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Comprehensive two-dimensional gas chromatography with time-of-flight mass spectrometry for the screening of potent swampy/septic odor-causing compounds in two drinking water sources in China

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Odor problems in drinking water, particularly swampy/septic odors, are normally triggered by a set of organic compounds with odor threshold concentrations (OTC) ranging from ng L^{-1} to $\mu\text{g L}^{-1}$. With such a low level of OTC, it has long been a challenge to effectively determine the odor-causing compounds in highly complex samples. The Huangpu and Huai rivers, as source waters in south China, have exhibited continuous swampy/septic odor over the entire year, yet the corresponding odor-causing compounds remain unclear. In order to screen the odor-causing compounds in these two rivers, a method to simultaneously determine fifty-four frequently encountered compounds with categories of thioethers, aldehydes, pyrazines, benzenes and phenols, has been developed using comprehensive two-dimensional gas chromatography with time-of-flight mass spectrometry (GC $\times$ GC-TOFMS) based on liquid–liquid extraction. The results indicated that this method could allow the analysis of different categories of compounds without derivatization at considerably higher sensitivities. Four thioether compounds, including dimethyl disulfide, diethyl disulfide, propyl sulfide, and amyl sulfide, and one ether compound (bis(2-chloroisopropyl) ether) were at least detected in one of the source waters with a concentration higher than their OTC value, suggesting that these compounds might be the main compounds causing the swampy/septic odor. At the same time, other compounds, including pyrazine, pyridine, 2-methyl-phenol, 2-nitro-phenol, and 2,6-dimethyl-phenol, were detected with a concentration lower than their respective OTC value. The contribution of these compounds to the swampy/septic odor requires further evaluation.

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1. Introduction

Odor problems in drinking water, which can impair the aesthetic aspects of water quality, have long been a major issue for both water suppliers and consumers.^{1,2} A wide range of compounds with different structural features, including algal metabolites and industrial pollutants, can cause odor problems in drinking water.³ An investigation of 111 waterworks in major cities across China showed that 80% of source water samples exhibited some type of odor problem with musty/earthy and swampy/septic odors being the two major odor types.⁴

In comparison to musty/earthy odors, which are usually triggered by a single compound, such as the algal metabolites, including 2-methylisoborneol (MIB) and geosmin,⁵ swampy/septic odors are considerably more complicated. A wide range of compounds, such as thioethers,⁶ thiols,⁷ pyrazines,⁸ pyridines,⁹ phenols,¹⁰ indoles,¹¹ have been reported to cause swampy/septic or similar odors even at a concentration of ng L^{-1} . These types of odor-causing compounds could be formed by different biological processes, including both aerobic and anaerobic conditions,² or could be associated with polluted source waters.¹² It is thus desirable to effectively establish an effective method, with high sensitivity and resolution, for the simultaneous detection of different odor-causing compounds in highly complex samples.

Gas chromatography with mass spectrometry (GC-MS) or gas chromatography with flame photometric detection (GC-FPD) have both been widely used for the determination of some typical odor compounds, including musty/earthy odor compounds, such as MIB and geosmin,¹³ and swampy/septic or

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Table 1 Information on the fifty-four odor compounds^a

