Quality of tap an drinking water

GERSTEL Twister sniffs out causes of bad odors

Authors

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Introduction

The presence of low levels of malodoros compounds in tap water can greatly influence the consumer's perception of the quality of the water. Most of the compounds present produce chlorine-like, earthy and musty odors. Although the compounds that produce the odors are present at harmless levels, the disagreeable smell gives the consumer doubts about drinking the water.

The target of our work was to develop a procedure to quickly and reliably analyze six organic odor compounds in water. The six were: Geosmin, 2-methylisoborneol, 2,4,6-trichloroanisole, 2,3,6-trichloroanisole, 2,3,4-trichloroanisole and 2,4,6-tribromoanisole.

Quantitation at the sub-nanogram level was needed. This represents detection levels at or below the compound's odor threshold level (Tab. 1). We used gas chomatography/mass spectroscopy (GC/MS) as the analytical instrumental technique and the GERSTEL Twister, or Stir Bar Sorptive Extraction (SBSE), for sampling and sample preparation. Compounds were thermally released from the Twister stir bar using a GERSTEL Thermal Desorption System (TDS).

Results and discussion

Influence of extraction time

The kinetics of sorption of the six components into the PDMS coating of the Twister were examined. Spring water, spiked with 2 ng/L of each compound (Fig. 1), was extracted for different lengths of time in the 15 to 300 minute range. For each compound, sorption occurred relatively quickly for 120 minutes, and then slowed without reaching a plateau. An extraction time of 120 minutes was empirically chosen for routine analyses with high sample throughput.

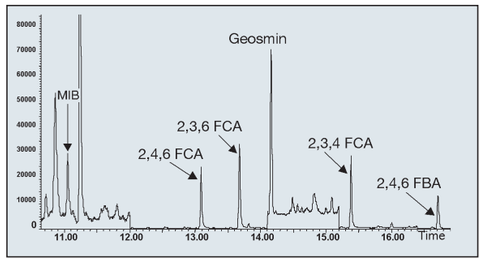

Figure 1: SIM chromatogram of spring water spiked with 2 ng/L of each component.

Name	Abbreviation	Taste	Odor threshold	CAS Number
2-Methylisoborneol	MIB	earthy	5 - 10 ng/L	n/a
2,4,6-Trichloroanisole	2,4,6-TCA	musty	0.1 - 2 ng/L	6130-75-2
2,3,6-Trichloroanisole	2,3,6-TCA	musty	0.2 - 2 ng/L	50375-10-5
Geosmin	Geosmin	camphor-like	1 - 10 ng/L	19700-21-1
2,3,4-Trichloroanisole	2,3,4-TCA	musty	0.2 - 2 ng/L	54135-80-7
2,4,6-Tribromoanisole	2,4,6-TBA	musty	0.15 - 10 ng/L	607-99-8

Table 1: Odor components determined

Influence of the sample volume

Maximum recoveries can be calculated from octanol-water distribution coefficients ($K_{O/W}$) using the KOWWIN software (SRC, 2000). Table 2 shows the experimentally determined and calculated log $K_{O/W}$ values for each compound. For the experiment, different volumes of spring water (10 to 200 mL) were spiked with 1 ng of each compound and extracted for 2 hours with the Twister (20 mm, 47 µL PDMS).

The experimental results were in agreement with theory – the larger the sample volume, the lower the recovery – but were below the anticipated values. Even after stirring for two hours, equilibrium had not been reached. The difference between experimental and anticipated values increased with increasing sample volume, depending on the particular compound.

Table 2: Octanol-water distribution coefficient ($K_{O/W}$) of the compounds analyzed

Name	experimental log K_{OW}	Calculated log K_{OW}
2-Methylisoborneol	3.31	2.85
2,4,6-Trichloroanisole	3.85	4.01
2,3,6-Trichloroanisole	3.64	4.01
Geosmin	n/a	3.57
2,3,4-Trichloroanisole	3.74	4.01
2,4,6-Tribromoanisole	4.48	4.75

The amount of compound concentrated in the PDMS coating increased with sample volume. For most compounds there was an increase up to 100 mL sample volume; increasing the sample volume to 200 mL brought no significant gain in response. To measure concentrations at the odor threshold level for each compound, two aliquots of 100 mL were extracted in parallel, each with a separate Twister. Both Twisters were subsequently desorbed at the same time.

