

Determination of earthy-musty odors in tap water by gas chromatography–mass spectrometry with silica solid-phase extraction

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ABSTRACT

This research aimed to develop an effective method for detecting semivolatile earthy-musty odors without using the conventional sample processing equipment used for volatile compounds. The concurrent isolation of 2-methylisoborneol (2-MIB), *trans*-1,10-dimethyl-*trans*-9-decalol (geosmin, GSM), 2-isopropyl-3-methoxy pyrazine (IPMP), and 2-isobutyl-3-methoxy pyrazine (IBMP) in tap water was successfully achieved by employing a combination of n-hexane liquid–liquid extraction (LLE) and silica solid-phase extraction (SPE) techniques. Gas chromatography–mass spectrometry (GC–MS) was utilized for the identification of these targets, with the inclusion of borneol (BN) as an internal reference. This robust method was optimized and validated. It was found that the method showed good linearity in the range of 0.5–100 ng/mL and produced good recoveries (84.6 %–103 %) with satisfactory relative standard deviations (1.50 %–10.1 %). The determined limits of detection (LODs) for the group of four substances were found to vary from 0.3 to 0.9 ng/L, whereas the limits of quantitation (LOQs) exhibited variations between 1 and 3 ng/L. The subsequent implementation of this methodology to evaluate the four previously described off-flavor chemicals in tap water resulted in satisfactory results.

1. Introduction

Taste and odor (T&O) problems in tap water are a common global issue and impact water supplies in many countries [1]. Earthy and musty odors are particularly unpleasant and troublesome and are often encountered in water [2]. While geosmin has been linked to altered energy metabolism and behavioral changes in fauna [3,4], environmentally relevant concentrations of off-flavor compounds have not exhibited serious health effects on humans [5]. However, consumer complaints concerning T&O in reservoir-sourced tap water, especially during elevated temperatures, remain prevalent [6]. Given this, it is necessary that these unpleasant odors be regularly monitored, and treated where needed, before reaching the consumer. Compounds such as 2-Methylisoborneol (2-MIB), *trans*-1,10-dimethyl-*trans*-9-decalol (geosmin, GSM), 2-isopropyl-3-methoxy pyrazine (IPMP), and 2-isobutyl-3-methoxy pyrazine

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(IBMP) have been identified as principal agents of earthy-musty odors in water [7], often originating from metabolites of cyanobacteria [8], actinomycetes [7,9] and myxobacteria [10]. The odor thresholds of humans for these compounds are extremely low, for example, 2-MIB, GSM, IPMP and IBMP have odor concentrations of as low as 1–10 ng/L, 4–10 ng/L, 2–16 ng/L, and 1–16 ng/L, respectively, in water [11]. As a result, nations including China [12] and Japan [13] have established a maximum permissible concentration of 10 ng/L for 2-MIB and GSM in potable water. As such, analytical techniques for these compounds must demonstrate exceptional sensitivity, selectivity, and incorporate effective pretreatment.

In the past, solid-phase microextraction (SPME) [14,15] is the most commonly used pre-conditioning method for the analysis of earthy-musty odors in water. Nevertheless, the utilization of a solitary SPME fiber for several samples presented potential hazards of cross-contamination and reduced effectiveness of the fiber over time [16]. Additionally, while employing SPME for the direct analysis of 2-MIB and GSM in tap water, an experimental error range of 10 ~ 70 % was observed due to the presence of residual chlorine [17]. Additional methodologies, such as purge and trap(P&T) [18] and solid-phase extraction (SPE) [19] have been occasionally reported in environmental waters. However, their effectiveness in the analysis of tap water is found to be restricted. The limits observed can be due to various reasons, such as the presence of chlorine residuals, which hinder the sequestration of GSM in C18 SPE methods [16]. The utilization of liquid-liquid microextraction (LLME) [20] was employed in determination of earthy-musty odors in drinking water. However, it exhibited poor efficiency in the extraction process. In light of these issues, it is necessary to explore a new method to overcome the limitations of the above methods.

This study introduced a new effective method for quantitative determination of 2-MIB, GSM, IPMP and IBMP in tap water with liquid-liquid extraction (LLE) and SPE techniques. The extraction and concentration conditions were optimized, and GC-MS was used to identify and quantify these compounds. This technology presents a potentially advantageous for detecting the odors in environmental and biological samples.