No.	Category	Compounds	Odor description	OTC ^a (μg L ⁻¹)	CAS	References
1	Aldehydes	Hexanal	Herbal flavor, almond	4.5 ^d	66-25-1	23
2		Heptanal	Fishy	3.0 ^d	111-71-7	7
3		Benzaldehyde	Herbal flavor	4.5 ^d	100-52-7	7
4		2,4-Heptadienal	Fishy/oily	5.0 ^d	4313-03-5	24
5		2-Octenal	Irritant	n.a. ^b	2548-87-0	7
6		Nonanal	Fruity, fragrance	n.a.	124-19-6	25
7		2,6-Nonadienal	Herbal flavor/cucumber	0.08 ^d	17587-33-6	26
8		Decanal	Orange flavor	n.a.	112-31-2	7
9		2,4-Decadienal	Oily	0.029 ^c	2363-88-4	24
10	Benzenes	2,6,6-Trimethyl-1-cyclohexene-1-carboxaldehyde	Sweet, fragrance	n.a.	432-25-7	27
11		Ethylbenzene	Plastic, oily, chemical	150.0 ^d	100-41-4	8
12		<i>p</i> -Xylene	Chemical	n.a.	106-42-3	7 and 8
13		1,4-Dichloro-benzene	Almond, sweet	4.5 ^d	106-46-7	8
14	Ethers	1,3,5-Trichloro-2-methoxy-benzene	Musty	0.002 ^d	108-70-3	28
15		Bis(2-chloroisopropyl) ether	Medicinal odor	0.017 ^c	39638-32-9	29
16	Esters	Butanoic acid, propyl ester	Alcohol	n.a.	105-66-8	30
17	Indoles	Indole	Stinky	0.1 ^d	120-72-9	31
18		3-Methyl-indole	Stinky	1.0 ^d	83-34-1	11 and 31
19	Ketones	Ionone	Fragrance	0.007 ^d	8013-90-9	32 and 62
20	Pyrazines	Tetramethyl pyrazine	Sour, fragrance	2.6 ^c	1124-11-4	33
21		Pyrazine	Fragrance	2.7 ^c	290-37-9	33
22		2-Methoxy-3-(2-methylethyl)-pyrazine/IPMP	Musty	0.0002 ^d	25773-40-4	8
23	Pyridines	2-Methoxy-3-(2-methylpropyl)-pyrazine/IBMP	Musty	0.001 ^d	24683-00-9	8
24		Pyridine	Amine, stinky	1.1 ^c	110-86-1	9 and 34
25	Phenols	2-Methyl-phenol	Medicinal odor	14.7 ^c	95-48-7	10
26		4-Bromo-phenol	Medicinal odor	n.a.	106-41-2	35
27		3-Methyl-phenol	Medicinal odor	12.8 ^c	108-39-4	10
28		2-Nitro-phenol	Medicinal odor	11.0 ^c	88-75-5	10
29		2,6-Dimethyl-phenol	Medicinal odor, musty	11.0 ^c	576-26-1	10
30		2-Chloro-phenol	Chemical, musty, floral	0.088 ^d	95-57-8	8 and 10
31	Thioethers	Dimethyl sulfide	Rotten cabbage	1.0 ^d	75-18-3	12
32		Diethyl sulfide	Swampy, septic	n.a.	352-93-2	7
33		Dimethyl disulfide	Swampy, septic	0.03 ^c	624-92-0	12 and 32
34		Diisopropyl sulfide	Swampy, septic	n.a.	625-80-9	36
35		Propyl sulfide	Swampy, septic	0.0019 ^c	111-47-7	37
36		Diethyl disulfide	Swampy, septic	0.02 ^c	110-81-6	7
37		Dimethyl trisulfide	Swampy, septic	0.01 ^d	3658-80-8	32 and 37
38		Butyl sulfide	Swampy, septic	0.00189 ^c	544-40-1	38
39		Dipropyl disulfide	Swampy, septic	n.a.	629-19-6	7
40		Amyl sulfide	Swampy, septic	0.0011 ^c	872-10-6	6
41		Dibutyl disulfide	Swampy, septic	n.a.	629-45-8	6
42		Dipentyl disulfide	Swampy, septic	n.a.	112-51-6	6
43	Thiols	Benzyl disulfide	Foul smell	n.a.	150-60-7	6
44		1-Pentanethiol	Rancid, stinky	n.a.	110-66-7	7
45		1-Heptanethiol	Rancid, stinky	n.a.	1639-09-4	7
46		1-Octanethiol	Rancid, stinky	n.a.	111-88-6	7
47		1-Nonanethiol	Rancid, stinky	n.a.	1455-21-6	7
48		Thiomorpholine	Fishy, stinky	n.a.	123-90-0	7
49		Thiazole	Foul smell	n.a.	288-47-1	39
50		Pentachlorothioanisole	Medicinal	n.a.	1825-19-0	8
51		Indane	Musk, fragrance	n.a.	496-11-7	40
52		Eucalyptol	Peppermint	n.a.	470-82-6	41
53		2-Methylisoborneol	Musty	0.01 ^d	2371-42-8	42
54		Geosmin	Earthy	0.004 ^d	19700-21-1	3

^a Odor threshold concentration.

other odor compounds, such as thioethers,¹² thiols,⁷ indoles,¹¹ phenols,¹⁰ and aldehydes (after derivatization),¹⁴ in drinking water and wastewater. However, due to the limited separation capacity and co-elution of some of the key compounds, the above odor-causing compounds could not be simultaneously

detected using the conventional one-dimensional GC-MS.¹⁵ Because of its high resolution, sensitivity, and separation capacity features in comparison with one-dimensional gas chromatography, comprehensive two-dimensional gas chromatography combined with time-of-flight mass spectrometry

Table 2 GC × GC column sets

Parameters	First column	Second column
Length (m)	30	1.79
Diameter (mm)	0.25	0.10
Stationary phase	Rxi-5silv	Rxi-17
Film thickness (μm)	0.25	0.10
Corporation	Restek	Restek

(GC × GC-TOFMS) is considered to be suitable for the analysis of highly complex samples.¹⁵ GC × GC-TOFMS has been used to simultaneously analyze a large variety of compounds in petroleum, food, wine, perfume, fruit, and environmental samples.^{16–20} However, to date, the application of this method for the quantitative analysis of odor-causing compounds in the environment has been very limited.

Huangpu River (HP) and Huai River (HH) in China are two water sources that frequently encounter swampy/septic odor problems.^{4,21,22} To date, compounds responsible for the odor have not been detected due to the lack of an effective method. In this study, fifty-four odor compounds frequently encountered in drinking water with different odor characteristics,^{7,8} including thioethers, aldehydes, pyrazines, benzenes and phenols, were simultaneously analyzed by employing the GC × GC-TOFMS method. The aim of this work was to apply GC × GC-TOFMS for screening odor-causing compounds qualitatively and quantitatively. This is the first study that simultaneously investigates several potential compounds to clarify the potent swampy/septic odor problems in drinking water, and provide vital support to the odor problem control in these areas.

2. Experimental

2.1. Chemicals and reagents

All of the fifty-four odor compounds used in this study (Table 1) were purchased from Sigma-Aldrich Co., USA. Stock solutions of 1000 μg L⁻¹ were prepared by diluting different standard solutions with chromatographically pure methanol. The fifty-four compounds were classified into three groups according to their respective characteristics in time-of-flight mass spectrometry. Group I includes forty-two odor causing compounds; Group II includes nine compounds: 4-bromo-phenol, 3-methyl-phenol, thiomorpholine, 1-octanethiol, 2-nitro-phenol, 2,3-dimethyl-phenol, decanal, 1-nonanethiol, indole; and Group III includes three compounds: 2,4-heptadienal, bis(2-chloroisopropyl) ether, and 2,6-nonadienal. The calibration concentration ranges for Groups I, II, and III were 10 to 500 μg L⁻¹, 20 to 1000 μg L⁻¹ and 100 to 5000 μg L⁻¹ in methylene chloride, respectively. NaCl and Na₂SO₄ of guaranteed reagent standard used for the liquid–liquid extraction and extract dehydration were obtained from Beijing Chemicals Ltd, China, and heated to 450 °C for two hours before use.

