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GC/MS Application Note

FOOD SAFETY ENVIRONMENTAL

Determination of Odor Compounds in Water by SPME Arrow Gas Chromatography/Mass Spectrometry

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Determination of Odor Compounds in Water by SPME Arrow Gas Chromatography/Mass Spectrometry

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Abstract

In this application the typical off-odor substances in drinking water 2-Methylisoborneol (2-MIB) and Geosmin are determined using the SPME Arrow device with gas chromatography/mass spectrometry (GC-MS) detection, and applied to the control of actual water samples. The method is robust, has high sensitivity compared conventional detection methods, and is fully automated. The detection limit is decreased by one order of magnitude with high accuracy. The precision and reproducibility is very good with RSD values of less than 3.7%, and the interday reproducibility at trace level is less than 8.7% RSD. The performance of this method satisfies the standard test requirements of 2-MIB and Geosmin in drinking water. The test results are very good for actual drinking water samples.

Keywords

Drinking water control, Geosmin, 2-MIB, SPME Arrow, SPME headspace extraction, GC-MS, China official regulation

Introduction

In recent years, problems with off-odors in domestic and foreign drinking water were frequently reported. This contamination increasingly affects the quality of drinking water. The two most common off-odor substances monitored are Geosmin and 2-methylisoborneol (2-MIB) with their chemical structures shown in Figures 1 and 2. Geosmin and 2-MIB are produced by cyanobacteria and are responsible for an unpleasant muddy or earthy off-flavor in drinking water, potentially also known from seafood. The olfactory thresholds are extremely low in the ppt level with 5 ng/L for Geosmin and even 1 ng/L for 2-MIB. The regulated maximum limit value is 10 ng/L in the China hygienic standard for domestic drinking water (GB5749-2006) for both off-flavor components. In 2016 the China National Standard test method GB/T 32470-2016 for Geosmin and 2-MIB testing in drinking water was established. Therefore, the requirement for a rapid, high sensitivity and reliable analysis method of trace off-odor levels is of special significance to the efficient control regional drinking water, and provide an early warning in case of an unexpected incident of peculiar water quality impact in our country.

At present, the developments on methods for off-odor analysis and determination are mainly focused on optimization of the instrumental analysis. For water samples the qualitative and quantitative detection is typically performed by GC-MS. The commonly used sample preparation methods include a wide variety of analytical solutions like the closed loop stripping analysis (CLSA), liquid-liquid extraction (LLE), solid phase extraction (SPE) technology, solid phase microextraction (SPME), liquid phase microextraction (LPME), ultrasonic assisted emulsification micro-extraction (USAEME), or the stir bar sorptive extraction (SBSE) technique. Many of the before mentioned methods have shortcomings such as a complex technical realization, lack of automation, the need of a larger amount of organic solvents, or low sensitivity. SPME in general is a "green" solventless extraction technique for small sample volumes and automated high sensitivity analyses. The SPME Arrow is a new patented SPME device with innovative improvements for ruggedness and high sample throughput, speed of extraction and high sensitivity for low LODs. The SPME Arrow comprises an arrow-shaped tip, which penetrates more easily and with less force and damage vial and injection port septa. The sorbent material coating provides a larger surface area and higher sorbent volume than fibers, increasing the extraction capacity, thus greatly improving the detection sensitivity. This method has the advantages of time saving, high extraction efficiency, no solvent use, less matrix interference, and ease of automation for large sample series. In this paper, an efficient and rugged SPME Arrow-GC-MS analysis method of the typical off-odors Geosmin and 2-MIB in water was established and successfully applied in the actual control of drinking water.

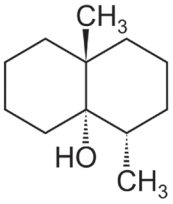

Fig 1: Geosmin

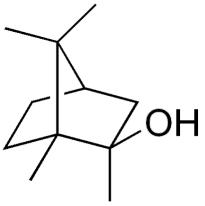

Fig 2: 2-Methylisoborneol (2-MIB)

Experimental

Instruments and Reagents

Instruments:

- Agilent PAL3 RSI or RTC automatic sample pretreatment platform, equipped with Agitator, Conditioning module, Heatex Stirrer module.
- Agilent 7890B 5977B single quadrupole GC-MS system.
- SPME Arrow Tool.
- SPME Arrow Holder.
- SPME Arrow: 1.1mm OD, DVB/CAR/PDMS sorbent phase, p/n: ARR11-DVB/CWR120/20-P5. Before first use condition the Arrow at 270 °C for 1 h.
- Injection port assembly for SPME Arrow operation, p/n: ARR-SSL-Inj-GC7890.
- Special inlet liner for SPME Arrow operation, p/n: ARRLIN17-GC7890-1.

