



HS-GC-IMS and HS-SPME/GC-MS coupled with E-nose and E-tongue reveal the flavors of raw milk from different regions of China

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ARTICLE INFO

Handling Editor: Professor Aiqian Ye

Keywords:

HS-SPME/GC-MS

Flavor

GC-IMS

Raw milk

Sensory

ABSTRACT

Milk authentication requires identification of the origin and assessment of the aroma characteristics. In this study, we analyzed 24 raw milk samples from different regions of China by profiling volatile flavors using headspace solid phase microextraction-gas chromatography-mass spectrometry, headspace gas chromatography-ion mobility spectrometry, and intelligent sensory technology (E-tongue and E-nose). The flavor of raw milk in Southern and Northern China had evident differences based on the intelligent sensory technology. However, the differences among the samples from the northeast, northwest, and central regions were not significant. Correlations between milk origin and volatile compounds based on variable importance prediction > 1 and principal component analysis results revealed differential compounds including pyridine, nonanal, dodecane, furfural, 1-decene, octanoic acid, and 1,3,5,7-cyclooctatetraene. Our study findings provided a deeper understanding of the geographical differences in raw milk volatile compounds in China.

1. Introduction

Flavor contributes to sensory characteristics, and aroma and taste are important factors in the assessment of dairy product quality (Claeys et al., 2013; Braggins et al., 2020). Due to its light aroma and taste, raw milk is susceptible to external factors, and is an essential control point in the flavor formation of dairy products (Chi et al., 2022; Evanowski et al., 2023).

Studies have evaluated the association between geographical location and flavor of dairy products. Climate, soil, and animal feed can impact raw milk flavor (Braggins et al., 2020; Zheng et al., 2021; T. Feng et al., 2022). In addition, the health status, nutrient status, and chemical contamination of dairy animals may alter the taste and odor of raw milk (Bendall, 2001; Coppa et al., 2011; O'Callaghan et al., 2016). With sustainable economic development and advances in logistics conditions, the cross-regional distribution of food products is becoming common (Wang et al., 2021). Flavor differences expand the traditional dairy market, and geographical flavor differences are features sought after by producers (Watkins et al., 2021). Flavor information enables the identification of the geographical origin and the selection of potential volatile organic compounds (VOCs) for origin certification (He et al., 2009;

Su et al., 2022). Raw milk from different geographical regions has different organoleptic qualities. Compounds that positively affect flavor can help turn regional differences into geographical advantages.

Flavor compounds of dairy products are analyzed by gas chromatography-mass spectrometry (GC-MS) (Delgado et al., 2011; Bhumireddy et al., 2021; Liu et al., 2022). Gas chromatography-ion mobility spectrometry (GC-IMS) is widely used in the dairy industry for VOC analysis during processing and metabolic footprint analysis during fermentation (X. Feng et al., 2022; Yao et al., 2022). Headspace-solid phase microextraction (HS-SPME/GC-MS) allows accurate qualitative and quantitative analysis of different aromatic compounds but fails to provide any organoleptic information. Evaluations requiring consumption are not feasible for unpasteurized milk due to pathogen risks. E-nose and E-tongue, which simulate olfaction and gustation, respectively, are electronic instruments that simulate the human senses. These instruments can complement the vague, subjective, and indeterminate senses, and simplify complex analytical methods such as chromatography (Duan et al., 2021; Chi et al., 2022; Lu et al., 2022). Aroma and taste have been gradually used to characterize and distinguish foods with distinctive geographical characteristics. For example, the origin of cured ham (Li et al., 2021), rice (Zhao et al., 2022), and

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<https://doi.org/10.1016/j.crf.2023.100673>

Received 9 September 2023; Received in revised form 7 November 2023; Accepted 27 December 2023

Available online 30 December 2023

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honey (Cheng et al., 2013), the grade of wine (Kallithraka et al., 2001; Claeys et al., 2013), the type of vinegar (Pizarro et al., 2008), and the variety of apples (Aprea et al., 2012).

Therefore, the objective of this work was to focus on the flavor of raw milk from 24 different pastures in China. We generated characteristic fingerprints by chromatography and intelligent sensory technology and evaluated the factors that affect the sensory quality of raw milk. This study discussed and successfully applied flavor as a tool to discriminate the origin of raw milk samples from several places of China. Preliminary results confirm the usefulness of GC-MS, GC-IMS, electronic nose and electronic tongue for classification and future quality control purposes of raw milk.