2. Materials and methods

2.1. Reagents and materials

N-hexane, ethyl acetate, acetone and acetonitrile were all of HPLC grade and supplied by CNW Technologies (Shanghai, China). 2-MIB ($\geq 98\%$), GSM ($\geq 98\%$), IPMP ($\geq 98\%$), IBMP ($\geq 98\%$) and borneol(BN) ($\geq 98\%$) were obtained from Dr. Ehrenstorfer GmbH (Bgm Schlosser-Str., Augsburg, Germany). Sodium chloride was provided by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Silica SPE cartridges (200 mg, 3 mL), C18, neutral alumina (N-alumina), silica, florisil and alkaline alumina (Al-alumina) were purchased from Agela Technologies (Tianjin, China). Chitosan was sourced from Aladdin (Shanghai, China). Standard mixtures of 2-MIB, GSM, IPMP and IBMP were constituted in n-hexane and stored at $-18\text{ }^{\circ}\text{C}$ in darkness. The concentration level of the standard solution was 0.5, 1, 10, 50 and 100 ng/mL.

2.2. Apparatus

The analytical platform for gas chromatography-mass spectrometry (GC-MS) utilized was the TSQ QUANTUM GC from Thermo Fisher Scientific (Waltham, MA, USA). SPE operations were facilitated using a device from Supelco (Bellefonte, PA, USA). Homogenization of solutions was achieved using a vortex mixer from IKA (Staufen, Germany).

2.3. Absorbent material adsorption profile test

To 5 mL of a 50 ng/mL standard solution of n-hexane, ethyl acetate, acetone and acetonitrile, 0.5 g of C18, N-alumina, silica, Florisil, chitosan and Al-alumina were added. Following vortex mixing, The solutions were allowed to stand to collect the supernatant, which was detected by GC-MS. Duplicate tests were performed for each sorbent.

2.4. Isolation and concentration of 2-MIB, GSM, IPMP and IBMP from tap water

Within a separating funnel, 100 ng borneol was combined with a 250 mL water aliquot. Dissolution of sodium chloride (12.5 g) was then performed in the water aliquot. This was succeeded by the addition of 15 mL n-hexane, vigorous shaking for 3 min, and subsequent stratification. The n-hexane layer was then removed into a collection tube.

The silica SPE cartridge was preconditioned with n-hexane before the extraction solution was passed through. Then, the cartridge was rinsed with 1 mL of n-hexane and dried under vacuum. The target analytes were eluted with 1 mL of n-hexane/ethyl acetate (v/v, 2/1). The eluate was vortexed for GC-MS analysis.

2.5. GC-MS determination

The GC instrument was equipped with an HP-5 MS fused silica capillary column ($30\text{ m} \times 0.25\text{ mm} \times 0.5\text{ }\mu\text{m}$). The carrier gas was helium (purity $>99.99\%$) with a flow rate maintained at 1.0 mL/min. The injector was held at $250\text{ }^{\circ}\text{C}$ in splitless mode. The oven temperature was held at $50\text{ }^{\circ}\text{C}$ for 1 min, increased to $180\text{ }^{\circ}\text{C}$ at $5\text{ }^{\circ}\text{C}/\text{min}$, and maintained at $180\text{ }^{\circ}\text{C}$ for 1 min. Then, it was increased to $280\text{ }^{\circ}\text{C}$ at $20\text{ }^{\circ}\text{C}/\text{min}$ and maintained at $280\text{ }^{\circ}\text{C}$ for 5 min.

