Application Note

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Determination of Off-Odor Compounds in Drinking Water Using an SPME Device with Gas Chromatography and Mass Spectrometry

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Abstract

In this Application Note, the determination of the typical off-odor substances in drinking water, 2-methyl isobutyl alcohol (2-MIB) and geosmin, using an SPME device with gas chromatography/mass spectrometry (GC/MS) detection is described, and applied to the control of actual water samples. The method is robust, has high sensitivity compared to conventional detection methods, and is fully automated. The detection limit was decreased by one order of magnitude with high accuracy. The precision and reproducibility were good with RSD values of less than 3.7%, and the interday reproducibility at trace level was less than 8.7% RSD. The performance of this method satisfied the standard test requirements of 2-MIB and geosmin in drinking water. The test results for actual drinking water samples were excellent.

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). 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, which is 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 provides an early warning in case of an unexpected incident of peculiar water quality.

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 gas chromatography/mass spectrometry (GC/MS). The commonly used sample preparation methods include a wide variety of analytical solutions such as closed-loop stripping analysis (CLSA), liquid-liquid extraction (LLE), solid phase extraction (SPE), solid phase microextraction (SPME), liquid phase microextraction (LPME), ultrasonic assisted emulsification microextraction (USAEME), or stir-bar sorptive extraction (SBSE). Many of these methods have shortcomings such as complex technical realization, lack of automation, the need for larger amounts 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, high sample throughput, speed of extraction, and high sensitivity for low limits of detection (LODs). The SPME Arrow device comprises an arrow-shaped tip, which penetrates vial and injection port septa more easily and with less force or damage. The sorbent material coating provides a larger surface area and higher sorbent volume than fibers, increasing the extraction capacity and thereby greatly improving the detection sensitivity. This method has the advantages of time saving, high extraction efficiency, zero solvent use, less matrix interference, and ease of automation for large sample series. In this study, an efficient and rugged SPME-GC/MS analysis method of the typical off-odors geosmin and 2-MIB in water was established and successfully applied in the control of drinking water.

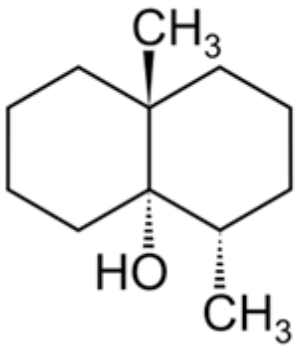

Figure 1. Chemical structure of geosmin

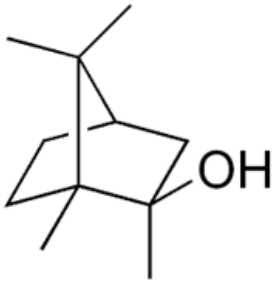

Figure 2. Chemical structure of 2-methyl-iso-borneol (2-MIB)

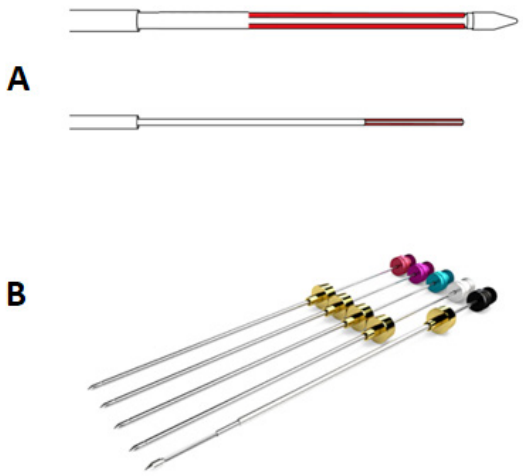

Figure 3. A: SPME Arrow device (top) compared to SPME Fiber device (bottom). B. Color coded SPME Arrow devices

Experimental

Instrumentation

The following instrumentation was used to perform the experiments.

Sample pretreatment platform	Agilent PAL3 RSI or RTC sample handling system with SPME Arrow accessory, including Arrow tool, Heatex stirrer, injection port assembly, and liner. Optional conditioning module and agitator.
SPME Arrow	1.1 mm od, DVB/CAR/PDMS sorbent phase, p/n 5191-5861. Before first use, the SPME Arrow was conditioned at 270 °C for 1 h
GC/MS platform	Agilent 7890B GC and Agilent 5977B single quadrupole GC/MS system

Reagents

- Standard solution of targets 2-MIB and geosmin, each 100 mg/L in methanol (Accustandard), as certified standard solution
- Internal standard of 2-isobutyl-3-methoxypyrazine, 100 mg/L in methanol solution (Accustandard), as certified standard solution
- Sodium chloride, analytical grade (Group Chemical Reagent Co., Ltd.), baked at 450 °C for 2 h
- Methanol, chromatographic purity (Merck)
- Water, ultrapure/HPLC quality

SPME Arrow extraction procedure

1.5 g of sodium chloride were placed in an empty 20 mL screw cap vial. 5 mL of a water sample were added followed by 5 µL of internal standard solution (2-isobutyl-3-methoxypyrazine, 10 ng/mL). The cap was tightened, and the vial placed in the PAL system sample rack for analysis.

