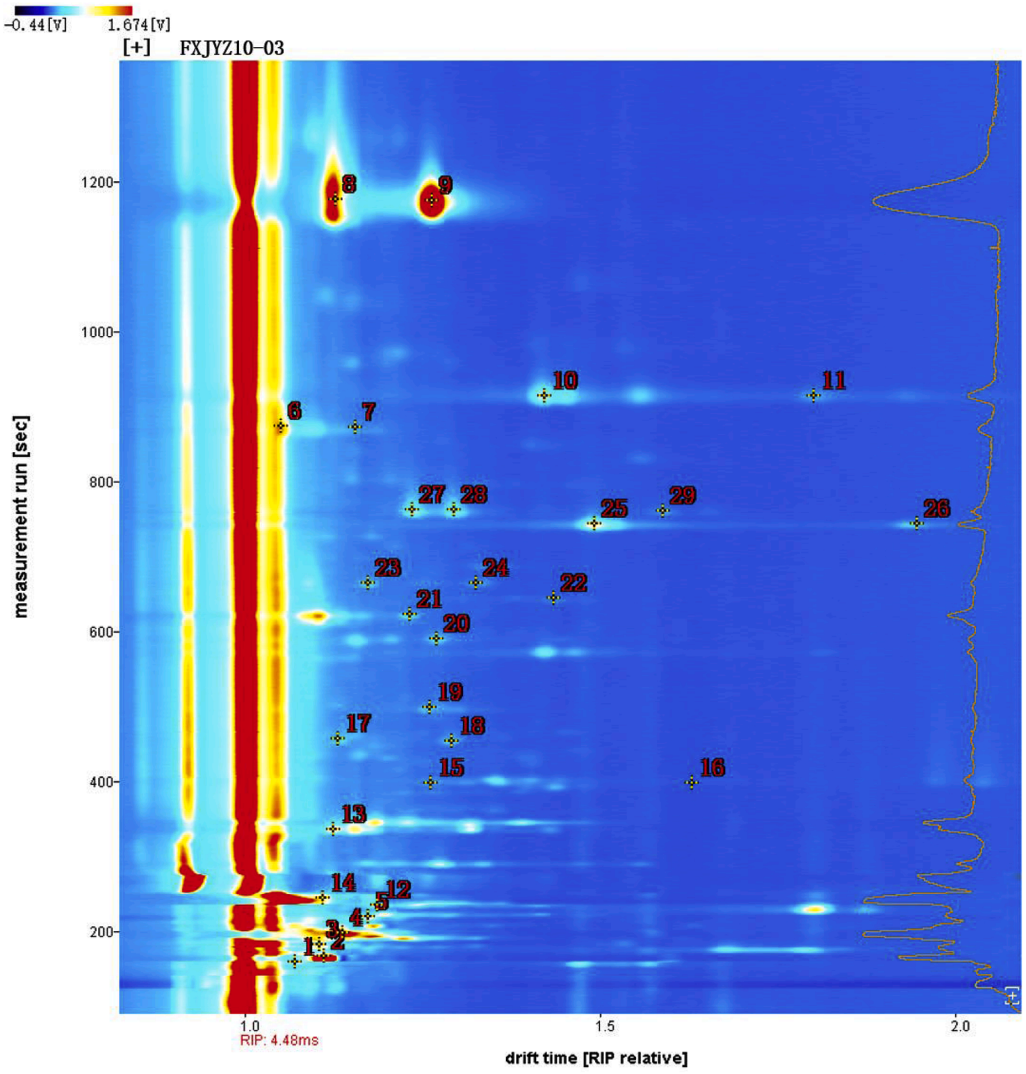

Figure 4. Result of volatile substances identified by GC-IMS reporter plots.

Table 1
Qualitative determination results of cigarette paper samples by GC-IMS.[a]