The “d” in Table 1 indicates that the odor threshold concentrations (OTCs) of the compounds could be found in

related references, “b” indicates that the OTCs were not available in references, while “c” indicates that the OTCs of some screened compounds were tested by 3-alternative forced choices (3-AFCs)⁴³ in this study.

The procedure for the 3-AFCs was as follows: two of the three samples are used as controls and one is the spiked sample. Six panelists were presented with eighteen conical flasks, corresponding to six 3-AFCs with six spiked levels, each level differed by a factor of 2 (X/64, X/32, X/16, X/8, X/4 and X/2) compared to the preceding and were evaluated in ascending order beginning from the most diluted one. All the conical flasks were labeled with a randomized 3 letters (A/B/C). Panelists were instructed to smell and choose the spiked sample in each set of three flasks; they were instructed to guess one if they could not perceive a difference (forced choice). The final OTC was averaged among all the panelists.

2.2. Sample collection and preparation

Water samples were collected in June 2013 from two water sources suffering odor problems, *i.e.*, the Huangpu River (HP) and the Huai River (HH). For comparison, a sample was also taken from the Yangtze River (CJ) as a control sample, and this has seldom been associated with odor problems.

The sampling locations for HP, HH, and CJ were water inlets for water treatment plants distributed in Minhang District, in Chongming County of Shanghai City, and in Tianjiaan District of Huainan City, respectively. All the samples were taken in 1 L amber laboratory bottles, with the bottles first being washed, oven dried and rinsed several times by raw water before taking the samples. Then, the samples were immediately transported to laboratories in a thermotank with added ice bags for maintaining the temperature below 4 °C. After filtering with glass fiber (GF/C, 1.2 μm, Whatman, UK), the samples were preconcentrated using the method described below.

Preconcentration was performed as follows: 500 mL water samples were extracted using HPLC grade dichloromethane twice (50 mL and 30 mL dichloromethane for the first and second extraction, respectively), and then dehydration was carried out with Na₂SO₄; the samples were then concentrated to a final volume of 500 μL, followed by rotary evaporation and blowing off under a gentle nitrogen stream. The pressure of the rotary evaporation chamber was 920 mbar, while the temperatures of the water bath and cooling cycling water were 28 °C and 10 °C, respectively. The overall preconcentration factor was 1000. Extraction blanks consisting of ultrapure water extracted with dichloromethane and solvent blanks were also analyzed to ensure the absence of contaminants in the solvents and laboratory air.

2.3. Odor evaluation

Flavor profile analysis (FPA) was used for odor evaluation. A detailed description of the training and applications for the FPA method can be found in the Standard Methods for Water and Wastewater.⁴⁴ The panels were made up of at least four panelists for each test. Seven-point scales of 1–12 were used to describe

Table 3 Target compounds, quantitative ions, and retention times in GC-MS and GC × GC-TOFMS

Compounds	Masses	1 st dimension time (s)	2 nd dimension time (s)	Retention time in GC-MS (min)
Dimethyl sulfide	57	290	1.71	—
Diethyl sulfide	75	310	2.22	—
Pyrazine	80	345	2.96	—
Thiazole	58	345	3.03	—
Dimethyl disulfide	94	355	2.71	—
Pyridine	79	365	2.9	—
Diisopropyl sulfide	61	410	2.39	4.72
Hexanal	56	420	2.69	4.87
1-Pentanethiol	104	445	2.58	—
Ethylbenzene	91	510	2.96	6.22
<i>p</i> -Xylene	91	525	2.93	6.45
Propyl sulfide	61	555	2.75	6.90
Butanoic acid, propyl ester	71	565	2.83	—
Heptanal	70	575	2.93	7.20
Diethyl disulfide	94	615	3.32	7.80
Benzaldehyde	106	690	4.1	—
Dimethyl trisulfide	126	700	4.05	9.07
2-Chloro-phenol	128	735	3.82	—
2,4-Heptadienal	81	775	3.53	—
1,4-Dichloro-benzene	146	785	3.57	—
1-Heptanethiol	70	795	2.9	—
Eucalyptol	71	815	3.08	10.80
Indane	117	820	3.68	10.87
2-Methyl-phenol	107	845	4.02	—
Bis(2-chloroisopropyl) ether	121	850	3.49	—
2-Octenal	70	860	3.2	11.47
4-Bromo-phenol	174	880	4.19	—
3-Methyl-phenol	108	885	3.98	11.85
Tetramethyl-pyrazine	54	905	3.72	12.15
Butyl sulfide	61	915	2.88	12.30
2-Methoxy-3-(2-methylethyl)-pyrazine	137	935	2.58	12.60
Nonanal	57	945	3	—
Dipropyl disulfide	150	955	3.29	12.90
Thiomorpholine	103	965	0.95	13.05
1-Octanethiol	56	990	2.91	—
2-Nitro-phenol	139	1000	4.28	13.57
2,6-Dimethyl-phenol	107	1020	3.95	—
2,6-Nonadienal	69	1030	3.41	14.02
2-Methoxy-3-(2-methylpropyl)-pyrazine	124	1075	3.45	14.70
2-Methylisoborneol	107	1110	3.29	15.22
Decanal	57	1125	2.97	—
Amyl sulfide	61	1130	2.78	—
Disulfide, dibutyl	57	1135	3.06	15.60
2,6,6-Trimethyl-1-cyclohexene-1-carboxaldehyde	109	1160	3.68	—
1-Nonanethiol	56	1175	2.87	—
Indole	117	1290	0.32	17.92
2,4-Decadienal	81	1325	3.28	—
1,3,5-Trichloro-2-methoxy-benzene	195	1340	3.8	18.67
3-Methyl-indole	130	1450	0.02	20.32
Geosmin	112	1490	3.51	20.92
Ionone	177	1580	3.6	22.27
Dipentyl disulfide	71	1620	3.09	22.87
Pentachlorothioanisole	296	2215	4.62	31.80
Benzyl disulfide	91	2365	0.07	34.05