2. Materials and methods

2.1. Materials

We purchased C7–C40 n-alkanes, 98.0% acetone, and 2-methyl-3-heptanone from Sigma-Aldrich Co., Ltd. (St. Louis, MO, USA). We obtained 24 raw milk samples from Holstein cows collected between March and April 2022 from 17 provinces, including Inner Mongolia, Heilongjiang, Tianjin, Hebei, Beijing, Gansu, Shaanxi, Henan, Jiangsu, Shanghai, Shandong, Fujian, Guangdong, Chongqing, Guizhou, and Yunnan. The samples were divided into four regions: A, samples 1 through 5 were from Inner Mongolia and Northeast China, B, samples 6 through 10 were from North China, C, samples 11 through 16 were from Central China, and D, samples 17 through 24 were from Southern China (Table 1). The lactating cows were milked twice daily in a milking parlour. We collected raw milk from the tanks after the first milking and immediately cooled the samples to $-20\text{ }^{\circ}\text{C}$, except for raw milk used to somatic cell count which was stored at $4\text{ }^{\circ}\text{C}$, transported to the laboratory immediately on dry ice, and stored in an appropriately $-80\text{ }^{\circ}\text{C}$ freezer until flavor compound analysis.

2.2. Physical and chemical analysis

We analyzed milk components, including fat, protein, total solids, non-fat milk solids, and lactose, using a MilkoScan™ 7 RM (Foss Electric, Hillerød, Denmark). Somatic cells were detected using

Table 1
Milk sample Information.

Group	Sample	Fat (%)	Protein (%)	Total solid (%)	Non-fat milk solids (%)	Lactose (%)	somatic cell count
A	1_KS	4.30	3.34	13.25	9.16	5.14	136500
	2_GN	4.16	3.26	13.07	9.10	5.17	86000
	3_HL	3.64	3.38	12.82	9.31	5.12	148000
	4_AL	3.55	3.32	12.59	9.16	5.04	133500
	5_FY	3.71	3.31	12.70	9.10	4.98	198000
B	6_XD	3.73	3.20	12.54	8.99	5.13	166000
	7_KP	4.03	3.31	12.89	9.04	5.08	223500
	8_LN	3.83	3.22	12.60	8.94	5.09	268500
	9_ZD	2.94	3.30	12.13	9.34	5.24	58500
	10_FY	3.51	3.23	12.33	8.97	5.13	196000
C	11_ZK	3.78	3.31	12.90	9.25	5.14	151000
	12_RJ	4.22	3.52	13.59	9.52	5.17	102500
	13_QM	4.62	3.30	13.68	9.20	5.09	156500
	14_RD	3.89	3.30	12.91	9.15	5.18	164300
	15_DY	3.82	3.27	12.91	9.23	5.16	132500
	16_RY	3.67	3.28	12.57	9.02	5.10	117500
D	17_SN	3.92	3.18	12.74	8.99	5.17	149000
	18_JD	3.85	3.22	12.48	8.80	5.05	11000
	19_CY	4.45	3.41	13.34	9.09	5.02	359500
	20_LZ	4.19	3.44	13.17	9.24	5.15	49500
	21_ZJ	4.13	3.28	12.79	8.85	5.01	289000
	22_XL	4.30	3.33	13.41	9.25	5.11	80500
	23_GZX	4.43	3.65	13.26	9.01	4.70	857000
	24_XH	4.18	3.13	12.98	8.98	5.19	19600

Fossomatic™ 7 DC (Foss Electric, Hillerød, Denmark).

2.3. HS-GC-IMS analysis

We analyzed VOCs by GC-IMS Flavor Spec (G.A.S, Beijing, China) coupled to an MXT-5 column ($15\text{ m} \times 0.53\text{ mm} \times 1.0\text{ }\mu\text{m}$). We injected 3 mL of sample into the headspace vial and incubated at $40\text{ }^{\circ}\text{C}$ for 30 min (Chi et al., 2022).

The column temperature was kept at $60\text{ }^{\circ}\text{C}$. The analysis took 35 min. Data were obtained using LAV software, and VOCs were characterized using the GC-IMS companion library. The experiment was repeated three times.

2.4. HS-SPME/GC-MS analysis

VOCs were identified and quantified using HS-SPME/GC-MS. Raw milk (10 mL) and 20 μL internal standard (100 mg/kg) were placed in vials. The samples were equilibrated for 30 min in a $40\text{ }^{\circ}\text{C}$ -water bath and stirred constantly. Fiber (1 cm) coated with divinylbenzene/carboxen/poly-dimethylsiloxane (50/30 μm) was used in the extraction. Then, the adsorption time was 30 min after inserting the SPME extraction fiber into the headspace vial. Subsequently, the sampler was removed from the headspace vial and inserted into the GC injector. The aroma compounds adsorbed on the SPME fiber were desorbed by heating ($250\text{ }^{\circ}\text{C}$), and the desorption time was 5 min. GC-MS was performed using an Agilent 7890A instrument coupled to an Agilent 5975C mass selective detector and a DB-WAX UI column ($30\text{ m} \times 0.25\text{ mm} \times 0.25\text{ }\mu\text{m}$). The initial temperature was $30\text{ }^{\circ}\text{C}$, which was kept for 6 min, increased to $220\text{ }^{\circ}\text{C}$ at $5\text{ }^{\circ}\text{C}/\text{min}$, and kept at $220\text{ }^{\circ}\text{C}$ for 3 min. The entire process was carried out in full scan mode. For accuracy, three replicate analyses were conducted for each sample.