No.	Compounds	CAS#	Formula	MW	RI	Rt [sec]	Dt [RIP rel]
1	propionaldehyde	123-38-6	C_3H_6O	58.1	790.4	158.686	1.07208
2	acetone	67-64-1	C_3H_6O	58.1	817.7	166.517	1.11202
3	butanal	123-72-8	C_4H_8O	72.1	876.4	183.31	1.10583
4	ethanol	64-17-5	C_2H_6O	46.1	924	198.024	1.13918
5	butane-2,3-dione (diacetyl)	431-03-8	$C_4H_6O_2$	86.1	981.3	219.622	1.17428
6	acetic acid monomer	64-19-7	$C_2H_4O_2$	60.1	1476	874.559	1.05258
7	propylene glycol monomer	57-55-6	$C_3H_8O_2$	76.1	1660.4	1175.724	1.12837
8	propylene glycol dimer	57-55-6	$C_3H_8O_2$	76.1	1659.6	1174.413	1.2646
9	2-ethyl-1-hexanol monomer	104-76-7	$C_8H_{18}O$	130.2	1500	913.775	1.42315
10	2-ethyl-1-hexanol dimer	104-76-7	$C_8H_{18}O$	130.2	1500	913.775	1.80138
11	methyl 2-methylbutanoate	868-57-5	$C_6H_{12}O_2$	116.2	1011.6	235.094	1.1868
12	butyl acetate	123-86-4	$C_6H_{12}O_2$	116.2	1134.2	336.552	1.12602
13	1-propanol	71-23-8	C_3H_8O	60.1	1024.7	243.918	1.11095
14	2-heptanone monomer	110-43-0	$C_7H_{14}O$	114.2	1185.8	398.123	1.26208
15	2-heptanone dimer	110-43-0	$C_7H_{14}O$	114.2	1186	398.42	1.63085
16	methyl furoate	611-13-2	$C_6H_6O_3$	126.1	1222.4	456.691	1.1322
17	benzaldehyde	100-52-7	C_7H_6O	106.1	1221.1	454.61	1.29194
18	1-pentanol	71-41-0	$C_5H_{12}O$	88.1	1247.2	498.611	1.26059
19	caprylic aldehyde	124-13-0	$C_8H_{16}O$	128.2	1294.2	577.881	1.41356
20	1-octen-3-one	4312-99-6	$C_8H_{14}O$	126.2	1301.8	590.161	1.27131
21	1-hydroxypropan-2-one	116-09-6	$C_3H_6O_2$	74.1	1321.4	622.162	1.2335
22	hexyl propionate	2445-76-3	$C_9H_{18}O_2$	158.2	1334.7	643.94	1.43628
23	6-methylhept-5-en-2-one	110-93-0	$C_8H_{14}O$	126.2	1347.2	664.385	1.17507
24	1-hexanol	111-27-3	$C_6H_{14}O$	102.2	1347.5	664.83	1.3263
25	nonanal monomer	124-19-6	$C_9H_{18}O$	142.2	1396.2	744.388	1.49299
26	nonanal dimer	124-19-6	$C_9H_{18}O$	142.2	1395.7	743.499	1.94666
27	2-butoxyethanol monomer	111-76-2	$C_6H_{14}O_2$	118.2	1406.9	761.722	1.23694
28	2-butoxyethanol dimer	111-76-2	$C_6H_{14}O_2$	118.2	1407.4	762.558	1.29463
29	β-damascenone	23696-85-7	$C_{13}H_{18}O$	192.3	1405.9	760.244	1.58956

[a] : The serial number corresponds to Figure 4.

with soft, light and permeable characters, which plays a significant role in aroma enhancement for cigarettes [28]. At the same time, GC-QTOF/MS was employed to a qualitatively detection on the volatile substances of different flavored cigarette paper samples, there were 27 compounds with matching degree greater than 90, and the results were shown in Table 2. Due to different detection

Table 2
Qualitative determination results of cigarette paper samples by GC-QTOF/MS.

No.	Compounds	Retention time	Formula	Peak area	fit
1	2-methyl-2-Butenal	4.7	C_5H_8O	4437274.6	92.1
2	Acetic acid	5.23	$C_2H_4O_2$	190827.3	90.4
3	Cyclohexanone	8.26	$C_6H_{10}O$	515484.5	90.1
4	Benzaldehyde	10.14	C_7H_6O	3794806.6	95.4
5	Benzyl alcohol	12.34	C_7H_8O	2736882.6	93.9
6	caprylic aldehyde	12.53	$C_8H_{16}O$	44259.3	90.5
7	6-methylhept-5-en-2-one	13.02	$C_8H_{14}O$	61891.9	90.8
8	nonanal	13.31	$C_9H_{18}O$	68659.9	918
9	hexyl propionate	14.05	$C_9H_{18}O_2$	156064.4	90.3
10	Phorone	14.6	$C_9H_{14}O$	359890.9	92.8
11	Phenylethyl Alcohol	14.72	$C_8H_{10}O$	1862653.5	90.4
12	Methyl salicylate	17.07	$C_8H_8O_3$	28853.8	91.2
13	Dodecane	17.14	$C_{12}H_{26}$	98139.3	92
14	1-Decanol, 2-ethyl-	17.52	$C_{12}H_{26}O$	36371.3	92.5
15	Tridecane	19.88	$C_{13}H_{28}$	68412.1	92.9
16	β-damascenone	18.72	$C_{13}H_{18}O$	224136.9	95
17	Eugenol	21.48	$C_{10}H_{12}O_2$	99172.1	87.3
18	Tetradecane	22.49	$C_{14}H_{30}$	245385.3	95.5
19	1H-Pyrazole, 3-methyl-1-phenyl-	24.19	$C_{10}H_{10}N_2$	93503.9	90.1
20	Pentadecane	24.33	$C_{15}H_{32}$	214184.5	95.1
21	2,4-Di-tert-butylphenol	24.5	$C_{14}H_{22}O$	3567270	96.2
22	Pentadecane, 3-methyl-	25.08	$C_{16}H_{34}$	43448.9	91.5
23	Hexadecane	25.33	$C_{16}H_{34}$	202726.3	94.4
24	Heptadecane	26.03	$C_{17}H_{36}$	84253.9	95
25	heneicosane	27.01	$C_{21}H_{44}$	4162.8	93
26	pentacosane	27.21	$C_{25}H_{52}$	65305.5	92.1
27	Hentriacontane	27.84	$C_{31}H_{64}$	92224.1	91.8

conditions, the column temperature of GC-IMS was relatively low, while the column temperature of GC-QTOF/MS was relatively high. The former focused on low boiling point and volatile substances, while the latter focused on volatile and semi-volatile substances. Therefore, the qualitative results were less identical and more different.