Before SPME extraction, the sample was transferred by the PAL system to the Heatex stirrer and incubated at 60 °C for 2 min. The SPME Arrow penetrated the vial septum and its sorbent phase was 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 Arrow was moved to the injection port and thermally desorbed at 250 °C for 5 min. During the desorption time, the injector split was closed.

GC/MS analysis conditions

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

Table 1. GC/MS parameter settings

GC column and temperature program	DB-5MS UI, 30 m × 0.25 mm × 0.25 µm, p/n 122-5532-UI 60 °C (2 min) at 10 °C/min to 270 °C (2 min)
Detector type and 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

Results and Discussion

Chromatogram and linearity of standard samples

The standard stock solution was prepared with ultrapure water at a concentration of 100 ng/L. The SPME Arrow extraction of the stock solution provided the chromatogram shown in Figure 4.

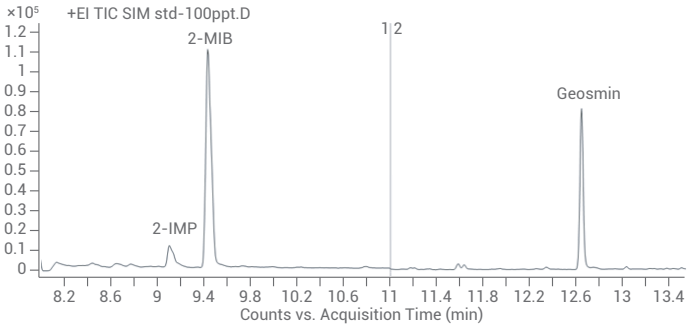

Figure 4. GC/MS chromatogram of 2-MIB and geosmin aqueous solution (100 ng/L) by SPME Arrow extraction

A series of standard dilutions with concentration of 1, 10, 20, 50, and 100 ng/L were prepared from the stock solution. The calibration curves were generated by calculating the relative response relative to the internal standard. The calibration curves of 2-MIB and geosmin were obtained with good precision and linearity as shown in Figure 5. The calibration precision was excellent with the linear correlation coefficient better than 0.999 for both compounds.

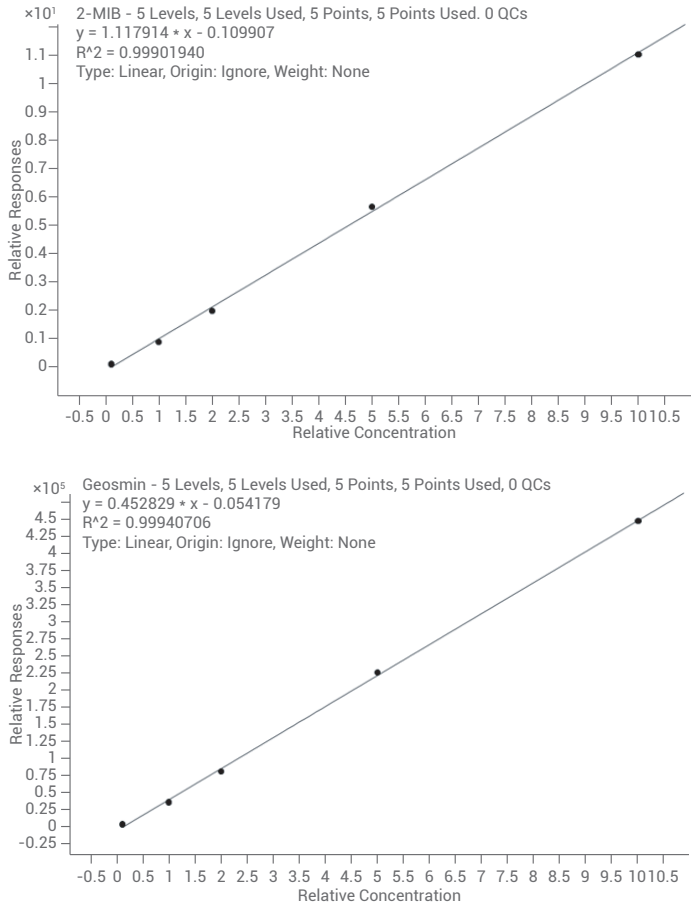

Figure 5. Calibration curves of 2-MIB (top) and geosmin (bottom), both in the range of 1 to 100 ng/L with precision better than $R^2 = 0.999$

