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Taihu Lake Safety Management and Determination Technologies Based on Odor Test

Ping He

School of management, Wuhan Institute of Technology, Wuhan 430205, China
heping366@126.com

There is a more diverse set of substances that may cause special odors in water bodies, so that it is difficult to analyze many factors that will make an increasing impact on the social and economic environment, thus seriously hobbling the people's demand for better life. Against this backdrop, how to quickly and accurately test smelly substances in water, ensure the safety of water areas, and make up for the gaps of the existing technologies has become a worthy focus of concern. In this paper, the headspace solid phase microextraction and the Gas Chromatography/Mass Spectrometry (GC/MS) are incorporated to analyze the smelly substances, in order to determine the optimal extraction and experiment conditions. In this way, the method has been proven to be effective in determining the smelly substances. Study results show that the accuracy every time reaches above 93%, which suggests that the test and identification technology for smelly substances is feasible. For example, test odorous substances in Taihu Lake, it provides the clues to deodorizing water and ensure the water safety of Taihu Lake and other water areas.

1. Introduction

In recent years, water pollution as a safety issue has led to plenty of waste of water resources. More than anything else, water pollution accidents occurred frequently has caused tremendous pressure on the ecological environment. In particular, the harmful secondary metabolites produced by water bloom enter the environmental water source, which easily induces water odor, impairs the function of water bodies, increases the difficulty of water treatment. Worse still, the fishery will suffer a heavy loss caused by this issue (Benanou, et al., 2003; DãAz et al., 2005; Elhadi et al., 2004). Although China has focused on the developing the comprehensive treatment approaches, it takes time to accumulate experience, so that a mature and reliable treatment program has not yet been developed till now.

Water safety is mainly unpinned in the water odor that is mainly caused by three factors: decomposers of organic matter such as inorganic ions, plants, microorganism, and algae metabolites. Among them, algae can produce a substantial amount of different odorous substances during the proliferation, growth and death process (Worley et al., 2003; Howgate, 2004; Klausen et al., 2010). For example, diatoms are an important source of earthy smell; dead algae act as actinomycetes to produce odorous compounds; rotten blue-green algae produce sulfides such as dimethyl sulfide and dimethyl trisulfate.

There are two types of frequently used methods, i.e. the instrumental analysis and sensory analysis (Lanciotti et al., 2003; Lin et al., 2003; Lawton et al., 2003). Instrumental analysis features high sensitivity and high accuracy, but its sample treatment is difficult and time-consuming; sensory analysis seems direct, simple and qualitative, but it is highly demanding for olfactory sensitivity and more awkward to quantitatively analyze the samples.

It is just because of diverse substances, many factors that may cause odors, and the analysis awkwardness that relevant scholars have started conducting the survey on this field (Lu et al., 2003; Sugiura et al., 2010; Spiteller et al., 2002). Huang Xianhuai et al. analyzed the odor of Chaohu Lake and identified that the odor was mainly attributed to algae, actinomycetes, and other creatures and organic pollutants. Li Lin et al. conducted a comprehensive analysis of environmental factors and odor compounds in the Great Lotus Lake. It was found that β-ring citral and β-ionone had a direct bearing on total algae and light intensity, and the concentration of 2-methylisoborneol was related to the anabaena.

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In order to carry out the water safety management (Yang, 2018) and further improve the reliability, veracity and rapidity of odor test and analysis technologies, analyze the composition and reasons of water odor substances, this paper uses the headspace solid phase microextraction-gas chromatography/mass spectrometry to analyze the odorous substances and relevant algal decomposers in Taihu Lake. The analysis results will provide the clues to deodorizing water body polluted by algae, and maintaining water safety and cleanliness.

2. Experimental analysis

According to relevant literature (Sung et al., 2005; Szczurek and Maciejewska, 2005; Zaitlin et al., 2003), there are 4 kinds of compounds, i.e. 2-methylisoborneol (MIB), geosmin (GEO), β-ring citral and β-ionone, all of which play a key function on the water odor. Choose them to build the headspace solid phase microextraction-gas chromatography/mass spectrometry (HS-SPME-GC/MS), and the experimental conditions are optimized.

