

Determination of VOCs Release Behaviour of Smoked Bamboo at Different Temperatures by TD-GC-MS

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Abstract—This research aimed at analysing the chemical composition of volatile organic compounds (VOCs) in smoked bamboo at different temperatures to evaluate its environmental performance in the process of storage, drying and processing. The VOCs were identified by the method of TD-GC-MS at temperature of 40°C, 180°C and 300°C. The results show that 21 VOCs can be identified at 40°C mainly including Acetic acid(22.15%), 1,1,1,5,7,7,7-heptamethyl-3,3-bis(trimethylsiloxy)tetrasiloxane(16.03%), 1h-indole-2-carboxylic acid,6-(4-ethoxyphenyl)-3-methyl-4-oxo-4,5,6,7-tetrahydro-, isopropyl ester(13.35%) and Cyclooctasiloxane, hexadecamethyl- (11.30%), etc., 42 VOCs can be identified at 180°C especially including Acetic acid(39.61%), and 24 VOCs were identified at 300°C mainly including Hydrazine, ethyl-(23.24%), 2(3H)-Furanone, dihydro-4-hydroxy-(13.76%), Phenol, 2,6-dimethoxy-(10.96%) and Benzaldehyde, 2-methyl-(10.28%),etc., which suggested VOCs emitted from smoked bamboo would not pollute air and harm human health but some of which were biomedicine components so as to have good environmental performance.

Index Terms—Smoked bamboo, VOCs, TD-GC-MS, Chemical composition, Different temperatures, Data fitting, Environmental performance

1 INTRODUCTION

Bamboo is one of the world-famous fast growing plants. Currently, bamboo is mainly distributed in Asia, Africa and other places. China, India, Japan, Myanmar and other countries have a lot of bamboo planting plantation and the plantation area is up to 20 million hectares with an annual output of 18 million tons of bamboo. In our country, the amount of the counties (cities) with the bamboo forest areas of 10,000 hectares are more than 130 and 7 million hectare areas are mostly dominated by Moso bamboo [1]. Bamboo is commonly used as a food source, and also used to make a variety of household goods such as furniture, dinnerware, sporting goods, jewellery and handbags [2]. However, bamboo has the defects of easily mildewing and rotting which direct to affect the service life of bamboo products. The existing body of literature suggests that scholars have studied in a large amount on overcoming the defects. Bamboo is treated in the atmosphere of shibakusa smoke at the temperature of 150°C-170°C to become a modified bamboo called smoked bamboo. The new bamboo material has wonderful economic nature such as anti-moulds, insect-resistant, non-warping, non-fissile, good mechanical properties and excellent weather stand-ability compared with common bamboo [3]. So smoked bamboo has intensively potential applied in the fields of furniture, decoration and building, etc. On the other hand, with the rapid development of people's living standard, the demand on living environment is also growing increasingly. Indoor environmental contamination is becoming more and more serious in recent years [4]. Most indoor air pollution comes from wood products inside the building which may emit volatile organic compounds (VOCs) [5], and the outdoor air that enters

the building can also be the main source of indoor air VOC pollution [6]. Therefore, It is necessary to determinate the chemical components of volatile organic compounds in smoked bamboo at different temperatures to assess its environmental performance in order to meet different operating requirements. In this research, thermal desorption-gas chromatography-mass spectrometry (TD-GC-MS) method was evaluated for the analysis of liquid-phase volatile organic compounds emitting from smoked bamboo in the process of storage, drying and processing to evaluate its environmental performance at different environmental temperatures, which will provide a scientific basis for the widely application of smoked bamboo.

2 MATERIALS AND METHODS

2.1 Samples preparation

A 5-year-old Moso bamboo, obtained from the Executive Forest Farm, Jiangxi province, P. R. China in September 2012, was modified in the atmosphere of shibakusa smoke at the temperature of 150°C-170°C to turn into the smoked bamboo. Then the samples of smoked bamboo were processed into 200 mesh powder and stored in a dark place for analysis.