Influence of storage after extraction

Six samples of spring water spiked with 2 ng/L of each compound were extracted. 10 mL of each sample was extracted with a Twister for two hours. One Twister was immediately desorbed, the other five were stored in vials at 4°C for later analysis.

Result: Even after storage for one week no loss of compounds was seen from the Twisters. This allows the conclusion to be drawn that when chromatographic analysis cannot be performed immediately, it is better to extract and then store the Twister than to store the original sample. When complaints are received about off-odors or bad taste of water, the compounds causing the problem should promptly be extracted and trapped. Water samples themselves need not be sent to a laboratory, however, as extractions can be made on the spot by the customer.

Equipment used and analytical conditions

Gas chromatograph 6890 (Agilent Technologies)

Column: HP5-MS, length 30 m, i.d. 0.25 mm, film thickness 0.25 µm

Carrier gas: Helium

Flow: 1.5 mL/min (constant)

Temperature profile: 50 °C – 2 min – 10 °C/min – 200 °C – 25 °C/min – 300 °C (2 min)

Mass spectrometer 5973 (Agilent Technologies)

Mode: Single-Ion-Monitoring

Thermal Desorption System (TDS A) (GERSTEL)

Mode: Split

Temperature program: 30 °C (0.8 min) – 60 °C/min – 280 °C (5 min)

Cooled Injection System (CIS 4) (GERSTEL)

Cryofocusing at -100 °C. Subsequent heating at 10 °C/s to 300°C, holding 2 minutes. Injection is made with solvent venting.

Twister (GERSTEL)

20 mm, 0.5 mm PDMS

Chemical standards and reagents

- Methanol (pesticide quality, Merck, Darmstadt)
- Spring water for blanks and standards
- 2-methylisoborneol, 2,4,6-trichloroanisole, 2,3,6-trichloroanisole, 2,3,4-trichloroanisole, 2,3,6-tribromoanisole, geosmin and 2,4,6-trichloroanisole D5 (Promochem, France)
- Stock solution, consisting of spring water and 1 µg/L each of MIB, geosmin and the haloanisoles. Stable for 1 month at 4°C.
- Internal standard: 2,4,6-TCA D5 in spring water (20 µg/L). Stable for 1 month at 4°C.

Extraction

Extractions of analytes done in parallel: 100 mL water sample, 5 mL methanol, 40 µL internal standard and a Twister were placed into a 125 mL volumetric flask. The water sample was stirred for two hours at room temperature. The Twister was removed, patted dry, transferred into a glass desorption tube and desorbed in the TDS.

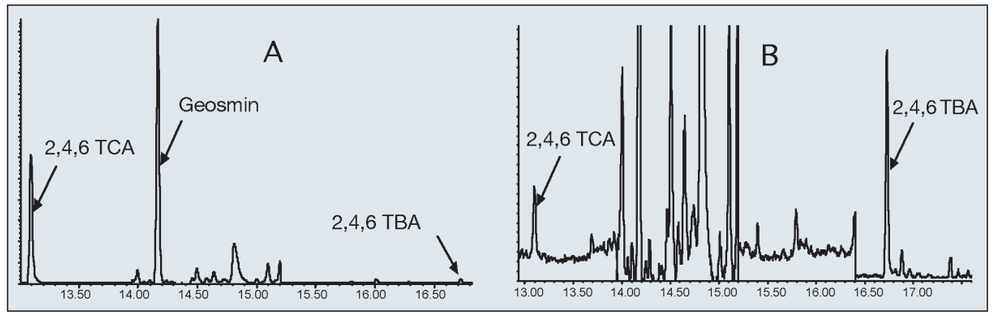

Figure 2: Chromatograms obtained for samples A and B in SIM-mode (case 1)

Validation of the method

The method was validated according to Guidelines XP T 90-210 of AFNOR, the French Institute for Standardization and member of the ISO; the validation criteria were fulfilled for all target compounds (Tab. 3). Practical tests were made using real water samples that had been analyzed after complaints of bad taste and odour.

Case 1

Two samples (A and B) were taken in the household of a customer: Sample A had a pronounced musty smell, sample B a somewhat musty but pronounced metallic smell. Extraction was carried out with the Twister, the determination of MIB, geosmin and haloanisoles was performed using GC/MS in SIM-mode. Table 4 shows the quantitative results, figure 2 the chromatograms.