Reagents:

- Standard solutions:
  - Targets: 2-MIB and Geosmin: Mixed standard solution (100 mg/L, methanol solution).
  - Internal standard: 2-isobutyl-methyl-methoxy-pyrrolidone (100 mg/L, methanol solution), both from Accustandard, as a certified standard solution.
- Sodium chloride, analytical grade (Group Chemical Reagent Co., Ltd.), 450 °C baked for 2 h.
- Methanol, chromatographic purity (Merck).
- Water, ultra pure/HPLC quality.

SPME Arrow Extraction Parameters

Add 1.5 g sodium chloride in an empty 20 mL screw cap vial. Add 5 mL of a water sample, and add 5 µL internal standard solution (2-isobutyl-methyl-methoxy-piperazine, 10 ng/mL). Tighten the cap and place the vial into the PAL System sample rack for analysis.
Before SPME extraction, the sample is incubated at 60 °C for 2 min, then the vial is transferred by the PAL System to the Heatex stirrer. The SPME Arrow penetrates the vial septum and its sorbent phase is extended into the air phase above the water sample, while maintaining the vial temperature at 60 °C for a 30 min headspace extraction. For analysis the SPME Arow moves to the injection port and is thermally desorbed at 250 °C for 5 min. During the desorption time the injector split is closed.

GC-MS Analysis Conditions

The analysis parameters of the GC-MS instrument are shown in Table 1.

Fig 3: SPME Arrow dimensions (top and middle) compared to SPME Fiber (bottom)

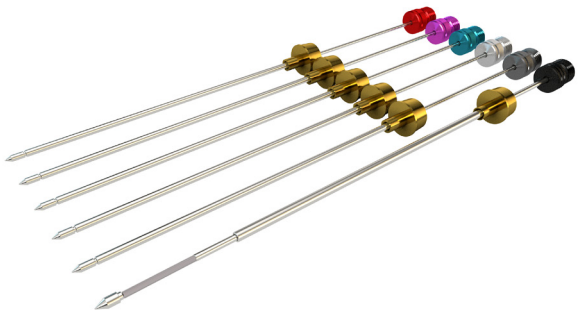

Fig 4: Color coded SPME ARROW devices

GC column and temperature program	DB-5MS UI, 30 m × 0.25 mm × 0.25µm, p/n 122-5532-UI 60 °C (2min) - 10 °C/min to 270 °C (2min)
Detector type, operating parameter	MS detector Transfer line temperature 280 °C Ion source temperature 250 °C
Acquisition mode and masses	Selective Ion Monitoring mode (SIM): 2-MIB: m/z 95,107,108 Geosmin: m/z 111,112,125 ISTD: m/z 94, 124
Injection parameter	Temperature 250 °C, splitless 2 min
Carrier gas and flow rate	He, 5.0 quality, constant flow mode, 1 mL/min

Table 1: GC-MS parameter setting

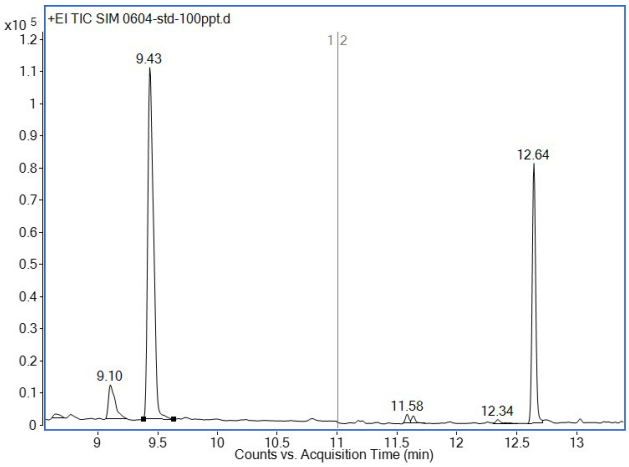

Fig 5: GC-MS chromatogram of 2-MIB and Geosmin aqueous solution (100 ng/L) by SPME Arrow extraction