Retention index (RI) values for each VOC were calculated from GC-MS results for n-alkanes under similar conditions. The NIST 08 library was used to identify unknown compounds. Quantification was achieved using internal standards.

2.5. E-nose analysis

Overall odor characteristics were obtained using the PEN3 E-nose

(Win Muster Airsense Analytics Inc., Schwerin, Germany). The E-nose has a metal oxide semiconductor sensor array containing 10 sensors. When VOCs pass through the instrument, the “odor fingerprint” is detected by the sensors (Chi et al., 2022; S. Wang et al., 2022). Prior to injection, we placed the sample in a vial and incubated it for 300 s at 40 °C under constant stirring. The data acquisition time was 120 s, and the flushing time was 300 s.

2.6. E-tongue analysis

Overall taste characteristics were obtained using an SA 402B E-tongue (Intelligent Sensor Technology Co., Ltd., Atsugi, Japan). The E-tongue contains five sensors that respond to eight tastes: umami, richness (aftertaste-umami), astringency, aftertaste-astringency, bitterness, aftertaste-bitterness, sourness, and saltiness (Chi et al., 2022). Sensors and reference electrodes were activated for at least 24 h. Samples were diluted and filtered at room temperature. The experiment was repeated three times per sample.

2.7. Statistical analysis

The concentration of VOCs was semi quantitatively estimated using internal standards. Multivariate analyses, including partial least

squares-discriminant analysis (PLS-DA) model, principal component analysis (PCA), and heat map, were performed using Metabo Analyst 4.0 (<https://metaboanalyst.ca/>) and SIMCA 14.1 (Umetrics, Malmö, Sweden). Other data analyses and image processing were conducted using Excel (Microsoft, USA) and Origin 8.0 (Microsoft Corp., United States).

3. Results and discussion

3.1. HS-GC-IMS analysis

In a previous study, we identified the optimal conditions for the analysis of VOCs in dairy products by HS-GC-IMS. The pretreatment temperature was over 60 °C, and the incubation was over 20 min. Considering the heat sensitivity of raw milk, we lowered the incubation temperature and extended the incubation time.

The response in the GC-IMS 2D profile was generated as a fingerprint (Fig. 1) to ensure the characteristic peak areas of raw milk from different regions of China (Yao et al., 2022). Each dot represents a VOC. The brighter the color of the dot, the higher the concentration of the VOC. In fingerprints, the number means that the response did not match the spectral library (Li et al., 2021).

Some samples from the four regions were selected for fingerprinting. Ethyl trans-2-butenate was detected at low concentrations in the