3.3. Fingerprint analysis

In order to obtain a comprehensively result of differences of aromatic compounds in different manufacturers and batches among flavored cigarette paper, the fingerprint plots and the peak intensity of identified VFCs were performed by using LAV software, each experiment was repeated three times. As shown in Figure 5, each point presented a volatile flavor compound. There were obvious similarities among different batches of flavored cigarette paper samples from the same manufacturer, and the main difference was the concentration. However, the samples from different manufacturers showed obvious differences, and the volatile substances in the samples had their own characteristic peak regions, and also had common similar regions. "A" area referred to the compounds of A manufacturer's samples whose content was significantly different from the other two samples, while "B" area referred to the compounds whose content was significantly higher in B manufacturer's samples than the other two manufacturer's samples. The 14 components in "C" area increased significantly, which could be used as the characteristic fragrance markers of samples from manufacturer C.

3.4. PCA analysis

Principal component analysis (PCA) was proposed by British statistician Carl Pearson in 1901. PCA was the most classical and

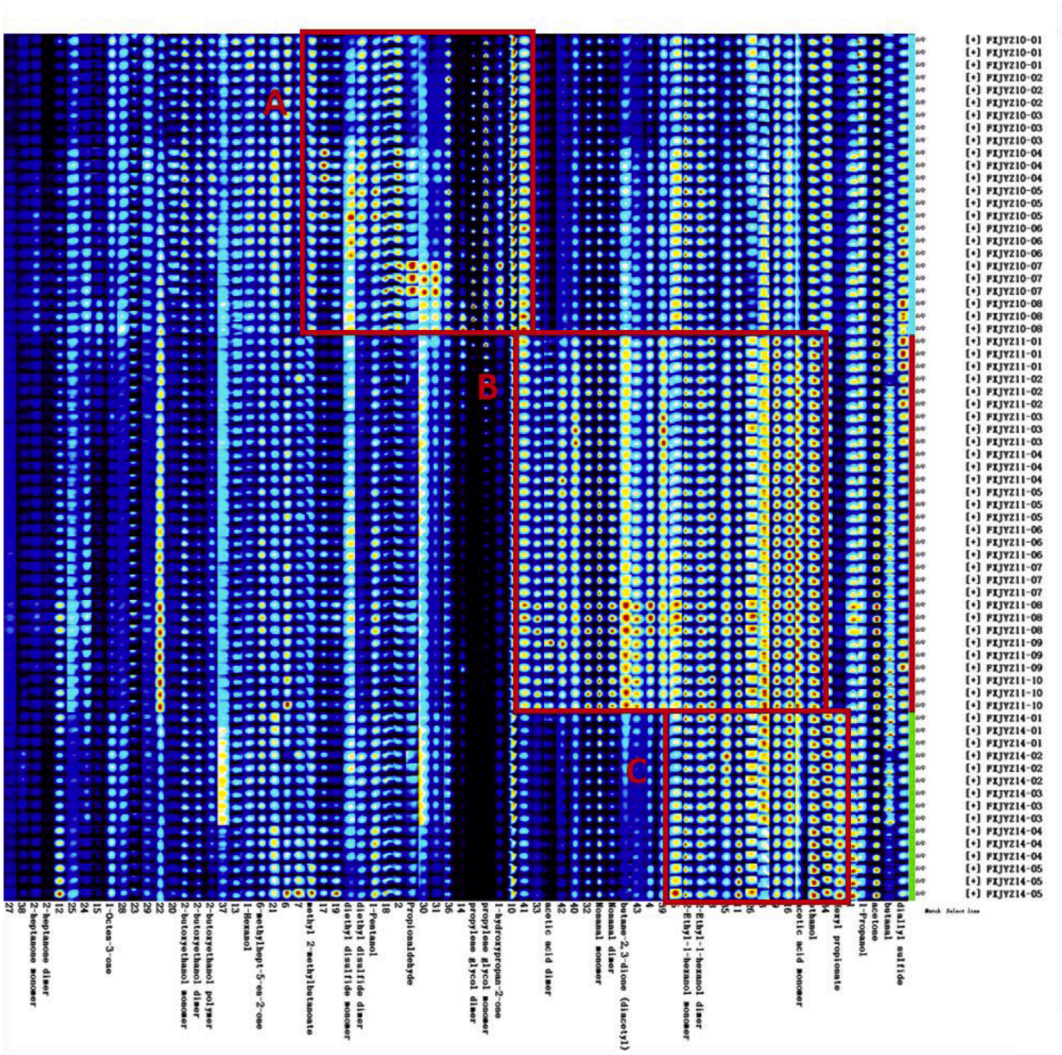

Figure 5. GC - IMS fingerprints of samples among different flavored cigarette paper.

widely used multivariate statistical method based on eigenvector analysis [29]. Through the PCA scatter score plot of sample markers in three dimensional spaces to analyze and compare the differences in the aroma components of cigarette paper from different manufacturers intuitively. In this paper, each sample was measured 5 times as parallel samples in PCA analysis, the result had been shown in Figure 6. The contribution (loading) of the individual compounds in the principal components had been shown in Table 3. The software automatically selected three principal components for analysis to unsupervised distinguish the samples. Among them, the contribution rate of the first principal component was 53.40%, the contribution rate of the second principal component was 15.21%, the contribution rate of the third principal component was 5.17%, and the cumulative contribution of the three principal components reached 73.78%, which indicated that different flavored cigarette paper samples were well separated. After the characteristic variables in the cigarette paper samples were processed by PCA, it could be directly observed through the three-dimensional plane data point distribution map: the flavored cigarette paper samples of the same manufacturer and different batches basically showed an aggregated distribution, which had good regional attribution. There was no overlap between the regions of samples from different manufacturers, which indicated that cigarette paper samples from different manufacturers could be well separated, and the characteristic aroma substances between samples had certain differences.

