PO-CON1557E

SHIMADZU
Excellence in Science

# Determination of 5 odorous compounds in water by GC-MS/MS using purge-and-trap technique

ASMS 2015 ThP 136

Xiaohua Liu, Ying Ye, Ning Yuan, Hui Hu, Wenyi Kang, Song Zhan, Taohong Huang, Shin-ichi Kawano, Yuki Hashi
Shimadzu Global COE, Shimadzu (China) Co., Ltd.

# Determination of 5 odorous compounds in water by GC-MS/MS using purge-and-trap technique

## Overview

A method for determination of 5 kinds of odorous compounds in water by gas chromatography-triple quadruple mass spectrometry was established using purge-and-trap technique. This method showed good linearity within the range of 0.01~0.5 μg/L (Isophorone: 1~50 μg/L). All the correlation coefficients were greater than 0.999, the limits of detection were in the range of 0.05~11.6 ng/L, respectively. The recoveries and the RSD of the real samples ranged from 87.2〜118.2% and 1.0~4.9%, respectively.

## Introduction

In recent years, odor incidents of drinking water keep happening in the world, odor substances in water become the hotspot of social attention. Research shows that most of the odorous substances in drinking water are microbial metabolites, such as 2-methylisoborneol (2-MIB) and geosmin (GSM), etc., the olfactory threshold concentration of such materials is very low, about 10 ng/L. The drinking water health standards of China (GB5749-2006) clearly defined MIB and GSM in drinking water should not exceed 10 ng/L. The objectives of the current studies were to develop a selective and sensitive GC-MS/MS method to determine of odor substances in water.

## Methods

### Sample Preparation

(1) Fill the bottle (40 mL) with water and tighten the cap.
(2) The sample (5 mL) was subjected to purge-and-trap pretreatment with the O.I. Eclipse 4660 (USA) equipped with the 4552 auto injector.

### GC-MS/MS Analysis

(1) The analysis was performed on a Shimadzu GCMS-TQ8040 (Kyoto, Japan).
(2) The separation was carried out on a Shimadzu Rtx-624 column (60 m x 0.32 mmi.d, 1.8 μm df) .
(3) Analytical conditions

The GC system used helium as the carrier gas in a linear velocity mode (36.1 cm/sec). Injector temperature was at 200 °C. Through the GC inlet liner, the oven temperature ramped to 110 °C (held for 1 min) at a rate of 8 °C/min from an initial temperature of 40 °C (held for 2 min), and then ramped to 220 °C (held for 10 min) at a rate of 10 °C/min from the temperature of 110 °C.

The MS was operated in EI mode with a detector voltage of 1.33 kV and ionization energy of 70 eV. Temperatures of ion source and transfer line were 220 °C and 240 °C, respectively. MS data were acquired in both full scan mode (*m/z* 40–200) for identification and multiple reaction monitoring (MRM) mode for quantification. MRM parameters are summarized in Table 1.

# Determination of 5 odorous compounds in water by GC-MS/MS using purge-and-trap technique

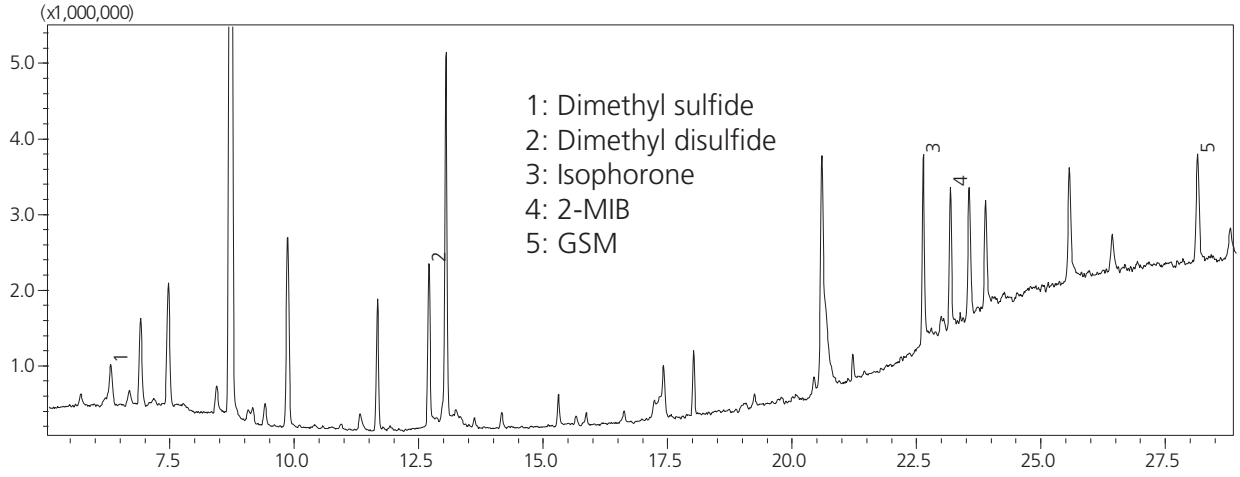


Figure 1 TIC chromatogram of 5 odorous compounds standard (2 µg/L each)