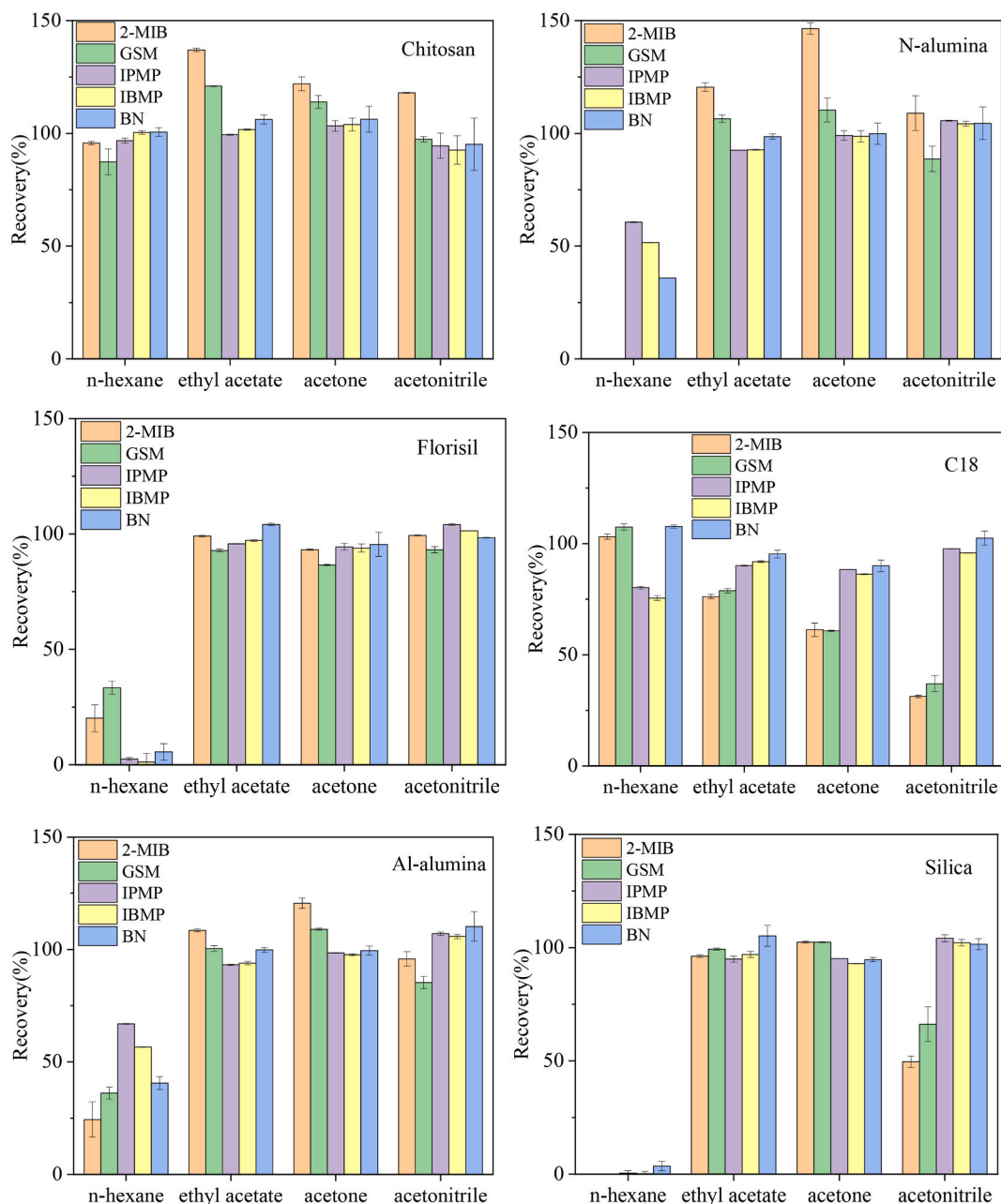
In the MS analysis, electron ionization (EI) mode was used with an electron energy of 70 eV, source temperature of $250\text{ }^{\circ}\text{C}$, and MS

Table 1

Selected ions, Linearity, limit of detection (LOD), limit of quantitation (LOQ) and enrichment factor (EF) for target compounds.

Compound	Selected ions	Linear equation	R ²	linear range (ng/mL)	LOD (ng/L)	LOQ (ng/L)	EF
2-MIB	94.9, 107.9, 134.9	$Y = -0.0061731 + 0.138881X$	0.9990	0.5–100	0.3	1	278
GSM	111.9, 124.9, 96.9	$Y = -0.0116947 + 0.158083X$	0.9996	0.5–100	0.9	3	247
IPMP	136.9, 151.8, 123.8	$Y = 0.0109084 + 0.117478X$	0.9992	0.5–100	0.6	2	266
IBMP	123.8, 150.9, 93.9	$Y = -0.013399 + 0.231933X$	0.9992	0.5–100	0.5	1.5	270
BN	107.9, 94.9, 151.9	—	—	—	—	—	—

—Not needed.