Results and Discussion

Chromatogram and linearity of standard samples

The standard stock solution was prepared with ultra-pure water for 100 ng/L concentration. The SPME Arrow extraction of the stock solution provided the chromatogram as shown in Figure 5 (previous page).
A series of standard dilutions with concentration of 1 ng/L, 10 ng/L, 20 ng/L, 50 ng/L and 100 ng/L were prepared from the stock solution. The calibration curve was generated calculating the relative response relative to the internal standard. The calibration curve of 2-MIB and Geosmin is obtained with very good precision and linearity as shown in Fig. 6. The calibration precision is excellent with the linear correlation coefficient better than 0.999 for both compounds.

Reproducibility

The standard solution for the 10 ng/L level of 2-MIB and Geosmin was measured 5 consecutive times to obtain the intraday reproducibility data of this method. The GC-MS chromatograms are shown in Figure 7. The area precision of 2-MIB and Geosmin repeat measurements were 1.65% and 3.7% RSD (n=5) respectively. Figure 8 shows the overlaid chromatograms of these measurements, the reproducibility of the SPME Arrow method is very good, as demonstrated by graphs and data.

Also the interday reproducibility of this method was evaluated. The 10 ng/L aqueous solution was measured during 5 consecutive days by this method. The reproducibility for 2-MIB and Geosmin was obtained with a precision of the peak area of 5.24% and 8.57% RSD respectively. The results of the measurement are shown in Fig. 8. It can be seen from these results that this method also has a very good day-to-day stability and satisfies completely the requirement of reproducible detection at trace levels.

Sensitivity of the SPME Arrow Method

The described method uses the newest SPME Arrow patented technology, which delivers greatly improved detection sensitivity. The method detection limit (MDL) of 2-MIB and Geosmin achieved with this method were 0.37 ng/L for 2-MIB and 0.22 ng/L for Geosmin, calculated from 8 consecutive runs of a 2 ng/L dilution. The chromatograms obtained from the sample extraction at the lowest level of 0.5 ng/L are shown in Figure 10. The peak shape is symmetrical with little interference for 2-MIB. At this very low concentration level a signal-to-noise ratio S/N =4.6 is achieved for 2-MIB, and S/N = 6 for Geosmin.

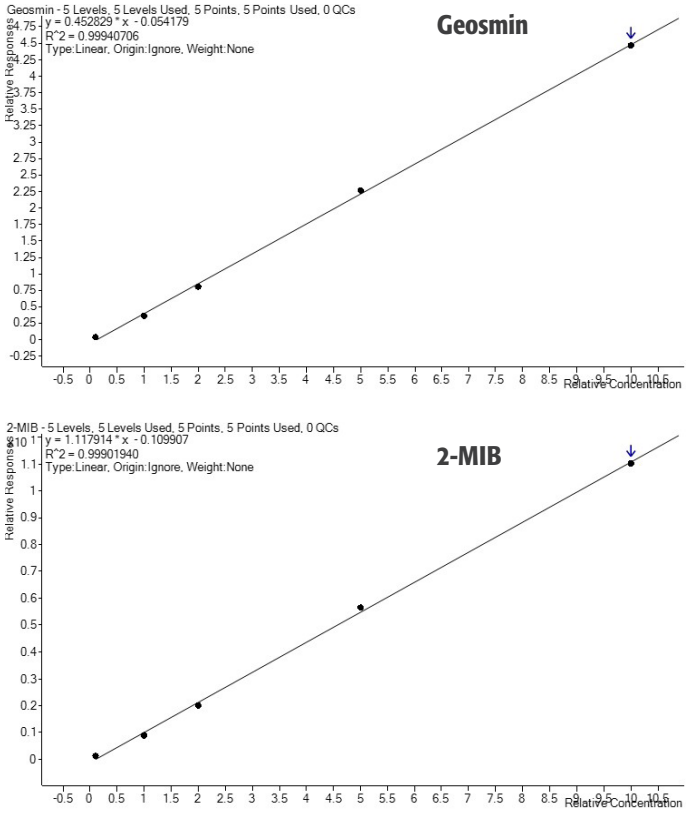

Fig 6: Calibration curves of Geosmin (top) and 2-MIB (bottom), both in the range of 1 to 100 ng/L with precision better than R2=0.999

