

Original Research

# An Investigation of the Formation of Taste and Odour Contaminants in Surface Water Using the Headspace SPME-GC/MS Method

M. Ligor, B. Buszewski\*

Department of Environmental Chemistry and Ecoanalytics, Faculty of Chemistry, Nicolaus Copernicus University,  
7 Gagarin St, 87-100 Toruń, Poland

Received: July 20, 2005

Accepted: November 20, 2005

## Abstract

The aim of this study was to optimize of a method for determining of compounds which are responsible for the earthy/musty odour in surface water. Among taste and odour contaminants the following compounds are mentioned: (+/-)-geosmin, 2-methylisoborneol, 2,4,6-trichloroanisole, 2-isopropyl-3-methoxypyrazine and 2-isobutyl-3-methoxypyrazine.

Some experiments were performed to examine the extraction conditions such as fiber exposure time, temperature of extraction and salt addition. Various SPME fibers such as PDMS, CAR/PDMS and PDMS/DVB coatings were used for the isolation of tested compounds from water samples. As tested, compounds 2-methylisoborneol, 2-isopropyl-3-methoxypyrazine and 2-isobutyl-3-methoxypyrazine were used.

After SPME optimization, real surface water samples were examined using the SPME-GC/MS method. Based on preliminary experiments the qualitative and quantitative analyses for the determination of (+/-)-geosmin, 2-methylisoborneol and 2,4,6-trichloroanisole were performed. The regression coefficients for calibration curves for examined compounds are  $R^2 \geq 0.990$ . This shows that the used method is linear in the examined concentration range (from 20.32 to 168.00 ng/L). One of the reasons for the formation of taste and odour contaminants can be surface water pollution. The changes of water conditions such as temperature, pH and conductivity were examined. And, for the test of periodical changes of geosmin concentration in surface water samples, the experiments were performed in various seasons.

**Keywords:** volatile organic compounds, water analysis, sample preparation, SPME, GC/MS

## Introduction

An earthy and musty odour of surface water is a common problem which occurs especially during late spring and summer. Among the compounds mainly responsible for this odour are particularly: 2-methylisoborneol (MIB), 2,4,6-trichloroanisole (TCA) and geosmin ([4S-(4 $\alpha$ ,4 $\alpha$ ,8 $\alpha$ )]-octahydro-4,8a-dimethyl-4a(2H)-naphthalenol or *trans*-1,10-di-

methyl-*trans*-9 decalol). These compounds can be detected by the human nose at a concentration as low as 10 ng/L [1]. Geosmin, as an actinomycetes metabolite, is produced by *Streptomyces* species, and by strains of *Nocardia*, *Micromonospora*, *Microbispora*, *Oscillatoria*, and *Phormidium* as well as *Penicillium* species [2-13]. The high concentration of geosmin in water also has been connected with the presence of algae [4-13]. 2-methylisoborneol occurs as a metabolite of actinomycetes, blue alga, *Oscillatoria tenuis*, and *Phormidium* species [4]. However, musty-earthy odour

---

\*Corresponding author; e-mail: bbusz@chem.uni.torun.pl

compounds were determined not only in water. An important source of MIB and geosmin are food products (wheat grain) [14], but TCA was determined in chicken meat, green coffee, packed dried fruit and wine [4]. These compounds are very difficult to remove by conventional water treatment processes and sometimes occur at concentrations above the odor threshold in consumer tap water.

For the isolation and determination of these compounds, which are on the low concentration level (ppb, ppt) in water samples, only sensitive and selective methods such as the solid phase microextraction (SPME), stir bar sorptive extraction (SBSE) and other methods coupled with gas chromatography/mass spectrometry (GC/MS) can be used [15-17]. SPME is a modern, simple, solventless sample preparation method which can be used for the isolation of odour compounds at low concentrations [18-24]. It is an inexpensive method that can easily be moved from laboratory to field and should prove useful for the monitoring of water quality (surface and potable water supplies). The coupling of SPME with GC provides a fast, reliable method for the analysis of MIB, TCA and geosmin in water samples. The selective nature of SPME allows the use of an inexpensive flame ionization detector for analyses at the  $\mu\text{g/mL}$  level. Analysis of solutions of known concentration shows that SPME provides precision and limits of detection comparable to smaller sample volumes. The analysis of algae cultures demonstrates that this method is applicable to real samples. The maximum selectivity for analysis of MIB, TCA and geosmin may be achieved if instrumental coupling techniques such as GC/MS are used for the identification and quantification of volatile odour compounds in water samples.

