Microwave-assisted purge-and-trap extraction device coupled with gas chromatography and mass spectrometry for the determination of five predominant odors in sediment, fish tissues, and algal cells

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ABSTRACT

Off-flavors are among the most troublesome compounds in the environment worldwide. The lack of a viable theory for studying the sources, distribution, and effect of odors has necessitated the accurate measurement of odors from environmental compartments. A rapid and flexible microwave-assisted purge-and-trap extraction device for simultaneously determining five predominant odors, namely, dimethyltrisulfide, 2-methylisoborneol, geosmin, β-cyclocitral and β-ionone, from the primary sources and sinks is demonstrated. This instrument facilitates the extraction and concentration of odors from quite different matrices simultaneously. This device is a solvent-free automated system that does not require cleaning and is timesaving. The calibration curves of the five odor compounds showed good linearity in the range of 1–500 ng/L, with correlation coefficients above 0.999 (levels = 7) and with residuals ranging from approximately 77% to 104%. The limits of detection (S/N = 3) were below 0.15 ng/L in algae sample and 0.07 ng/g in sediment and fish tissue samples. The relative standard deviations were between 2.65% and 7.29% ($n = 6$). Thus the proposed design is ready for rapid translation into a standard analytical tool and is useful for multiple applications in the analysis of off-flavors.

1. Introduction

Off-flavors produced by algae, fungi, and actinomycetes in environment have been widely reported [1–6]. Dimethyltrisulfide (DMTS), 2-methylisoborneol (MIB), geosmin (GSM), β-cyclocitral, and β-ionone are the frequently encountered odors during cyanobacteria bloom episodes [7–10]. These notorious compounds are a serious nuisance in municipal water supplies [11–14] and aquaculture [15,16] worldwide. The evaluation of off-flavors in water is essential in water science [17], environmental science [10,18], ecology [19,20], toxicology [21], and epidemiology [22].

A rapid, sensitive device for the determination of odors from environmental samples could be helpful in the management of these environmental odors and will reduce losses incurred by water treatment plants and aquaculture industries. Algae and sediment are the sources of off-flavors in natural water environments, whereas fish and water serve as sinks. However, the detection of odor compounds in solid samples (such as sediment, fish tissues, and algal cells) are not as straightforward as

that in water because of the lack of effectual method and/or equipment for the extraction of these compounds from different matrices. Solid phase microextraction (SPME) [23–26] and purge-and-trap (P&T) [27–30] are the most commonly used methods in the extraction of odors from water samples. However, these techniques are ineffective in extracting odors from fish tissues. The techniques used in the extraction of off-flavors from fish tissues include microwave distillation–cold trap extraction [31], microwave distillation–solid phase extraction (SPE) [32], and microwave distillation–SPME [33,34]. However, these methods cannot effectively extract off-flavors from sediment, and the efficiency of the closed-loop stripping analysis (CLSA) [31,35] used in the extraction of odors from sediment is reduced by solvent interference. Moreover, rare reports are available on the extraction of odors from algal cells. The lack of effective extraction methods from these matrices makes research on the sources of odors difficult. Therefore, an urgent need exists to develop devices or methods that will facilitate the extraction of off-flavors from different environmental samples.

The aforementioned methods utilize enrichment techniques with cold-trap, SPE, SPME, and CLSA extraction devices that have several disadvantages, thus limiting their direct application. For instance, the fatal flaws of a cold trap include the loss of odors,
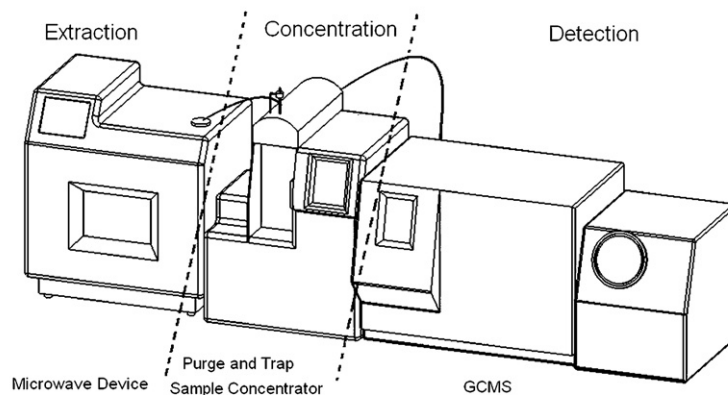
(a) MAPTE-GCMS System