3.5. PLS analysis

Partial least squares regression had been widely used in stoichiometric analysis and had become a standard multivariate modeling tool [30]. The PLS-DA analysis had been applied to analyze the three types of samples. The leave-one-out method in cross-validation was used to extract and establish the validation sets one by one, so as to evaluate the generalization degree and over-fitting degree of the model. The results showed that when the number of latent variables was 3 or 5, the model achieved the best classification recognition rate and, the recognition rate was between 99% and 100% ($R^2Y = 0.995$, $Q^2 = 0.994$). PLS-DA score chart from Figure 7 indicated that there was significant difference in the composition of volatile compounds in cigarette paper, and three types of samples were well distinguished within 95% confidence interval (shown by the oval) of Totelling's T2, which revealed a perfect cluster performance of different flavored cigarette paper samples, came to a significant discrimination among cigarette paper samples from

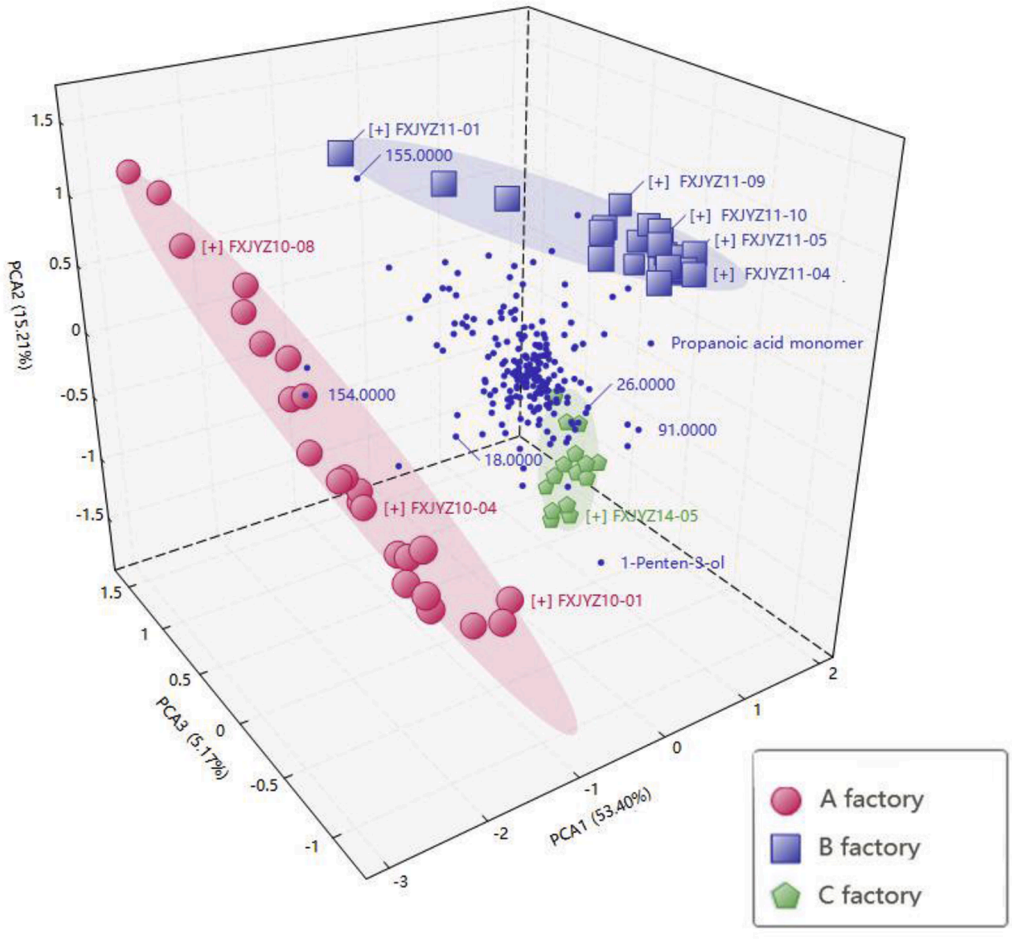

Figure 6. PCA plot of flavored cigarette paper.

Table 3
The contribution (loading) of the individual compounds in the principal components.