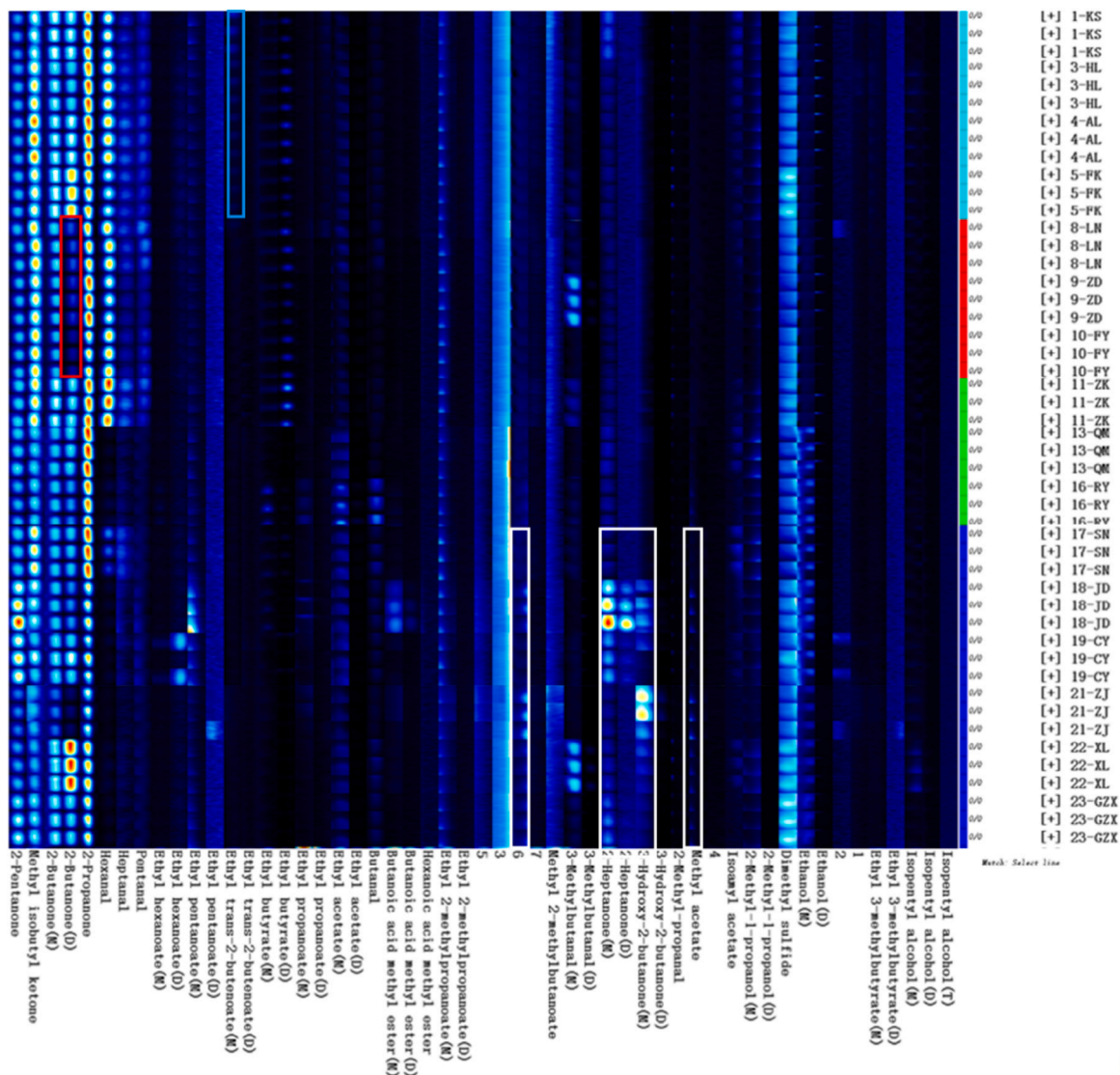


Fig. 1. Gallery plot of volatile flavors.

samples from Northeast and Inner Mongolia, while no marker was detected in other samples. Ethyl trans-2-butenate, which imparts a fruity and sweet aroma, is present in cashews, prunes, and sweet passion fruit (Garruti et al., 2003). The compound 2-butanone was present in low concentrations in the samples from group B. 2-Butanone is transferred from feed to raw milk (Valdivielso et al., 2016; Faulkner et al., 2018). The fingerprint profile showed that hexanal was present in raw milk from northern pastures, while it was very low or not detected in raw milk from southern pastures. Hexanal can be used as a marker to distinguish raw milk from different regions. Hexanal is produced from the degradation of oleic and linoleic acids. The high hexanal concentrations may be directly related to the high linoleic acid concentrations in raw milk (Kilcawley et al., 2018; Zheng et al., 2021). The separation between group C and the other groups was not obvious. The samples in group D were mainly from southern pastures. Methyl acetate, 2-heptanone, and 3-hydroxy-2-butanone were the characteristic VOCs identified by GC-IMS in group D. Acetoin (3-hydroxy-2-butanone) is an indicator of changes in raw milk during storage (Li et al., 2022). Acetoin, which is present in mature cheese, is odorless and easily oxidizes to diacetyl. Diacetyl imparts creamy aroma and sweetness (Nalepa et al., 2018; Teter et al., 2020). The accumulation of 3-hydroxy-2-butanone is associated with temperature changes and microbial metabolism (Yang et al., 2022). All cows are Holstein and raised indoors, so we excluded the influence of feeding method and cow breed. On this basis, the results of volatile compounds in raw milk showed that the southern and northern samples were clustered separately. So, Flavor differences in raw milk from southern and northern pastures may be attributed to the ambient temperature and humidity. Therefore, the GC-IMS results revealed that there are regional odor differences in raw milk. Most samples can be distinguished by the type and content of VOCs. Samples from southern and northern pastures were better differentiated, but the more accurate and detailed differentiation of raw milk from Inner Mongolia and Northeast pastures was not particularly good. We characterized and quantified VOCs by GC-MS and performed aroma and taste analyses using E-tongue and E-nose.

3.2. GC-MS analysis

We detected 42 VOCs by GC-MS, including 13 acids, 8 hydrocarbons, 7 alcohols, 5 aldehydes, 3 ketones, 3 esters, 1 nitrogenous compound, and 1 sulfur compound (Table 2). VOCs were identified by comparing their mass spectra with those in the NIST library, their retention time with those of standards, and their retention indices on DB-Wax column with those in the literature.