Table 1 MRM parameters

| No. | Compound | Target ion (*m/z*) | CE(V) | Ref. ion (*m/z*) | CE(V) |
|---|---|---|---|---|---|
| 1 | Dimethyl sulfide | 62.0>47.0 | 12 | 62.0>46.0 | 10 |
| 2 | Dimethyl disulfide | 94.0>79.0 | 12 | 94.0>61.0 | 10 |
| 3 | Isophorone | 82.0>54.0 | 8 | 82.0>39.0 | 12 |
| 4 | 2-MIB | 95.1>67.0 | 12 | 95.1>55.0 | 18 |
| 5 | GSM | 112.1>97.0 | 14 | 112.1>83.0 | 12 |

# Results

Chromatograms of 5 odorous compounds are shown in Fig. 1. Table.2 shows the calibration curve of 5 odorous compounds. Excellent linearity was demonstrated in the rang of 0.01~0.2 µg/L (Isophorone is 1~20 µg/L) with a coefficient of determination greater than 0.999. The limits of detection were ranged from 0.05 ng/L to 11.6 ng/L. The recoveries of the method ranged from 87.2% to 118.2%. The repeatability of 5 odorous compounds in real samples were investigated, and the area RSD(%) were ranged from 1.0% to 4.9%, as show in Table 3.