Recently, the effective isolation of MIB, TCA and geosmin from drinking water samples was performed using the SBSE method [25]. The mentioned compounds were extracted with high recovery and, in comparison with other methods such as the closed-loop stripping analysis (CLSA), this method provides a higher sample throughput with a better sensitivity, reproducibility and accuracy [25].

In the current paper, optimization of the method for the determination of earthy/musty odour compounds in surface water was performed. Among analyzed earthy/musty odour compounds were the following substances: MIB, 2-isopropyl-3-methoxypyrazine, 2-isobutyl-3-methoxypyrazine, (+/-)-geosmin, as well as TCA. As tested substances for SPME optimization of 2-methylisoborneol, 2-isopropyl-3-methoxypyrazine and 2-isobutyl-3-methoxypyrazine were chosen. Extraction conditions such as: fiber exposure time, temperature of extraction, salt addition and the SPME fibers choice were examined. After SPME optimization, real surface water samples were examined using the SPME–GC/MS method. Based on preliminary experiments the qualitative and quantitative analyses for the determination of (+/-)-geosmin, MIB and TCA were performed. Therefore, when optimal conditions were applied, the test of periodical changes of geosmin concentration in surface water samples was performed particularly during ten days in the middle of spring and sporadically in the early spring, in the summer and in the autumn. As it was proved, the reason for the formation of taste and odour contaminants can be surface water pollution. Some parameters of surface water such as: conductivity, pH, and temperature were determined. Conductivity was informative about the pollution of examined water samples.

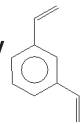
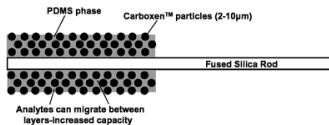
## Experimental

### Apparatus

The SPME apparatus (*Supelco Inc.*, Bellefonte, PA, USA) with polydimethylsiloxane (PDMS – thickness 100  $\mu\text{m}$ ), polydimethylsiloxane/divinylbenzene (PDMS/DVB – thickness 65  $\mu\text{m}$ ) and Carboxen/polydimethylsiloxane (CAR/PDMS – thickness 75  $\mu\text{m}$ ) coating fibers were used for the determination of analytes.

Chromatographic analysis was performed by GC/MS, gas chromatograph - Autosystem XL, mass spectrometer

Table 1. The characterization of the SPME fiber coatings used in the presented experiments.

Stationary phase	Description	Film thickness	Type of function group (structure)
Polydimethylsiloxane (PDMS)	volatile compounds	100 $\mu\text{m}$ (non bonded phase)	$\left[ \begin{array}{cccccc} \text{CH}_3 & \text{CH}_3 & \text{CH}_3 & \text{CH}_3 & \text{CH}_3 & \text{CH}_3 \\   &   &   &   &   &   \\ -\text{Si}- & \text{O}-\text{Si}- & \text{O}-\text{Si}- & \text{O}-\text{Si}- & \text{O}-\text{Si}- & \text{O}-\text{Si}- \\   &   &   &   &   &   \\ \text{CH}_3 & \text{CH}_3 & \text{CH}_3 & \text{CH}_3 & \text{CH}_3 & \text{CH}_3 \end{array} \right]_n$
polydimethylsiloxane/divinylbenzene (PDMS/DVB)	volatile, amine, and nitroaromatic compounds	65 $\mu\text{m}$ (partially crosslinked phase)	$\left[ \begin{array}{cccccc} \text{CH}_3 & \text{CH}_3 & \text{CH}_3 & \text{CH}_3 & \text{CH}_3 & \text{CH}_3 \\   &   &   &   &   &   \\ -\text{Si}- & \text{O}-\text{Si}- & \text{O}-\text{Si}- & \text{O}-\text{Si}- & \text{O}-\text{Si}- & \text{O}-\text{Si}- \\   &   &   &   &   &   \\ \text{CH}_3 & \text{CH}_3 & \text{CH}_3 & \text{CH}_3 & \text{CH}_3 & \text{CH}_3 \end{array} \right]_n$ 
Carboxen/polydimethylsiloxane (CAR/PDMS)	gases and low molecular weight compounds	75 $\mu\text{m}$ (partially crosslinked phase)	

– Turbo Mass (Perkin Elmer, Shelton, CT, USA), mass spectrum libraries Wiley and NIST. The RTX-5MS column (Restek, Bellefonte, PA, USA) with parameters: 30 m  $\times$  0.25 mm  $\times$  0.25  $\mu$ m was used.

### Sorption and Desorption Conditions

The spiked standards or determined analytes were isolated from 25.00 mL of water sample by static headspace (SHS). SHS vials (120 mL volume) were used in all experiments.

