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Application Note 147

Solid Phase Microextraction of Odors in Drinking Water, for Analysis by GC/MS

A new method involving the use of Solid Phase Microextraction (SPME)* has been developed for the analysis of trace odor components such as geosmin, methylisoborneol (MIB), isopropylmethoxypyrazine (IPMP) and isobutylmethoxypyrazine (IBMP) from drinking water at parts per trillion (ppt) concentration for analysis by gas chromatography/mass spectrometry (GC/MS). The simple to use, and cost effective method, 6040D, developed by the American Water Works Association (AWWA) describes the use of SPME for odor determination in drinking water.

Musty odors in drinking water often are caused by chemical by-products from the growth of blue-green algae, commonly found in lakes an reservoirs. Some people can smell the odor analytes in drinking water at concentrations of 10ppt or less. Thus many water utility companies and beverage manufacturers must detect geosmin, MIB, IPMP and IBMP at concentrations of 1-3ppt.

Previously to SPME, the methods for extracting these analytes were closed-loop stripping, and purge and trap (dynamic headspace). With closed-loop stripping, a liter of water sample is passed through a small absorbent bed. This is a time consuming procedure and the instrumentation is not always reliable. In addition, if solvent is used to elute the analytes off the adsorbent bed, the analytes are diluted, losing the advantage of the large sample volume. In purge and trap, to trap a sufficient amount of analytes, a 25mL vessel must be used. The sparging of 25mL water samples is not very efficient compared to 5mL samples. This results in only a portion of the sample reaching the trap.

SPME, a simple solventless sample preparation technique, can be used to extract the odor compounds at concentrations as low as 1ppt for analysis by GC/MS. Analytes from the sample are adsorbed in the coating of the SPME fiber and are desorbed from the fiber in the heated GC injection port. This is a low cost, simple yet reliable alternative method for the extraction of water odors.

In 1999, a new odor method incorporating the dual-coated SPME fiber was proposed to the committee on Odor Methods of the AWWA as an alternative to closed-loop stripping and purge and trap. Andy Eaton (1) and Steve Foster (2) described the proposed method 6040D, Analysis of Taste and Odor Compounds by SPME at the AWWA annual meeting in 1999. The method calls for the SPME fiber to be inserted into the headspace of a 60mL vial containing 45mL of water with 25% NaCl heated to 65°C. After a 30-minute exposure of the SPME fiber in the vial, the fiber was removed and inserted directly into the heated injection port (260°C) of the GC/MS system. The MS analysis is either recommended in the single ion mode for quadrupole instruments or a reduced mass range for ion trap instruments. The analytes are quantified by single ions shown in Table 1. Method 6040D verified

Table 1. Quantitation Ions and Secondary Ions for Odor Agents

Odor	Quant Ion	Sec. Ion
IPMP	137	124, 152
IBMP	124	151
MIB	95	107
Geosmin	112	125
2,4,6-TCA	197	195, 212

Figure A. Odors by SPME/GC/MS at 2 Parts per Trillion in Water

Column:	**Equity-5, 30m x 0.25mm, 0.25µm film**
Cat. No.:	**28089-U**
SPME Fiber:	2cm StableFlex coated with 50/30µm DVB/Carboxen/PDMS, Cat. No. 57348-U
Extraction:	headspace, 65°C (30 min)
Desorption:	3 min at 260°C
Oven:	60°C (2 min) to 200°C at 8°C/min
GC Liner:	0.75mm SPME liner
Detector:	5973 MSD, selected ions (SIM) 95, 112, 124, 137, 197; interface at 280°C
Flow:	Helium, 37cm/sec @ 60°C (1mL/min constant flow)
Injection:	SPME fiber, splitless opened at after 1 min at 50mL/min
Sample:	25mL of water containing 25% NaCl and drinking water odors kit, Cat. No. 47529-U

1. 2-Isopropyl-3-methoxypyrazine, 2ppt
2. 2-Isobutyl-3-methoxypyrazine, 2ppt
3. 2-Methylisoborneol, 2ppt
4. 2,4,6-Trichloroanisole (internal standard), 8ppt
5. (±)Geosmin, 2ppt

