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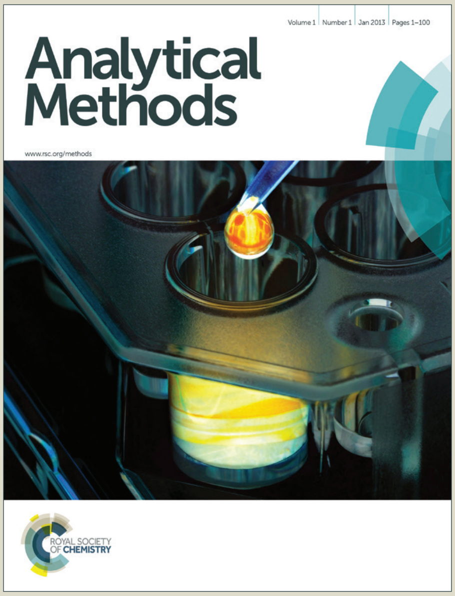

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Comprehensive two-dimensional gas chromatography with time-of-flight mass spectrometry for screening of potent swampy/septic odor causing compounds in two drinking water sources of China

Qingyuan Guo[a], Xia Li[a], Jianwei Yu[a,*], Haifeng Zhang[a], Yu Zhang[a], Min Yang[b], Ning Lu[c], Dong Zhang[c]

[a] Key Laboratory of Drinking Water Science and Technology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing, 100085, China.

[b] State Key Laboratory of Environmental Aquatic Chemistry, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing, 100085, China.

[c] Shanghai National Engineering Research Center of Urban Water Resources Co., Ltd., Shanghai 200082, China

* Corresponding author

E-mail: jwyu@rcees.ac.cn

Abstract

Odor problems in drinking water, particularly the swampy/septic odors, are normally triggered by a set of organic compounds with odor threshold concentrations (OTC) ranging from ng L^{-1} to μg L^{-1}. With such a low level of OTC, it has been a challenge to determine the odor causing compounds in highly complex samples effectively. Huangpu and Huai River as source waters in south China have exhibited continuous swampy/septic odor over the whole year, and 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, phenols, etc., was developed using comprehensive two-dimensional gas chromatography with time-of-flight mass spectrometry (GC×GC-TOFMS) based on liquid-liquid extraction. The results indicated that this method allowed the analysis of different categories of compounds without derivatization at much 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 evaluated.

Keywords: comprehensive two-dimensional gas chromatography, time-of-flight mass spectrometry, drinking water, thioethers, qualitative screening, quantitative analysis

1. Introduction

Odor problems in drinking water, which can impair its 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 kind 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 much more complicated. A wide range of compounds, such as the thioethers,[6] thiols,[7] pyrazines,[8] pyridines,[9] phenols,[10] indoles,[11,] have been reported to cause the swampy/septic or similar odors even at a concentration of ng L^{-1}. This kind of odor causing compounds could be formed by different biological processes including both aerobic and anerobic conditions,[2] or associated with polluted source waters.[12] So it is desirable to establish an effective method with high sensitivity and resolution for the simultaneous detection of different odor causing compounds in highly complex samples effectively.

Gas chromatography with mass spectrometry (GC-MS) or gas chromatography with flame photometric detection (GC-FPD) have been widely used for the determination of some typical odor compounds, including the musty/earthy odor compounds, like MIB and geosmin,[13] and the swampy/septic or other odor compounds, like thioethers,[12] thiols,[7] indoles,[11] phenols,[10] and aldehydes (after derivatization),[14] in drinking water and wastewater. However, due to limited separation capacity and co-elution of some key compounds, the above odor causing compounds could not be detected simultaneously using the conventional one-dimensional GC-MS.[15] Because of its high resolution, sensitivity and separation capacity features in comparison with the one-dimensional gas chromatography, comprehensive two-dimensional gas chromatography combined with time-of-flight mass spectrometry (GC×GC-TOFMS) is considered to be suitable for the analysis of highly complex samples.[15] The 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] The application of this method for quantitative analysis of odor causing compounds in environments, however, has been very limited so far.