As preliminary study some experiments were performed to examine extraction conditions such as fiber exposure time (10, 20, 30, 35, and 40 min), temperature of extraction (30, 40, 60, 70°C) and sodium chloride addition (0, 15, 25, 30, 35%). Various SPME fibers such as PDMS, CAR/PDMS and PDMS/DVB coatings (Table 1) were compared for the isolation of tested compounds from water samples.

The tested substances 2-methylisoborneol ( $c = 0.824 \mu\text{g/mL}$ ), 2-isopropyl-3-methoxypyrazine ( $c = 1.289 \mu\text{g/mL}$ ) and 2-isobutyl-3-methoxypyrazine ( $c = 1.154 \mu\text{g/mL}$ ) were selected and used. Analyzed standard solutions were prepared in water.

Experimental conditions for the comparison of extraction efficiency of MIB and other compounds with various coated fibers were used as follows: the SPME fibers PDMS, CAR/PDMS, PDMS/DVB; water sample volume spiked with standards 25.00 mL; sorption time of 40 min; temperature of 40°C; NaCl concentration of 25%.

Experimental conditions for the study of salt concentration effects on extraction efficiency of MIB and other compounds were used as follows: the SPME fiber CAR/PDMS; water sample volume spiked with standards 25.00 mL; sorption time of 40 min; 40°C temperature.

Experimental conditions for the study of the extraction time profile corresponding to extracted mass of MIB and other compounds were used as follows: the SPME fiber CAR/PDMS; water sample volume spiked with standards 25.00 mL; NaCl concentration of 25%; 40°C temperature.

Experimental conditions for the study of temperature dependence of extracted mass of MIB and other compounds were used as follows: the SPME fiber CAR/PDMS; water sample volume spiked with standards 25.00 mL; NaCl concentration of 25%; sorption time 40 min.

Finally, examined standards for the preparation of calibration curves and real sample solutions contained an optimum 25% of sodium chloride salt (6.25 g of NaCl for 25 mL of water sample). The optimal temperature of isolation ( $40 \pm 1^\circ\text{C}$ ) was obtained by refrigerated circulator Julabo F 25 (Julabo Labortechnik GmbH, Seelbach, Germany). The stirring was not used during isolation. An optimum sorption time of 40 min was applied. All samples were incubated during 40 min at  $40 \pm 1^\circ\text{C}$  before extraction by SPME. Temperature of desorption was 220°C. The fiber was exposed in the injection port to desorbed volatiles for 1 min (splitless). The carryover tests of the analyte desorption process for 2 and 5 min were performed. All the analytes were desorbed during 1 min, after which the oven temperature programme was started (split). Total GC run-time was 23 min. The SPME fibers were preconditioned (220°C, 10 min) before and after all analyses.

### Samples and Standard Preparation

The calibration was performed by external standard method. For the calibration procedures methanol standard solutions of (+/-)-geosmin (concentration 101.9 ng/mL), MIB (concentration 101.6 ng/mL) and TCA (concentration 56.0 ng/mL) were diluted in water.

Standard solutions were dissolved in water (free of volatile organic compounds and obtained from Milli-Q apparatus (Millipore, El Paso, TX, USA). Final concentration of analyzed compounds was in the range from 20.32 to 168.00 ng/L. The calibration curves for determined compounds in various samples were evaluated. The calibration data are listed in Table 2.

The calibration procedure and determination of (+/-)-geosmin, MIB and TCA in real surface water samples was carried out in the same analysis conditions.

Table 2. The calibration data of standard mixtures by SPME-GC/MS method (n=5).

Compound Parameter	2-methylisoborneol (MIB)	2,4,6-trichloroanisole (TCA)	(+/-)-geosmin
Average of retention time ( $t_R$ )	10.93 min	13.54 min	14.86 min
Calibration curve	$y=1174.5x + 56251$	$y=345.9x - 5191.3$	$y=2137.9x - 39301$
Correlation coefficient ( $R^2$ )	0.9904	0.9991	0.9971
Range of concentration of standard solution	20.32 – 152.40 ng/L	56.00 – 168.00 ng/L	20.38 – 152.85 ng/L
Detection limit	15 ng/L	5 ng/L	10 ng/L

### GC/MS Conditions

Carrier gas: helium (99.999%) – linear velocity – 30 cm/s. The temperature of the split-splitless inlet was 220°C (splitless time – 1.0 min).