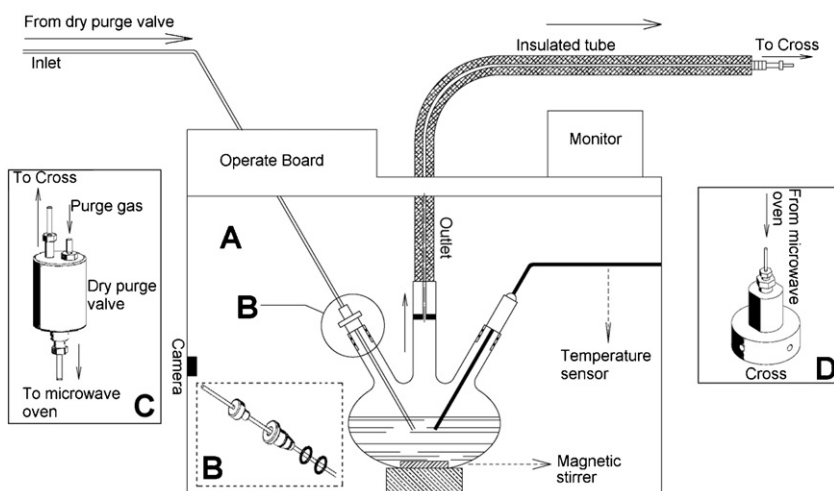## (b) The schematic diagram of microwave device

Fig. 1. (a) The MAPTE coupled with the GCMS system; (b) schematic diagram of the MAPTE apparatus (C and D are parts of the P&T Sample Concentrator).

which are mostly volatile organic compounds, when the recovery temperature changes from −80 °C to room temperature, and the condensation of air moisture compromises gas chromatography and mass spectrometry (GCMS). SPE and CLSA are time-consuming, labor-intensive and are unsuitable for trapping low-boiling-point odors [7,30,36]. Selecting a fiber suitable for the large-scale analysis of odors from different matrices is difficult in SPME [7,25,37]. Finally, all of these enrichment techniques initially extract analytes and then concentrate or subject these extracts to other processes (e.g., removal of sodium chloride) before injecting them into detectors. These step-by-step methods are time-consuming, labor-intensive, and result in a loss of analytes and often do not yield good results. Furthermore, none of these methods could be applied to extract off-flavors from three different matrices simultaneously.

Microwave-assisted extraction (MAE) is widely used in sample preparation [38,39]. Rapid heating, timesaving, and large sample throughput are the primary advantages of this technique [38], demonstrating that MAE has great potential in the extraction of odors from environmental samples. This potential can be harnessed if a device capable of trapping and purging odors from different

matrices is incorporated into MAE. P&T satisfies these requirements. First, this technique is solvent-free and purges the analytes from matrices. Therefore, no solvent interference will occur, and the matrix interference would be decreased [30]. Second, this technique is suitable for a large-scale analysis of odors from different matrices [30,40]. Third, P&T has an excellent performance in the extraction of odors, and it is easy to operate and is timesaving [30,40].

In the present paper, a novel assembled online device for the simple, flexible, and direct measurement of five predominant off-flavor compounds from fish tissue, sediment, and algal cells using customized microwave and P&T devices coupled with GCMS was demonstrated. The microwave-assisted purge-and-trap extraction (MAPTE) system combined the advantages of both the microwave and P&T, making it possible to extract and concentrate simultaneously, and thereby significantly saving time and labor and reducing the loss of analytes. This device was solvent-free (during extraction, concentration, and system clean-up), easy to operate, and efficient, with low limits of detection (LOD) and high accuracy. Finally, the proposed approach was further demonstrated with custom devices to simultaneously and directly analyze odors in different
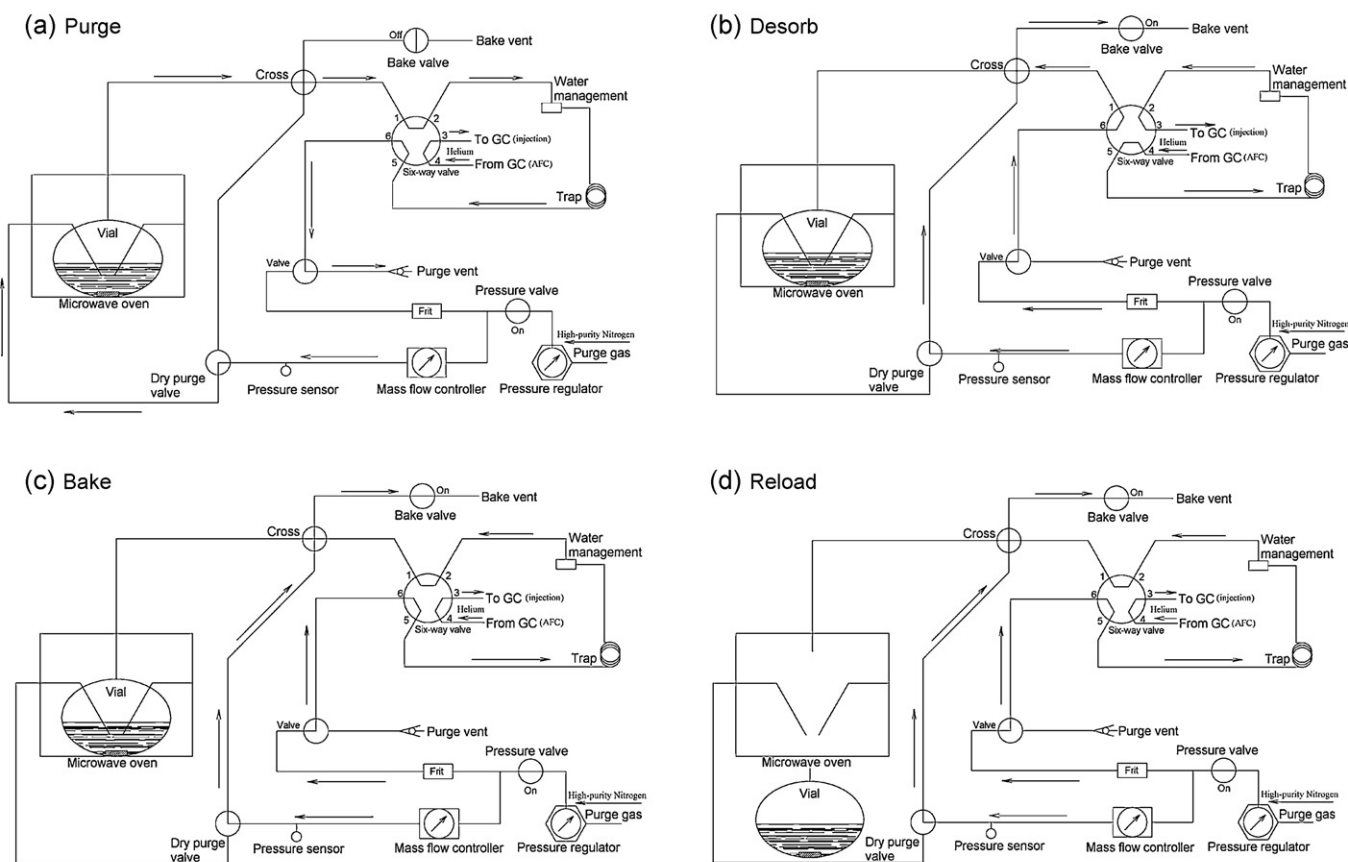
Fig. 2. Flow charts of the entire extraction procedure of MATPE–GCMS. Parts of the charts were cited from the operating manuals of Eclipse-V 2.0.