No.	Compounds	PC 1	PC 2
1	propionaldehyde	0.050355	0.055244
2	acetone	0.189714	-0.05178
3	butanal	0.074659	0.172057
4	ethanol	0.001407	0.046004
5	butane-2,3-dione (diacetyl)	-0.01853	0.004339
6	acetic acid monomer	0.083051	0.092754
7	propylene glycol monomer	0.044032	0.019738
8	propylene glycol dimer	0.049967	0.005458
9	2-ethyl-1-hexanol monomer	-0.03415	-0.01378
10	2-ethyl-1-hexanol dimer	-0.00722	0.011439
11	methyl 2-methylbutanoate	0.025063	-0.09877
12	butyl acetate	0.042726	-0.05727
13	1-propanol	-0.01156	-0.01195
14	2-heptanone monomer	-0.21066	-0.32272
15	2-heptanone dimer	-0.13537	-0.08821
16	methyl furoate	-0.01718	-0.02361
17	benzaldehyde	-0.07521	-0.0584
18	1-pentanol	-0.08013	-0.18785
19	octaldehyde	0.017355	-0.0834
20	1-octen-3-one	0.104452	0.156615
21	1-hydroxypropan-2-one	-0.0003	0.011858
22	hexyl propionate	-0.06992	0.015522
23	6-methylhept-5-en-2-one	0.006436	0.396618
24	1-hexanol	0.028065	0.054332
25	nonanal monomer	-0.13261	-0.19523
26	nonanal dimer	-0.05661	-0.07724
27	2-butoxyethanol monomer	0.026583	0.014926
28	2-butoxyethanol dimer	0.646389	-0.25856
29	β-damascenone	0.401356	-0.24762
30	unknown compound 1	-0.06852	0.090481
31	unknown compound 2	0.093988	-0.03953
32	unknown compound 3	-0.02304	0.017666
33	unknown compound 4	-0.08562	-0.14485
34	unknown compound 5	-0.00115	0.033749
35	unknown compound 6	-0.00123	-0.02978
36	unknown compound 7	-0.03973	0.079064
37	unknown compound 8	-0.05647	0.012563
38	unknown compound 9	-0.05132	-0.0415
39	unknown compound 10	0.050238	0.027312
40	unknown compound 11	-0.08041	0.026247
41	unknown compound 12	-0.13372	0.059354
42	unknown compound 13	0.046238	-0.00752
43	unknown compound 14	0.07674	-0.23755
44	unknown compound 15	0.115308	-0.11059
45	unknown compound 16	-0.03392	0.011965
46	unknown compound 17	0.055787	0.078863
47	unknown compound 18	0.115004	0.103553
48	unknown compound 19	0.035116	0.006456
49	unknown compound 20	0.1337	0.027291
50	unknown compound 21	0.034969	0.081432
51	unknown compound 22	-0.09436	-0.1517
52	unknown compound 23	0.048473	-0.0772
53	unknown compound 24	-0.01372	-0.11803
54	unknown compound 25	0.027581	-0.05866
55	unknown compound 26	-0.09796	0.038877
56	unknown compound 27	-0.01917	-0.02165
57	unknown compound 28	0.089623	0.093334
58	unknown compound 29	0.084957	0.060679
59	unknown compound 30	-0.06919	-0.00227
60	unknown compound 31	0.011818	-0.0781
61	unknown compound 32	-0.11138	-0.16598
62	unknown compound 33	-0.11583	-0.2211
63	unknown compound 34	0.011593	0.075623
64	unknown compound 35	-0.08221	-0.03173
65	unknown compound 36	0.05883	-0.01156
66	unknown compound 37	0.008336	0.066759
67	unknown compound 38	-0.02077	0.0981
68	unknown compound 39	-0.05626	-0.10789

(*continued on next page*)

Table 3 (*continued*)

No.	Compounds	PC 1	PC 2
69	unknown compound 40	-0.07569	-0.13029
70	unknown compound 41	0.029875	-0.1364
71	unknown compound 42	-0.18943	-0.13871
72	unknown compound 43	-0.09226	-0.23278

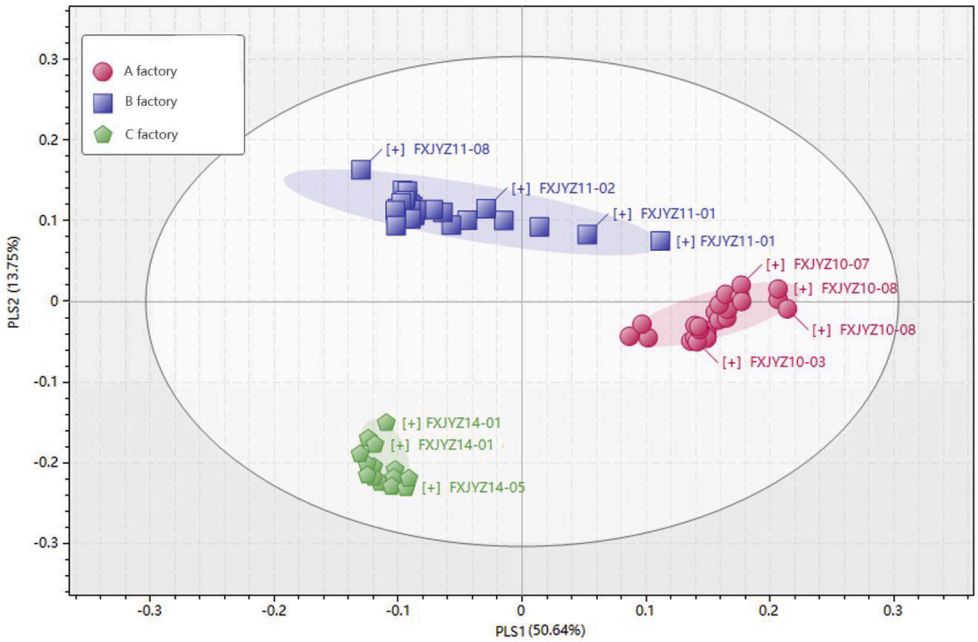

Figure 7. PLS-DA plot of flavored cigarette paper.

