Analysis of Unknown Odorous Compound with GC/MS combined with Olfactometry

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INTRODUCTION

In order to supply safe, tasty water to the public, the Tokyo Waterworks Bureau has implemented advanced water treatment facilities that use biological activated carbon and ozonation at our major purification plants. We have also set up 131 water quality monitoring sites for tap water in Tokyo and conduct regular water examinations, in addition to maintaining continuous 24-hour water quality monitoring via automatic water quality testing devices. Due to initiatives such as these, a 2014 Tokyo Waterworks Bureau satisfaction survey of Tokyo residents found that public satisfaction with tap water had risen to over 60%. However, it was also discovered that many Tokyo residents continued to express dissatisfaction with the “smell” of Tokyo tap water. This suggests the possibility that there remains an unknown odorous substance in tap water that cannot be sufficiently treated even by advanced water treatment methods.

Therefore, Tokyo Waterworks installed “GC/MS/Olfactometry” (hereinafter referred to as “GC/MS/O”), which combines olfactometry with a gas chromatography/mass spectrometer at Water Quality Center, to enable us to rapidly identify compounds causing odors in tap water and to begin studying countermeasures. These devices combine methods sensory test and instrumental analysis, and they are effective identifying unknown odorous compounds, having been used to analyze flavor compounds of food or odorous compounds of environmental water. Although these techniques have seldom been applied to tap water, it is considered that can be used to analyze unknown odorous compounds in tap water. Therefore, to verify the applicability of these devices to tap water for use in future odor-related countermeasures, we attempted an analysis of the unknown odorous compounds that created a “putrid odor of onion” in a past water-quality incident involving water resources.

Materials & Methods

1. Analytical equipment, measurement flowchart

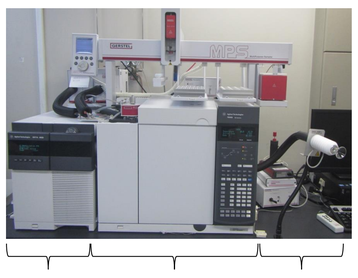


Figure 1: GC/MS/O

GC/MS/O

- Consisting of Gas Chromatograph, Mass Spectrometer and Olfactory detection port.
- Odorous compound is detected with a mass spectrometer and confirmed with human nose at the same time.

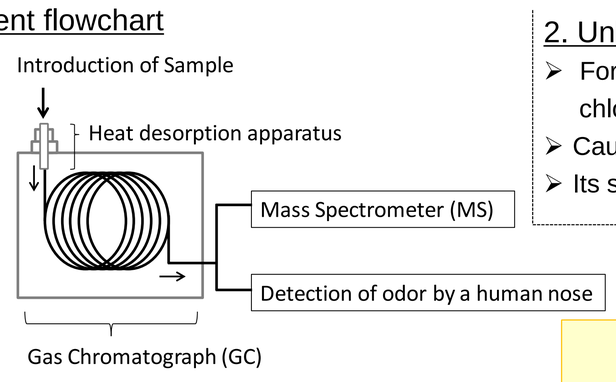


Figure 2: General analysis flowchart

Flow of analysis

- After extracting using a twister (Fig. 3), the target component is separated via heating and introduced into a GC.
- The GC outlet is branched to analyze simultaneously on the MS detector side and olfactory port side.

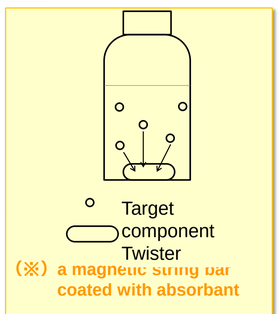


Figure 3: Star bar extraction method

2. Unknown odorous compound that was analyzed

- Formed by a reaction between cyclohexylamine and chlorine; produces the ”putrid odor of onion” (Fig. 4).
- Caused a water quality incident in the past.
- Its structure and other details are still unidentified.

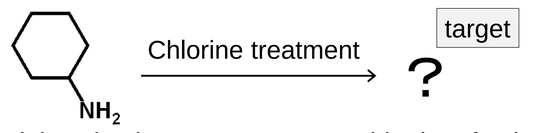


Figure 4: Reaction product of cyclohexylamine and chlorine

3. Analysis specifications

Twister	PDMS Twister, film thickness of 0.5 mm
GC	Agilent 7890B GC System
Separation column	HP-5MS UI
Twister extraction temperature	Two patterns of execution: 260℃ and 160℃
Oven temperature	40℃ (3.5min) → 280℃ (5min) Temperature increase of 10℃ / min
MS	Agilent 5977A MSD
Ionization method	EI^+
Measurement mode	Scan
Ion source temperature	230℃
Interface temperature	250℃