the intensity of the samples ((1) odor threshold, (2)–(4) weak odor intensity, (6)–(8) moderate odor intensity, (10)–(12) strong odor intensity). Odor standards with different intensities were used to remind the panel of the odor descriptors and intensities with each batch of samples.

2.4. GC × GC-TOFMS analysis

As shown in Table 2, a Pegasus-4D GC × GC-TOFMS system (LECO, USA) equipped with a multipurpose sampler (Gerstel, Germany) was used for the analysis of the extracts. Comprehensive two-dimensional gas chromatography was linked by a

Table 3 shows the specific quantification ions selected for each odor compound. After the automatically generated ion chromatograms of all the odor compounds were confirmed manually, the calibration curves were reconstructed using software. The limits of detection and quantification for the odor compounds were determined by the analysis of the odor compounds' standard dilutions in dichloromethane when the signal to noise ratio (S/N) was three and ten, respectively, and then divided by one thousand (the preconcentration factor). The overall method recovery and repeatability were evaluated by analyzing samples spiked into ultrapure water and source water samples at three levels: blank (0), the first levels for Groups I, II, and III with 20, 40 and 200 ng L⁻¹ additions, respectively, and the second levels for Groups I, II, and III with 100, 200 and 1000 ng L⁻¹ additions, respectively.

For GC $\times$ GC-TOFMS analysis, the conditions were optimized as follows: second dimension separation time, 5 s; second oven offset temperature, 5 $^{\circ}$ C; temperature programming rate, 5 $^{\circ}$ C; modulator temperature offset, 20 $^{\circ}$ C; hot pulse time, 1 s. As shown in Fig. 1, the fifty-four odor compounds were completely distributed in the chromatogram (contour plot) under the optimized conditions. The quantitative ions and two-dimensional retention times are shown in Table 3. It is clear that the