To assess the differences among samples more intuitively, one sample from each region was selected as a representative, and the VOC response under different retention times was presented on a total ion current diagram (Fig. 2). The outflows of sample 3-HL and sample 8-LN on the column were similar, but significantly different from those of sample 13-QM and sample 24-XH.

Based on the GC-MS results, more than 10 VOCs were detected in each sample, and most of them were acid compounds. Acid compounds are retained better on polar columns. The VOCs in raw milk were alcohols, acids, and esters. Aldehydes are formed from amino acid enzymolysis or lipid oxidation during fermentation and are rapidly oxidized to acids (Capuano et al., 2014; Bergamaschi et al., 2015; O'Callaghan et al., 2016). Therefore, only few aldehydes, such as hexanal and nonanal, were detected and at low concentrations. Aldehydes have low threshold. Therefore, even at low concentrations, aldehydes contribute to flavor, e.g., acetaldehyde imparts milky aroma and octanal and nonanal impart a green odor (Coppa et al., 2011; Faulkner et al., 2018; Magan et al., 2021).

We performed PLS-DA based on the qualitative and quantitative results. In Fig. 3, samples No. 2 and No. 14 were outliers, and the other samples could be separated. Group D (red) and the other three groups were completely separated. However, the distribution of group A

Table 2

VOCs detected in raw milk by GC-MS.

No.	RT	Compounds	CAS	RI (Cal.)	RI (Ref.)
1	9.572	p-Xylene	106-42-3	1078	1119
2	10.767	Dodecane	112-40-3	1150	1200
3	10.838	Undecane	1120-21-4	1154	1100
4	11.024	Pyridine	110-86-1	1166	1176
5	11.344	1-Decyne	764-93-2	1185	1221
6	11.665	Hexanoic acid ethyl ester	123-66-0	1206	1223
7	11.699	3-methyl-1-Butanol	123-51-3	1208	1185
8	11.979	1,3,5,7-Cyclooctatetraene	629-20-9	1227	1226
9	12.016	Styrene	100-42-5	1229	1241
10	12.287	1-ethyl-2-methyl- Benzene	611-14-3	1247	1249
11	12.564	Octanal	124-13-0	1266	1267
12	13.863	1-Hexanol	111-27-3	1355	1360
13	14.289	2-Nonanone	821-55-6	1385	1390
14	14.292	Nonanal	124-19-6	1385	1387
15	14.903	Octanoic acid ethyl ester	106-32-1	1431	1433
16	14.933	1-ethenyl-3-ethyl- Benzene	7525-62-4	1433	1424
17	15.217	Furfural	98-01-1	1455	1457
18	15.221	1-Heptanol	111-70-6	1455	1459
19	15.632	2-ethyl-1-Hexanol	104-76-7	1478	1484
20	16.658	5-methyl-2-Furancarboxaldehyde	620-02-0	1567	1567
21	16.783	4-Cyclopentene-1,3-dione	930-60-9	1576	1573
22	17.064	2-Undecanone	112-12-9	1598	1598
23	17.344	Butyrolactone	3068-88-0	1622	1623
24	17.344	Butanoic acid	5434-68-4	1622	1624
25	17.715	2-Furanmethanol	623-19-8	1654	1656
26	17.843	3-methyl-Butanoic acid	503-74-2	1664	1677
27	18.212	2-Propenamide	1432-45-7	1696	1943
28	19.812	Hexanoic acid	58454-07-2	1840	1841
29	20.352	Dimethyl sulfone	67-71-0	1891	1895
30	20.538	Phenylethyl Alcohol	60-12-8	1909	1914
31	20.946	Heptanoic acid	111-14-8	1948	1954
32	21.085	Maltol	118-71-8	1962	1965
33	22.02	Octanoic acid	124-07-2	2055	2051
34	23.036	Nonanoic acid	112-05-0	2158	2149
35	24.005	n-Decanoic acid	334-48-5	2261	2262
36	24.552	9-Decenoic acid	14436-32-9	2322	2335
37	25.569	Benzoic acid	117500-35-3	2441	2446
38	25.845	Dodecanoic acid	143-07-7	2473	2471
39	25.852	Undecanoic acid	112-37-8	2474	2421
40	25.906	5-Hydroxymethylfurfural	67-47-0	2480	2485
41	27.567	Tetradecanoic acid	544-63-8	2682	2685
42	29.759	n-Hexadecanoic acid	57-10-3	2895	2899

Note, RI (Cal.), Retention indices calculated on DB-WAX column against n-alkanes, RI (Ref.), Retention indices reported by <http://webbook.nist.gov/chemistry/cas-ser.html>, RT, retention time.