RESULTS & DISCUSSION

1. Twister extraction temperature: Results at 260℃

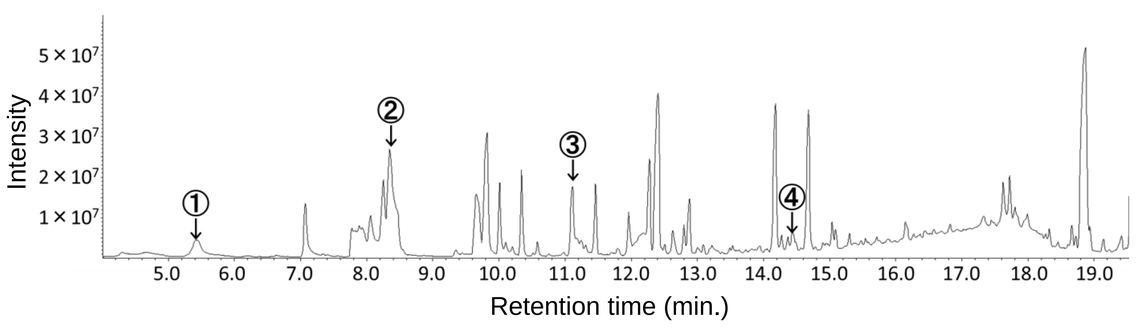
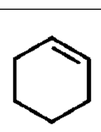
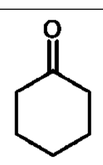
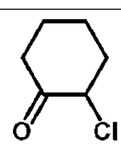
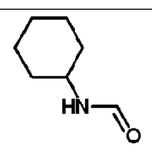


Figure 5: GC/MS/O under the 260℃ extraction condition

Compound number	1	2	3	4
Compound name	Cyclohexene	Cyclohexanone	2-Chlorocyclohexanone	N-Cyclohexylformamide
Structural formula				
Odor	Solvent odor	Solvent odor	Solvent odor	Solvent odor

- Confirmed more than 50 numbers of odor.
- ”Putrid odor of onion” was not detected.
- Four peaks were identified as 1) Cyclohexene, 2) Cyclohexanone, 3) 2 - Chlorocyclohexanone, and 4) N-Cyclohexylformamide.
- All four of these odors were solvent odors.

2. Twister extraction temperature: Results at 160℃

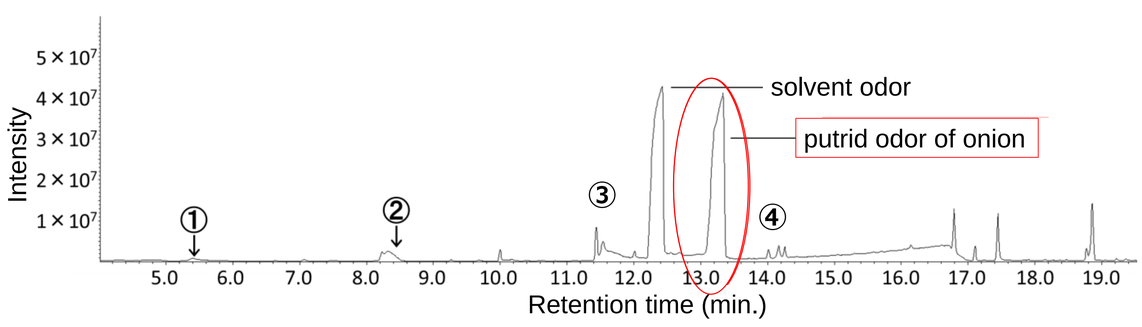


Figure 6: GC/MS/O under the 160℃ extraction condition

- Fewer peaks than in the results at the 260℃ extraction temperature.
- At 12.2 minutes of retention time, a solvent odor similar to dichloromethane was detected (A).
- At 13.2 minutes of retention time, the “putrid odor of onion” was detected (B)

- **The “putrid odor of onion” was detected from one of the reaction products of cyclohexylamine and chlorine.**
- **The compound that produces the “putrid odor of onion” breaks down or changes into another compound at 260℃.**

- **We used GC/MS/O to acquire information (peak intensity, retention time) about the compound that causes the “putrid odor of onion”.**
- **We confirmed that GC/MS/O is effective at estimating the causes of abnormal odors and tastes.**

CONCLUSIONS

- We used “GC/MS/Olfactometry” (“GC/MS/O”) to attempt to analyze unknown odorous compounds.
- The target of the analysis was the reaction product of cyclohexylamine and chlorine, which produces a “putrid odor of onion” that has caused a water-quality incident involving water resources in the past.
- In analysis of the target substance, a strong “putrid odor of onion” was detected at one of the peaks separated via GC.
- We confirmed that GC/MS/O is effective at estimating the causes of abnormal odors and tastes.
- We are continuing the work to identify the isolated substance(s) that produce the “putrid odor of onion.”