Reproducibility

The standard solution for the 10 ng/L level of 2-MIB and geosmin was measured five consecutive times to obtain the intraday reproducibility data of this method. The GC/MS chromatograms are shown in Figure 6. The area precision of 2-MIB and geosmin repeat measurements were 1.65 and 3.7% RSD (n = 5) respectively. Figure 7 shows the overlaid chromatograms of these measurements, the reproducibility of the SPME Arrow method is good, as demonstrated by the graphs and data.

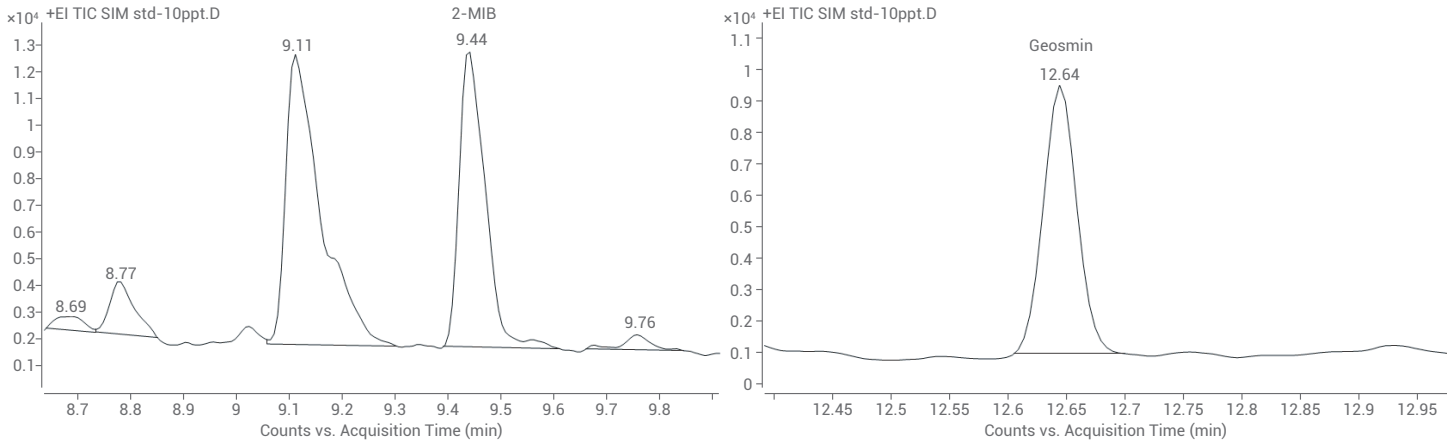

Figure 6. GC/MS chromatograms of 2-MIB and geosmin at the regulated decision level 10 ng/L

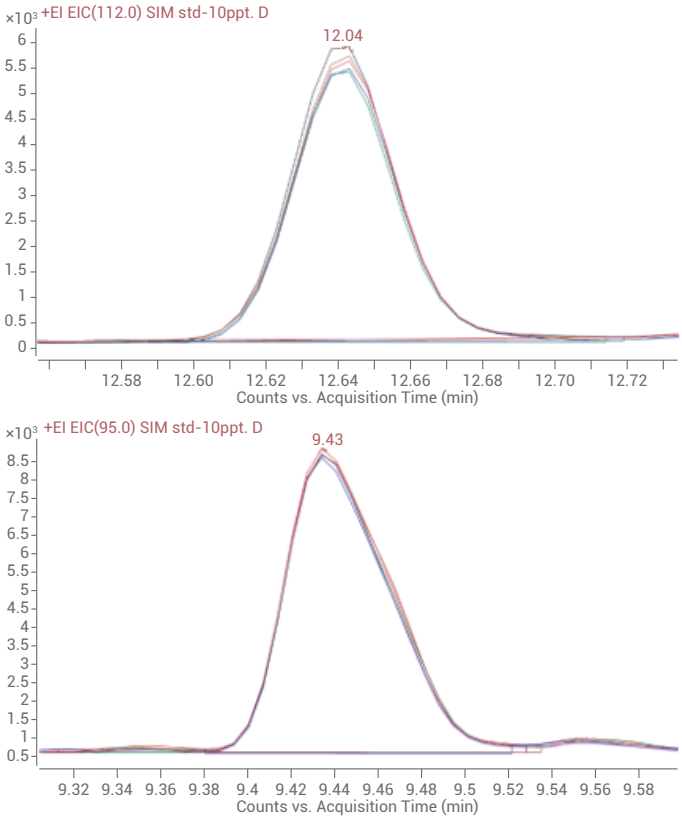

Figure 7. Intraday reproducibility data for geosmin and 2-MIB (10 ng/L, n = 5)