**Fig. 1.** Recoveries of 2-MIB, GSM, IPMP, IBMP, and BN by chitosan, N- alumina, florisil, C18, Al-alumina and silica in n-hexane, ethyl acetate, acetone and acetonitrile.

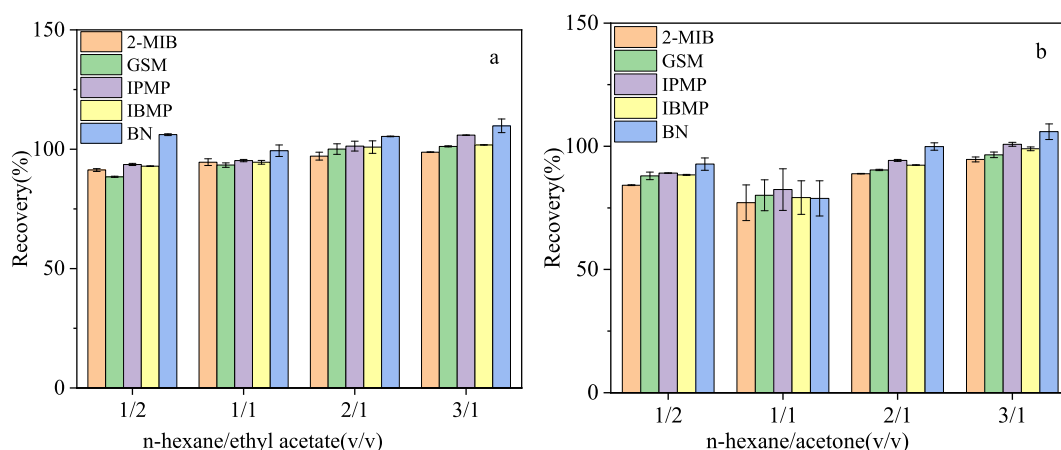


Fig. 2. Elution efficiencies of n-hexane/ethyl acetate (a) and n-hexane/acetone (b) with different volume ratios.

transfer line temperature of 280 °C. Mass spectra were obtained at m/z (50–350) to confirm the appropriate masses for selected ion monitoring (SIM), detailed in Table 1.

3. Results and discussion

3.1. Mass spectrometric characteristics of the off-flavor compounds

Comprehensive mass spectrometric analysis was performed on standard solution (2 µg/mL) of 2-MIB, GSM, IPMP, IBMP, and BN, prepared in n-hexane. The target peaks were identified by cross-referencing a mass spectrometry database with the characteristic ions described in prior research. Qualitative and quantitative ions were classified based on their abundance and specificity in the full scan. The resulting data was organized and recorded in Table 1.

3.2. Optimization of chromatographic conditions

Traditionally, initial oven temperatures of 40–60 °C [20–22] have been utilized to study 2-MIB and GSM. But there is no any information regarding the analysis of IPMP and IBMP. As a result, the present study examined initial oven temperatures ranging from 40 °C to 80 °C. While the peak areas of IPMP and IBMP increased as the initial oven temperatures were raised, a decrease in peak height was detected after reaching 50 °C. The peak height of IPMP at 60–80 °C initial oven temperature was 18.6 %–34.2 % lower than 50 °C, while the reduction for IBMP was 1.4 %–32.2 %. Based on the observations above, 50 °C was the optimum initial temperature.

3.3. Adsorption characteristics of absorbents in different organic reagents

In the past, LLE for extracting off-flavor compounds was commonly performed without concentration [23] or with post-concentration using a gentle stream of nitrogen or argon at room temperature [21,24]. Nevertheless, focusing on nitrogen flux resulted in substantial losses of analytes, surpassing 67 %. To address this issue, an optimized adsorption material was implemented in the present investigation.