environmental samples to trace the fate of target odors in the aquatic environment, providing insight into risk assessment and management.

## 2. Experimental

2.1. Chemicals and materials

DMTS (Cas no. 3658-80-8, percent >98.0%) was purchased from Tokyo Chemical Industry (Tokyo, Japan). MIB (Cas no. 2371-42-8, percent >99.8%), GSM (Cas no. 19700-21-1, percent >99.9%), and β-cyclocitral (Cas no. 432-25-7, percent >90.0%) were purchased from Sigma–Aldrich (Shanghai, China). β-ionone (Cas no. 14901-07-6, percent >96.0%) was purchased from Acros Organics (Fair Lawn, USA). MIB and GSM were mixed in a standard solution of 100 μg/mL methanol (in a 1 mL ampoule). Anhydrous calcium chloride (CaCl$_2$, AR) and sodium chloride (NaCl, AR) were purchased from Sinopharm Chemical Reagent (Shanghai, China). CaCl$_2$ and NaCl were baked at 450 °C for 4 h before use. In addition, NaCl was dissolved in HPLC grade water to yield a solution at a concentration of 250 g/L. Then, 10 mg of each of these odor compounds (except for MIB and GSM) was weighed and dissolved in methanol (MERCK, HPLC grade) to yield a mixed stock solution at an approximate concentration of 100 μg/mL for each. This solution, as well as the mixed standard solution of MIB and GSM, was sealed up and stored at 4 °C as the first stock solution. The second stock solution was diluted from the first stock solutions with HPLC grade water at a concentration of 10 μg/L for each compound. Standard series used for standard curves were diluted from the second stock solution

with the NaCl solution. In order to avoid the sample volatilization, all procedures were performed as soon as possible, and the second stock solution and the standard series used for standard curves were generated before daily use and used once only.

2.2. Sample preparation

Sediment, fish tissue, and algal cells were collected from Taihu, Chaohu and Poyang Lakes (three of the five largest freshwater lakes in China). Algal biomass was estimated, and the algae in one liter water were filtered through 0.45 μm pore glass-fiber-filter (GF/C, Whatman, England), and then the filters were packed by foil, sealed up and stored at −80 °C. Well mixed sediments collected from the lakes were divided to 5 g per sample (wet weight) evenly on the spot and then sealed up and stored at −80 °C. The fish was sliced to fillets immediately before frozen at −80 °C, and then were homogenized by a high-speed disintegrator (model: FW80, Tianjin Taisite Instrument Co., Ltd., China). This disintegrator, equipped with small crushing chamber (diameter: ϕ 8 cm) and high speed blade (rotational speed: 10,000 r/min), can expeditiously crush the frozen fish 30 s and then the fish samples (uniform mixing and sufficient low temperature, <0 °C) were divided into 2.5 g per sample (fresh weight) and packed by foil, sealed up and stored at −80 °C. All the samples (algal cells, sediment, and fish tissues) were prepared carefully and quickly, and repeated freezing (at −80 °C) and thawing (at 4 °C) (to rupture the cells of samples) before use.