Oven temperature program: the initial temperature of 60°C was kept for 2 min, then raised 8°C/min to 220°C (kept for 4 min). The sample was ionized by electron ionization (EI) at an energy of 70 eV and MS (quadrupol) ion range  $m/z = 35 \div 500$  amu (quant. ions 95, 107, 108, 195, 197, 212, 112, 125 and 149, or ions for selected ion monitoring). The temperature of the interface was 200°C.

### Results and Discussion

In order to compare the extraction efficiency of musty-earthly odour compounds from the water sample with SPME fibers such as PDMS, PDMS/DVB and CAR/PDMS, the extracted mass of MIB, 2-isopropyl-3-methoxypyrazine and 2-isobutyl-3-methoxypyrazine were used. This comparison is presented in Fig. 1.

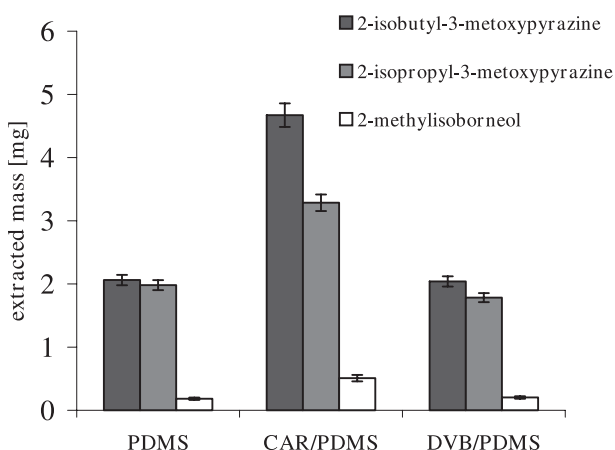


Fig. 1. A comparison of extraction efficiency of MIB and other compounds by SPME with various coated fibers.

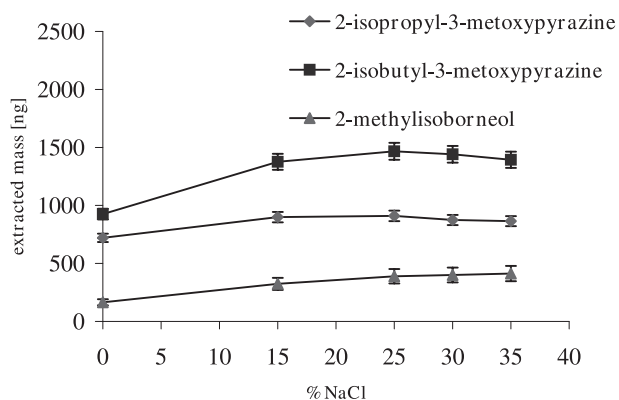


Fig. 2. The effect of salt concentration on MIB and other compound extractions performed by SPME.

The highest extraction efficiency for 2-isobutyl-3-methoxypyrazine is observed. The most satisfactory results were obtained when CAR/PDMS fiber was used. This information is helpful in choosing the appropriate SPME fiber for optimal extraction of volatile organic compounds from water samples. Therefore, obtained data confirm that the thickness of coatings and their chemical properties exert an influence on extraction recoveries.

On the other hand, in order to optimize the sorption and desorption processes, accounts were taken of all the factors influencing the equilibrium between the analytes in the water samples and on the fiber. For example, the matrix in which the extraction takes place has a great influence on the extraction rate. The matrix effect includes a number of factors affecting the equilibrium between the sample and the coating, in particular salt concentration, time, and temperature of extraction. The dependence of compounds extracted mass on salt concentration for MIB, 2-isopropyl-3-methoxypyrazine and 2-isobutyl-3-methoxypyrazine shows that the extracted mass increases with the growth of the salt concentration until saturation of the sample (Fig. 2).

For final analyses of surface water samples a 25% salt concentration was used. This amount of salt in the ana-

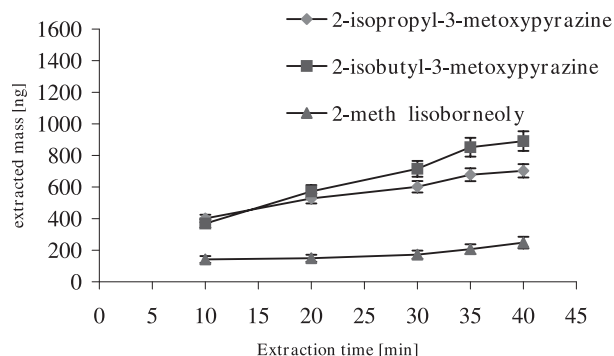


Fig. 3. The extraction time profile corresponding to extracted mass of MIB and other compounds by SPME.