The adsorption rates of 2-MIB, GSM, IMP, IBMP, and BN were explored with the method presented in Section 2.3. The results are shown in Fig. 1. The adsorption rates of chitosan for the five compounds were consistently below 13 % in different organic reagents. N-alumina and florisil sorption rates were observed to be below 8 % in ethyl acetate, less than 14 % in acetone, and did not surpass 12 % in acetonitrile. The experimental results revealed that N-alumina exhibited total adsorption of 2-MIB and GSM in n-hexane, but adsorption percentages ranging from 40 % to 65 % were recorded for IPMP, IBMP and BN. In contrast, it was observed that the adsorption of IPMP, IBMP, and BN by florisil in n-hexane exceeded 94 %, whereas the adsorption of 2-MIB and GSM ranged from 67 % to 80 %. C18 and Al-alumina showed inconsistent adsorption rates (0–76 %) for the five compounds in different organic reagents. The adsorption rate of silica for the five compounds was found to be remarkably high, more than 96 % in n-hexane. However, the adsorption rate was below 5.1 % and 7.1 %, in ethyl acetate and acetone respectively. Based on the observed results, it can be concluded that n-hexane is a suitable solvent for extracting the five earthy-musty odors. Additionally, silica has been found to absorb the target compounds in hexane with ethyl acetate or acetone as elution reagent.

3.4. Optimization of elution solvent for silica SPE

After adsorbing 50 ng of the five compounds, the silica SPE method was utilized to eluent the compounds using 1 mL of n-hexane/ethyl acetate and n-hexane/acetone in different proportions (v/v, 1/2, 1/1, 2/1, 3/1, 4/1). The elution efficiencies were illustrated

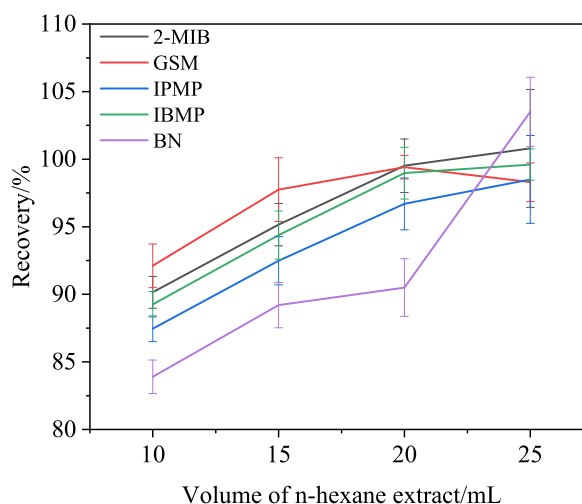


Fig. 3. Extraction efficiency versus n-hexane volume.

Table 2

Standard recoveries and RSDs of four off-flavor compounds (n = 6).

Compound	4 ng/L		8 ng/L		40 ng/L		200 ng/L	
	recovery/%	RSD/%	recovery/%	RSD/%	recovery/%	RSD/%	recovery/%	RSD/%
2-MIB	96.2	1.77	94.9	1.50	95.2	4.48	95.6	4.47
GSM	94.5	2.08	89.6	3.29	97.1	3.47	94.2	2.48
IPMP	103	10.1	84.9	4.18	85.5	5.48	89.8	4.69
IBMP	98.7	6.28	84.6	4.53	86.2	3.94	90.3	4.15

respectively in Fig. 2(a) and (b). The results of the comparative analysis demonstrated that the elution rates were significantly more precise when utilizing n-hexane/ethyl acetate than n-hexane/acetone. As a result, the eluent of choice for this study was determined to be n-hexane/ethyl acetate. The elution rates of n-hexane/ethyl acetate (v/v, 2/1, 3/1, 4/1) were observed to vary between 97.1 % and 105.9 % for 2-MIB, GSM, IPMP and IBMP. In the contrast, the elution rates of n-hexane/ethyl acetate (v/v, 1/2, 1/1) were 88.5 %–93.6 % and 93.4 %–95.2 %, respectively. Based on the results obtained, it was determined that n-hexane/ethyl acetate (v/v, 2/1, 3/1, 4/1) exhibited favorable characteristics for the intended purpose, and the selected eluent for this study was n-hexane/ethyl acetate (v/v, 2/1).