Huangpu River (HP) and Huai River (HH) are two source waters frequently encountering swampy/septic odor problems in China.[4,21-22] Until now, compounds responsible for the odor have not yet been revealed 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, phenols, etc., , were analyzed simultaneously by employing the method of GC×GC-TOFMS. 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 investigates so many potential compounds simultaneously to clarify the potent swampy/septic odor problems in drinking water, which should give a vital support for 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, 2,6-nonadienal. The calibration concentration ranges for Group 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 Na_2SO_4 of guaranteed reagent standard used for liquid-liquid extraction and extract dehydration were obtained from Beijing Chemicals Ltd., China and heated to 450 ºC for two hours before use.

Table1 Information of the fifty-four odor compounds

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		2,6,6-Trimethyl-1-Cyclohexene-1-carboxaldehyde	Sweet, fragrance	n.a.	432-25-7	27
11	Benzenes	Ethylbenzene	Plastic，oily，chemical	150.0 ^{d}	100-41-4	8
12		p-Xylene	Chemical	n.a.	106-42-3	7,8
13		1,4-Dichloro-benzene	Almond，sweet	4.5 ^{d}	106-46-7	8
14		1,3,5-Trichloro-2-methoxy-benzene	Musty	0.002 ^{d}	108-70-3	28

15	Ethers	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	Stink	0.1[d]	120-72-9	[31]
18		3-methyl-indole	Stink	1.0[d]	83-34-1	[11,31]
19	Ketones	Ionone	Fragrance	0.007[d]	8013-90-9	[6232]
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		2-Methoxy-3-(2-methylpropyl)-pyrazine/IBMP	Musty	0.001[d]	24683-00-9	[8]
24	Pyridines	Pyridine	Amine, stink	1.1[c]	110-86-1	[9,34]
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	[8,10]
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	[12,32]
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	[32,37]

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		Benzyl disulfide	Foul smell	n.a.	150-60-7	6
44	Thiols	1-Pentanethiol	Rancid, stink	n.a.	110-66-7	7
45		1-Heptanethiol	Rancid, stink	n.a.	1639-09-4	7
46		1-Octanethiol	Rancid, stink	n.a.	111-88-6	7
47		1-Nonanethiol	Rancid, stink	n.a.	1455-21-6	7
48		Thiomorpholine	Fishy, stink	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

The “d” in Table 1 means that the odor threshold concentrations (OTCs) of the compounds could be found in related references, “b” means that OTCs were not available in references, while “c” means that OTCs of some screened compounds were tested by 3-alternative forced choice (3-AFC) [43] in this study.

The procedures of 3-AFC as follows: two of three samples are 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 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 would guess one if they could not perceive a difference (forced choice). The final OTC was averaged among all panelists.

2.2. Sample collection and preparation

Water samples were collected in June 2013 from two source waters suffering odor problems, the Huangpu River (HP) and the Huai River (HH). For comparison, a sample was also taken from the Yangtze River (CJ) as control sample, which 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, Chongming County of Shanghai City and Tianjiaan District of Huainan City, respectively. All samples were taken in 1-L amber laboratory bottles fully, the bottles were washed clean, oven dried and rinsed several times by raw water before taking samples. Then the samples were transported to laboratories immediately in thermotank added ice bags for keeping temperature below 4 ºC. After filtering with glass fiber (GF/C, 1.2μm, 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); then dehydration was carried out with Na_2SO_4; samples were then concentrated to a final volume of 500 µL, following rotary evaporation and blowing off under a gentle nitrogen stream. The pressure of rotary evaporation chamber was