2.2 Thermal desorption-gas chromatography-mass spectrometry (TD-GC-MS)

Extraction of VOCs was carried out with the help of Master TD thermal desorption device made by DANI Co., Ltd, Italy. 9g powder samples were separated into three parts (3g of each) and placed in the sample tubes of thermal desorption device which ejected by the carrier gas of helium (99.999%) at the temperature of 40°C, 180°C and 300°C for 20 minutes with the trap adsorption temperature of 0°C, the trap resolution temperature of 350°C, valve temperature of 320°C, and the transfer line temperature of 330°C, respectively. Then the obtained

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VOCs were instantly desorbed thermally in an online linked injector of gas chromatography and analysed using the GC-MS technique. GC-MS analysis was performed in an Agilent 6890 A gas chromatograph (Agilent Technologies, Santa Clara, CA, USA) and Agilent 5973 N mass spectrometer (Agilent Technologies). The GC device was equipped with HP-5MS column (5% phenylmethylsiloxane) size 30m×0.25mm×0.25µm film thickness. The carrier gas was helium (99.999%) at a constant flow rate of 1.3 ml/min. The temperature program was as follows: initial temperature 400°C held for 3 min, from 40°C to 180°C at 10°C/min, from 180°C to 300 °C at 20 °C/min, and final temperature holding for 5 min. The ion source was operated in the electron ionisation mode (EI; 70 eV). Full scan mode data were acquired to determine appropriate masses for the later acquisition in selected ion monitoring mode (SIM), under the conditions of mass range from 10 to 200 amu with the scan rate of 0.2 s/scan.

The identification of the VOCs was based on computer matching with the reference mass spectra of the Wiley7, Mainlib and NIST05 libraries by comparing their retention times.

3 RESULTS AND DISCUSSION

The total ion chromatogram of VOCs in smoked bamboo at the temperature of 40°C, 180°C and 300°C was shown in Figure 1, Figure 2 and Figure 3, respectively. The mass fractions of all compounds were calculated with the area normalization method. So the Chemical compositions of VOCs were shown in Table 1, Table 2 and Table 3 according to the MS data in Figure 1, Figure 2 and Figure 3, respectively.

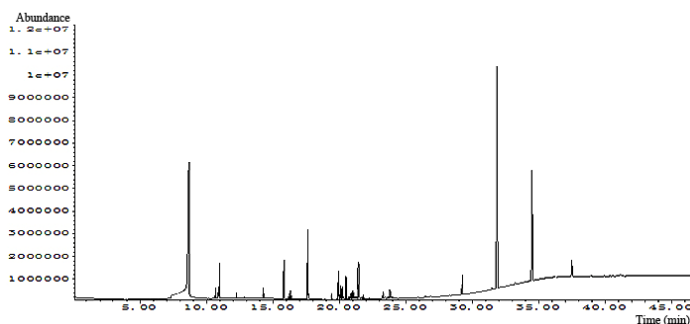


Fig. 1. The total ion chromatogram of VOCs in smoked bamboo at the temperature of 40°C

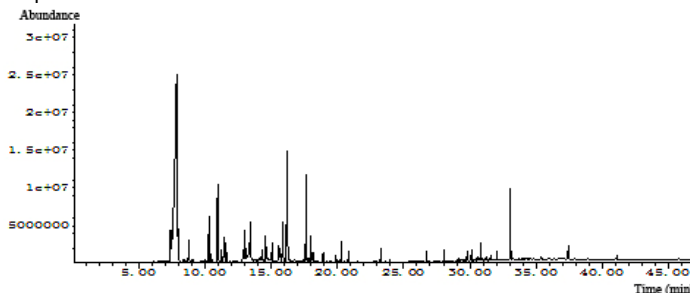


Fig. 2. The total ion chromatogram of VOCs in smoked bamboo at the temperature of 180°C

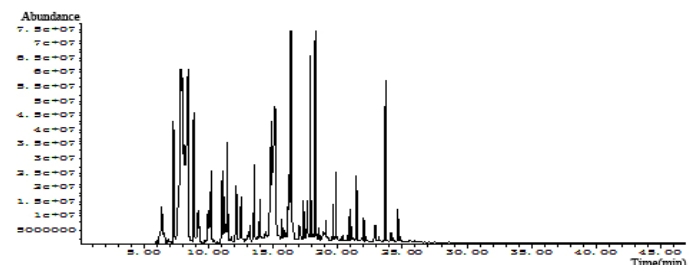


Fig. 3. The total ion chromatogram of VOCs in smoked bamboo at the temperature of 300°C