The interday reproducibility of this method was also evaluated. The 10 ng/L aqueous solution was measured by this method during five consecutive days. 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 measurements are shown in Figure 8. It can be seen from these results that this method also has good day-to-day stability and satisfies completely the requirements of reproducible detection at trace levels.

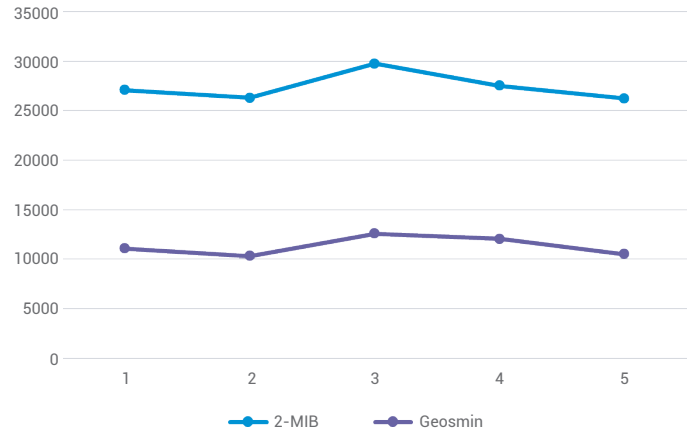

Figure 8. Day-to-day reproducibility of 2-MIB and geosmin SPME Arrow analysis (10 ng/L)

Sensitivity of the SPME Arrow method

The 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 eight 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 9. The peak shape is symmetrical with little interference for 2-MIB. At this low concentration level, a signal-to-noise ratio (S/N) of4.6 was achieved for 2-MIB and an S/N of 6 for geosmin.

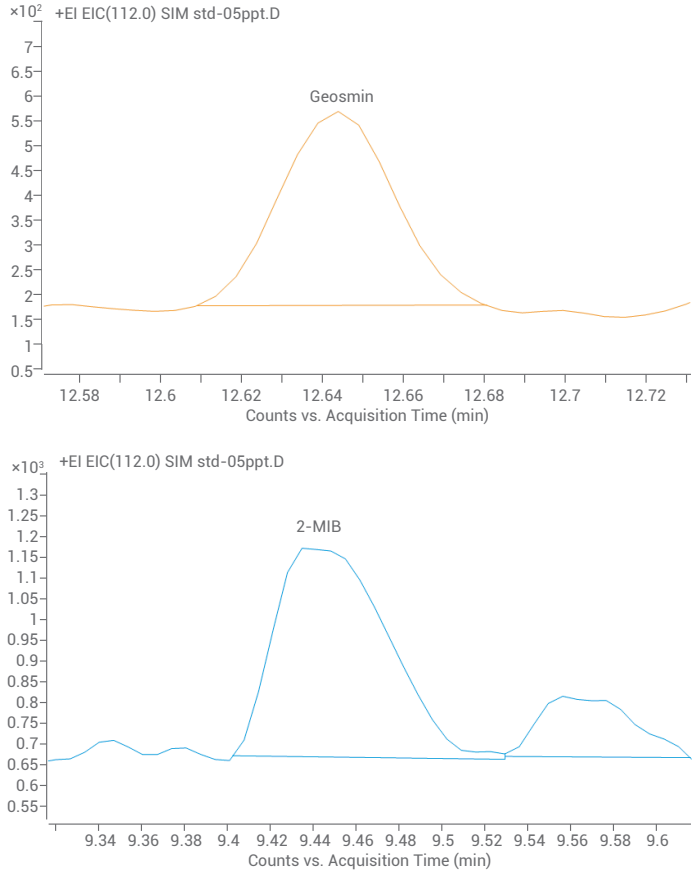

Figure 9. Chromatograms of the lowest concentration level measured (0.5 ng/L)

Real-life water analyses

Regular tap water was tested. The spiked standard was 10 ng/L, with repeated threefold measurements. The recovery rates of 2-MIB and geosmin were measured at 116% and 98.4%. The precision for 2-MIB and geosmin in the repeat measurements of the real-life samples was 3.8% and 2.8% RSD.

