Analysis of off-flavor compounds in water at sub part per trillion level by GC/MS with programmable temperature vaporizer inlet

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Abstract "Earthy-musty" off-flavor problems in water samples are due to organic compounds present at the sub part per trillion level. Most of the studies in the analysis of tastes and odorous compounds focus on the extraction pre concentration technique, with detection at picogram per liter level of the earthy-musty off-flavor compounds, which are difficult to achieve. The objective of this study is to develop a new method involving the GC/MS with programmable temperature vaporizer (PTV) inlet via large volume injection (LVI) or solid phase micro-extraction (SPME), to attain analytical sensitivity equal to or better than olfactory sensitivity. Six "earthy-musty" organic compounds; 2-methylisoborneol (MIB); geosmin; 2, 4, 6-trichloroanisole (2,4,6-TCA); 2, 3, 6-trichloroanisole (2,3,6-TCA); 2, 3, 4-trichloroanisole (2,3,4-TCA); and 2, 4, 6-tribromoanisole (2,4,6-TBA), were used as probes for this study. It was found that LVI via PTV could greatly improve system sensitivity towards the detection of off-flavor compounds with low volatility such as haloanisoles. For those off-flavor compounds with high volatility, eg MIB, SPME coupled with PTV-GC-MS with cool initial temperature has always demonstrated the best sensitivity.

Keywords GC-MS; large volume injection (LVI); off-flavor; programmable temperature vaporizing (PTV); solid phase micro-extraction (SPME); water

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Introduction

Surface water supplies are more likely to be affected by substances causing undesirable tastes and odors. As a result, taste and odor account for the largest single class of consumer complaints submitted to water utilities (Levallois *et al.*, 1999). Nearly all water treatment plants utilize chemicals or adsorbents to control these problems. Treating water so that it meets taste and odor standards set by the EPA (Environmental Protection Agency) makes up a significant portion of total water treatment costs. It was commonly accepted that earthy-musty smell is associated with the presence of geosmin, MIB and haloanisoles (Mallevialle and Suffet, 1987; Jensen *et al.*, 1994; Bruchet, 1999). Among the eight odor groups described in the water flavor wheel, the earthy-musty odors are especially troublesome because they are particularly unpleasant and often encountered in water (Suffet *et al.*, 1996). These semi-volatile compounds have a muddy, musty odor described by the human nose when present at concentrations greater than 0.004–0.02 μg/L for geosmin and MIB (Krasner *et al.*, 1983; Persson, 1983; Mallevialle and Suffet, 1987; Young *et al.*, 1996), as well as 30 pg/L for haloanisoles in water (Malleret and Bruchet, 2001; Malleret *et al.*, 2001). These olfactory detection limits are well below the conventional analytical methods.

Traditional analytical methods for monitoring these taste and odor concentrations include closed-loop stripping (McGuire *et al.*, 1981), liquid–liquid extraction (Johnsen and Kuan, 1987; Bao *et al.*, 1997), steam distillation (Anselme *et al.*, 1985) and purge and trap (USEPA, 1988; Johnsen and Lloyd, 1992). Some of these methods have poor sensitivity while some of them have more complex sample preparation or analysis. Most

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of the developments in the analysis of taste and odor compounds focus on the extraction preconcentration technique, such as membrane based extraction (Zander and Pingert, 1997), microliquid–liquid extraction (Bao *et al.*, 1997), solid phase microextraction (Lloyd *et al.*, 1998) and stir bar sorptive extraction (Nobuo *et al.*, 2001; Benanou *et al.*, 2003). However, detection at picogram per liter level of the earthy-musty off-flavor compounds has not been achieved, although numerous extraction techniques have been applied.

Since GC-MS is highly selective and sensitive, it is often the method of choice for organic residue analysis and/or confirmation (Arrebola *et al.*, 2004; Diaz *et al.*, 2005). However, for the analysis of taste and odor compounds at picogram per liter level, sensitivity of GC-MS is usually a challenge. With the development of PTV technique, which offers capability of LVI (Grob *et al.*, 1985; Engewald *et al.*, 1999), sensitivity of GC analysis can be greatly improved. PTV coupled with GC/MS offers great possibility in simple sample preparation and extreme high sensitivity.