TABLE 1

THE ANALYTICAL RESULTS OF VOCs IN SMOKED BAMBOO AT THE TEMPERATURE OF 40°C

PK	RT	% of total	Identified component	Qual
1	8.563	22.15	Acetic acid	99
2	10.567	0.91	2-Ethoxypropane	96
3	10.953	1.92	Furfural	95
4	12.263	0.76	Cyclohexasiloxane, dodecamethyl-	91
5	14.322	0.92	Cyclohexasiloxane, dodecamethyl-	98
6	15.863	2.65	Bicyclo[2.2.1]heptan-2-one, 1,7,7- trimethyl-, (1S)-	96
7	17.360	0.91	3-Cyclohexene-1-methanol, .alpha.alpha.4-trimethyl-	97
8	17.592	4.23	1,3-Benzodioxole, 5-(2-propenyl)-	96
9	19.523	0.42	Copaene	79
10	19.935	3.62	Tricyclo[2.2.1.0(2,6)]heptane, 1,7-dimethyl-7-(4-methyl-3-pentenyl)-,(-)-	98
11	20.623	1.32	Bicyclo[2.2.1]heptane, 2-methyl-3- methylene-2-(4-methyl-3-pentenyl)- , (1S-exo)-	96
12	21.103	1.45	Cyclohexene, 1-methyl-4-(5-methyl-1-methylene-4-hexenyl)-, (S)-	94
13	21.536	2.85	Naphthalene,1,2,3,5,6,8a-hexahydro-4,7-dimethyl-1-(1-methylethyl)-, (1S-cis)-	92
14	23.461	0.86	Cedrol	94
15	23.903	1.22	Bicyclo[4.4.0]dec-1-ene,2-isoprop yl-5-methyl-9-methylene-	93
16	26.523	0.13	Octasiloxane,1,1,3,3,5,5,7,7,9,9, 11,11,13,13,15,15-hexadecamethyl-	86

17	29.125	0.35	Eicosamethylcyclodecasiloxane	94
18	31.521	1.36	Silane,trimethyl[5-methyl-2-(1-methyl-ethyl)phenoxy]-	96
19	31.560	11.30	Cyclooctasiloxane, hexadecamethyl-	86
20	34.492	16.03	1,1,1,5,7,7,7-Heptamethyl-3,3-bis(trimethylsiloxy)tetrasiloxane	99
21	37.486	13.35	1H-Indole-2-carboxylic acid,6-(4-ethoxyphenyl)-3-methyl-4-oxo-4,5,6,7-tetrahydro-,isopropyl ester	69
22	38.952	3.64	Cyclotrisiloxane, hexamethyl-	85
23	41.095	0.62	Cyclotrisiloxane, hexamethyl-	74

