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Determination of geosmin and 2-methylisoborneol in source water by dispersive liquid-liquid micro-extraction combined with gas chromatography-mass spectrometry

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Abstract: A method using dispersive liquid-liquid micro-extraction (DLLME) and gas chromatography-mass spectrometry (GC-MS) was developed to analyze geosmin(GSM, trans-1,10-dimethyl-trans-9-decalol) and 2-methylisoborneol (2-MIB) in source water. The mass spectrometry was operated in selective ion monitoring (SIM) mode. Three kinds of dispersants and four extraction solvents were compared, acetonitrile was chosen as optimum dispersant, and chlorobenzene was chosen as the optimum extraction solvent. It was found that the method showed good linearity in the range of 5–100 ng/mL and gave limit of quantitation of 0.1ng/mL for GSM and 0.15ng/mL for 2-MIB. Good recoveries (82.6%–112%) and relative standard deviations (2.56%–6.23%) were also obtained.

Introduction

Taste and odor is the quality traits of drinking water which people can directly perceived .Taste and odor problems in water have received increasing attention in the past decades [1] .In china, residents life has been brought serious problems due to the source water quality deterioration [2,3]. Geosmin(GSM) and 2-methylisoborneol (2-MIB) which cause an earthy-musty smell have commonly been regarded as the dominant taste and odor compounds in surface water [4,5], and the olfactory threshold concentration of people is very low [6].

Because the GSM and 2-MIB usually occur at very low concentration in source water, it is necessary and essential to concentrate these compounds before analysis[7].The techniques have been developed to concentrate GSM and 2-MIB include liquid-liquid extraction, closed-loop stripping, purge and trap technique, solid-phase extraction, headspace solid phase micro-extraction. However, these methods have some shortcomings, which hinder their wide application. For example, closed loop stripping requires relatively complex instrumentation. Liquid-liquid extraction needs to use relatively more toxic solvent, and the concentration is a problem on account of the volatile feature of the target compound. Solid-phase extraction was quick and simple, but appropriate solid phase extraction columns were needed. Both purge and trap technique and headspace solid phase micro-extraction is time-consuming and inferior stability, and need some special tools. Dispersive liquid-liquid micro-extraction is a new micro-extraction technique, that needs less extraction solvent, and could increase the contact area between extraction solvent and the sample solution by dispersant. The operation is simpler and the extraction time is shorter, so this method was researched.

Gas chromatography-mass spectrometry (GC-MS) is the common method to identify GSM and 2-MIB in water. In this paper, we describe a method using dispersive liquid-liquid micro-extraction and gas chromatography–mass spectrometry for the analysis of the two taste and odor compounds in source water.

Materials and method

Reagents and materials

The standards of GSM and 2-MIB were purchased from Dr.Ehrenstorfer Company. Both standards were 100 μg · mL^{-1} in methanol.

Mixed stock standard solution of 1μg · mL^{-1} was prepared by diluting each standard in n-hexane.

Calibration mixtures at various concentration levels were obtained by combing aliquots of stock solutions with n-hexane and stored at -20°C.

Acetonitrile, n-hexane and chlorobenzene were HPLC-grade, and purchased from J.T.Baker Chemical Company.

Apparatus

The GC-MS analysis was carried out on a Thermo TRACE-DSQ (Thermo Fisher, USA) gas chromatography mass spectrometry, and a DB-5 ms fused silica capillary column (5% phenyl polysiloxane as non-polar stationary phase, 30m, 0.25 mm i.d. and 0.25 μm film thickness) from Agilent (J&W Scientific, Folson, CA,USA) was used for separation. The specific analysis conditions are as follows. The oven temperature program was held at 60°C for 4 min, raised to 250°C at increments of 12°C · min^{-1}, and sustained for 2 min. The carrier gas was ultra-pure helium (99.9999%) and was kept at 1 mL · min^{-1} constant flow rate. The injection port was set at 250°C in splitless mode and injection volume was 1μL. The transfer-line temperature was 250°C, and ion source temperature was set at 230°C. The mass spectrometer was operated in the EI positive mode(70 eV). The mass spectrometry was operated in the selective ion monitoring (SIM) mode. The selected ions (m/z) of GSM and 2-MIB are listed in Table 1 .