These three types of samples used for the analysis of recoveries were added into a 50 mL solution of NaCl and 5 g CaCl$_2$. Then
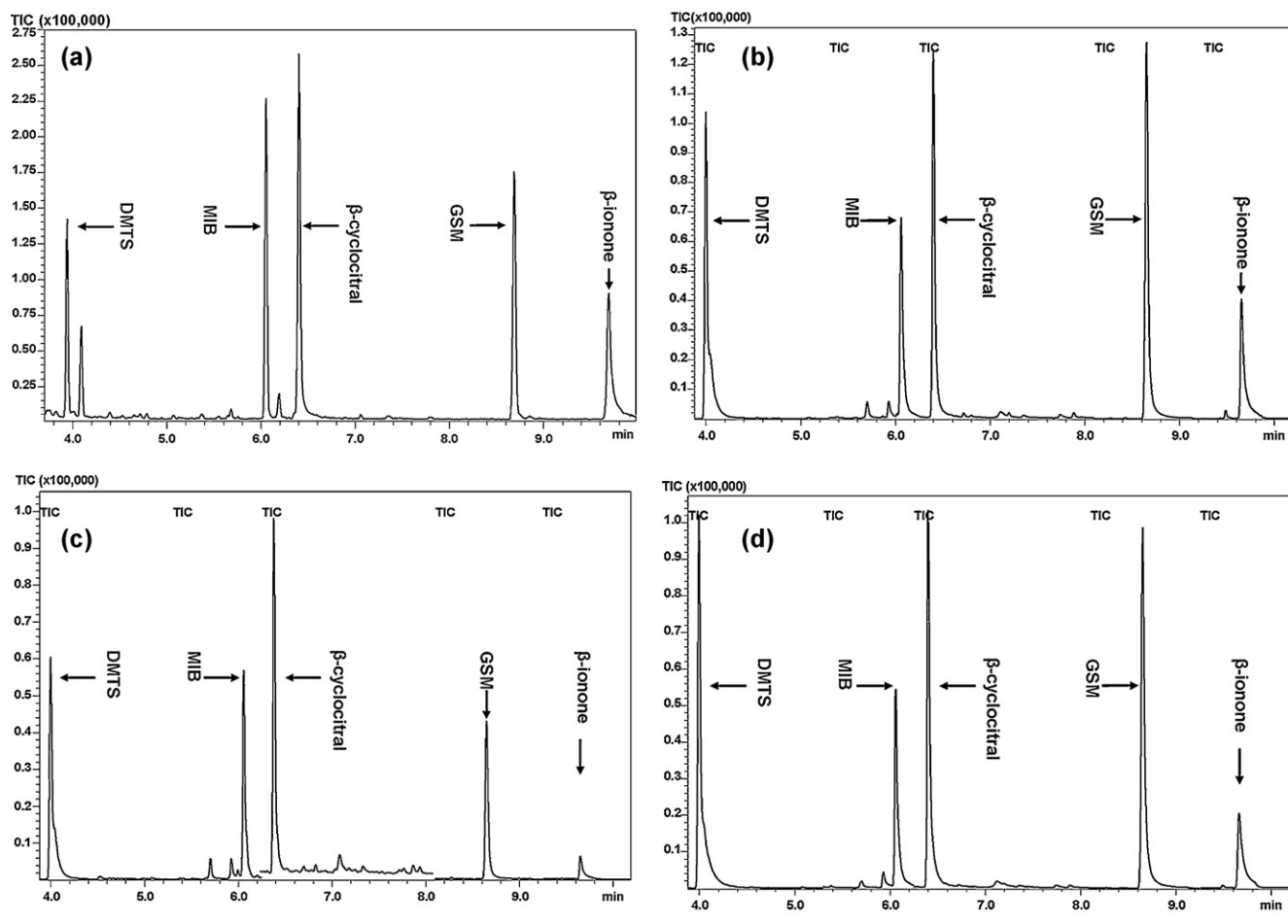
Fig. 3. Chromatograms of the five predominant odors produced by MAPTE–GCMS. (a) Identification of all five odors in injection mode, and the full scan mass spectra from 3.7 to 10 min obtained with an m/z range of 75–180 u; (b)–(d) are the chromatograms of the spiked samples (sediment, fish tissues, and algal cells) in SIM mode.

the samples were spiked at two concentrations (10 and 500 ng/L) with the second stock solution (see Section 2.1) to evaluate the recoveries of the method.

2.3. Instrumentation

The MAPTE coupled with GCMS used in the present study is shown in Figs. 1 and 2.

Microwave radiation was performed in an 800 W microwave oven (APEX Microwave Chemistry Workstation, YiYao Microwave Chemistry Company, Shanghai) (Fig. 1b-A), which was modified as described below. An inlet gas transfer line (1/16 in., steel tube) was inserted through the microwave oven, covering the bottom of a reaction still (Fig. 1b-B). The reaction still was a 100 mL oblique three round-bottomed flask, with a temperature probe inserted sideways. This microwave oven is equipped with a magnetic stirrer, which has a maximum speed of 2000 r/min. An outlet gas transfer line (1/16 in., silicon steel tube) was inserted through the middle hole of the reaction still. This outlet gas transfer line was heated to 220 °C to prevent the condensation of the target compounds (Fig. 1b).