PK=Peak, RT=Retention time (min), Qual= Reference Quality

TABLE 2
THE ANALYTICAL RESULTS OF VOCs IN SMOKED BAMBOO AT THE TEMPERATURE OF 180°C

PK	RT	% of total	Identified component	Qual
1	6.533	0.56	Benzeneethanamine, N-methyl-	76
2	7.864	39.61	Acetic acid	99
3	8.425	1.23	1,3-Butanediol, (S)-	86
4	9.865	0.86	1,2-Propanediol, 3-methoxy-	89
5	10.362	1.75	2,3-Butanediol	96
6	10.869	3.02	Furfural	98
7	11.369	2.63	Methyltartronic acid	85
8	13.520	6.85	3(5)-[[1,2-Dihydroxy-3-propoxy]methyl]-4-hydroxy-1H-pyrazole-5(3)-carboxamide	85
9	14.421	1.63	Eucalyptol	98
10	14.692	1.95	2(1H)-Pyridinone	96
11	15.123	0.98	Pyrimidine-4,6-diol, 5-methyl-	79
12	15.632	2.03	Phenol, 4-ethyl-	91
13	15.903	1.92	Bicyclo[2.2.1]heptan-2-one, 1,7,7-trimethyl-, (1R)-	97
14	16.065	7.40	Benzofuran, 2,3-dihydro-	65
15	16.750	0.68	Hydroquinone	86
16	17.526	4.03	1,3-Benzodioxole, 5-(2-propenyl)-	98
17	17.989	2.36	Benzaldehyde, 4-hydroxy-	96
18	19.012	0.81	Vanillin	95
19	19.635	0.23	Tricyclo[2.2.1.0(2,6)]heptane, 1,7-dimethyl-7-(4-methyl-3-pentenyl)-, (-)-	99
20	20.156	0.30	Naphthalene,1,2,3,5,6,7,8,8a-octahydro-1,8a-dimethyl-7-(1-methylethenyl)-,[1R-(1.alpha.,7.beta.,8a.alpha.)]-	93
21	20.506	0.07	Bicyclo[2.2.1]heptane,2-methyl-3-methylene-2-(4-methyl-3-pentenyl)-, (1S-endo)-	86
22	20.756	0.35	Cycloheptasiloxane, tetradecamethyl-	90
23	21.623	0.36	3,4-Dimethoxy-6-methylpyrocatechol	78
24	23.641	0.56	Benzaldehyde, 4-hydroxy-3,5-dimethoxy-	95
25	23.768	0.62	Cedrol	91
26	23.984	0.63	6-(3,5-Dimethyl-1H-pyrazol-1-yl)-N-benzyl-1,2,4,5-tetrazine-3-amine	87
27	25.778	0.23	1-[1-[2-Pyridyl]ethyl]hydrazinethiocarboxamide	70
28	26.201	0.30	Phenanthrene	96
29	27.703	0.16	Methanol, [4-(1,1-dimethylethyl)phenoxy]-, acetate	82
30	29.503	0.56	5-Amino-4-nitrozo-2-phenyl(2H)benzotriazole	89
31	30.201	0.78	1H-Naphtho[2,1-b]pyran,3-ethenyldodecahydro-3,4a,7,7,10a-pentamethyl-, [3R-(3.alpha.,4a.beta.,6a.alpha.,10a.beta.,10b.alpha.)]-	91
32	30.691	1.25	5-Acetamido-4,7-dioxo-4,7-dihydrobenzofurazan	76
33	31.654	0.95	Perylene, eicosahydro-	86
34	32.078	0.34	Fluoranthene	83
35	33.560	3.56	1-Phenanthrenecarboxaldehyde,7-ethenyl-1,2,3,4,4a,4b,5,6,7,9,10,10a-dodecahydro-1,4a,7-trimethyl-, [1R-(1.alpha.,4a.beta.,4b.alpha.,7.beta.,10a.alpha.)]-	80
36	34.021	0.82	1H-Indole, 1-methyl-2-phenyl-	91
37	34.512	0.68	1H-Indole-2-carboxylic acid,6-(4-ethoxyphenyl)-3-methyl-4-oxo-4,5,6,7-tetrahydro-, isopropyl ester	80

38	34.902	0.80	Cyclotrisiloxane, hexamethyl-	86
39	35.641	0.59	1-Phenanthrenecarboxylic acid, 1,2,3,4,4a,9,10,10a-octahydro-1,4a-di methyl-7-(1-methylethyl)-, methyl ester, [1R-(1.alpha.,4a.beta.,10a.alpha.)]-	92
40	36.614	0.85	Cyclotrisiloxane, hexamethyl-	84
41	37.896	0.91	Cyclononasiloxane, octadecamethyl-	99
42	42.021	0.24	Octasiloxane, 1,1,3,3,5,5,7,7,9,9, 11,11,13,13,15,15-hexadecamethyl-	83