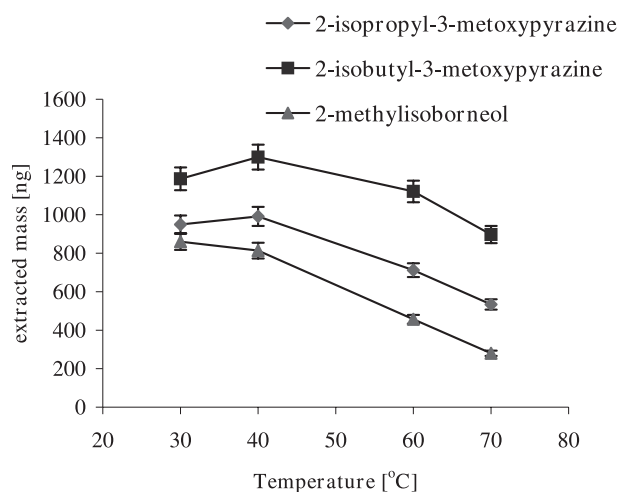


Fig. 4. The temperature dependence of extracted mass of MIB and other compounds by SPME.

lyzed samples is enough to obtain a high extraction efficiency of the determined compounds. Obtained data, for the selection of extraction time confirm that the time, 40 min, is adequate for the highest extraction efficiency of MIB, 2-isopropyl-3-methoxypyrazine and 2-isobutyl-3-methoxypyrazine extracted from water sample (Fig. 3).

As shown in Fig. 4, the choice of extraction temperature depends on the extracted mass of compounds. For SPME method it is necessary to extract the highest possible quantity of compounds. Sorption temperature of 40°C was taken into consideration as suitable for the extraction of components of water samples.

In these investigations a thermal desorption of compounds from water sample was complete after 1 minute at the injector port at 220°C. This is the optimal temperature for total desorption of determined compounds without destruction of these as well as the fiber coating, according to ref. [6-8].

According to preliminary experiments the qualitative and quantitative analyses for the determination of MIB, TCA and (+/-)-geosmin from water samples were performed. Water samples were taken from the lake in the town park (Toruń, Poland). The presence of MIB, TCA

and geosmin in real surface water sample is confirmed by SPME-GC/MS analysis (Fig. 5).

A complex matrix such as the surface water samples requires the appropriate method of preparation. The presence of a variety of substances (eg. lipids, humic acids and other) would reduce the amount of musty/earthy odour compounds in the headspace of the sample and results in low detection. These substances could influence the matrix effect in surface water. Additionally, examined compounds are characterized by lipophilic properties. For the preparation of standard solutions all standards in methanol were diluted with water. The quantitative analysis of determined compounds was performed by the external standard method. The presented SPME method has been optimized for rapid analysis of limited sample volume. The use of large sample volumes (25 mL), long exposure time (40 min) and mass spectrometric detection in selected ion monitoring mode permits the analyses at concentrations as low as 5 ng/L (for TCA standard solution). The regression coefficients of the calibration curves for the examined compounds are as follows: MIB –  $R^2 = 0.9904$ , TCA –  $R^2 = 0.9991$ , and for geosmin  $R^2 = 0.9971$ . This shows that the used method is linear in the examined concentration range.

The presence of musty/earthy odour compounds in water samples can be connected with the fact that atmospheric factors like temperature or sunlight and the concentration of nutrients (phosphorus and nitrogen) caused the growth of organisms, which produce these compounds in water. The highest concentrations of the determined compounds in real surface water samples by SPME-GC/MS method are presented in Table 3.

In the middle of spring the highest concentration of MIB, TCA and geosmin in surface water were determined.

Table 3. The highest concentrations of determined compounds in real surface water samples by SPME-GC/MS method (n=3).

Compounds	Surface water c [ng/L]
2-methylisoborneol (MIB)	38.49 ± 4.62
2,4,6-trichloroanisole (TCA)	17.54 ± 2.11
(+/-)-geosmin	126.16 ± 12.88