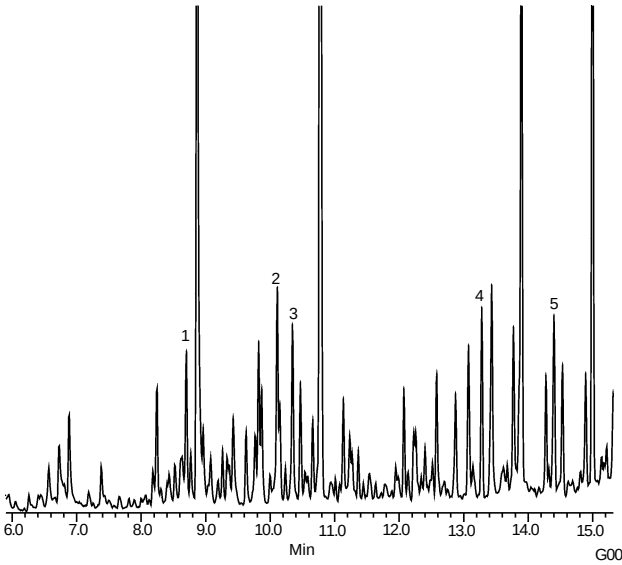
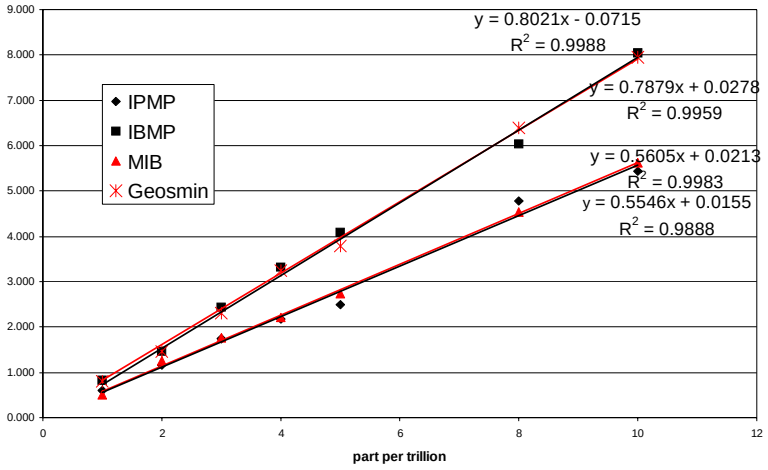


Figure B. Linearity of Relative Responses with Respect to TCA



analysis of these 4 odor causing agents using one of the methoxypyrazines as an internal standard. Method 6040D can be downloaded from the web at www.standardmethods.org.

A special 2cm SPME fiber, DVB-Carboxen-PDMS was specifically designed for this analysis. It contains an inner layer of Carboxen in PDMS coating overlaid with a divinylbenzene (DVB)-PDMS layer. Both adsorbents have a high affinity for the odor agents, but the fiber can easily release them in the heated injection port of the GC.

Figure A shows the results of extracting of 4 odor agents at 2ppt in water along with an internal standard (IS) 2,4,6-trichloroanisole (TCA) at 8ppt. TCA was added at a higher concentration due to the high degree of fragmentation when ionized by the MS. TCA may be present as an odor-causing agent. If so, IPMP or IBMP can be use as the IS. Always run a sample without an IS to determine which analytes are present. We prepared the sample by placing 25mL of the water in a 40mL vial containing 6g of NaCl and a stirring bar. The vial was placed in a 40mL aluminum-heating block preset at 65°C on a stirring heat plate. The 2cm fiber was placed in the headspace of the vial and the sample was extracted for 30 minutes with rapid stirring. The fiber was desorbed in the injection port containing a 0.75mm ID liner at 260°C, and the analytes were resolved on an Equity-5 capillary column. The good resolution of this column enabled the analytes to be detected down to 1ppt. The linearity of this analysis as relative responses is shown in Figure B. The good correlation coefficients of 0.99 or better and y intercepts within 0.08 of zero for the odor agents, indicate that the method is reliable.

References

1. Eaton, A., Nguyen, D., Suhady, L. Proceeding of American Water Works Association, Water Quality Conference, November 1999, M3-2.
2. Foster, S., Nanci, J., Owen, C., Proceeding of American Water Works Association, Water Quality Conference, November 1999, M3-3.

Ordering Information:

Description	Cat. No.
SPME Fiber Assemblies, for odor analysis, pk. of 3**	
Divinylbenzene/Carboxen/polydimethylsiloxane coating	
For both manual and autosampling, 2cm	**57348-U**
SPME Fiber Holder**	
For manual sampling	**57330-U**
For Varian 8100/8200 AutoSampler or HPLC	**57331**
For CombiPal and Gerstel autosampler	**57347-U**
Equity-5 Capillary Column	
30m x 0.25mm ID x 0.25 df	**28089-U**
40mL Vial Heating Block	
Use with heat/stir plate	
(capacity 6 vials)	**33313-U**
Screw Top Vials	
Precleaned, pk. of 72	
Clear, 40mL	**23188**
Amber, 40mL	**23189**
Drinking Water Odor Standards	
100µg/mL in 1mL methanol	
(±)-Geosmin	**47522-U**
2-Methylisoborneol	**47523-U**
(±)-Geosmin and 2-Methylisoborneol	**47525-U**
2,4,6-Trichloroanisole	**47526-U**
2-Isopropyl-3-methoxpyrazine	**47527-U**
2-Isobutyl-3-methoxypyrazine	**47528-U**
Drinking Water Odor Standards Kit	
1mL of each standard listed above	**47529-U**

*Solid phase microextraction technology is licensed exclusively to Supelco (US patent 5,691,206; European patent #0523092).

** Initially you must order both the fiber holder and the fiber assembly. The holder is reusable indefinitely. Use of the holder with AutoSampler requires a Varian SPME upgrade kit (available from Varian).

Carboxen is a trademark of Sigma-Aldrich Co.

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