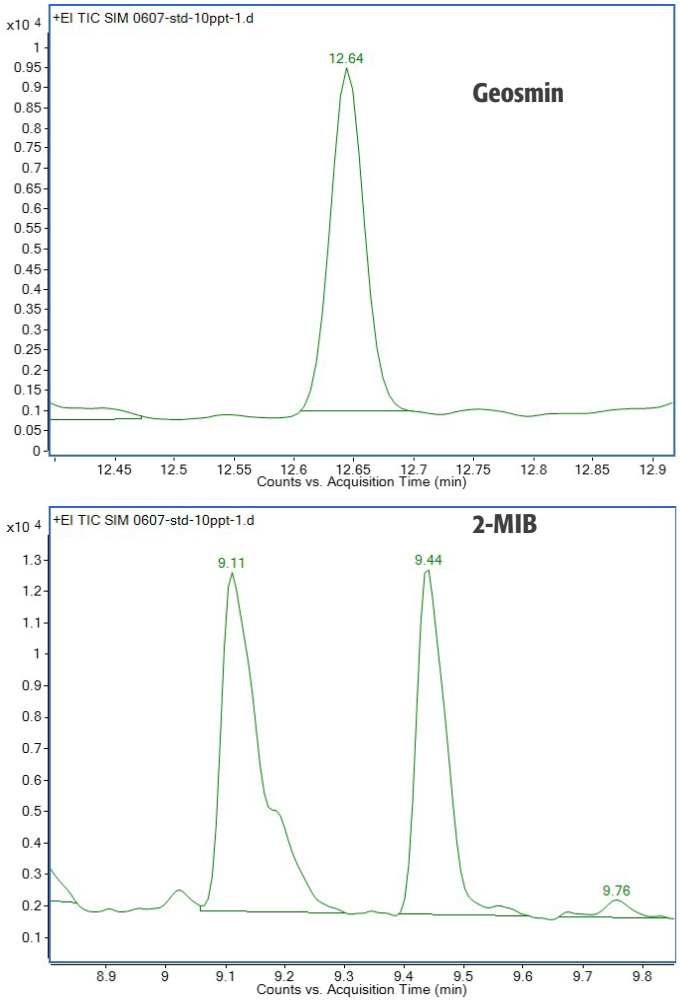

Fig 7: GC-MS chromatograms of Geosmin (top) and 2-MIB (bottom) at the regulated decision level 10 ng/L

Real Life Water Analyses

Regular tap water was tested. The spiked standard was 10 ng/L, with repeated 3-fold measurements. The recovery rate of 2-MIB and Geosmin was measured with 116% and 98.4%. The measurement precision for 2-MIB and Geosmin in the actual samples repeat measurements was 3.8% and 2.8% RSD. The total ion chromatogram obtained from the actual sample determination is shown in Figure 11. The actual real life sample background does not interfere with the determination of the target compounds at retention times 9.43 min for 2-MIB and 12.64 min for Geosmin.

Conclusion

An analytical SPME method for the determination of 2-MIB and Geosmin in water with GC-MS detection was established in this study. This method demonstrated the following advantages:

- ✓ Using the robust SPME Arrow technology provides high sensitivity, rugged and highly reproducible quantitative determinations.
- ✓ Green analytical method. No need to use organic solvents, reduce environmental pollution, and protect the safety of operators.
- ✓ Small sample volumes required, less interference by the matrix, easy to achieve on-line monitoring.
- ✓ The used SPME Arrow device is robust, unbreakable, has a long life and lasts for several hundreds of analyses and GC-MS injections.

The described SPME Arrow GC-MS method for off-flavors is not only simple in operation and automated, but also fast and accurate, and satisfies completely the hygienic test requirements of drinking water and water source control in the China hygienic standard of drinking water (GB5749-2006).