2.1 Experimental conditions

2.1.1 Solution preparation

Take the methyl alcohol as the solvent, prepare 1000mg/L β-Cyclocitral and β-Ionone as the storing solutions, 10mg/L MIB, GEO, β-Cyclocitral and β-Ionone as the working solution, 1mg/L mixed standard solution, store them at 4°C in the refrigerator for use.

2.1.2 Optimize GC/MS conditions

Mass spectrometry full scan (30-350 amu) and selective ion storage (SIS) (quantitative characteristic ions: m/z 95, 137, 112, 177; monitored characteristic ions: m/z 107, 126, 152, 135) are adopted to optimize sample inlet temperature, split ratio, and column temperature.

2.1.3 Optimize HS-SPME conditions

The HS SPME is optimized by thermal resolution time, extraction time and temperature and ionic strength.

2.1.4 Precision and accuracy analysis

The precision and accuracy of the HS SPME GC/MS are analyzed under the optimal experimental conditions.

2.2 Analysis of results

2.2.1 GC/MS analysis conditions

With the optimization analysis, the chromatographic conditions: sample inlet temperature 250°C, splitless sampling mode, the column temperature for temperature programming, and the high purity He as the carrier gas; the mass spectrometry conditions: 260°C and 180°C as the transmission line and ion trap temperatures; the EI ionization source is also used.

2.2.2 Thermal resolution time and Impact of extraction time on extraction efficiency

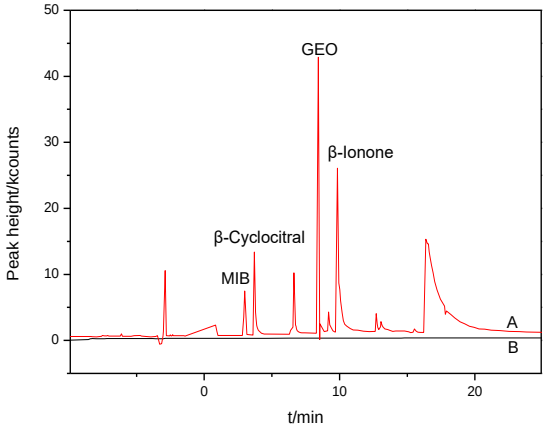

Figure 1: Comparison of 3 min thermal resolution effect

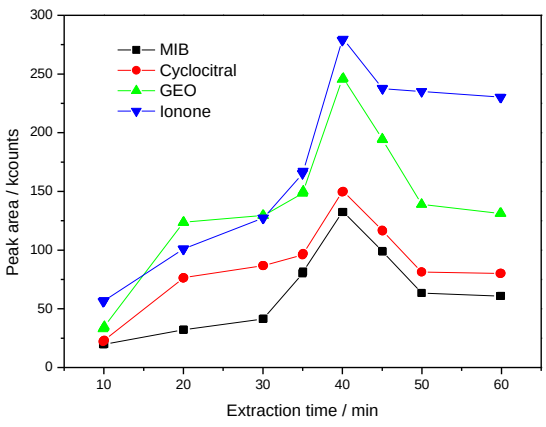

Figure 2: Impact of extraction time on extraction effect

A and B in Fig. 1 represent the total ion chromatograms after the extraction and the first sample injection. It is known from the figure that after 3 min extraction, individual compound can be completely resolved without the interference with other samples. Moreover, in order to ensure the activation of the extraction head, the thermal resolution time is finally selected as 3 min.

Since the principle of solid phase microextraction is the enrichment of substances under test on the modified fused silica optical fiber adsorbent, so that the time lapse will affect the extraction effect. As shown in Fig. 2, the extraction effect first increases over time, and then decreases when it reaches the peak, and finally maintains at a certain stable level. As a result, in order to minimize the extraction time and ensure the optimal extraction effect, the extraction time is determined as 40 min.