(green) and group B (purple) was close. In summary, the samples from the southern and northern regions could be separated. Samples from Northeast and North China had similar components, which were difficult to be completely distinguished and need to be evaluated in combination with the taste results. Eighteen variables were considered to contribute significantly (VIP > 1), including two aldehydes (nonanal and furfural), three alcohols (2-ethyl-1-hexanol, phenylethyl alcohol, and 3-methyl-1-butanol), seven hydrocarbons (dodecane, 1-decyne, 1,3,5,7-cyclooctatetraene, undecane, styrene, 2-undecanone, and 1-ethenyl-3-ethyl-benzene), five acids (3-methyl-butanoic acid, octanoic acid, hexanoic acid, butanoic acid, and 9-decenoic acid), and one heterocyclic compound (pyridine). Nonanal is a contributor to fatty flavor and a marker of lipid oxidation, with a low threshold and a high impact on flavor (Zhang et al., 2022). As a potential indicator that can assess the freshness of milk, pyridine is sensitive to temperature and time (Li et al., 2022). Studies have indicated that VOCs like 3-methyl-1-butanol and phenylethanol may be derived from the secondary metabolism of pasture plants and transferred to milk through the feed (Bovolenta et al., 2014; O'Callaghan et al., 2016). 3-Methylbutyric acid, octanoic acid,

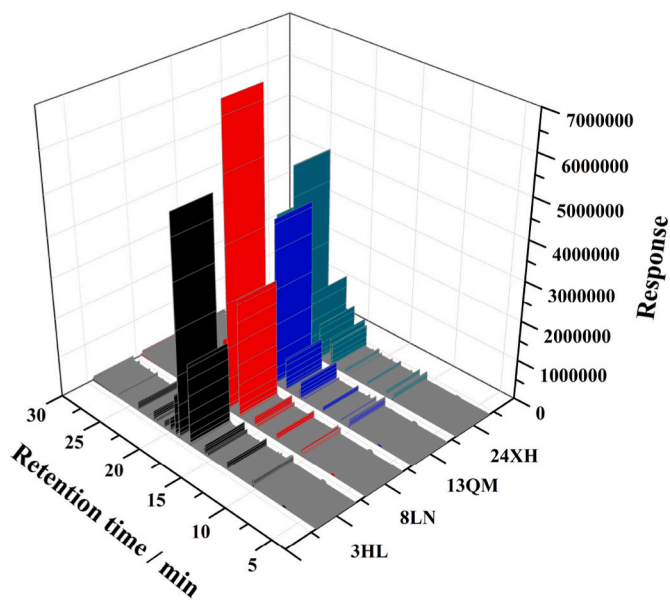


Fig. 2. Total ion current diagram of representative samples from four regions in China.

and butyric acid are volatile acids closely linked to seasonality and characteristic components of silage (Tornambe et al., 2006; Boltar et al., 2014). The results of the differentiation of compounds and the intelligent sensory analysis were consistent. In the subsequent results of electronic nose and electronic tongue, the overall trend is consistent with the results of GC-MS, and the difference between groups is obvious. But there is no regularity of raw milk flavor in the northern regions. Combined with the pasture information we obtained, the diet of two pastures in the northern region are the same, even though their geographical distance is far away, it is still difficult to distinguish. We speculated that the diet information leads to no significant differences in raw milk between the group A and the group B. Therefore, we speculate that environment and feed are the main reasons for the differences between raw milk from northern and southern farms.

3.3. E-nose analysis

The E-nose is widely used for aroma identification and

differentiation and can accurately provide the overall characteristics of VOCs (Lu et al., 2022). Studies have reported that the E-nose can distinguish different milk samples due to differences in VOCs, such as different processing conditions, storage time, and milk varieties (Labreche et al., 2005; Wang et al., 2010). During E-nose analysis, the response value of each sensor can be observed. In this study, raw milk samples from 24 pastures were detected by E-nose. All samples reached equilibrium within 90s–150 s.

The response curve shows that the first and highest response corresponded to the W5S sensor, followed by the W2S and W1S sensors, indicating that this is a specific response for raw milk samples (Fig. 4A). Nitrogen oxides, short chain alkanes, and alcohols are present in raw milk. The sensors that contributed the most to the differentiation of samples were W3S, W6S, and W5S, especially W3S and W6S. Even though their response values were not significant, the differences between the samples were obvious. Sensors W3S, W6S, and W5S played an important role in differentiating raw milk long-chain alkanes and compounds containing hydrogen from different regions of pastures in China.

Further correlation analysis was performed by combining the GC-MS results with the E-nose sensor response values (Fig. 4B). The W6S, W5S, and W3S sensors were the closest in distribution to the characteristic compounds (blue). The distribution of VOCs with VIP > 1 and sensors with larger contributions was consistent (Fig. 5), indicating a strong correlation between them. Overall, these results confirm the results from GC-MS.