920 mbar, the temperatures of water bath and cooling cycling water were 28 ºC and 10 ºC, respectively. The overall pre-concentration 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 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 the intensity of 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 analysis of the extracts. Comprehensive two-dimensional gas chromatography was linked by a two-stage modulator. In the first dimension a low polarity capillary column was used, and the second dimension column was a polar one mounted in a separate oven installed in the main GC oven. Liquid nitrogen was filled into a Dewar using a liquid leveler automatically which was for cold pulses. Ultrapure helium (He ≥ 99.999%) was used as the carrier gas at the constant flow of 1 mL/min. One μL extracts were introduced using a programmed temperature vaporizing injector at 50 μL/s in a splitless mode with the inlet temperature of 250 ºC. Mixtures of different categories of odor compound standards were injected for the optimization of the following conditions: second dimension separation time (3, 5, 7 s), second oven offset temperature (5, 10, 15 ºC above the first GC oven temperature), temperature programming rate (5, 10, 15 ºC), modulator temperature offset (10, 20, 30 ºC), and hot pulse time (0.5, 1, 1.5 s).

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

Finally, the temperature program of the first column (main GC oven) was optimized as follows: 40 ºC (0.2 min) →280 ºC (at 5 ºC/min) →280 ºC (5 min). The temperature of the second oven was programmed from 45 ºC (0.2 min) to 285 ºC at a rate of 5 ºC/min with a final hold time of 5 min. The modulator temperature offset was 20 ºC above the first GC oven temperature. The second-dimension separation time (modulation time) was 5.0 s divided into a hot pulse time of 1.0 s and a cold pulse time of 1.5 s. The transfer line linking the secondary oven with the mass spectrometer was maintained at 250 ºC. The electron energy was -70 eV, and the detector voltage was set at 1575 eV. The data acquisition rate was 100 spectra/s, covering a mass range of 50-500 m/z. The temperature of the ion source was set at 250 ºC.

To compare the separation and detection effects, a GC-MS analysis in scan mode was also carried at the same conditions in GC×GC-TOFMS, including injection speed, constant flow, inlet temperature, temperature programming rate of first column and scan mass range. The temperatures of the MS Source and MS Quadrupole were set at 230 ºC and 150 ºC, respectively.

2.5. Data processing and quantification

Data pre-processing was done using a ChromaTOF version 4.50.8.0 via the following steps: the baseline was computed through average noise, and peak finding and deconvolution were achieved with an S/N ratio of 6 and peak width of 0.1 s. The S/N threshold was set to a relatively low level in order to avoid losing small molecule modulation peaks at low concentrations. Based on repeated experiments, a similarity value of 700 was set to be most practical for screening. Library searching was carried out using the NIST Mass Spectral Library (NIST11).

Table 3 shows the specific quantification ions selected for each odor compound. After the automatically generated ion chromatograms of all 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 analysis of odor compounds standard dilutions in dichloromethane when the Signal to Noise Ratio (S/N) was three and ten, respectively, then divided by one thousand (the pre-concentration 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 Group I, II and III with 20, 40 and 200 ng L^{-1} additions, respectively, and the second levels for Group I, II and III with 100, 200 and 1000ng L^{-1} additions, respectively.

3. Results and discussion

3.1. GC×GC-TOFMS optimization

For GC×GC-TOFMS analysis, the conditions were optimized as follows: second dimension separation time, 5s; second oven offset temperature, 5ºC; temperature programming rate, 5ºC; modulator temperature offset, 20ºC; hot pulse time, 1 s. As shown in Figure 1, the fifty-four odor compounds were completely distributed in the chromatogram (contour plot) under the optimized condition. The quantitative ions and two-dimensional retention times are shown in Table 3. It is clear that the fifty-four odor compounds were separated well over the two-dimensional space without the occurrence of the wrap-around phenomena.[15] It is known that the 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 by using GC-MS. Some compounds, such as pyrazine and thiazole, eucalyptol and indane, which couldn't be separated in GC-MS analysis, were separated well in GC×GC-TOFMS. Furthermore, the group-type separation[15] of odor compounds could be identified in Figure 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.