3.5. Evaluation of extraction volume

Water samples containing 500 ng of 2-MIB, GSM, IPMP, IBMP, and BN were subjected to extraction using n-hexane volumes of 10 mL, 15 mL, 20 mL, and 25 mL. The associated extraction efficiencies are shown in Fig. 3. The extraction recoveries for the aforementioned volumes were 83.9 %–92.1 %, 89.2 %–97.8 %, 90.5 %–99.5 % and 98.3 %–103.5 %, respectively. While increasing the solvent volume led to enhanced recovery, it simultaneously extended the time necessary for the subsequent concentration phase. Consequently, the optimal extraction volume was determined to be 15 mL.

3.6. Method validation

Calibration curves were generated for each compound using prepared concentrations of 0.5, 1, 10, 50 and 100 ng/mL, with 100 ng/mL BN as internal standard. The ratios of peak areas between the target analytes and the internal standard were plotted against the corresponding concentration, as outlined in Table 1. This analysis confirmed the strong linearity of the calibration curves. The calculation formula for the calibration curves and the concentrations of sample is as follows:

$$X = \frac{C \times V}{M}$$

where X, C, V, M are the concentration of analyte in water sample (ng/L), concentration of analyte in eluent quantified by standard curve (ng/mL), volume of eluent (mL), and volume of water sample (L), respectively.

The limits of detection (LODs), based on signal-to-noise ratio (S/N) of 3, ranged from 0.3 to 0.9 ng/L. The limits of quantitation (LOQs), based on signal-to-noise ratio (S/N) of 10, ranged from 1.0 to 3.0 ng/L. The enrichment factor (EF) was defined as the ratio of

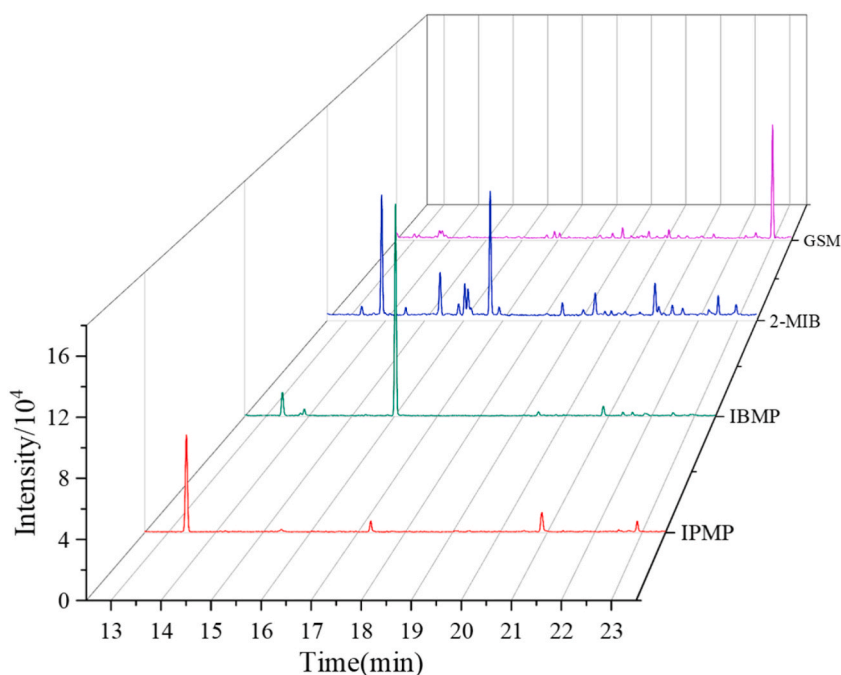


Fig. 4. Typical chromatograms of IPMP (13.39 min), IBMP (16.03 min), 2-MIB (16.67 min) and GSM (22.97 min) in tap water (200 ng/L) after sample preparation.

Table 3

Comparison of methods published for determining 2-MIB, GSM, IPMP and IBMP in tap water samples.