2.2.3 Impact of extraction temperature on extraction effect and Impact of ionic strength on extraction effect

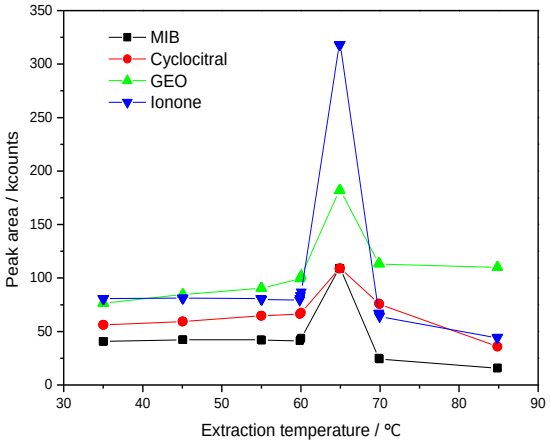

Figure 3: Impact of extraction temperature on the extraction effect

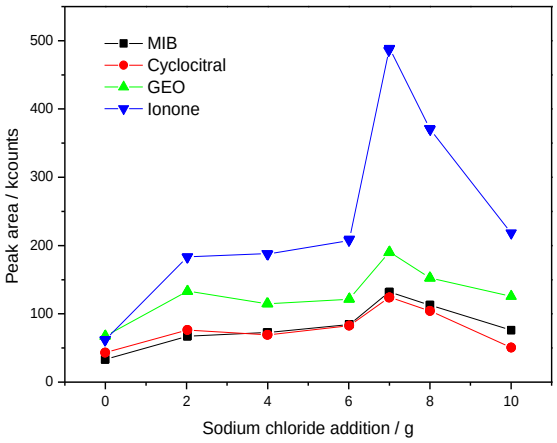

Figure 4: Impact of ion strength on extraction effect

The solid phase microextraction is characterized by the equilibrium, so that the temperature plays a key role in the equilibrium acceleration and disequilibrium. As shown in Fig. 3, as the time goes on, the extraction effect is slightly improved, and reaches a peak at a specific temperature (65 ° C), then decreases as the time goes by. For this reason, the extraction time is chosen to be 65 °C.

The ionic strength will produce an effect on the compound solubility in the aqueous phase. As shown in Fig. 4, the extraction effect gets better when the ionic strength increases. However, the ionic strength will limit the extraction effect after reaching a specific level. Therefore, the sodium chloride added may reach 29%.

2.3 Precision

In summary, the optimal extraction conditions are determined as follows: thermal resolution time 3 min; the extraction temperature 65 °C; the extraction time 40 min, and the sodium chloride content 29%.

Table 1: Relative standard deviation of individual substance in different scanning modes

Chemical compound	Relative standard deviation / %	
	Full scan mode	SIS mode
MIB	3.4	4.5
β-Cyclocitral	8.0	9.3
GEO	5.3	5.6
β-Ionone	10.1	12.2

Under the optimal experimental conditions, the relative standard deviations of 4 compounds are analyzed by the mass spectrometry full scan (200 ng/L sample) and the selective ion storage (sample 20 ng/L). The results are shown in Table 1. As shown in the table, the two scanning determination methods have not much different precisions, and the full scanning mode is slightly better than the SIS mode.

2.4 Recovery

As shown in Tables 2 and 5, the recoveries of the four compounds are relatively high, the maximum falls on the GEO, i.e. 96.24%, and the minimum is 93.84%, which shows that the odor test technology is feasible.