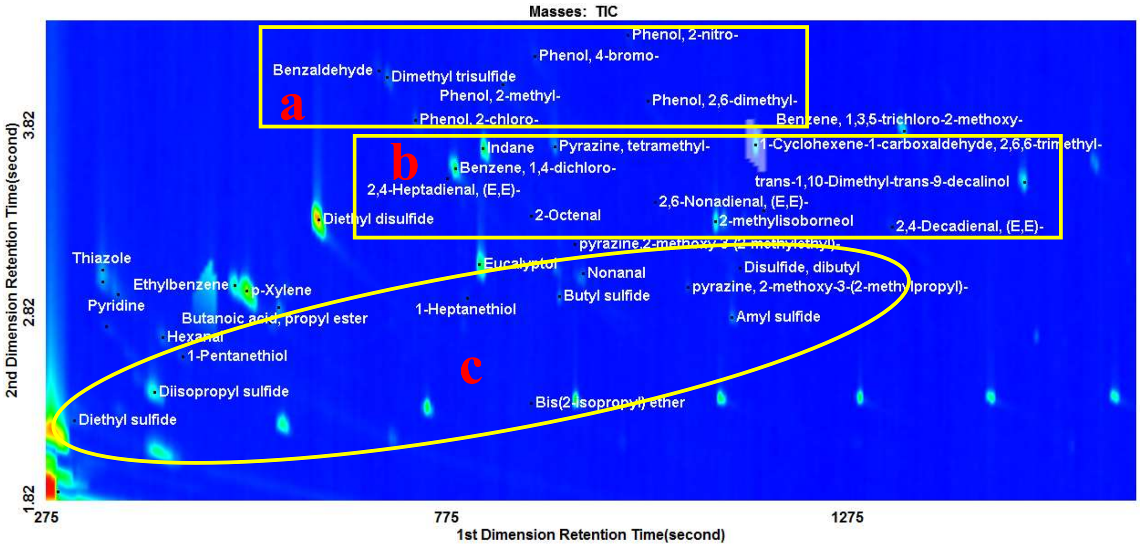

Fig.1. The two-dimensional chromatographic profile of fifty-four odor compounds analyzed by GC×GC-TOFMS

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

Compounds	Mass	1st Dimension	2nd Dimension	Retenti

	es	Time (s)	Time (s)	on 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
p-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

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 quantification of the compounds, LODs for Groups I, II, III were 0.01-5.29, 2.17-6.88 and 3.99-18.18 ng L^{-1}, and LOQs were 0.02-17.63, 7.22-22.92 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 much 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, much lower than the reported values (4.00 and 6.00 ng L^{-1}) acquired with GC-MS.[82] All these results indicated that, in comparison with the conventional GC-MS method (Table 3),[15] the GC×GC-TOFMS technique not only provided a better separation capacity, but also a much lower detection limit, making it a sound approach for the simultaneous analysis of complicated odor compounds.

Table 4 Method performance data

Compounds	Correlation coefficients	LOD (ng L^{-1})	LOQ (ng L^{-1})	The first levels for Group I, II and III (n=5)				The second levels for Group 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
p-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

3.3. Method accuracy and precision

As shown in Table 4, the average recoveries in ultrapure water and 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, 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, 2-notrophenol were a bit 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×GC-TOFMS method allowed simultaneous analysis of different groups of compounds without derivatization, and save a lot of time and cost.

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

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

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		p-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		2-Methoxy-3-(2-methylpropyl)-pyrazine/IBMP	n.d.	n.d.	n.d.
24	Pyridines	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		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	Thiols	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.

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 results are shown in Table 5. A swampy or septic odor with intensity of 6 and 3, and a musty odor with intensity 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 has been 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 been clarified.