The P&T system was carried by the Eclipse 4660 P&T Sample Concentrator (OI Analytical Company, USA) and had a # 07 trap (OI Analytical Company, USA). The conjunction of the microwave oven and the Eclipse 4660 P&T Sample Concentrator can be described as follows: The inlet gas transfer line (in the microwave described above) was fixed at the dry purge valve of the Eclipse 4660 P&T Sample Concentrator (Fig. 1b-C). The outlet gas transfer line (in the

microwave described above) was fixed at the cross, which was also part of the concentrator (Fig. 1b-D).

GCMS analysis was performed using a GCMS (QP2010Plus, Shimadzu Corporation, Japan) with an HP-5MS UI column (30 m × 0.25 mm × 0.25 μm; J&W Scientific, USA) and with helium as carrier gas. The GCMS was connected to the six-port valve of the Eclipse 4660 P&T Sample Concentrator (Fig. 2).

2.4. Procedure

GC was operated under the following settings: injection temperature of 270 °C, total flow rate of 14 mL/min (carry gas, helium), column flow rate of 1 mL/min, and split ratio of 10:1. The oven temperature was programmed from 60 °C to 150 °C (15 °C/min) and finally, to 220 °C (5 °C/min). MS was equipped with an electron ionization source and set as follows: Ion-source temperature of 200 °C, interface temperature of 250 °C, solvent cut time of 3.7 min, electron energy of 70 eV, and selected ion mode (SIM). All other parameters were defined by automatic tuning.

P&T was programmed and set as follows: Target compounds were purged from the sample and absorbed onto the trap for 10 min (Fig. 2a). Purge gas was high-purity nitrogen (99.999%), with a flow rate of 40 mL/min. Water manager temperature was set at 110 °C, and trap temperature was set at 30 °C during the purge step. Subsequently, the trap was heated. The trapped components were desorbed by helium for 4 min, meanwhile, transferred directly to the GC system (helium was from AFC of GC, and passed the trap of P&T, and then went

to the injection of GC) (Fig. 2b). Water manager temperature was set at 0 °C, and trap temperature was set at 180 °C (pre-desorb at 170 °C) during the desorb step. And then the trap was baked for 12 min to clean the purge system (Fig. 2c). Water manager temperature was set at 240 °C, and trap temperature was set at 200 °C during the bake step. The no sampler mode, desorb without drain mode, and bake without purge mode were selected, and the six-way valve temperature and transfer line temperature were set at 250 °C and 270 °C respectively during the whole process.

The procedure for the microwave-assisted apparatus was set as follows: a 100 mL flask mode was selected, and the sample was then heated to 70 °C. To keep pace with P&T, the heating time of the sample was set at 10 min (heating time equals to purge time). Meanwhile, the magnetic stirrer work synchronized with the purge process at 2000 r/min, allowing the matrix to be purged evenly.

After all parameters of the apparatus were fixed, a 50 mL solution of NaCl (m:v, 25%) and 5 g CaCl$_2$ was placed in the still (a 100 mL vial), and a sample was then added (Fig. 2d). NaCl, which were used in the present experiment, could result in the low solubility of odor compounds [40,41]. And CaCl$_2$ was used to prevent the production of bubbles by matrix. Then, the still was loaded, the oven door was closed, and the microwave procedure was started. After 10 min of extraction (Fig. 2a), the analytes were absorbed on the trap, and desorption started within 4 min (Fig. 2b). After desorption, the system started to bake for cleaning (Fig. 2c). At this point, the sample can be reloaded (Fig. 2d).

3. Results and discussion

To define the quantitative and qualitative ions, the five odors were injected into the GC and identified in scan mode. The ions selected are listed in Table 1, and the chromatogram is shown in Fig. 3a. The five target compounds were separated within 10 min.

3.1. MAPTE of taste and odor compounds

To verify the feasibility of the proposed apparatus in the extraction of odor compounds, several parameters were tested. For P&T parameters, trap # 7 and desorb within 4 min were selected based on a previous work [30]. The energy of the microwave (800 W) and purge gas flow (40 mL/min) were held constant following the previously mentioned instructions. The efficiency of the extraction was affected by both time and the temperature of microwave heating during the extraction process, these two factors had to be optimized. In this study, according to Salemi et al. and Deng et al., one-at-a-time optimization scheme was used to evaluate the effect of each parameter on the sensitivity of the method [30,40]. To keep pace with P&T, the heating time of the sample was set synchronously with the purge time (discussed below).