Table 3: Scan chromatogram of sample A (case 1)

	R	LOQ ng/L	Repeatability %	Trueness %	Reproducibility %
MIB	0.9987	1	4-10	89	13
2,4,6-TCA	0.9998	0.1	1-5	97	4
2,3,6-TCA	0.9998	0.1	4-11	97	5
Geosmin	0.9991	0.5	2-10	83	9
2,3,4-TCA	0.9998	0.2	7-15	87	13
2,4,6-TCA	1.0000	0.2	2- 9	91	15

The compound concentrations found in the samples explain the musty smell. To identify further compounds which could cause the off-odor, the samples were again extracted with the Twister, this time without internal standards, and analyzed using GC/MS in SCAN-mode.

The olfactory detection of sample A gave a pronounced musty smell at the retention times for 2,4,6-TCA and geosmin; also obvious was a typical medical smell at 8 minutes, and a smell of solvent at 14 minutes. The olfactory detection of the B sample gave a medium musty smell at the retention time for 2,4,6-TBA as well as a typical medicinal smell at about 8 minutes.

The mass spectrum and isotope relationships of sample A showed a brominated component after 8.4 minutes and a chlorinated component after 13.9 minutes. The medicinal smell could be attributed to dibromomethyliodide, a chlorinated by-product, the smell of solvent to tetrachlorobenzene (Fig. 3). Dibromomethyliodide was also shown to be present in sample B.

Table 4: Concentration of the target components in sample A and B

	Sample A[C] (ng/L)	Sample B[C] (ng/L)
2-Methylisoborneol	< 1	< 1
2,4,6-Trichloranisole	8.9	0.2
2,3,6-Trichloranisole	< 0.1	< 0.1
Geosmin	5.2	< 0.5
2,3,4-Trichloranisole	< 0.2	< 0.2
2,4,6-Tribromanisole	0.4	1.3

Case 2

Water from a tank near Paris had an off-odor. The reason was unknown. During sampling, cracks in the tank were noticed, and taste analysis of the water taken indicated a chlorinated taste, overlaid with an intense musty taste (threshold test No. 5). But what caused this drinking water, which was sourced from ground water, to have such an intense off-odor? Prior to being stored in the tank as drinking water, the ground water was treated as follows:

It was aerated and filtered through sand to remove iron, then chlorinated at the tank inlet to kill bacteria. The coating of the tank was impermeable to water, consisting of synthetic cement produced by mixing a grey, elastic cement with a white synthetic resin in aqueous solution. The coating was very elastic, but released no organic compounds. The filtered and chlorinated water was extracted with the Twister and quantitatively analyzed to determine the previously mentioned compounds.

Table 5 shows the results. The only one of the six taste compounds found in the chlorinated water was 2,4,6-tribromoanisole at a concentration of 5.6 ng/L. This explained the musty taste of the water; the filtered water appeared not to contain any of the six target compounds known to cause off-odor.

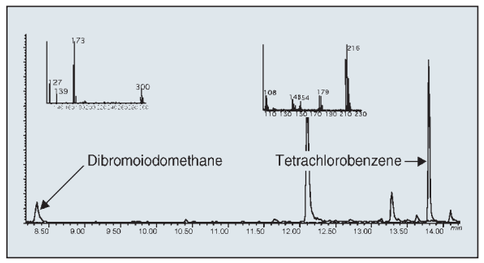

Figure 3: Scan chromatogram of sample A (case 1)

Olfactory detection of the filtered water did not bring any characteristic odor to the fore. Analysis of the chlorinated water, however, brought forward a very musty odour at the retention time of 2,4,6-TBA as well as various phenolic odors at 8, 14 and 17 minutes.

In order to analyze the phenolic components by gas chromatography, they were derivatized in a 10 mL water sample with 1 g K_2CO_3 and 500 µL of acetic anhydride; GC/MS detection was performed in SCAN-mode. This procedure enabled us to determine that the sample contained 2,4,6-trichlorophenol and 2,4,6-tribromophenol alongside phenol. The result of the sniff-test and MS detection are summarized in Table 6. Figure 4 shows the chromatograms obtained.

On the basis of these results, the assumption was made that the tank coating had released phenol, which reacted with excess chlorine and free bromide to 2,4,6-TCP and 2,4,6-TBP. In addition, 2,4,6-TBA may well have been synthesized by organisms that had settled on the surface of the coating. No answer was given as to why only 2,4,6-TBA was formed, despite the presence of 2,4,6-TCP and 2,4,6-TBP.