PK=Peak, RT=Retention time (min), Qual= Reference Quality

TABLE 3
THE ANALYTICAL RESULTS OF VOCs IN SMOKED BAMBOO AT THE TEMPERATURE OF 300°C

PK	RT	% of total	Identified component	Qual
1	6.532	2.63	Hydrazinecarboxylic acid, ethyl ester	89
2	7.362	2.48	Formic acid	86
3	7.902	23.24	Hydrazine, ethyl-	99
4	8.913	3.82	2-Propanone, 1-hydroxy-	95
5	10.213	2.95	1-Hydroxy-2-butanone	86
6	11.068	4.23	Furfural	94
7	12.302	3.65	2H-Pyran, 3,4-dihydro-	78
8	13.562	2.98	2-Methyliminoperhydro-1,3-oxazine	63
9	15.362	13.76	2(3H)-Furanone, dihydro-4-hydroxy-	95
10	16.356	10.28	Benzaldehyde, 2-methyl-	96
11	18.654	10.96	Phenol, 2,6-dimethoxy-	96
12	19.856	1.65	Benzaldehyde, 3-hydroxy-4-methoxy-	98
13	19.903	1.95	Phenol, 2-methoxy-4-(1-propenyl)-, (E)-	96
14	20.403	0.63	Ethanone, 1-(4-hydroxy-3-methoxyphenyl)-	95
15	20.995	1.56	2-Propanone, 1-(4-hydroxy-3-methoxyphenyl)-	86
16	21.506	2.17	2,3,5,6-Tetrafluoroanisole	83
17	22.910	1.23	Benzaldehyde, 4-hydroxy-3,5-dimethoxy-	96
18	23.905	2.62	Phenol, 2,6-dimethoxy-4-(2-propenyl)-	91
19	25.034	1.62	Ethanone,1-(4-hydroxy-3,5-dimethoxyphenyl)-	97
20	25.603	0.85	2-Heptanone, 6-(3-acetyl-1-cyclopropen-1-yl)-3-hydroxy-6-methyl-, (R*,R*)-	75
21	27.410	0.26	Benzofuran-2-one, 2,3-dihydro-3,3-dimethyl-4-nitro-	91
22	28.562	0.65	2-Butenenitrile, 2-chloro-3-(4-methoxyphenyl)-	84
23	30.605	0.20	Octasiloxane, 1,1,3,3,5,5,7,7,9,9, 11,11,13,13,15,15-hexadecamethyl-	91
24	32.625	0.64	Silane, 1,4-phenylenebis(trimethyl	90

PK=Peak, RT=Retention time (min), Qual= Reference Quality

According to the results in Table 1, 21 VOCs were detected which account for 92.97% of the total peak areas with the reference quality>69. The main compounds can be grouped as follows: Acetic acid(22.15%), 1,1,1,5,7,7,7-heptamethyl-3,3-bis(trimethylsiloxy)tetrasiloxane(16.03%), 1h-indole-2-carboxylic acid,6-(4-ethoxyphenyl)-3-methyl-4-oxo-4,5,6,7-tetrahydro-, isopropyl ester(13.35%), Cyclooctasiloxane, hexadecamethyl- (11.30%), Cyclotrisiloxane, hexamethyl-(4.26%), 1,3-benzodioxole, 5-(2-propenyl)- (4.23%), Tricyclo[2.2.1.0(2,6)]heptane, 1,7-dimethyl-7-(4-methyl-3-pentenyl)-,(-) (3.62%), naphthalene,1,2,3,5,6,8a-hexahydro-4,7-dimethyl-1-(1-methylethyl)-, (1s-cis)- (2.85%), bicyclo[2.2.1]heptan-2-one, 1,7,7- trimethyl-, (1s)- (2.65%), furfural(1.92%), cyclohexasiloxane, dodecamethyl-(1.68%), cyclohexene, 1-methyl-4-(5-methyl-1-methylene-4-hexenyl)-, (s)- (1.45%), silane,trimethyl[5-methyl-2-(1-methylethyl)phenoxy]- (1.36%), bicyclo[2.2.1]heptane, 2-methyl-3-methylene-2-(4-methyl-3-

pentenyl)-, (1s-exo)- (1.32%) and bicyclo[4.4.0]dec-1-ene,2-isopropyl-5-methyl-9-methylene-(1.22%), etc.