different manufacturers. At last, variable importance in the projection (VIP) plot were applied to screen the significantly differential VFCs. In general, the compounds with VIP >1.5 was considered as significantly differential VFCs . As shown in Table 4 and 21 compounds (1-propanol, nonanal monomer, propylene glycol monomer, 2-heptanone monomer, unknown compound 26, et al.) were

Table 4
Results of variable importance in the projection of aromatic substances in flavored cigarette paper.

No.	Compounds	Class		
		Covariance	Correlation	VIP value
1	1-Propanol	-0.544	-0.866	6.015
2	Nonanal monomer	-0.515	-0.842	5.244
3	propylene glycol monomer	-0.324	-0.840	3.631
4	2-heptanone monomer	-0.214	-0.654	2.716
5	unknown compound 26	0.178	0.663	2.243
6	octaldehyde	0.188	0.668	2.152
7	butane-2,3-dione	-0.220	-0.842	2.086
8	butanal	-0.141	-0.573	2.048
9	Butyl acetate	0.108	0.423	1.990
10	unknown compound 43	-0.159	-0.743	1.906
11	methyl 2-methylbutanoate	0.187	0.776	1.763
12	acetic acid monomer	0.216	0.559	1.754
13	unknown compound 31	-0.117	-0.520	1.708
14	Propionaldehyde	0.211	0. 560	1.696
15	ethanol	-0.136	-0.675	1.696
16	unknown compound 17	-0.151	-0.531	1.667
17	unknown compound 15	-0.127	-0.559	1.659
18	unknown compound 10	-0.143	-0.644	1.646
19	2-Ethyl-1-hexanol monomer	0.171	0.812	1.620
20	Benzaldehyde	0.147	0.780	1.523
21	1-Hexanol	0.141	0.716	1.515

screened as significantly differential VFCs. It could be seen from Figure 8 that volatile flavor substances near the central axis were substances with small differences in the two groups of samples. The variables in lower left and upper right quadrants in S-plot were the main volatile substances that distinguish three groups of samples, which had been marked with red in S-plot.

3.6. Clustering heatmap analysis

Clustering heatmap was one of the methods which had been widely used in data mining in recent years. Its principle was to display the results in a progressive and intuitive way on the basis of aggregating a large amount of experimental data, while density and frequency of the data were achieved, as well as the difference and change of the key research objects [31]. After preprocessing the GC-IMS data of 23 cigarette paper samples by UV scaling algorithm, ModelLab Matman software had been applied to set the distance function to "Euclidean distance"; the connection function to "Far Neighbor Method" to draw poly Similar heat map (in the figure, the color from blue to yellow represented the content from low to high). The results in Figure 9 showed that 23 batches of samples could be grouped into 4 different categories (differentiated by color), the fragranced cigarette paper samples from different manufacturers could be well separated, which might be related to the different production processes of different manufacturers.

3.7. ANN analysis

Artificial neural network was a bionic system and mathematical model that simulates the structure and intelligent behavior of the human brain. It was an important research content in the field of artificial intelligence and machine learning [32]. GC-IMS data of different cigarette paper samples had been analyzed through the self-organizing map (SOM) model of the self-organizing map neural network, the neighbor radius coefficient was 0.96; the learning speed coefficient was 0.99, and the training expected residual was 0.1 %. The neural network clustering results in Figure 10 showed that the four different types (differentiated by color in Figure 10(A)) of scented cigarette paper samples were well separated, and no sample misclassification occurred. The SOM observation matrix showed significant differences in the composition of volatile compounds in different categories, indicating obvious regional division among the four categories (by the bright line in Figure 10(B)). ANN analysis could be used to distinguish scented cigarette paper samples from different manufacturers accurately and conveniently, which was helpful for the identification of products from different processing manufacturers.

4. Conclusions

In this study, head space-gas chromatography-ion migration spectrometry was used to study the difference of aroma components of 23 different batches of flavored cigarette paper samples for the first time. A total of 73 kinds of common volatile substances were detected from different samples, and 29 kinds of monomer and dimer substances were identified, while contents of different compounds were different. Through fingerprint analysis and data visualization research, it could be found that different batches of cigarette paper samples had the same kinds of volatile substances, while certain differences in the content of volatile substances from different manufacturer's samples. Through the analysis of stoichiometric model, paper samples from different manufacturers could be well separated, which was helpful for the identification of products from different processing manufacturers. HS-GC-IMS technology combined with stoichiometric models made up for the inadequacy of current detection methods. Compared with traditional cigarette paper detection methods [33, 34], this method performed advantages of high sensitivity, less sample consumption, convenient operation and high efficiency, which was promising to investigate the differences of volatile substances among complex system of cigarette paper. It also played a positive role in promoting the quality and stability maintenance of multi-point processed varieties of cigarette paper products and the development of new products.