Table 1 MS Parameters for GSM and 2-MIB

compound	molecular weight	selected ion [m/z]	Rent time [min]
GSM	182.3	111.9*，124.9，96.9	12.8
2-MIB	168.3	95.0*，107.9，134.9	10.0

*quantitative ion

Method

Water samples should be filtered to remove the solid matter, and the pH must be greater than 6. About 10mL of water was weighed into a 15mL test tube with conical bottom. Then, 400μLof acetonitrile was added and mixed fully. 100μL of chlorobenzene was then added, and the tube was shaken vigorously by hand for 3 min. Afterwards, the mixed solution was frozen for 0.5 hour at -20°Cin refrigerator, and thawing under the condition of 4 °C. Finally, the cloudy solution was centrifuged at 2000 r/min for 8 min, the enriched analytes in the chlorobenzene were taken to detect by GC-MS.

Dispersant and extracting solvent optimization

A solvent system in dispersive liquid–liquid micro-extraction (DLLME) contains a mixture of water-immiscible extraction solvent and water-miscible disperser solvent. The type of solvent is an important factor in influencing extraction efficiency. Acetonitrile, methanol and acetone were selected as disperser solvent, and methylene chloride, chloroform, tetrachloromethane, chlorobenzene and tetrachloroethylene were selected as extraction solvent to experiment. Ten milliliter of water was added into a 15 ml test tube with conical bottom. 50 ng of analytes was added into the water, and mixed.400μl of disperser solvent and 100μl of extraction solvent was injected into the sample solution. The next steps follow the above method.

Results and discussion

Chromatographic conditions optimization

There are some chromatographic conditions can affect the detection sensitivity, include injection port temperature, the initial column temperature, the oven temperature program.

The result of the injection port temperature 200 °C, 250 °C and 280 °C compared experiment for the detection sensitivity of GSM and 2-MIB showed that the peak areas under different temperature were similar, but when temperature is 250 °C, the signal-to-noise ratio of the signal is highest, in order to improve the detection sensitivity, the injection port temperature 250 °C was chose.

The initial column temperature 60 °C and 100 °C were compared by experiment, it was found that when the initial temperature is lower, the sensitivity of detection signal is higher, so the initial column temperature of 60 °C was selected.

Different oven heating rate of 2, 5, 8, 8.5, 9, 10, 11, 12, 13, 14, 15 °C · min^{-1} was tried, the results showed that with the improvement of column heating rate, the peak areas of GSM and 2-MIB were similar ,but the corresponding signal to noise ratio (S/N) was increasing. When the heating rate was greater than 12 °C · min^{-1}, the increase of the S/N was not obvious. The heating rate of 12 °C · min^{-1} was chose in order to get higher sensitivity and better degree of separation of target peak and impurity peak .

Dispersant and extraction solvent optimization

The dispersant and extracting solvent optimization experiments were conducted, and the figure1 shows the result. The extraction efficiency of methanol-chlorobenzene for GSM and 2-MIB was low. The extraction efficiency of acetonitrile-methylene dichloride, acetonitrile-chloroform, acetone-methylene chloride, acetone-chloroform and acetone-chlorobenzene was too low to suitable for 2-MIB extraction. The extraction efficiency of acetonitrile-tetrachloromethane, acetonitrile-tetrachloroethylene, methanol-methylene dichloride, methanol-chloroform, methanol-tetrachlormethane, methanol-tetrachloroethylene, acetone-tetrachloroethylene for GSM and 2-MIB extraction was high but the recovery was very different. The recovery of acetonitrile-chlorobenzene for GSM and 2-MIB was 90%-120%, and the extraction efficiency is similar, so the acetonitrile-chlorobenzene was the best choice.