Among the swampy/septic odor compounds, thioethers are frequently reported ones.[2] Two thioether compounds, dimethyl disulfide (72.5 ng L^{-1}) and diethyl disulfide (36.6 ng L^{-1}) were detected in HP samples, while three were detected in 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 color, foul smell and hyper-eutrophic freshwater lakes, even being detected as high as μg/L level.[55] Yang et al.[2] has reported that a high concentration of 11399 ng L^{-1} ever occurred in Taihu Lake due to distinct black water "agglomerate", which triggered the water crisis in Wuxi in 2007. Meanwhile, concentrations of dimethyl sulfide and dimethyl trisulfide as high as 62331.8 and 12413.3 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, which can be broken down by many bacteria (e.g., *Pseudomonas sp.*) into methylmercaptan or dimethylpolysulfides.[56-58] These compounds were also conformed occuring in the algea-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 rivers [61] were also reported the major source of some thioethers. As far as HP and HH River, whose water was partly originated from Taihu Lake and easily being polluted by the wastewater discharges, respectively, both degradation of biomasses and pollution might be the major reason for thioether compounds occurrence.

By using the 3-AFC method, OTCs of dimethyl trisulfide, dimethyl disulfide, diethyl disulfide, propyl sulfide and amyl sulfide were determined as 10.0, 30.0, 20.0, 1.9 and 1.1 ng L^{-1}, respectively, among which, only OTC of dimethyl trisulfide has been reported with the same value.[71] 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 with dimethyl disulfide and diethyl disulfide, while that in the HH sample might be related with propyl sulfide and amyl sulfide. Bis (2-chloroisopropyl) ether, usually causing medicinal odor problem and identified as odor-causing compounds in different source waters of China,[62] was detected in both the HP and HH samples with a concentration higher than its OTC (17 ng L^{-1}) 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, 9.2, and 52.4 ng L^{-1} for pyridine, pyrazine and tetramethyl pyrazine in HP samples, and 16.9, 0, 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 unpleasant fishy odor, which exceeded 2390 times of its odor threshold concentration. In this study, the OTC values for pyridine, pyrazine and tetramethyl obtained using the 3-AFC method were 1.1, 2.7 and 2.6 μg L^{-1}, respectively, all of which were much higher than those detected in the water samples. Therefore, 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 HP and HH samples, concentrations of which were much lower than their corresponding OTCs of 14.7, 11.0 and 11.0 μg L^{-1}, respectively. Phenolic compounds can exist extensively in water environment, which are usually arisen from natural substance degradation, industrial activities and agricultural practices.[16] The contribution of these phenol compounds might be limited, too. Besides, 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 HH and HP rivers was 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 HH and HP samples, which could further deduce the different odor sources. Among these, 3-methylindole was 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 HH samples, which was related to industrial wastewater discharge,[41] algal metabolite[32] and industrial additive or solvent,[73] respectively. Thus combing 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 much more correlated with algal induced activities.

MIB and geosmin are two major musty odor causing compounds ever reported in drinking water.[4] For HP River, an MIB concentration between 28.6 and 71.0 ng L^{-1} was ever reported.[5] In this study, 12.9 ng L^{-1} MIB and 11.1 ng L^{-1} geosmin were both detected in the sample of HP River While for HH River, much higher concentration of geosmin (45.7 ng L^{-1}) was detected compared with MIB (9.8 ng L^{-1}). Only low level of MIB and geomin were detected in CJ River (MIB 10.0 ng L^{-1} and geosmin 3.0 ng L^{-1}). These two compounds were correlated with the musty odor in the two water samples.[74]

4. Conclusion

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 co-elution of peaks when analyzing complicated water samples with significant matrix effects, and 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 problem, 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 value. These compounds might have 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. The contribution to the swampy/septic odor should be further studied. In the future, the method will be improved by adding much more odor causing compounds, and the contribution of the major odorous compounds to the swampy/septic odor will be evaluated.