SPME is a solvent free extraction technique that enables the extraction and concentration steps to be carried out simultaneously. It has received much more attention in recent years due to its high efficiency for the extraction of organic compounds with different polarity, volatility and solubility from water samples. A manufacturer's report described a headspace SPME (HS-SPME) method for the analysis of MIB and geosmin with excellent linearity from 1–10 ng/L for standards in water.

So far, all the reported SPME processes were performed on the hot GC injection inlet, since most of the gas chromatograph systems are equipped with standard split/splitless type inlets. One Gerstel application note firstly demonstrated the advantage of combination of hot PTV inlet and SMPE technique. The significant improvement versus split/splitless type inlet was considered to be contributed from the use of septumless head (SLH) instead of a septum for sealing the inlet. However, the main advantage of the application of PTV inlet is that the sample is not introduced into a hot oxidative environment, but into a cool system followed by an increasing temperature ramp to minimize the thermal decomposition of the labile analytes. Unfortunately to this date, there is no report on the combination of SPME and PTV process starting from a cool inlet.

The objective of this study is to develop and validate a reliable and efficient method for analysis of taste and odor compounds at sub part per trillion level in water using LVI-PTV-GC/MS and SPME-PTV-GC/MS techniques. Variable LVI-PTV-GC/MS and SPME-PTV-GC/MS conditions will be investigated in detail.

Experimental

Chemicals and reagents

The standard compounds of 2-methylisoborneol (MIB), geosmin, 2, 3, 4-trichloroanisole and 2, 4, 6-tribromoanisole were purchased from Dr. Ehrenstorfer Gmbh (Bgm Schlosser-Str., Augsburg). 2, 4, 6-Trichloroanisole and 2, 3, 6-trichloroanisole were purchased from Aldrich Chem. Co. (Saint Quentin Fallavier, France). Methanol, dichloromethane, diethyl ether, acetone were HPLC grade and obtained from Merck KGaA (Darmstadt, Germany). Off-flavor standard mixture solutions were prepared in methanol, and subsequently diluted to achieve a calibration standard for LVI-PTV-GC/MS. The aqueous standards for SPME-PTV-GC/MS were prepared by spiking off-flavor mixture standard in deionized water, which was obtained by passing tap water through an USF-ELGA option 15 system and an USF Maxima system (VivendiWater, UK) with the resistance greater than 18.2 $M\Omega.cm^{-1}$ and on-line TOC less than 2 μg/L.

Equipment

The gas chromatograph used for this study is Agilent 6890 series GC coupled with 5973 series mass spectral detector. An Agilent programmable temperature vaporizing inlet (G2619A Septumless head, Agilent, USA) with PTV liner (Part No. 5183-2041 and 5183-2037 PTV liner, Agilent, USA) was applied as the sample injector. The GC column used was HP-5MS 30 m × 0.25 mm × 0.25 μm. The carrier gas was helium with a flow rate at 1.2 ml/min. The GC/MS transfer line temperature was maintained at 280°C. The electron impact (EI) ionization mode was used with an electron energy of 70 eV and tune to perfluorotributylamine (PFTBA). The mass spectrum was obtained at a mass-to-charge ratio scan range of 50–700 amu to determine appropriate masses for selected ion monitoring (SIM). The EI ion source of the mass spectrometer was 230°C. The solvent delay time was set to 3 minutes. Selected ion monitoring mode was used in quantitation. The dwell time was set to 100 ms for each ion.

Materials

SPME fiber assembly holder and six commercial available fibers (polydiemthylsiloxane (PDMS) 100 mum, non-bonded; polydiemthylsiloxane/divinylbenzene (PDMS/DVB) 65 mum, partially crosslinked; polydiemthylsiloxane/divinylbenzene (PDMS/DVB) stableflex 65 mum, highly crosslinked; polyacrylate (PA) 85 mum, partially crosslinked; carbowax/divinylbenzene (CW/DVB) 65 mum, partially crosslinked; stableflex divinylbenzene/carb oxen/polydiemthylsioxane (DVB/CAR/PDMS) 50/30 mum, highly crosslinked) were ob tained from Supelco (Bellefonte, PA, USA). 22 mL headspace vials with PTFE-coated silicone septa were purchased from Agilent Technologies (Singapore).