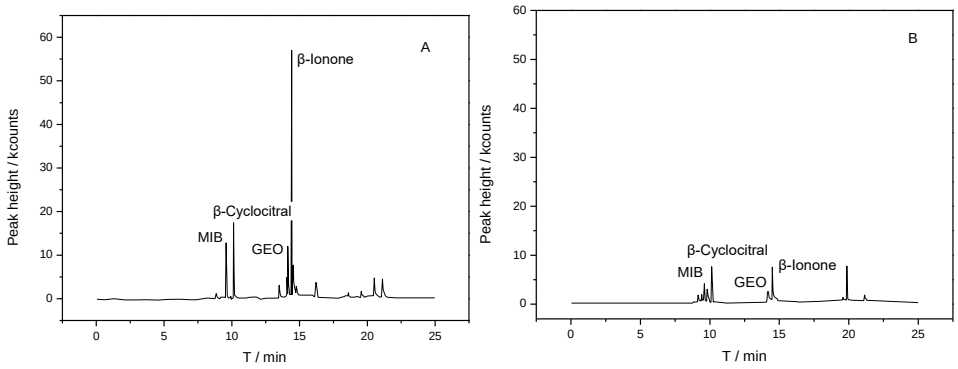

Figure 5: Total ion chromatograms before and after sample spike (A: after spiked; B: experimental water sample)

Table 2: Standard recovery of individual substance

Chemical compound	Content (ng/L)	Amount of addition (ng/L)	Measured value (ng/L)	Rate of recovery /%
MIB	57.77	50	102.29	94.92
β-Cyclocitral	207.32	100	288.38	93.84
GEO	82.06	100	175.12	96.24
β-Ionone	28.31	30	54.66	94.74

3. Empirical analysis

In order to further verify the reliability of the odor measurement method, this paper takes the Taihu water (Ahmad et al., 2018) body to test and analyze the above four compounds.

3.1 Water sampling

Select 6 different sampling sites around the Taihu Lake, collect the water samples from January to March using the clean glass bottles according to the collection operation, and well mark and record them.

3.2 Change in MIB concentration and Change in the β-Cyclocitral concentration

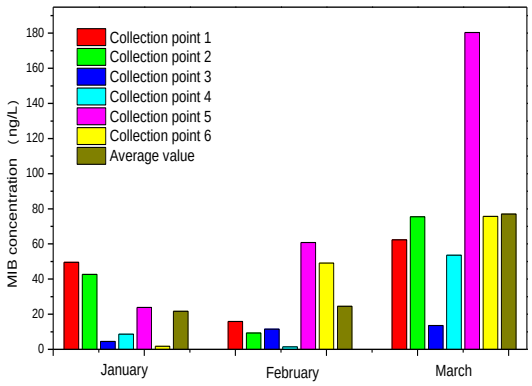

Figure 6: Change in MIB concentration

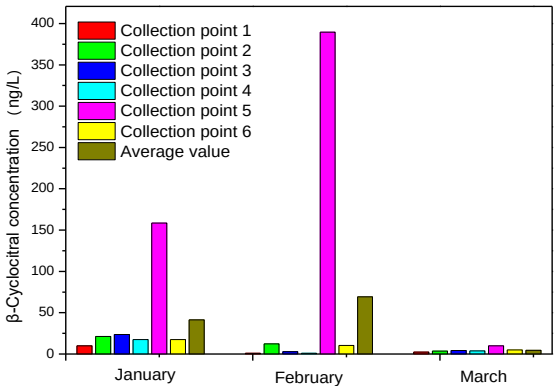

Figure 7: Tendency of β-Cyclocitral concentration

The change in MIB concentration is shown in Fig. 6. It is obvious that there are the lower MIB concentrations in January and February, and the maximum in March; the MIB concentration in three months increases as the

time goes on, but most significantly in March; the concentration of sample point 5 is the maximum and reaches the peak in March.
Figure 7 is a data map of β-Cyclocitral concentration. It can be seen from the figure that the concentration of sample point 5 reaches the maximum in each month, and the rangeabilities of other sampling points seem small. The average concentration in each month first increases and then decreases.