3.4. E-tongue analysis

The distinguishing results and important taste characteristics are presented in Fig. 5. And it can be used to assess the strength and explanatory power of the differences in the accumulation of each metabolite on the categorical discrimination of each group of samples. VIP ≥ 1 is a common criterion for differential screening (Fig. 5A) (Gao et al., 2021; Y. Wang et al., 2022).

Sourness, bitterness, and freshness were the main differential taste characteristics in raw milk samples from different regions. These taste characteristics played a critical role in E-tongue analysis. The 2-D loadings plot (Fig. 5B) clearly depicts the results of taste clustering of raw milk from different pastures in China. Except for samples No. 2 and No. 20, which showed more obvious outliers, the other samples had significant clustering. Samples No. 1 through 10 were closer together, and samples No. 1 through 24 were clustered in one group.

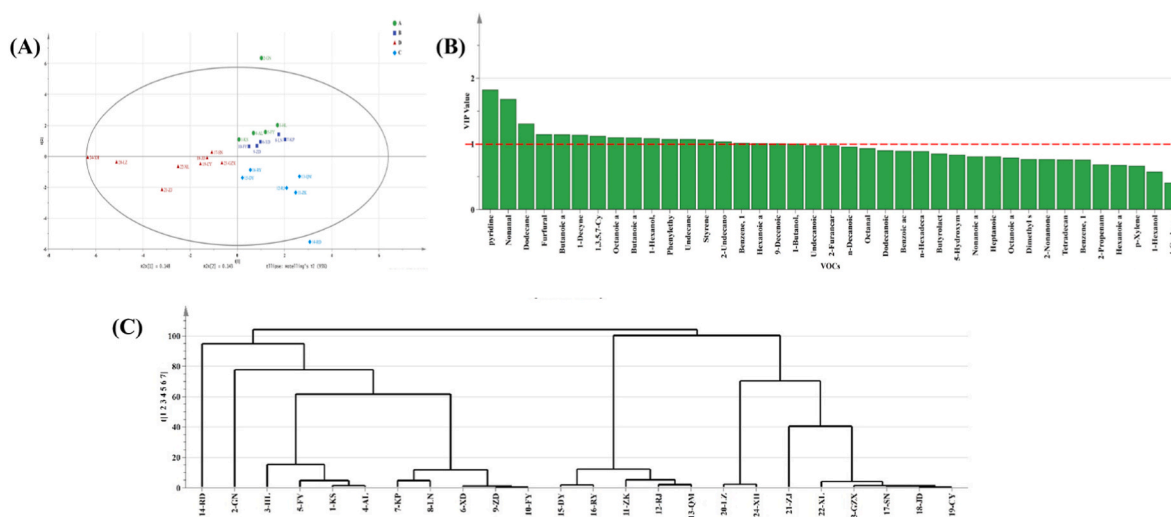


Fig. 3. Comparison of volatiles from different regions by HS-SPME/GC-MS. (A) PLS-DA score plot of volatiles in raw milk. (B) variable importance in the projection (VIP) scores in PLS-DA. (C) Cluster Analysis based on PLS-DA.

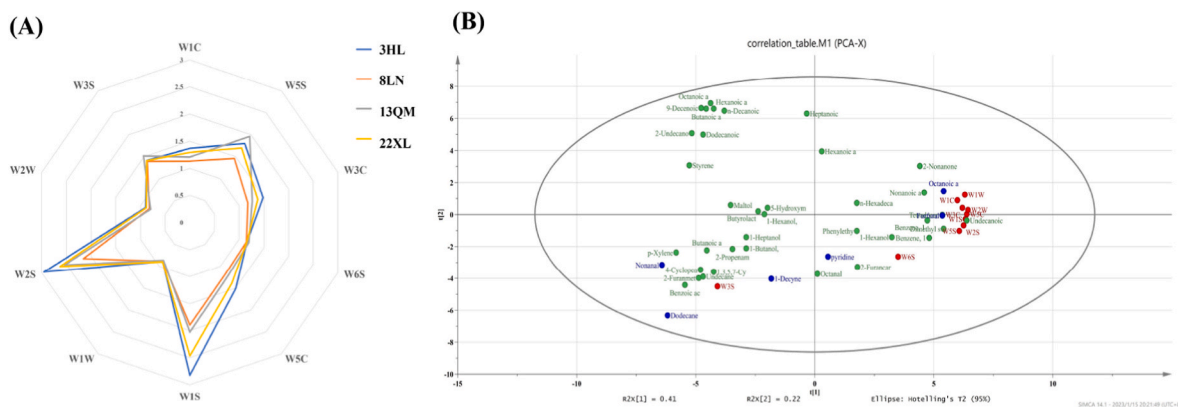


Fig. 4. (A) Radar chart of electronic nose sensors. (B) Correlation of Volatile organic compounds and electronic-nose sensors.