# Determination of 5 odorous compounds in water by GC-MS/MS using purge-and-trap technique

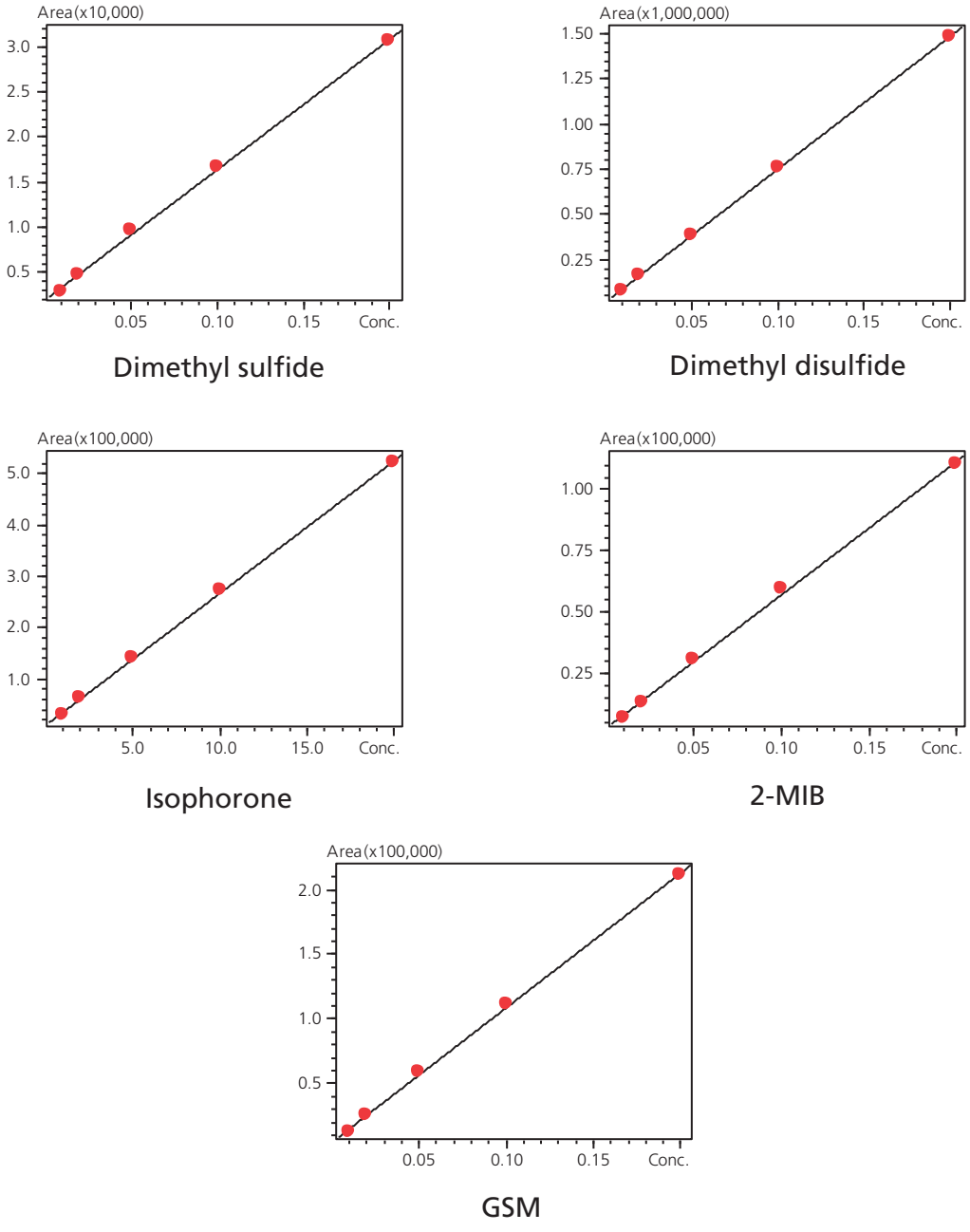


Figure 2 Calibration curve of of 5 odorous compounds

# Determination of 5 odorous compounds in water by GC-MS/MS using purge-and-trap technique

Table 2 Information on calibration curves of 5 odorous compounds

| No. | Compound | Calibration curve | Linear range (µg/L) | r | LOD (ng/L) |
|---|---|---|---|---|---|
| 1 | Dimethyl sulfide | Y = 144044.6X + 2063.41 | 0.01~0.2 | 0.9992 | 0.2 |
| 2 | Dimethyl disulfide | Y = 7387424X + 11428.64 | 0.01~0.2 | 0.9999 | 0.05 |
| 3 | Isophorone | Y = 25881.03X + 8050.912 | 1~20 | 0.9997 | 11.6 |
| 4 | 2-MIB | Y = 545774.4X + 2518.972 | 0.01~0.2 | 0.9993 | 0.2 |
| 5 | GSM | Y = 1048360X + 3478.089 | 0.01~0.2 | 0.9995 | 0.4 |

Table 3 Recovery, repeatability and results in a drinking water sample

| Compound | Spike recovery (%) | | | RSD (%,n=5) | Content (ng/L) |
|---|---|---|---|---|---|
| | 5 µg/L | 10 µg/L | 20 µg/L | | |
| Dimethyl sulfide | 87.2 | 119 | 112.4 | 4.9 | N.D |
| Dimethyl disulfide | 110.6 | 114.1 | 109.7 | 4.8 | 98.0 |
| Isophorone | 113.9 | 107.2 | 108.6 | 3.5 | N.D |
| 2-MIB | 114.4 | 116.6 | 118.2 | 2.2 | N.D |
| GSM | 117 | 119.7 | 113.8 | 1.0 | N.D |

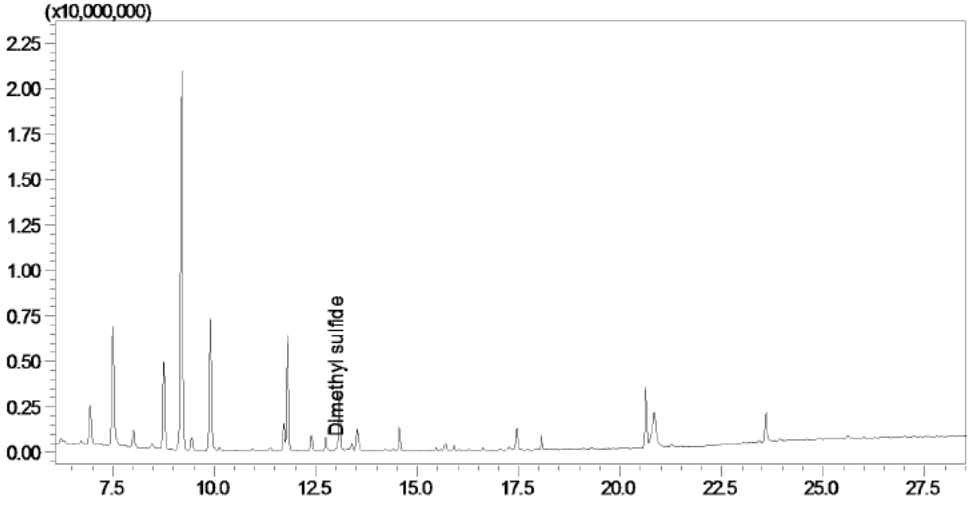


Figure 3 Representative TIC chromatogram of drinking water sample

# Determination of 5 odorous compounds in water by GC-MS/MS using purge-and-trap technique

## Conclusions

Good recoveries and RSDs were obtained for odorous compounds in our study. These results showed that a purge-and-trap technique method combined with GCMS-TQ8040 has strong anti-interference capability, accurate, high sensitivity, and can effectively monitor the odorous substance in drinking water. The limits of detection in this method were below 10 ng/L, which could best meet the requirements of the drinking water health standards of China (GB5749-2006).

First Edition: June, 2015

SHIMADZU

Shimadzu Corporation

**www.shimadzu.com/an/**