Linear ranges and detection limits

The performance of this method was investigated under optimum conditions. The peak areas were plotted against the corresponding concentrations to obtain the working curves of GSM and 2-MIB. The results are listed in Table 2.

The limits of quantitation were determined by injecting a series of low concentration extraction solvent to produce a signal-to-noise ratio (S/N) of 10, and then, the original concentrations were calculated as the limits of quantitation for the two compounds. The results are listed in Table 2.

Table 2 The equation, linear range, correlation coefficient and limit of quantitation (LOQ) of the method

compound	equation	linear range [ng · mL^{-1}]	Correlation coefficient	LOQ [μg · L^{-1}]
GSM	Y=2597.26X-482.407	5～100	0.9993	0.10
2-MIB	Y=2175.61X+1683.09	5～100	0.9989	0.15

Recoveries and relative standard deviation

The recoveries and relative standard deviation (RSD, n = 6) experiments were conducted, and the result are listed in Table 3.As shown in Table 6, the recoveries for GSM and 2-MIB were between 82.6%–112%, indicating that the method demonstrates good recovery.

Table 3 Standard recoveries and RSD of GSM and 2-MIB

compound	2μg · L^{-1}		10μg · L^{-1}		30μg · L^{-1}	
	Recovery[%]	RSD[%]	Recovery[%]	RSD[%]	Recovery[%]	RSD[%]
GSM	85.3	6.23	108	4.23	112	2.56
2-MIB	82.6	4.56	94.5	3.98	96.7	3.15

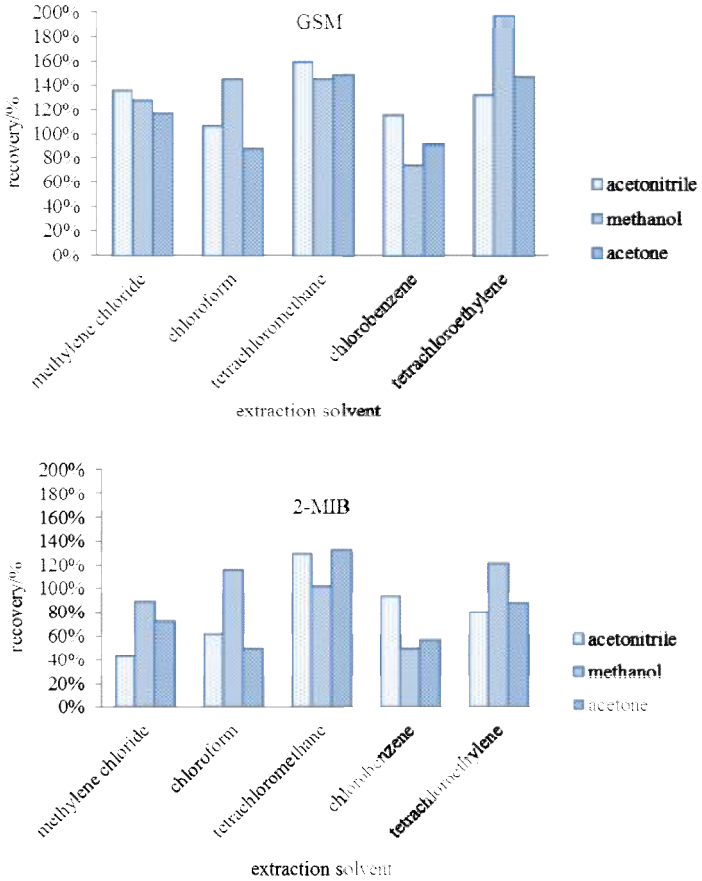

Fig.1 The recovery of GSM and 2-MIB in different dispersants and extraction solvents

Conclusions

In this investigation, a dispersive liquid-liquid micro-extraction method was developed for extraction of GSM and 2-MIB in source water. On the basis of optimization experiments, acetonitrile and chlorobenzene were chosen as dispersant and extraction solvent, respectively. The method clearly demonstrated good linearity, accuracy, and precision, so it could be used to analyze GSM and 2-MIB in source water.

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