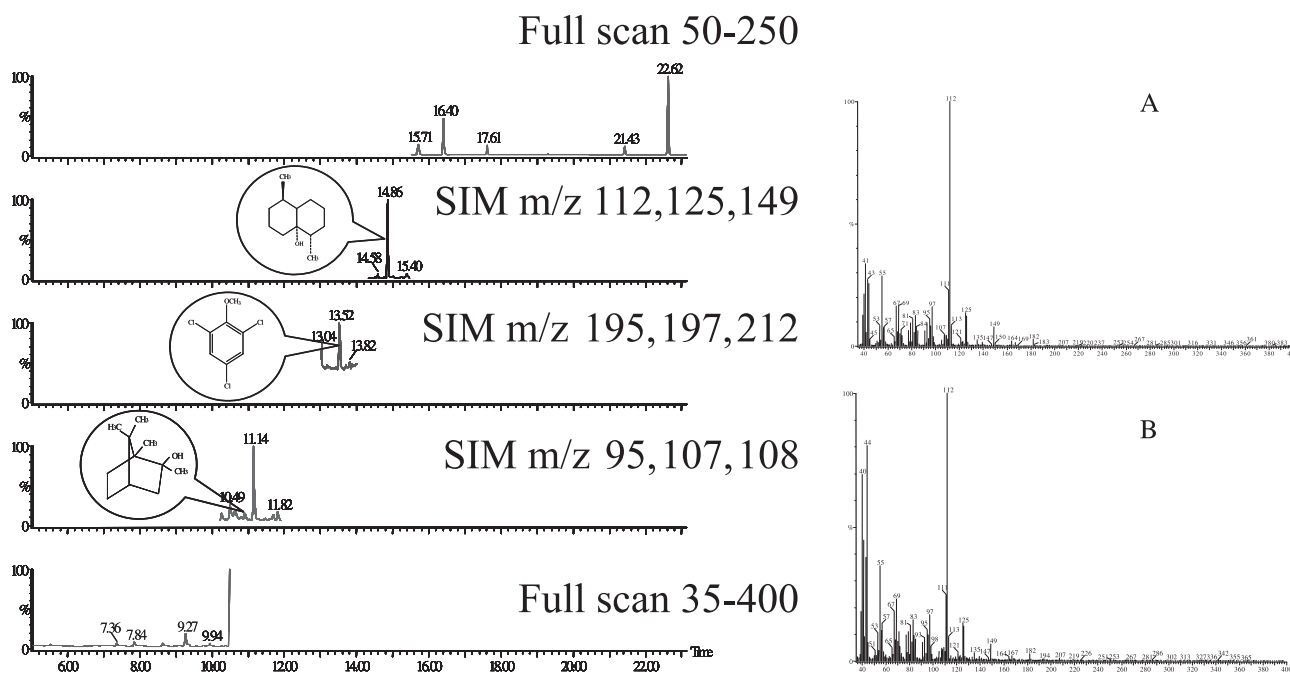


Fig. 5. The extracted ion chromatograms for MIB (ion m/z 95), TCA (ion m/z 197) and geosmin (ion m/z 112) from an analysis of odour compounds in surface water sample. Spectrum of geosmin compound – standard (A), real sample (B).