Case 3

In this case it was evident that the sensory water quality got worse along the municipal drinking water pipeline. Complaints came from consumers living far away from the waterworks. Two samples were taken: at the outlet from the waterworks (A), the second in the house of a consumer at the end of the pipe system (B). Sample A had a chlorinated odor, whereas sample B smelled musty, marshy and earthy (threshold test: > 10).

Measurement gave no contamination of sample A with geosmin, MIB or haloanisoles. In sample B, however, 2,4,6-TCA and 2,3,4-TCA were found in concentrations of 0.1 ng/L and 0.2 ng/L respectively; but this did not explain the taste and odor. The water samples were again extracted with the Twister, but this time without internal standards, and then analyzed by GC/MS with olfactory and SCAN-mode detection.

The olfactory examination of sample B gave several odours, whereas the olfactory examination of sample A was negative. The results of the sniff-test and MS analysis are given in Table 7. Seven different odours could be detected by sniffing, of which some were in agreement with the odor profile analysis.

Summary

A rapid **SBSE-GC-MS-Olfactory** method was developed for the determination of MIB, geosmin and haloanisole components in water.

The combination of GC/MS and the Twister (SBSE) led to very low detection limits for all components, near or below the odor threshold. The influence of extraction time, sample volume and storage time were examined, to improve the sensitivity of the measurement. The final method was validated according to AFNOR-Guidelines.

The linearity was examined with the correlation co-efficient (R) in the range from 0.9987 to 1.000. Repeatability and reproducibility were both below 15 percent and the recovery was between 87 and 117 percent depending on the component. After extraction with a Twister, the Twister could be stored for seven days under suitable conditions without any loss of analyte.

Table 6: Odors detected during the analysis of sample B (case 2)

Retention time (min)	Odor	Intensity	Qualification (acetate derivative)
8.5	phenolic	++++	Phenol
13.7	phenolic	++	2,4,6-Trichlorphenol
15.9	musty		2,4,6-Tribromanisole
16.8	phenolic	+++	2,4,6-Tribromphenol

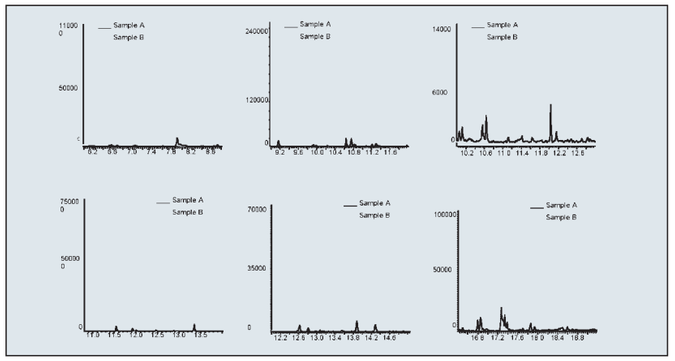

Figure 4: Comparion of the reconstructed chromatograms (retention indices, RIC) for each component smelled for samples A and B

When used for genuine, odor-loaded water samples, Stir Bar Sorptive Extraction (SBSE) provided good correlation between the odor profile analysis, the MS analysis and olfactory detection. SBSE was found to be a highly efficient and useful technique for the analysis of MIB, geosmin and haloanisoles.

Conclusion

The procedure described in this paper provides a means of identifying odorous compounds in water at very low concentration levels. The determination can be performed much faster than was previously possible using traditional techniques.

Table 5: Concentration of the target compounds in filtered and chlorinated water (case 2)

	Filtered water	Chlorinated water [C] (ng/L)
2-Methylisoborneol	< 1	< 1
2,4,6-Trichloranisole	< 0.1	< 0.1
2,3,6-Trichloranisole	< 0.1	< 0.1
Geosmin	< 0.5	< 0.5
2,3,4-Trichloranisole	< 0.2	< 0.2
2,4,6-Tribromanisole	< 0.2	5.6

Table 7: Odors detected during the examination of sample B (case 3)

Retention time	Odor	Compound
7	sweat	Phenylacetaldehyde
7.8	marshy	Dimethyltrisulfide
10.7	lemony	Decanal ?
12.8	sweat	not identifiable
12.9 to 15.2	musty	Alkylbromobenzene isomer
16.07	rancid	Isopropyldodecanoate ?
16.8 to 17.4	tar	Diisopropyl naphthalene
20.15	tar	Dodecahydrophenanthrene