3.1.1. Purge time (heating time)

A suitable purge time is very important for purge efficiency. Target compounds could not be purged within a short time, and would break through within a long time, which all result in low purge efficiencies and high LOD. Therefore, purge time was tested from 1 min to 14 min (heating time was set synchronously with the purge time). Fig. 4 shows the response of purge time with other parameters fixed. The maximum responses of DMTS, MIB, and β-ionone were achieved at 10 min, and the maximum responses of GSM and β-cyclocitral occurred at 12 min. The responses of DMTS and β-ionone descended rapidly after the maximum at 10 min, and the same phenomenon was observed for GSM and β-cyclocitral after their maximum at 12 min. The decline resulted from the breakthrough of analytes. Thus, purge time was set at 10 min.
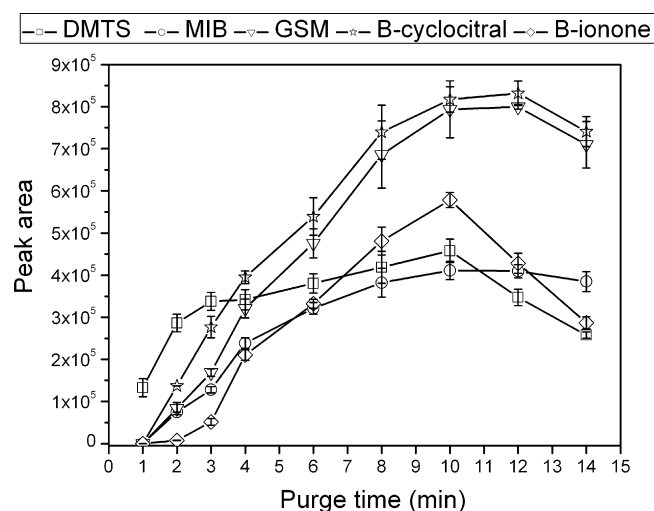

Fig. 4. Response of purge time with other parameters fixed.

3.1.2. Sample temperature

The principle of heating using microwave energy is based on the effect of microwaves on molecules by ionic conduction and dipole rotation [38]. In our design, the water (NaCl solution) acted as a medium in the extraction process. The electrophoretic migration of ions in water will result in friction and heat the water. And the realignment of dipoles in water will force molecular movement and heat the water [38]. The heat was delivered rapidly and evenly by water to solid samples. And the odors were released out rapidly from solid samples to water, and were purged evenly by nitrogen from water to trap. However, two important points should be indicated by exorbitant heat. Firstly, extra water would be purged to the trap, which can affect the quality of chromatography and shorten trap life. Secondly, breakthrough time (volume) would be shortened sharply. Therefore, a proper sample temperature is needed to explore. In this study, sample temperatures were tested at 50, 60, 70, 80, 90 °C (with purge 10 min). The effect of sample temperature on sensitivity is shown in Fig. 5. Among the different sample temperatures, 70 °C resulted in the best sensitivity of MIB, GSM, and β-cyclocitral, and the second sensitivity of DMTS and β-ionone. The maximum response of DMTS and β-ionone was achieved at 80 °C, however, the responses of MIB, GSM, and β-cyclocitral descended rapidly after the maximum at 70 °C. As the five target T&O compounds were simultaneously determined here, the sample temperature was set at 70 °C to yield chromatograms
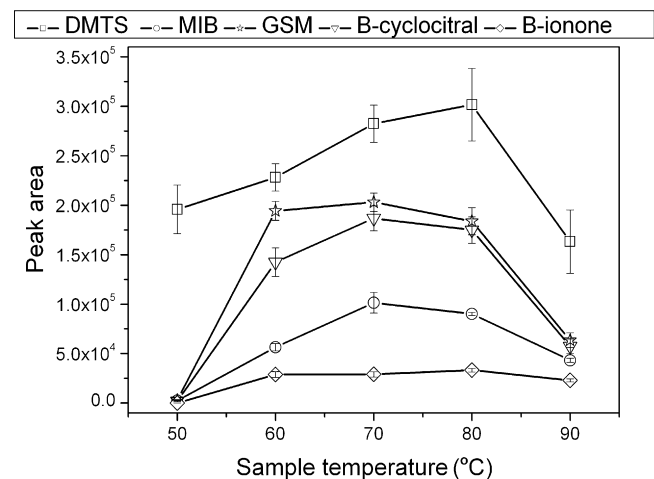

Fig. 5. Response of sample temperature with other parameters fixed.

Table 1
The selected ions, retention time, linearity, residual, relative standard deviation and limit of detection.

Analyte	Selected ions	t_R (min)	Linearity (R)	Residual range (% accuracy)	RSD % ($n = 6$)		LOD [a]		
					10 ng/L	500 ng/L	Sediment (ng/g)	Fish tissue (ng/g)	Algae [b] (ng/L)
DMTS	126[c], 79, 111	4.023	0.9992	98–104	6.98	3.29	0.02	0.03	0.08
MIB	95[c], 108, 135	6.092	0.9995	93–102	5.99	2.84	0.01	0.02	0.07
β-Cyclocitral	137[c], 152, 123, 109	6.441	0.9995	85–102	6.97	3.98	0.01	0.03	0.11
GSM	112[c], 125, 149	8.699	0.9993	86–102	4.77	2.65	0.03	0.02	0.07
β-Ionone	177[c], 91, 135	9.712	0.9991	77–101	7.29	3.51	0.03	0.07	0.15

[a] Limit of detection was calculated on the basis of S/N = 3, at a spiked concentration of 50 ng/L.
[b] One liter water was filtered, and the biomass of algae in the water was approximately 10^7 cells/L.
[c] Target ions for quantitation.