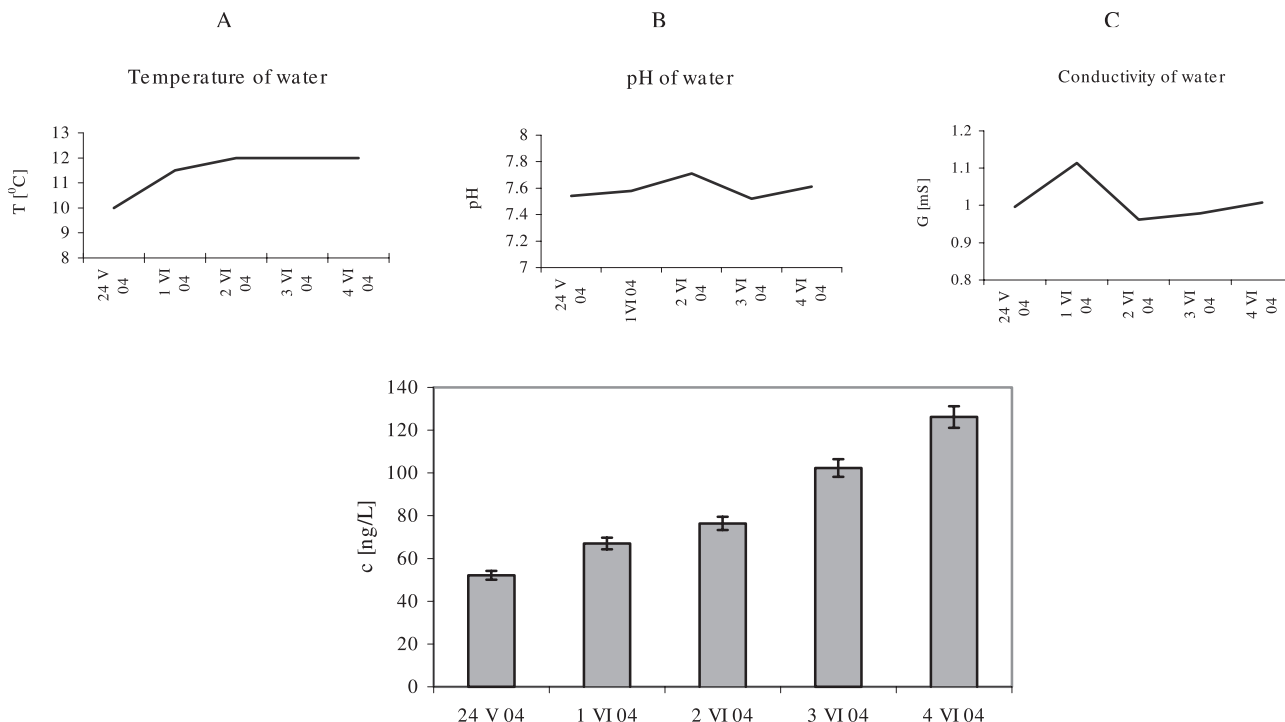


Fig. 6. The change of geosmin concentration in surface water samples during ten days, depending on water conditions: (A) temperature, (B) pH, (C) conductivity.

In other seasons these compounds were not detected in analyzed water (autumn, winter) or the concentration of MIB, TCA and geosmin were on lower levels (summer).

Additionally, for the test of periodical changes of geosmin concentration in surface water samples, some experiments were performed during ten days in the spring. Obtained data in this part of the study are presented in Fig. 6. Particularly, the changes of geosmin concentration in surface water samples during ten days, depending on water conditions such as temperature, pH, and conductivity of water, were taken into consideration.

The investigations, which were performed in various seasons particularly in the early spring, in the middle of spring, in the summer and in the autumn, allow the statement that musty/earthy odour compounds in surface water are formed generally in the middle of spring to be true. In the middle of spring the temperature of ambient air was about 20°C, also an intensive sunlight was observed and the concentration of nutrients was at a high level. And they caused a growth of microorganisms, which produce these compounds in water.

The water samples were obtained from the lake in a city park. The quality of water from this lake, particularly the presence of musty/earthy odour compounds in spring and summer, was important for people using the park. The musty/earthy odour from the lake water was unpleasant for older people and children. However, the way to remove this problem could be the oxygenation of this lake water. The oxygenation of lake water could be performed by using mixing or splash installations. But in the summer, in the autumn and in the winter the problem of lake water aroma

is not an issue, which is connected with the change of atmospheric factors. In cases when the surface water could be used for consumption, water treatment technology would be needed. In the removing of odour compounds from the surface water the chlorination and ozonization processes as well as the use of filters with activated charcoal have significance.

The SPME-GC/MS method for the determination of volatile organic odour compounds in water, which was optimized in this study, can be useful in the routine analysis in environmental laboratories.

## Conclusions

SPME is an inexpensive method that should prove its usefulness for monitoring water quality in potable water supplies and aquaculture systems. The coupling of SPME with the GC/MS technique provides a fast, reliable analysis of MIB, TCA, geosmin and other odour compounds in water samples. The selectivity of SPME helps obtain results with high precision and with limits of detection which are comparable to smaller sample sizes.

During a few days the concentration of geosmin in surface water has been changed in the increasing function from  $52.14 \pm 8.34$  ng/L to  $126.16 \pm 12.88$  ng/L, which corresponds to a higher ambient temperature and high water pollution (spring season). The water treatment technology based on the chlorination effect, which is applied for the preparation of potable water, is efficacious in the removal of geosmin from surface water.

### Acknowledgments

The authors thank K. Milinkiewicz, M.Sc., for technical assistance.