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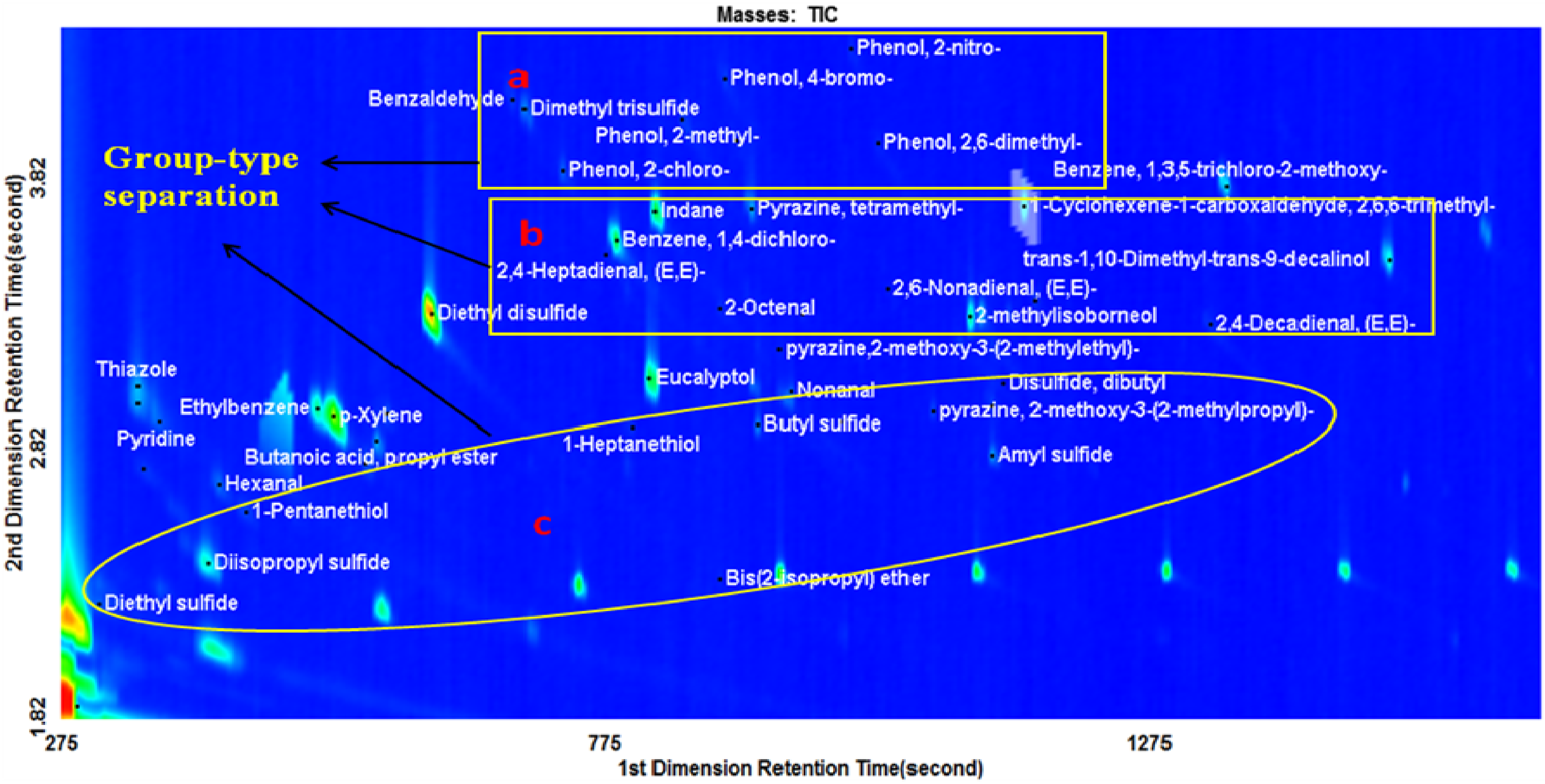

Fifty-four odor compounds → **Two-dimensional gas chromatography with time-of-flight mass spectrometry** → **Potent swampy/septic odor causing compounds**