Declarations

Author contribution statement

LI Chao, TIAN Senlin and LI E'xian: Conceived and designed the experiments; Performed the experiments; Wrote the paper.
FAN Duoqing, TIAN Runtao: Conceived and designed the experiments; Wrote the paper.
ZHU Zijian: Analyzed and interpreted the data.
WANG Chunqiong, WANG Qinghua: Contributed reagents, materials, Analysis tools or data; Wrote the paper.
YOU Junheng, LIU Jinyun: Performed the experiments; Analyze and interpret the data; wrote the paper.

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Data availability statement

Data will be made available on request.

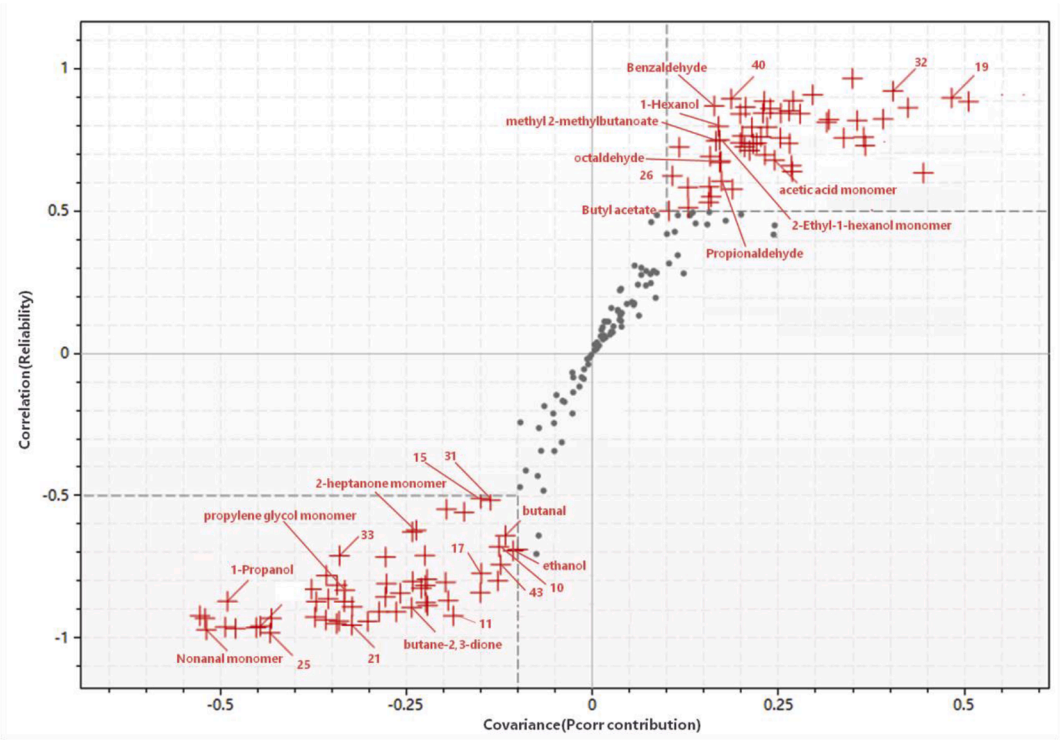

Figure 8. S-plot of flavored cigarette paper.