Table 4 Method performance data

Compounds	Correlation coefficients	LOD (ng L ⁻¹)	LOQ (ng L ⁻¹)	The first levels for Groups I, II, and III (n = 5)				The second levels for Groups I, II, and III (n = 5)			
				Ultrapure water		River water		Ultrapure water		River water	
				Mean recovery (%)	RSD (%)	Mean recovery (%)	RSD (%)	Mean recovery (%)	RSD (%)	Mean recovery (%)	RSD (%)
Dimethyl sulfide	0.9730	0.38	1.26	97.78	1.60	79.02	9.28	99.76	18.79	69.28	5.22
Diethyl sulfide	0.9950	0.72	2.39	76.33	13.19	75.90	8.63	90.00	29.22	86.39	1.55
Pyrazine	0.9923	0.15	0.49	86.95	4.69	85.68	10.19	84.00	20.23	75.82	3.23
Thiazole	0.9901	0.29	0.98	97.93	3.05	87.55	8.31	98.52	12.82	62.73	8.09
Dimethyl disulfide	0.9984	0.67	2.23	86.95	7.84	81.75	6.56	99.33	21.33	77.17	8.46
Pyridine	0.9996	2.51	8.37	83.75	6.43	76.03	11.58	86.38	16.25	62.26	11.57
Diisopropyl sulfide	0.9991	0.04	0.14	80.56	7.66	88.23	4.79	87.03	11.16	69.38	12.60
Hexanal	0.9993	0.43	1.42	69.06	5.61	76.29	17.72	94.08	8.60	69.81	2.99
1-Pentanethiol	0.9983	1.26	4.21	78.80	15.02	75.77	5.96	97.04	17.66	70.77	4.59
Ethylbenzene	0.9974	0.05	0.16	88.54	28.59	79.49	3.19	88.00	26.72	71.74	10.07
<i>p</i> -Xylene	0.9946	0.02	0.05	85.10	13.06	63.33	14.93	90.00	8.98	89.62	5.23
Propyl sulfide	0.9934	0.49	1.65	75.39	7.04	83.20	5.85	82.00	11.89	69.10	3.16
Butanoic acid, propyl ester	0.9941	0.42	1.40	88.27	3.98	82.53	12.08	91.00	10.41	82.90	6.60
Heptanal	0.9929	1.89	6.29	72.86	5.96	78.08	16.78	87.29	10.35	76.42	7.31
Diethyl disulfide	0.9972	0.01	0.02	82.94	7.52	72.64	7.80	74.58	10.29	70.50	4.89
Benzaldehyde	0.9916	3.26	10.87	124.67	34.94	95.26	13.54	112.78	7.32	91.44	7.73
Dimethyl trisulfide	0.9957	0.23	0.77	81.06	2.22	65.86	9.46	71.60	12.60	78.58	2.12
2-Chloro-phenol	0.9974	1.29	4.31	75.83	8.18	89.64	5.42	80.04	3.58	65.38	12.23
2,4-Heptadienal	0.9932	20.95	70.55	85.74	14.01	74.84	7.88	75.56	6.76	82.62	12.61
1,4-Dichloro-benzene	0.9950	0.19	0.63	121.86	25.50	105.59	5.76	71.08	9.93	81.29	9.57
1-Heptanethiol	0.9921	4.85	16.17	76.58	4.81	80.56	12.64	73.37	7.82	71.29	11.18
Eucalyptol	0.9953	0.19	0.62	77.32	3.06	83.81	17.28	75.65	5.70	78.54	3.96
Indane	0.9955	0.05	0.16	91.21	4.27	77.30	7.96	89.58	6.05	62.82	10.05
2-Methyl-phenol	0.9976	2.76	9.22	73.93	7.49	70.35	5.39	72.22	8.87	74.34	5.07
Bis(2-chloroisopropyl) ether	0.9905	10.4	34.8	83.67	22.15	91.97	10.19	74.51	6.76	72.17	13.45
2-Octenal	0.9942	2.50	8.33	86.82	9.49	77.75	6.08	73.54	7.44	92.40	22.11
4-Bromo-phenol	0.9913	4.89	16.30	80.24	8.94	82.24	6.16	95.01	14.67	70.68	4.99
3-Methyl-phenol	0.9803	3.82	12.74	81.83	3.02	90.21	4.76	90.21	9.64	68.58	4.23
Tetramethyl-pyrazine	0.9961	0.32	1.08	78.18	5.54	76.27	13.48	85.42	4.62	71.69	8.00
Butyl sulfide	0.9947	0.58	1.94	64.57	5.60	70.32	4.92	71.44	9.17	73.11	3.49
2-Methoxy-3-(2-methylethyl)-pyrazine	0.9926	0.35	1.18	65.12	9.70	74.04	3.59	92.22	13.84	65.81	24.12
Nonanal	0.9922	0.13	0.43	72.18	10.59	78.07	13.04	87.82	17.30	78.93	8.96
Dipropyl disulfide	0.9991	2.53	8.42	82.00	11.02	80.69	12.50	78.43	7.13	71.84	8.37
Thiomorpholine	0.9971	5.65	18.83	74.87	6.34	77.70	10.04	93.59	6.89	78.79	7.11
1-Octanethiol	0.9935	3.35	11.15	71.56	5.06	94.70	8.71	115.45	13.01	73.79	7.77
2-Nitro-phenol	0.9910	6.19	20.63	75.22	5.16	78.93	10.27	98.39	7.13	74.92	6.58
2,6-Dimethyl-phenol	0.9947	6.36	21.18	82.04	9.39	77.08	10.19	83.12	7.64	70.68	4.99
2,6-Nonadienal	0.9939	18.18	60.61	82.16	6.63	84.63	8.47	86.01	7.01	68.58	4.23
2-Methoxy-3-(2-methylpropyl)-pyrazine	0.9941	0.29	0.97	109.00	14.20	115.96	27.03	81.59	9.95	78.48	20.64
2-Methylisoborneol	0.9938	0.14	0.47	85.32	14.26	76.05	6.46	75.64	7.22	74.02	17.14
Decanal	0.9989	4.13	13.75	78.69	7.75	79.38	3.05	111.35	4.21	69.56	17.96
Amyl sulfide	0.9950	0.34	1.12	71.05	5.61	77.22	10.42	99.97	11.79	71.10	6.86
Dibutyl disulfide	0.9960	4.18	13.92	72.06	5.21	75.62	5.56	97.84	9.86	70.67	4.91
2,6,6-Trimethyl-1-cyclohexene-1-carboxaldehyde	0.9936	0.70	2.35	78.37	7.71	77.88	9.56	95.70	7.93	68.60	29.94
1-Nonanethiol	0.9920	2.17	7.22	85.70	11.09	87.69	3.09	128.34	6.47	70.88	3.54
Indole	0.9189	6.88	22.92	78.62	9.98	78.31	10.07	123.90	2.13	90.08	7.67
2,4-Decadienal	0.9996	2.76	9.21	80.58	7.40	85.89	9.10	112.04	6.22	73.18	8.92
1,3,5-Trichloro-2-methoxy-benzene	0.9923	0.64	2.13	82.02	5.46	87.59	5.33	100.17	10.30	67.76	10.65
3-Methyl-indole	0.9963	3.33	11.09	82.64	9.33	82.79	4.34	88.42	8.53	65.31	12.06
Geosmin	0.9951	0.25	0.83	77.40	18.31	83.00	5.49	76.68	6.77	79.83	8.02
Ionone	0.9915	0.27	0.91	82.79	10.44	122.58	31.34	86.90	8.25	89.01	14.61
Dipentyl disulfide	0.9923	5.29	17.63	78.53	7.67	82.10	9.45	94.86	9.21	76.62	16.00
Pentachlorothioanisole	0.9982	2.21	7.37	84.58	10.88	83.79	12.11	102.81	10.16	84.30	23.59
Benzyl disulfide	0.9820	0.29	0.98	84.70	13.58	66.99	3.48	152.21	18.14	88.20	16.99

Table 5 Flavor profile analysis for the environmental samples from three river water sources

Samples	CJ	HP	HH
Odor characterized by FPA (odor type and intensity)	Musty 2	Musty 4; swampy/septic 6	Musty 3; swampy/septic 3

fifty-four odor compounds were separated well over the two-dimensional space without the occurrence of wrap-around phenomena.¹⁵ It is known that a co-eluting problem is frequently encountered for the analysis of complicated samples in one-dimensional GC.¹⁵ As shown in Table 3, only eighteen odorants were separated among the fifty-four compounds using GC-MS. Some compounds, such as pyrazine and thiazole, eucalyptol, and indane, which could not be separated in GC-MS analysis, were separated well in GC $\times$ GC-TOFMS. Furthermore, the group-type separation¹⁵ of odor compounds could be identified, as shown in Fig. 1: phenols were located in region a, while most of the compounds identified as aldehydes and thioethers were located in regions b and c, respectively. All these results indicated that the columns and operational conditions used in this study were suitable for the analysis of the fifty-four compounds.