Table 2
The recoveries (±RSD %) of these compounds in the three matrices with two spiked concentration.

Analytes	Sediment		Fish tissue		Algal cells	
	10 ng/L	500 ng/L	10 ng/L	500 ng/L	10 ng/L	500 ng/L
DMTS	120.9 ± 1.2	85.5 ± 2.6	109.3 ± 1.6	91.9 ± 2.8	85.0 ± 2.4	84.6 ± 1.7
MIB	101.0 ± 8.7	97.9 ± 3.3	78.5 ± 6.4	81.2 ± 1.7	95.5 ± 9.3	102.3 ± 5.6
β-Cyclocitral	94.5 ± 6.1	98.9 ± 3.2	95.4 ± 6.2	84.3 ± 3.6	99.4 ± 9.2	101.2 ± 6.1
GSM	91.1 ± 8.7	109.4 ± 6.8	102.3 ± 6.3	85.4 ± 1.8	104.1 ± 9.8	108.0 ± 4.4
β-Ionone	109.3 ± 9.2	86.6 ± 4.9	109.1 ± 9.0	87.3 ± 6.1	88.9 ± 9.7	107.1 ± 2.1

Table 3
The concentrations of the five odors detected in the three types of samples from three eutrophic lakes in China (ng/g).

Lakes	Sample type	DMTS	MIB	β-Cyclocitral	GSM	β-Ionone
Poyang Lake	Sediment	51	22	49	49	259
Taihu Lake		3	3	18	ND[a]	29
Chaohu Lake		4	1	2	ND[a]	1
Poyang Lake	Fish tissue	274	9	9	3	35
Taihu Lake		33	33	6	1	70
Chaohu Lake		ND[a]	34	ND[a]	5	17
Poyang Lake	Algal cell [b]	ND[a]	ND[a]	113	ND[a]	117
Taihu Lake		ND[a]	64	475	ND[a]	207
Chaohu Lake		ND[a]	550	251	ND[a]	132

[a] No detected.
[b] The biomass of algae was expressed as mg/L, and the concentrations of odors were calculated by the biomass of total algae.

with "balanced" peak areas when all five analytes were present at a similar concentration level.

3.2. Calibration curves, repeatability, and LOD

Linearity was studied by purging the standard solutions of the five odor compounds at seven concentration levels, ranging from 1 ng/L to 500 ng/L. Table 1 shows the parameters for the calibration curves of the five odor compounds. Coefficients of correlation (R) were greater than 0.999, with residuals (accuracy) ranging from approximately 77% to 104%. The relative standard deviation (RSD %) estimated from six standard replicates and calculated at concentrations of 10 ng/L and 500 ng/L was between 2.65% and 7.29%. The LODs of these compounds were calculated on the basis of S/N = 3 in SIM mode at spiked concentration of 50 ng/L. And the LODs for sediment and fish tissue ranged from 0.01 ng/g to 0.07 ng/g, much lower than those reported by Martin et al. [31], Conte et al. [32], and Zhu et al. [33]. And the LODs for algae were between 0.07 ng/L and 0.15 ng/L, much lower than those reported by Hu et al. [42]. Since many studies have focused on the well-known earthy-musty algal metabolites GSM and MIB [31–33,35,36], whereas there are only a few studies on other cyanobacterial metabolites such as β-cyclocitral, β-ionone, we could only compare the repeatability and LODs for MIB and GSM obtained here with the reported studies. The values obtained in the present study are similar to those reported

by Machado et al. [41], and greatly improved when compared with those obtained by MAE-Cold Trap, MAE-SPE, and MAE-SPME techniques [31–33].

3.3. Applications

MAPTE of off-flavors from sediment, fish tissue, and algal cells was studied. To confirm the validity of this method, the possible matrix effect had to be evaluated. The samples and the same matrix spiked with target compounds were compared. The result showed that no interfering peak from the sample matrix occurred (Fig. 3b, c, and d). Accuracy was estimated for the five off-flavors in the three matrices, based on the recoveries obtained from the measurements of spiked samples. The two spiked concentrations (10 and 500 ng/L) in the three matrices were analyzed with six replicates. The recoveries (mean ± RSD) are shown in Table 2, and all these recoveries are in acceptable range. Fish tissue samples seem to be more influential to the recoveries of these odors, for example at 10 ng/L level, the recovery of MIB (78.5 ± 6.4%), and at 500 ng/L level, the recoveries of MIB (81.2 ± 1.7%) and β-cyclocitral (84.3 ± 3.6%) are susceptible to fish tissue samples, while all the compounds are quite tolerant to other matrices. This is similar to the results of Martin et al. and Zhu et al. [31,33]. Probably, such differences were caused by the interactions between these odors and matrices; for example, there

Table 4
Comparison of published and developed techniques.