3.3 Changes in the GEO concentration and Change in the β-Ionone concentration

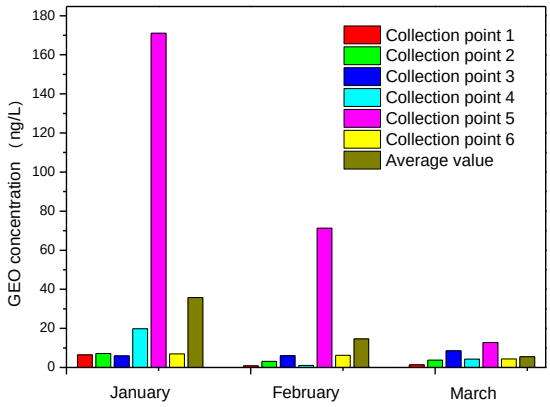

Figure 8: Tendency of GEO concentration

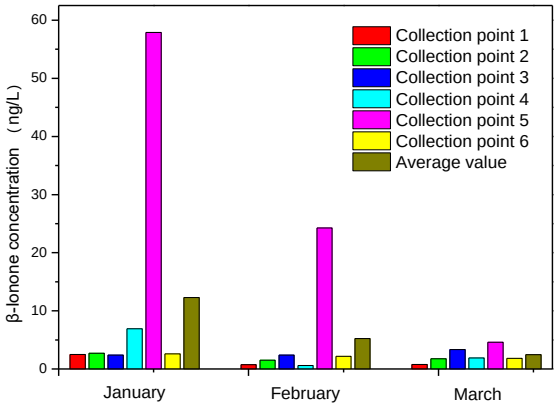

Figure 9: Change map of β-Ionone concentration

As shown in Fig. 8, it is a data map of GEO concentration at different time points and at different sampling points. It can be seen from the figure that the concentration of sample No. 5 is still the maximum, the concentration of sample No. 1 is the minimum; the average concentration decreases over the time.
As shown in Fig. 9, it is a data map of β-Ionone concentration at different time points and at different sampling points. It can be seen from the figure that the change trend of β-Ionone concentration is similar to that of GEO concentration, and the sampling point 5 is the maximum, and the overall trend is downward.
The well-established HS-SPME-GC/MS technology is used to test and identify the water in Taihu Lake, which shows that there are MIB, GEO, β-Cyclocitral and β-Ionone odor substances in Taihu Lake. The maximum concentrations are 180.39, 171.05, 389.62, 57.90 ng/L, respectively.

4. Conclusion

This paper uses the headspace solid phase microextraction and GC/MS to analyze the odorous substances that cause water safety and optimize the test conditions. The odorous substances in the Taihu Lake water areas are also tested and identified, providing the clues to deodorizing the Taihu Lake and other water areas.
4.1 The HS-SPME-GC/MS test technology is built for 4 kinds of odorous substances such as MIB, GEO, β-Cyclocitral and β-Ionone, and the optimal extraction conditions are given: the thermal analysis time lasts for 3 min, and the extraction temperature is 65 °C; the extraction time lasts for 40 min, and the sodium chloride reaches 29%; the best experiment conditions are as follows: for the chromatographic conditions, the sample inlet temperature is 250 ° C, the sampling mode is splitless, the column temperature uses the temperature programming, and the high purity He is the carrier gas; for the MS conditions, the transmission line temperature and the ion trap temperature fall over 260 ° C and 180 ° C, respectively, and an EI ionization source is used.
4.2 By analyzing the precision and accuracy of the measurement method under the optimal conditions, it is found that the GEO is the maximum recovery rate, up to 96.24%, and the β-Cyclocitral is 93.84% as the minimum, which shows that the odor test and determination technology has feasibility.
4.3 The method is verified by using water samples from the Taihu Lake. The results reveal that MIB, GEO, β-Cyclocitral and β-Ionone in Taihu Lake have the maximum concentrations, i.e. 180.39, 171.05, 389.62, 57.90ng/L, respectively.

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