3.2. Calibration, limits of detection, and quantification

The external standard method was used for the quantification of the odor compounds. The correlation coefficients of the linear calibration curves are shown in Table 4. Except for dimethyl sulfide (0.97), 3-methyl-phenol (0.98), indole (0.92), and benzyl disulfide (0.98), all of the other compounds exhibited a value over 0.99. For the quantification of the compounds, LODs for Groups I, II, III were 0.01–5.29 ng L⁻¹, 2.17–6.88 ng L⁻¹, and 3.99–18.18 ng L⁻¹, and LOQs were 0.02–17.63 ng L⁻¹, 7.22–22.92 ng L⁻¹, and 13.31–60.61 ng L⁻¹, respectively. Compared with other methods, a better quantification result could be obtained. For instance, the LODs for MIB and geosmin, were 0.14 and 0.25 ng L⁻¹, respectively, which were 8 and 13 times lower than those acquired with the solid-phase microextraction GC-MS method.²³ The LODs for hexanal, heptanal, nonanal, decanal, benzaldehyde were 0.43, 1.89, 0.13, 4.13 and 3.26 ng L⁻¹, respectively, which were 418, 84, 1076, 48, and 9 times lower than those acquired with GC-MS after derivatization.¹⁴ The LODs for 2-chlorophenol and 2-nitrophenol were 1.29 and 6.19 ng L⁻¹, respectively, which were also considerably lower than those using solid phase extraction (SPE) with atmospheric pressure chemical ionization-MS detection (48 ng L⁻¹ for 2-chlorophenol and 49 ng L⁻¹ for 2-nitrophenol, respectively).⁴⁵ The LODs for 2-isopropyl-3-methoxypyrazine and 2-isobutyl-3-methoxypyrazine were 0.35 and 0.29 ng L⁻¹, respectively, which is considerably lower than the reported values (4.00 and 6.00 ng L⁻¹) obtained using GC-MS.⁴⁶ All these results indicated that, in comparison with the conventional GC-MS method (Table 3),¹⁵ the GC $\times$ GC-TOFMS technique not only provided a better separation capacity, but also a considerably lower detection limit, making it a sound approach for the simultaneous analysis of complicated odor compounds.

3.3. Method accuracy and precision

As shown in Table 4, the average recoveries in ultrapure water and the source water samples of the HP river at the first level for Groups I, II, III (20, 40, 200 ng L⁻¹) were 64.57–124.67% and 63.33–122.58% with an average RSD of 9.50% and 9.39%, respectively. In general, the recoveries for most compounds were in the range of 70–90%, and the RSDs were below 15%. For the majority of the compounds at the second level for Groups I, II, III (100, 200, 1000 ng L⁻¹), the recoveries and RSDs were 70–100% and below 15%, respectively.

The recoveries for MIB and geosmin were 75.64% and 76.68%, respectively. The recoveries and precisions of 2-chlorophenol, 2-nitrophenol, 2-isopropyl-3-methoxypyrazine, and 2-isobutyl-3-methoxypyrazine were a little lower than those determined using high-pressure liquid chromatography or GC-MS.^{45,46} The recoveries for hexanal, heptanal, nonanal, decanal, benzaldehyde, 2-chlorophenol, and 2-nitrophenol were slightly lower than those using GC-MS with derivatization.¹⁴ In general, the recoveries for the compounds were slightly lower than the conventional methods. However, the use of the GC $\times$ GC-TOFMS method allowed simultaneous analysis of different groups of compounds without derivatization, and hence saves a lot of time and cost.

3.4. Application to environmental samples

HP and HH Rivers, which are used as the major water sources for some cities and towns along the rivers, have long been associated with complicated odor problems. Odor characterization was carried out and the results are shown in Table 5. A swampy or septic odor with an intensity of 6 and 3, and a musty odor with an intensity of 4 and 3 were present for HP and HH Rivers, respectively, while for CJ, only a weak musty odor of intensity 2 was present. MIB was identified as being mainly responsible for the musty/earthy odor in HP River in our previous study,⁵ but the compounds associated with the swampy/septic odors in the two rivers have not yet been clarified.