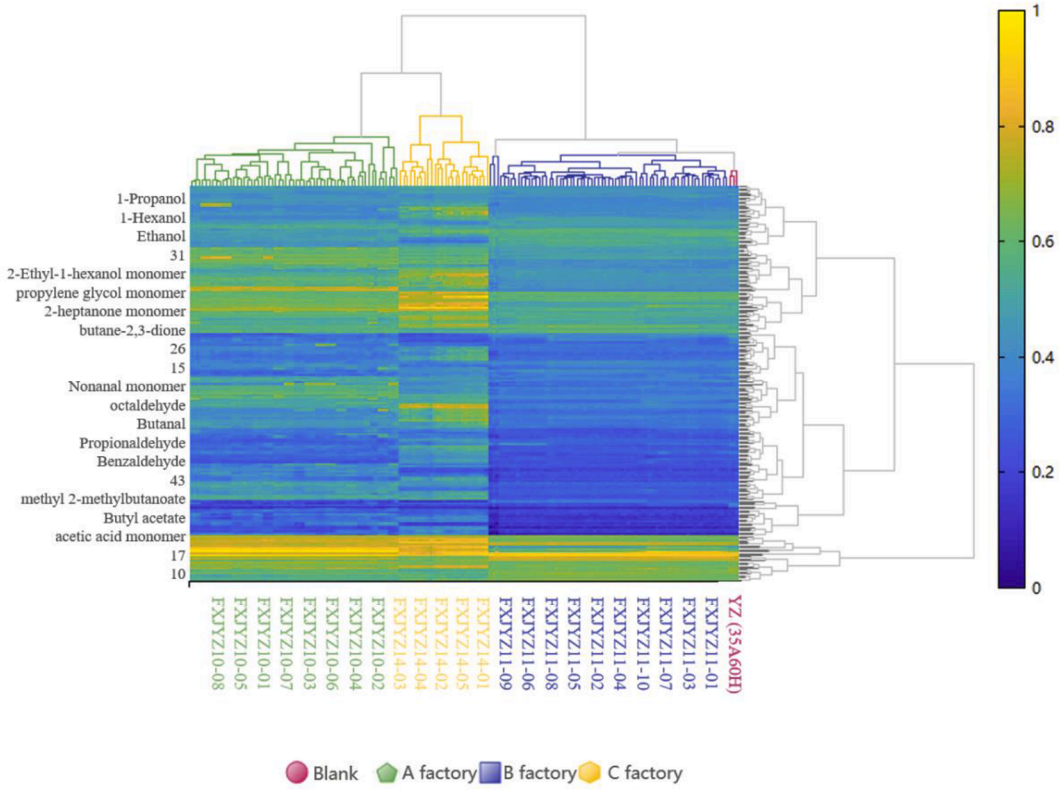

Figure 9. Heat map of cluster analysis of flavored cigarette paper.

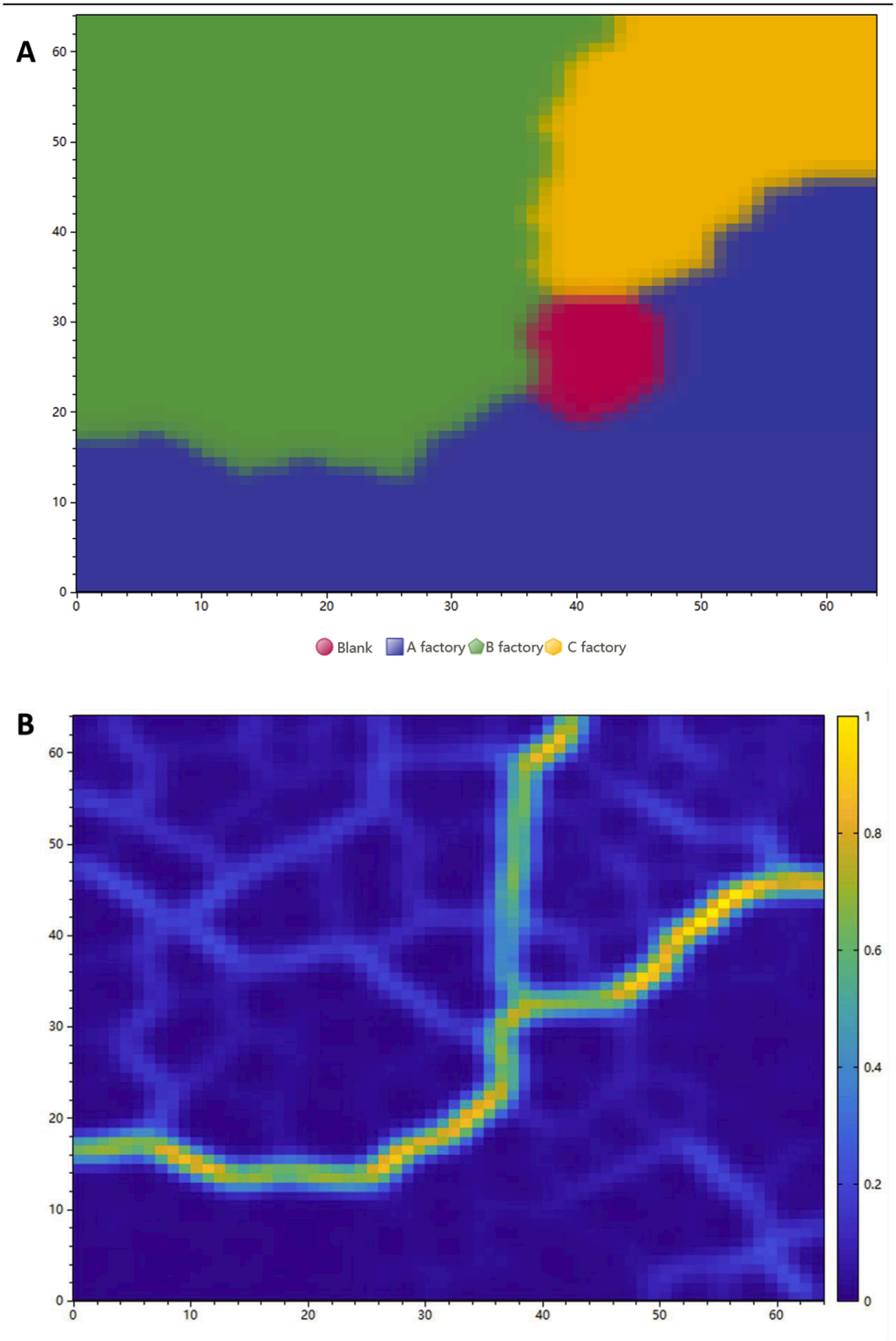

Figure 10. ANN analysis of SOM self-organizing mapping of GC-IMS data of flavored cigarette paper (A: SOM mapping clustering diagram of samples; B: SOM observation matrix).

Declaration of interests statement

The authors declare no competing interests.

Additional information

No additional information is available for this paper.

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