The total ion chromatogram obtained from the actual sample determination is shown in Figure 10. The real-life sample background does not interfere with the determination of the target compounds at retention times of 9.44 min for 2-MIB and 12.64 min for geosmin.

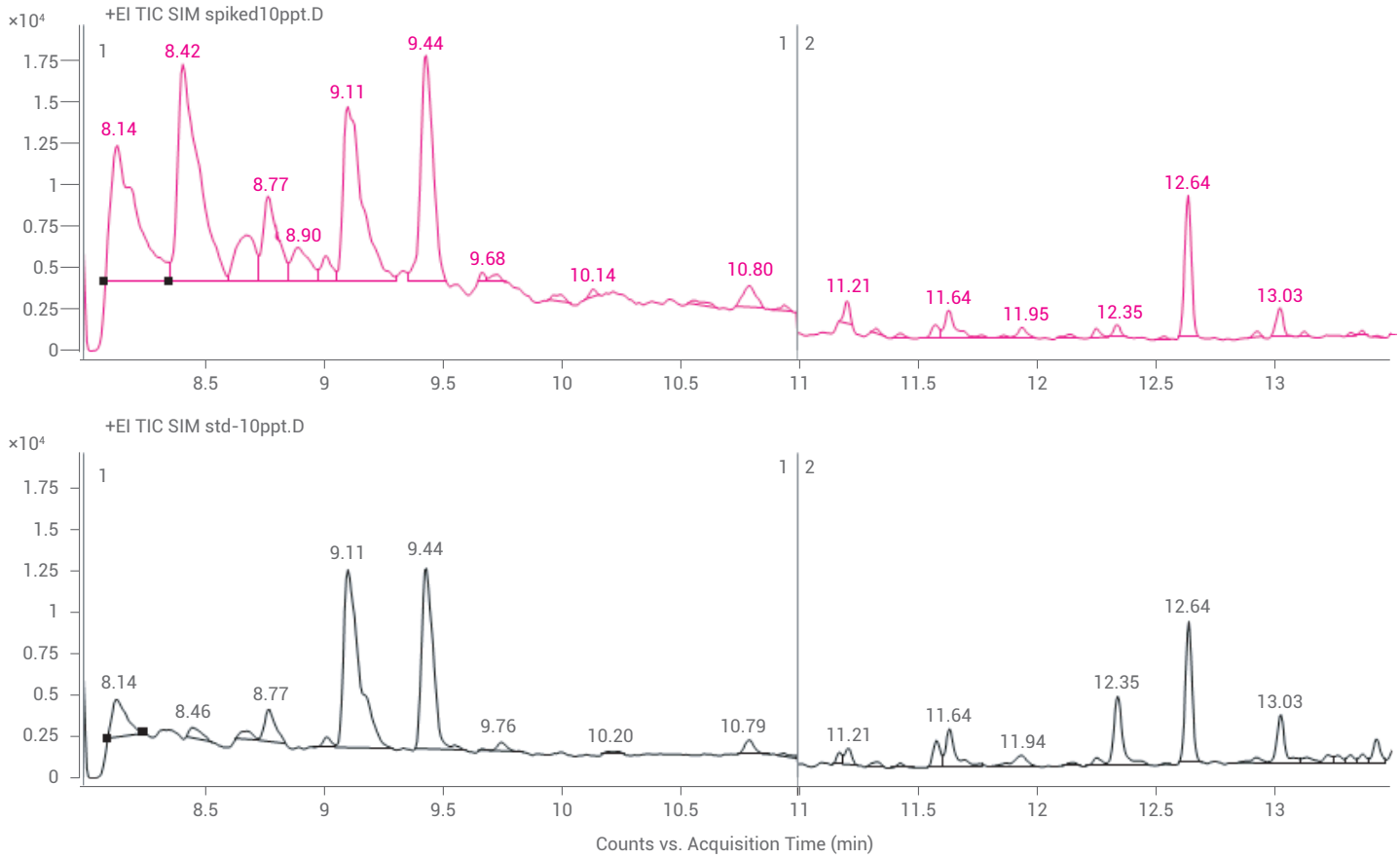

Figure 10. Water sample chromatograms, spiked at 10 ng/L (above, the spiked drinking water sample, below a spiked ultrapure water preparation)

Conclusions

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

- Robust SPME Arrow technology provides high sensitivity, and rugged and highly reproducible quantitative determinations
- Green analytical method eliminates the use organic solvents, reduces environmental pollution, and protects the safety of operators
- Method requires small sample volumes, exhibits less interference by the matrix, and is easy to deploy for online 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 national standard test method for drinking water (GB5749-2006).

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