Among the swampy/septic odor compounds, thioethers are frequently reported.² Two thioether compounds, dimethyl disulfide (72.5 ng L⁻¹) and diethyl disulfide (36.6 ng L⁻¹) were detected in the HP samples, while three were detected in the HH samples, including dimethyl trisulfide (4.0 ng L⁻¹), propyl sulfide (31.0 ng L⁻¹), and amyl sulfide (2.0 ng L⁻¹). No sulfur-containing compounds were detected in the CJ control samples. In general, sulfur-containing compounds are related to algal metabolism or anaerobic digestion of biomass.^{12,47–54} Different thioether compounds, including dimethyl sulfide, dimethyl disulfide, and dimethyl trisulfide, have been reported in black colored, foul smelling and hyper-eutrophic freshwater lakes,

Table 6 Detection results of the fifty-four odor-causing compounds in three river water sources^a

No.	Category	Compounds	Concentration (ng L ⁻¹)		
			CJ	HP	HH
1	Aldehydes	Hexanal	85.1	91.3	142.7
2		Heptanal	77.6	80.3	19.7
3		Benzaldehyde	560.3	656.3	185.9
4		2,4-Heptadienal	n.d. ^a	n.d.	n.d.
5		2-Octenal	1080.0	888.7	n.d.
6		Nonanal	648.0	n.d.	337.3
7		2,6-Nonadienal	n.d.	n.d.	n.d.
8		Decanal	73.0	192.5	93.2
9		2,4-Decadienal	n.d.	22.6	n.d.
10		2,6,6-Trimethyl-1-cyclohexene-1-carboxaldehyde	30.8	n.d.	n.d.
11	Benzenes	Ethylbenzene	49.4	64.6	3.4
12		<i>p</i> -Xylene	29.9	32.5	4.0
13		1,4-Dichloro-benzene	14.3	31.3	16.4
14		1,3,5-Trichloro-2-methoxy-benzene	n.d.	n.d.	n.d.
15	Ethers	Bis(2-chloroisopropyl) ether	37.7	51.9	32.0
16	Esters	Butanoic acid, propyl ester	n.d.	n.d.	n.d.
17	Indoles	Indole	n.d.	n.d.	n.d.
18		3-Methyl-indole	n.d.	n.d.	18.0
19	Ketones	Ionone	n.d.	n.d.	3.2
20	Pyrazines	Tetramethyl pyrazine	9.98	52.4	26.0
21		Pyrazine	n.d.	9.2	n.d.
22		2-Methoxy-3-(2-methylethyl)-pyrazine/IPMP	n.d.	n.d.	n.d.
23	Pyridines	2-Methoxy-3-(2-methylpropyl)-pyrazine/IBMP	n.d.	n.d.	n.d.
24		Pyridine	n.d.	27.3	16.9
25	Phenols	2-Methyl-phenol	n.d.	17.6	18.3
26		4-Bromo-phenol	n.d.	n.d.	n.d.
27		3-Methyl-phenol	n.d.	n.d.	n.d.
28		2-Nitro-phenol	21.4	86.9	48.5
29		2,6-Dimethyl-phenol	19.7	20.2	n.d.
30		2-Chloro-phenol	n.d.	n.d.	n.d.
31	Thioethers	Dimethyl sulfide	n.d.	n.d.	n.d.
32		Diethyl sulfide	n.d.	n.d.	n.d.
33		Dimethyl disulfide	n.d.	72.5	n.d.
34		Diisopropyl sulfide	n.d.	n.d.	n.d.
35		Propyl sulfide	n.d.	n.d.	31.0
36		Diethyl disulfide	n.d.	36.6	n.d.
37		Dimethyl trisulfide	n.d.	n.d.	4.0
38		Butyl sulfide	n.d.	n.d.	n.d.
39		Dipropyl disulfide	n.d.	n.d.	n.d.
40		Amyl sulfide	n.d.	n.d.	2.0
41	Thiols	Dibutyl disulfide	n.d.	n.d.	n.d.
42		Dipentyl disulfide	n.d.	n.d.	n.d.
43		Benzyl disulfide	n.d.	n.d.	n.d.
44		1-Pentanethiol	n.d.	n.d.	n.d.
45		1-Heptanethiol	n.d.	n.d.	n.d.
46		1-Octanethiol	n.d.	n.d.	n.d.
47		1-Nonanethiol	n.d.	n.d.	n.d.
48		Thiomorpholine	n.d.	n.d.	n.d.
49		Thiazole	n.d.	n.d.	n.d.
50		Pentachlorothioanisole	n.d.	n.d.	n.d.
51		Indane	n.d.	n.d.	2.1
52		Eucalyptol	n.d.	n.d.	2.0
53		2-Methylisoborneol	12.9	9.5	10.0
54		Geosmin	11.1	45.7	3.0

^a Not detected.

even being detected as high as the $\mu\text{g L}^{-1}$ level.⁵⁵ Yang *et al.*² reported that a high concentration of 11 399 ng L^{-1} even occurred in Taihu Lake, and was due to a distinct black water

“agglomerate”, which triggered the water crisis in Wuxi in 2007. Meanwhile, concentrations of dimethyl sulfide and dimethyl trisulfide as high as 62 331.8 ng L^{-1} and 12 413.3 ng L^{-1} ,

respectively, have also been detected from decaying cyanobacterial blooms of Taihu Lake.⁴⁷ The amino acids methionine and cysteine are important precursors of thioether compounds, and can be broken down by many bacteria (*e.g.*, *Pseudomonas* sp.) into methylmercaptan or dimethylpolysulfides.^{56–58} These compounds were also confirmed as occurring in the algae-induced black bloom of Taihu Lake.^{48,59} In addition, bio-industry (wastewater treatment plants, composting plants, rendering plants),^{11,60} swine operation processes,⁷ and polluted rivers⁶¹ were also reported to be major source of some thioethers. As far as the HP and HH rivers, whose waters partly originate in Taihu Lake and that are easily polluted by wastewater discharges, respectively, both the degradation of biomasses and pollution might be the major reasons for the occurrence of the thioether compounds.