### References

1. YOUNG W.F., HORTH H., CRANE R., OGDEN T., ARNOTT M. Taste and odour threshold concentrations of potential potable water contaminants. *Wat. Res.* **30** (2), 331, **1996**.
2. GRAHAM M. R., SUMMERS R. S., SIMPSON M. R., MACLEOD B. W. Modelling equilibrium adsorption of 2-methylisoborneol and geosmin in natural waters. *Wat. Res.* **34** (8), 2291, **2000**.
3. SAADOUN I. M. K., SCHRADER K. K., BLEVINS W. T. Environmental and nutritional factors affecting geosmin synthesis by *Anabaena* SP. *Wat. Res.*, **35** (5), 1209, **2001**.
4. JELEŃ H.H., MAJCHER M., WĄSOWICZ E., Analysis of microbial volatile metabolites responsible for musty-earthly odors by headspace solid-phase microextraction gas chromatography/mass spectrometry, in: *Handbook of flavour characterisation*, Marcel Dekker, New York, **2003**.
5. NAKAMURA S., DAISHIMA S. Simultaneous determination of 22 volatile organic compounds methyl-*tert*-butyl ether, 1,4-dioxane, 2-methylisoborneol and geosmin in water by headspace solid phase microextraction-gas chromatography-mass spectrometry. *Analytica Chimica Acta.* **548**, 79, **2005**.
6. IZAGUIRRE G., TAYLOR, W. D. Geosmin and 2-methylisoborneol production in a major aqueduct system. *Wat. Sci. Tech.* **31** (11), 41, **1995**.
7. MATTHEIS J.P., ROBERTS R.G. Identification of geosmine as a volatile of *Penicillium expansum*. *Appl. Environ. Microbiol.* **58**, 3170, **1992**.
8. HAYES K.P., BURCH M.D. *Wat. Res.* **23** (1), 115, **1989**.
9. WNOROWSKI A.U., SCOTT W.E. *Wat. Sci. Tech.* **25** (2), 225, **1992**.
10. DIETRICH A.M., HOEHN R.C., DUFRESNE L.C., BUF-FIN L.W., RASHASH D.M.C., PARKER B.C. Oxidation of odorous and non odorous algal metabolites by permanganate, chlorine, and chlorine dioxide. *Wat. Sci. Tech.*, **31** (11), 223, **1995**.
11. RASHASH D.M.C., DIETRICH A.M., HOEHN R.C. *JAW-WA*, **89** (2), 131, **1997**.
12. SUFFET I.H., KHIARI D., BRUCHET A. The drinking water taste and odour wheel for the millennium beyond geosmin and 2-methylisoborneol. *Wat. Sci. Tech.*, **40** (6), 1, **1999**.
13. YOUNG C.C., SUFFET I.H., CROZES G., BRUCHET A. Development of a standard method – analysis of compounds causing taste and odours in drinking water. *Wat. Sci. Tech.* **40** (6), 279, **1999**.
14. JELEŃ H.H., MAJCHER M., ZAWIRSKA-WOJTASIAK R., WIEWIÓRKOWSKA M., WĄSOWICZ E. Determination of geosmin, 2-methylisoborneol, and a musty-earthly odour in wheat grain by SPME-GC-MS, profiling volatiles, and sensory analysis. *J. Agric. Food Chem.* **51** (24), 7079, **2003**.
15. LLOYD S.W., LEA J. M., ZIMBA P. V., GRIMM C. Rapid analysis of geosmin and 2-methylisoborneol in water using solid phase microextraction procedures. *Wat. Res.* **32** (7), 2140, **1998**.
16. NAKAMURA S., NAKAMURA N., ITO S. Determination of 2-methylisoborneol and geosmin in water by gas chromatography-mass spectrometry using stir bar sorptive extraction. *J. Sep. Sci.* **24**, 674, **2001**.
17. WATSON S.B., BROWNLEE B., SATCHWILL T., HARGESHEIMER E.E. Quantitative analysis of trace levels of geosmin and mib in source and drinking water using headspace SPME. *Wat. Res.* **34** (10), 2818, **2000**.
18. LIGOR M., BUSZEWSKI B. Solid Phase Microextraction as a method for the preparation of environmental samples. *Pol. J. Environ. Stud.* **6** (5), 5, **1997**.
19. LIGOR M., ŚCIBIOREK M., BUSZEWSKI B. New coating surfaces of fibers for solid phase microextraction (SPME). *J. Microcolumn Sep.* **11/5**, 377, **1999**.
20. LIGOR M., BUSZEWSKI B. Determination of methol and methone in food and pharmaceutical product by SPME/GC. *J. Chromatogr. A.* **847**, 161, **1999**.
21. EISERT R., LEVSEN K. Solid-phase microextraction coupled to gas chromatography: a new method for the analysis of organics in water. *J. Chromatogr. A.* **733**, 143, **1996**.
22. LOUCH D., MOTLAGH S., PAWLISZYN J. Dynamics of organic compounds extraction from water using liquid-coated fused silica fibers. *Anal. Chem.* **64**, 1187, **1992**.
23. LORD H., PAWLISZYN J. Evolution of solid-phase microextraction technology. *J. Chromatogr. A.* **885**, 153, **2000**.
24. PAWLISZYN J. *Solid Phase Microextraction – Theory and Practise*. Wiley-VCH, New York, **1997**.
25. DAVID F., TIENPONT B., SANDRA P. Stir-bar sorptive extraction of trace organic compounds from aqueous matrices. *LC GC Europe.* **16** (7), 410, **2003**.