According to the results in Table 2, 42 VOCs were detected which account for 96.44% of the total peak areas with the reference quality>65. The main compounds can be grouped as follows: Acetic acid(39.61%), Benzofuran, 2,3-dihydro-(7.40%), 3(5)-[[1,2-Dihydroxy-3-propoxy]methyl]-4-hydroxy-1H-pyrazole-5(3)-carboxamide(6.85%), 1,3-Benzodioxole, 5-(2-propenyl)-(4.03%), 1-Phenanthrenecarboxaldehyde,7-ethenyl-1,2,3,4,4a,4b,5,6,7,9,10,10a-dodecahydro-1,4a,7-trimethyl-, [1R-(1.alpha.,4a.beta.,4b.alpha.,7.b eta.,10a.alpha.)]- (3.56%), Furfural(3.02%), Methyltartronic acid(2.63), Benzaldehyde, 4-hydroxy-(2.36%), Phenol, 4-ethyl-(2.03%), 2(1H)-Pyridinone(1.95%), Bicyclo[2.2.1]heptan-2-one, 1,7,7- trimethyl-, (1R)-(1.92%), 2,3-Butanediol(1.75%), Eucalyptol(1.63%), 5-Acetamido-4,7-dioxo-4,7-dihydrobenzofurazan(1.25%) and 1,3-Butanediol(1.23%), etc.

According to the results in Table 3, 24 VOCs were detected

which account for 97.01% of the total peak areas with the reference quality>75. The main compounds can be grouped as follows: Hydrazine, ethyl-(23.24%), 2(3H)-Furanone, dihydro-4-hydroxy-(13.76%), Phenol, 2,6-dimethoxy-(10.96%), Benzaldehyde, 2-methyl-(10.28%), Furfural(4.23%), 2-Propanone, 1-hydroxy-(3.82%), 2H-Pyran, 3,4-dihydro-(3.65%), 2-Methyliminoperhydro-1,3-oxazine(2.98%), 1-Hydroxy-2-butanone(2.95%), Hydrazinecarboxylic acid, ethyl ester(2.63%), Phenol, 2,6-dimethoxy-4-(2-propenyl)-(2.62%), Formic acid(2.48%), 2,3,5,6-Tetrafluoroanisole(2.17%), Phenol, 2-methoxy-4-(1-propenyl)-, (E)-(1.95%), Benzaldehyde, 3-hydroxy-4-methoxy-(1.65%), Ethanone,1-(4-hydroxy-3,5-dimethoxyphenyl)-(1.62%), 2-Propanone, 1-(4-hydroxy-3-methoxyphenyl)-(1.56%) and Benzaldehyde, 4-hydroxy-3,5-dimethoxy-(1.23%), etc.

The above results of analysis showed that the VOCs emitted from smoked bamboo would not cause air pollution and harm human health in the process of storage, drying and processing with different environmental temperatures. While some biomedicine components identified in the volatile organic compounds of smoked bamboo, which showed that the smoked bamboo biomaterial could release some biomedicines to have bio-health function. So Smoked bamboo is a kind of biomass materials with safety and environmental protection which can be widely used for green Furniture, building and other decorative products.

4 CONCLUSION

In this paper, the VOCs release behaviour of smoked bamboo was explored at different temperatures by TD-GC-MS. Our results shown that 21 VOCs can be identified occupying 92.97% of the total peak areas with the reference quality>69 at 40°C mainly including Acetic acid(22.15%), 1,1,1,5,7,7,7-heptamethyl-3,3-bis(trimethylsiloxy)tetrasiloxane(16.03%), 1h-indole-2-carboxylic acid,6-(4-ethoxyphenyl)-3-methyl-4-oxo-4,5,6,7-tetrahydro-, isopropyl ester(13.35%) and Cyclooctasiloxane, hexadecamethyl- (11.30%), etc., 42 VOCs can be identified occupying 96.44% of the total peak areas with the reference quality>65 at 180°C especially including Acetic acid(39.61%), and 24 VOCs were identified occupying 97.01% of the total peak areas with the reference quality>75 at 300°C mainly including Hydrazine, ethyl-(23.24%), 2(3H)-Furanone, dihydro-4-hydroxy-(13.76%), Phenol, 2,6-dimethoxy-(10.96%) and Benzaldehyde, 2-methyl-(10.28%),etc. This research suggests that the VOCs emitted from smoked bamboo not cause air pollution and harm human health and some of which are biomedicine components. Therefore, smoked bamboo is the better choice to make green products.

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