By using the 3-AFC method, OTCs of dimethyl trisulfide, dimethyl disulfide, diethyl disulfide, propyl sulfide, and amyl sulfide were determined as 10.0 ng L⁻¹, 30.0 ng L⁻¹, 20.0 ng L⁻¹, 1.9 ng L⁻¹, and 1.1 ng L⁻¹, respectively, among which, only the OTC of dimethyl trisulfide has been reported with the same value.³⁷ The concentrations of the four sulfide compounds (dimethyl disulfide, diethyl disulfide, propyl sulfide, and amyl sulfide) were higher than their corresponding OTCs in the HP and HH river samples. So the swampy/septic odor in the HP sample might be related to dimethyl disulfide and diethyl disulfide, while that in the HH sample might be related with propyl sulfide and amyl sulfide. Bis(2-chloroisopropyl) ether, which usually causes medicinal odor problems and has been identified as an odor-causing compound in different source waters in China,⁶² was detected in both the HP and HH samples with a concentration higher than its OTC (17 ng L⁻¹), as tested by 3-AFC. This compound might have also contributed to the swampy/septic odor to some extent.

Meanwhile, several nitrogen containing compounds existed in the water samples, with a concentration of 27.3 ng L⁻¹, 9.2 ng L⁻¹, and 52.4 ng L⁻¹ for pyridine, pyrazine and tetramethyl pyrazine in HP samples, and 16.9 ng L⁻¹, 0 ng L⁻¹, and 26.0 ng L⁻¹ in HH samples, respectively. Previous studies have reported these compounds were related with stinky/fishy/sour/medicinal-like odors to some extent.⁶³ For example, Pandey *et al.*⁹ reported that pyridine was detected in waste gas emissions with an unpleasant fishy odor, which exceeded 2390 times its odor threshold concentration. In this study, the OTC values for pyridine, pyrazine and tetramethyl obtained using the 3-AFC method were 1.1 ng L⁻¹, 2.7 ng L⁻¹, and 2.6 µg L⁻¹, respectively, all of which were much higher than those detected in the water samples. Therefore, the contribution of these nitrogen containing compounds might be limited.

Similar results were also obtained for phenol compounds. As indicated in Table 6, although several phenol compounds, including 2-methyl-phenol, 2-nitro-phenol, and 2,6-dimethyl phenol, were detected in the HP and HH samples, the concentrations were much lower than their corresponding OTCs of 14.7 ng L⁻¹, 11.0 ng L⁻¹, and 11.0 µg L⁻¹, respectively. Phenolic compounds can exist extensively in the water environment, and usually arise from natural substance degradation, industrial activities, and agricultural practices.¹⁶ The contribution of these

phenol compounds might be limited, too. Furthermore, considering the fact that the concentrations of benzenes and aldehydes in the CJ sample were even higher than those in the HH and HP samples, these compounds should not be responsible for the swampy/septic odor.

The occurrence of odor problems in the HH and HP rivers is surely associated with water pollution. The potassium permanganate index and ammonia nitrogen concentrations have been reported to be relatively high.^{64–66} Pollution by antibiotics, pharmaceuticals, and estrogenic endocrine has also been reported recently.^{67–71} However, there were also some differences for other compounds detected in the HH and HP samples, which could further deduce the different odor sources. Among these, 3-methylindole is a typical stinky odorant related with wastewater pollution,^{11,72} which was only detected in the HH sample. Besides, eucalyptol, ionone and indane were also only detected in the HH samples, which are related to industrial wastewater discharge,⁴¹ algal metabolite,³² and industrial additives or solvents,⁷³ respectively. Thus, combining with other results discussed above, although both algal-induced and wastewater contamination were doomed to correlate with the swampy/septic odor problems, there might be some differences in odor sources between the two rivers. For HH source water, the odor problem might be more associated with wastewater pollution, while for HP source water, it might be more correlated with algal-induced activities.

MIB and geosmin are two major musty odor-causing compounds even reported in drinking water.⁴ For HP River, an MIB concentration between 28.6 ng L⁻¹ and 71.0 ng L⁻¹ was even reported.⁵ In this study, 12.9 ng L⁻¹ MIB and 11.1 ng L⁻¹ geosmin were both detected in the sample from the HP River, while for the HH River, a much higher concentration of geosmin (45.7 ng L⁻¹) was detected compared with MIB (9.8 ng L⁻¹). Only low levels of MIB and geosmin were detected in the CJ River (MIB 10.0 ng L⁻¹ and geosmin 3.0 ng L⁻¹). These two compounds were thus correlated with the musty odor in the two water samples.⁷⁴

4. Conclusions

A method for the simultaneous determination of a total of fifty-four typical odorants in drinking water using GC × GC-TOFMS was successfully developed. This method could effectively prevent the occurrence of the co-elution of peaks when analyzing complicated water samples with significant matrix effects, and thus allow the simultaneous analysis of different groups of compounds without derivatization at much higher sensitivities. For the two source waters with continuing swampy/septic odor problems, four thioether compounds (dimethyl disulfide, diethyl disulfide, propyl sulfide, and amyl sulfide) and one ether compound (bis(2-chloroisopropyl) ether) were found with a concentration higher than their individual OTC values. These compounds might make a major contribution to the swampy/septic odor. For other compounds, including the nitrogen ones and the phenols, the concentrations were much lower than their OTCs; their contribution to the swampy/septic odor should be further studied. In the future,

the method will be improved by adding many more odor-causing compounds, and evaluating the contribution of the major odorous compounds to the swampy/septic odor.

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