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中华人民共和国国家标准

GB/T 32470—2016

生活饮用水臭味物质　土臭素和2-甲基异莰醇检验方法

Organic compounds in drinking water—Test methods of geosmin and 2-methylisoborneol

National standard method GB/T 32470-2016

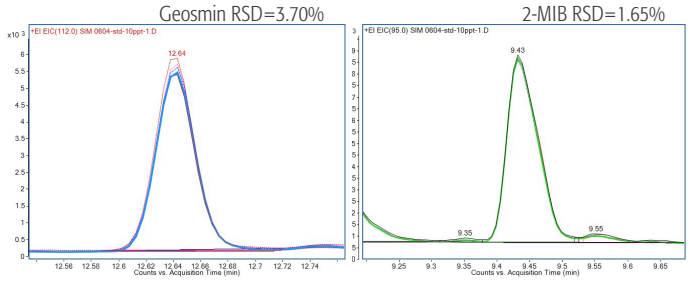

Fig 8: Intraday reproducibility data of Geosmin and 2-MIB (10ng/L, n=5)

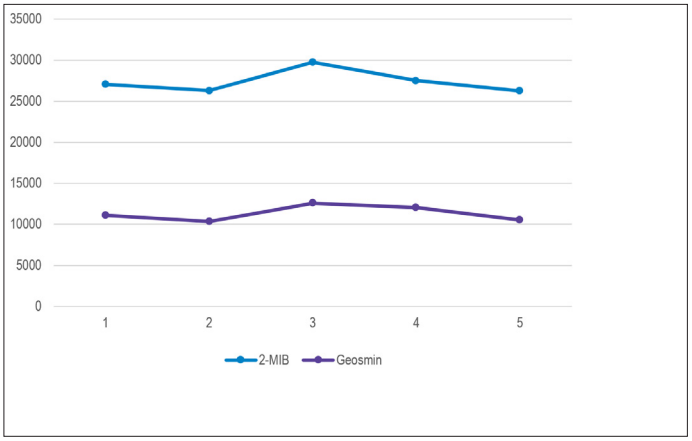

Fig 9: The day-to-day reproducibility of 2-MIB and Geosmin SPME ARROW analysis (10ng/L)

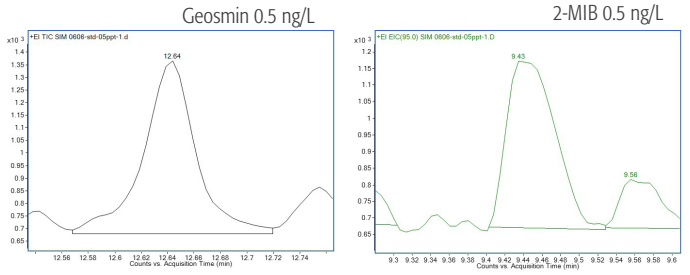

Fig 10: Chromatograms of the lowest concentration level measured (0.5 ng/L)

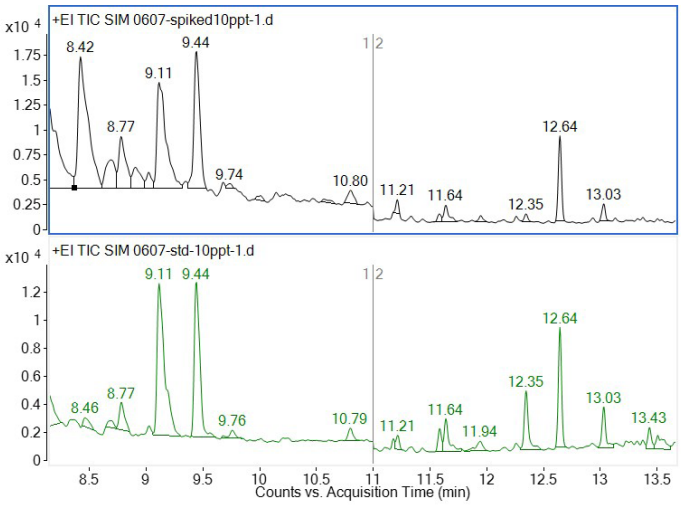

Fig 11: Water sample chromatograms, spiked at 10 ng/L (above, the spiked drinking water sample, below a spiked ultra-pure water preparation)

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