Methodology	Sample Volume (mL)	Extraction Temp. (°C)	LOD (ng/L)	Recovery (%)	RSD (%)	Standard curve	Reference
HS-SPME-GC/MS	8	60	0.25–0.46	80.00–125.37	3.20–11.37	Pretreatment required	[14]
HS-SPME-GC/MS	20	90	0.25–0.58	82.1–89.3	8.0–9.5		[23]
HS-SPME-GC/MS	20	70	0.39–0.51	100.7–107.3	3.8–6.8		[7]
HS-SPME-GC/MS	10	65	0.2–1	85.99–112.30	6.19–14.30		[26]
LLME-GC/MS	200	room temperature	0.1	55.4–105.1	3.1–10.9		[27]
HS-CI&TOF MS	100	room temperature	3.9–50.2 ^a	101–105	4–15		[28]
LLE-SPE-GC-EI-MS	250	room temperature	0.3–0.9	84.6–103	1.50–10.1	No pretreatment	this study

— Not mentioned. ^a For IPMP and IBMP.

the analyte concentration in the eluent to the initial concentration of analyte within the sample [25]. The results are listed in Table 1.

The recoveries and relative standard deviations (RSDs) were evaluated, and the results are listed in Table 2. Fig. 4 shows a typical chromatogram of IPMP, IBMP, 2-MIB, and GSM in tap water. As presented in Table 2, the recoveries of the four compounds were 84.6 %–103 %, indicating that the method demonstrated good recovery for a wide range of concentrations of taste and odor compounds. In addition, the calculated relative standard deviations (RSDs) for the four compounds were all below 10.1 %, hence confirming the precision of the employed methodology.

3.7. Method application

To further demonstrate the feasibility of the method, it was applied to determine the concentrations of four off-flavor compounds in Shanghai's tap water. Eight samples from different communities in Shanghai were analyzed, and the concentration of 2-MIB in one sample was 8.23 ng/L, while the three compounds were not detected in other samples.

3.8. Method comparison

This method was compared with the other existing methods used to detect the 2-MIB, GSM, IPMP and IBMP in tap water. The results of this comparison are presented in Table 3. As indicated by the data presented in Table 3, the effectiveness of the seven approaches exhibited variability in their ability to handle the group of earthy-musty odorous compounds. It is worth noting that Headspace and solid phase microextraction compounded with gas chromatography–mass spectrometry (HS-SPME-GC/M) are the most used method, which need a dechlorination step [14]. The pretreatment technology in this method can be conducted at room temperature,

eliminating the need for strict sealing procedures. This sets it apart from the HS-SPME method. Additionally, there is no cross contamination in this approach, which is a problem for SPME. The recovery of IPMP was less than 60 % by LLME [27]. The Headspace and chemi-ionization technique coupled with time-of-flight mass spectrometry (HS-CI&TOF MS) requires specific devices and the conventional experiment was unable to establish the LODs for GSM and 2-MIB [28]. All reference methods in Table 3 exhibit a common characteristic: the necessity for identical sample pretreatment in their calibration curves, which is not needed in this method. Therefore, this method provides improved ease of use while also resolving the inherent constraints found in other techniques.

4. Conclusion

A method of n-hexane extraction and silica SPE concentration coupled with GC/MS was developed, optimized, and evaluated for the determination of earthy-musty odorous compounds in tap water. Leveraging silica SPE concentration effectively addressed the issue of compound loss encountered during the gas-blowing concentration phase. The sensitivity of this method was high enough to produce satisfactory quantitative results below the odor thresholds of the examined off-flavor compounds. According to the analytical performance evaluation results, the method is a reliable, accurate and precise technique that can be implemented to analyze the practically relevant concentrations of earthy-musty odorous compounds in tap water samples. Potential extensions of this silica adsorption technique may include its application to environmental and biological matrices.

Data availability statement

The data used to support the findings of this study are available from the corresponding author upon request.

CRediT authorship contribution statement

Liangliang Tian: Writing – original draft, Visualization, Software, Project administration, Methodology, Funding acquisition, Data curation, Conceptualization. **Xin Qu:** Validation, Software, Methodology, Investigation, Data curation. **Dong-mei Huang:** Resources, Funding acquisition, Data curation. **Yong-fu Shi:** Software, Resources, Formal analysis. **Cong Kong:** Writing – review & editing, Investigation, Formal analysis. **Yuan Wang:** Writing – review & editing, Supervision, Project administration, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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