Techniques	CLSA[a]	MAE-Cold Trap[b]	MAE-SPE[c]	MAE-SPME[d]	MAE-P&T[e]
Matrices (size)	Water (1000 mL) Sediment	Fish tissue (40 g)	Fish tissue (20 g)	Fish tissue (10 g)	Sediment (5 g)/fish tissue (2.5 g)/Algae (10^7 cells/L)
Odors	MIB, GSM	MIB	MIB, GSM	MIB, GSM	DMTS, MIB, GSM, β-cyclocitral, β-ionone
Extraction time	2 h	3.5 min	10 min	6 min	10 min
Solvent	Acetone Carbon disulphide Methylene chloride	Hexane	Ethyl acetate Methanol	No usage	No usage
Linearity range	50 pg/L to 10 ng/L	–	0.5–500 µg/L	0.1–100 µg/L	1–500 ng/L
Regression coefficient	0.99	–	0.999	0.999	0.999
Recovery[f]	103%	>60%	>93%	>30%	>79%
Repeatability[f]	<14%	<17%	<10%	<17%	<6%
LOD[f]	30 pg/L	5 ng/g	217 ng/L	43 ng/L	0.02 ng/g
Advantages	Low detection limits	Fast extraction	Fast extraction	Fast extraction	Fast extraction
		Low detection limits	Low solvent volumes	No solvent usage	No solvent usage
					No clean-up required No needed to remove sodium chloride Extraction and concentration in one step Multiple extractions Automated systems Low detection limits Good repeatability
Drawbacks	Solvent needed	Large solvent volumes needed	Solvent needed to elute	Remove excess sodium chloride	Many parameters to optimize
	Long extraction times	Long concentration times needed before injection to detector	Extract was needed to dry	Long concentration times needed by SPME before injection to detector	
	Clean-up step needed	Clean-up of transfer lines step needed	Concentration needed before injection to detector	Clean-up of transfer lines step needed	
	Extraction and concentration not in one step	Extraction and concentration not in one step	Clean-up of transfer lines step needed	Extraction and concentration not in one step	
	Many parameters to optimize	Many parameters to optimize	Extraction and concentration not in one step	Many parameters to optimize	
		Poor repeatability	Many parameters to optimize Poor detection limits	Not too good detection limits	

[a] Closed-loop stripping analysis, and it was cited from [35,36].
[b] Microwave distillation-cold trap extraction, and it was cited from [31].
[c] Microwave distillation-solid phase extraction, and it was cited from [32].
[d] Microwave distillation-solid phase microextraction, and it was cited from [33].
[e] Microwave-assisted purge-and-trap extraction, present study.
[f] Comparison of the data of MIB.

are many reports about the strong correlation of MIB with fat levels in fish tissue [43,44].

Samples from different eutrophic lakes in China were analyzed, and the results are listed in Table 3. In these samples, the algal cells mainly contain MIB, β-cyclocitral and β-ionone, and half of fish tissue and sediment samples contain all these five odors, which highlights the importance to monitor these off-flavors in the lake ecosystems. Concentrations of these off-flavors seem quite variable among different lakes. For algal cells, the difference might be explained by the different composition of algal community. As we know, some taxa in cyanophyta and chlorophyta are the most common algae in eutrophic lakes [2,3], and some taxa in cyanophyta mainly produce DMTS, β-cyclocitral and β-ionone, for example *Microcystis aeruginosa*, and some also produce MIB and GSM, e.g.

Phormidium sp., whereas some taxa in chlorophyta could not produce these odors. For sediment, the odors are influenced not only by the producer in sediment (e.g. algae, fungi, and actinomyces), but also by the physical and chemical properties of sediment [2,3]. And the odors in fish tissue are influenced by the odors in its prey, water and sediment [16,31,45]. It should be noted that the concentrations of MIB (≥9 ng/g) and GSM (≥1 ng/g) in fish tissue samples are not only above the odor thresholds (between 0.1 ng/g and 0.2 ng/g for MIB, between 0.25 ng/g and 0.5 ng/g for GSM) [46], but also much higher than their corresponding LODs (Table 1). A comparison of advantages/disadvantages between previous techniques and the present ones is shown in Table 4. The MAPTE system is successfully applied to extract these five odors from sediment, fish tissue, and algae samples.

4. Conclusion

An online MAPTE device coupled with GCMS, to successfully detect the five predominant odor compounds, namely, DMTS, MIB, β-cyclocitral, GSM, and β-ionone, from sediment, fish tissue, and algal cell samples was developed.

The MAPTE system integrates extraction and concentration of off-flavors in one step, and requires no cleaning up, and is easy to operate. It greatly improved the efficiency of the analysis of odors from these matrices. And the developed method was validated to yield good results, e.g. good linearity, low LODs, and good repeatability. Especially, we applied the system to efficiently quantify five predominant odors in three different matrices, from eutrophic lakes. These may contribute to better understanding the environmental fate of eutrophication-related off-flavors, as well as providing insight into risk assessment and management.

Acknowledgments

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