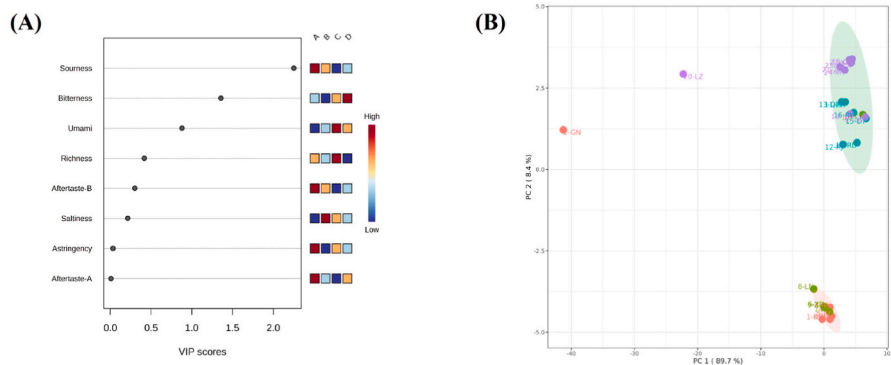


Fig. 5. Results of e-tongue analysis of 24 raw milk samples. (A) VIP-score from PLS-DA. (B) PCA score plot from PLS-DA.

Unfortunately, the raw milk samples from groups A, B, C, and D could not be completely separated. However, the differences in taste between the raw milk samples from the southern and northern regions were obvious. In combination with the VIP scores, raw milk from the northern farms had more sourness, while the raw milk from the southern farms showed more pronounced bitterness and umami (Fig. 5A).

Clustering algorithm using Ward. D. The heat map analysis shows the performance of raw milk from different regions in terms of taste characteristics (Fig. 6). Samples from group D (blue) were clustered and were mainly sour and bitter. Sample 2 is an outlier. Dark blue represents group C samples. Samples 17 and 18 from group D had similar taste characteristics, which we speculate is probably due to their geographical proximity to samples 15 and 16. Group C samples were distinguished from other groups by their astringent and bitter aftertaste. Group A samples (red) and group B samples (green) could not be separated, but they were well separated from the other two groups. When distinguishing 24 raw milk samples from these different regions, it seems

that taste is more important than smell.

4. Conclusion

We identified volatile aroma and taste compounds from 24 large and medium-sized pastures of China using chromatography and bionic instruments. Instead of human sensory evaluation, the characteristics of raw milk taste and aroma in different regions of China detected by electronic nose and electronic tongue. The discrimination effect of the E-nose was consistent with the VOCs. The W6S and W3S sensors played a major role. The E-tongue results revealed that saltiness and richness (aftertaste-umami) were most prominent in Northern China, while umami and astringency were predominant in Southern China. Pyridine, nonanal, dodecane, furfural, 1-decyne, octanoic acid, and 1,3,5,7-cyclooctetraene were the differential compounds between the north and south samples. Therefore, these compounds could be used as markers to ensure the origin of raw milk. Future studies should evaluate the

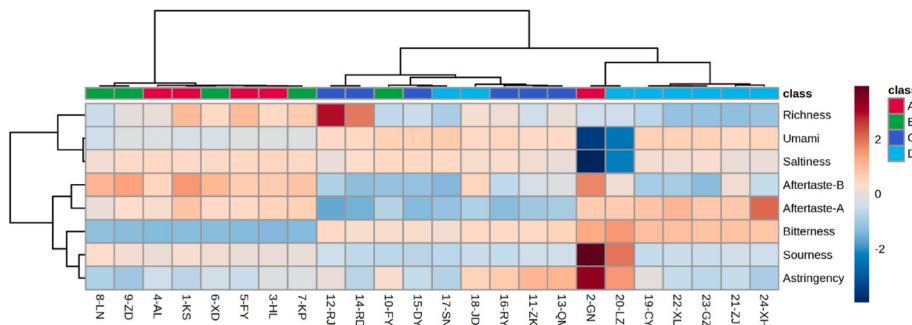


Fig. 6. Heatmap of volatile flavors base on electronic tongue.

mechanism for the variations in flavor accumulation in different geographical locations.

CRedit authorship contribution statement

Xuelu Chi: Conceptualization, Methodology, Data curation, Visualization, Formal analysis, Writing – original draft. **Yangdong Zhang:** Visualization, Writing – review & editing. **Nan Zheng:** Writing – review & editing. **Jiaqi Wang:** Funding acquisition, Project administration, Writing – review & editing. **Huimin Liu:** Formal analysis, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgments

This research was supported by National Key R&D Program of China (2022YFD1301003, 2022YFD1301004), the earmarked fund for CARS (CARS-36), the Agricultural Science and Technology Innovation Program (ASTIP-IAS12), the Xinjiang Tianshan Innovation Team (2022D14016), and the Xinjiang science and technology projects (2022A02006-3-1).

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