Extraction procedure

Continuous liquid-liquid extraction (CLLE). A measured volume of sample, usually 1 liter, was placed into a continuous liquid-liquid extractor, and extracted with 400 mL dichloromethane for 5 hours. The apparatus used for current continuous liquid–liquid extraction was made by UFO Pte Ltd., Singapore, with its design similar to that supplied by Kimble/Kontes (Part No. 584240) (Vineland New Jersey, USA). The temperature of water bath was controlled by a magnetic digital ceramic hotplates/stirrers SM26 (Stuart Scientific, Staffordshire, UK). The temperature of the water bath was set at 70°C, stirred at 700 rpm. After drying over anhydrous sodium sulphate followed by removal of dichloromethane, the extract was concentrated to 1 ml via nitrogen blow down.

Headspace-SPME procedure (HS-SPME). 10 ml of water sample was placed into a 22 mL headspace vial containing a magnetic stirrer (12 × 3 mm). After addition of 4.0 g of NaCl, the vial was sealed with a silicon-PTFE septum cap. The sealed vial was placed in a water-bath and stirred at 700 rpm, with the water bath temperature being controlled at 60 °C by magnetic digital ceramic hotplates/stirrers SM26 (Stuart Scientific, Staffordshire, UK). After the syringe needle of the SPME device was pierced through the septum, the fiber was plunged out to be exposed in the headspace for adsorption of the analyte. About 30 minutes later, the fiber was retracted back into the syringe and withdrawn from the vial, followed by the immediate fit into the PTV-GC/MS inlet for desorption. After plunging the fiber out from the syringe holder to desorb the extracted analytes, both the PTV program and GC program started. Eight minutes later, the SPME fiber was retracted back into holder, removed away from PTV inlet and used directly for next SPME extraction.

Results and discussion

Principle of LVI using PTV

Currently, there are two techniques which can be used for large volume injection: cool on-column (COC) and programmable temperature vaporizer inlet (PTV). Compared with LVI via cool on-column injector, which is most appreciate for clean samples with volatile components, LVI via PTV is ideal for trace analysis of later eluting solutes with boiling points approximately 100°C higher than solvent and for dirty samples.

LVI using PTV can improve GC system detection limits by 1–2 orders of magnitude over standard methods. The PTV inlet has the same basic functions as the split/splitless inlet except that it is temperature programmable from -60°C (using CO_2 cooling) or − 160°C (using liquid N_2 cooling) to 450°C at rates up to 720°C/min. At the "solvent vent" mode with multiple injections, system sensitivity can be greatly improved by LVI. Generally, three steps consisted in the LVI via PTV, injection and solvent elimination, split/splitless sample transfer to the GC column, and chromatographic separation

To achieve better sensitivity, two key points must be noted during method setup: 1) the vent end time must occur before the inlet starts to heat and release analysts; and 2) purge time must occur before the oven begins to heat and moves the sample through the column. However, due to the complicated PTV injection process, many factors can affect the performance of this system and its efficiency, such as solvent type, injection volume, initial temperature and ramp temperature of PTV inlet, etc. Therefore, many research studies must be conducted before an optimized method can be achieved.

Principle of HS-SPME

Solid phase microextraction consists of two processes: adsorption or absorption of the analytes on the fiber coating and then desorption of concentrated analytes into an analytical instrument. The first process is a multiphase equilibration of analytes partitioning between the sample and the coating on a silica fiber. The basic principle is "like dissolves like". In practice, if a liquid polymeric coating is used, the amount of analyte absorbed by the coating at equilibrium is directly related to its initial concentration in the sample. Desorption process for GC is a thermally desorbing procedure while it is a solvent eluting procedure for HPLC analysis.

SPME sampling can be performed in three basic modes: direct extraction, headspace extraction and extraction with membrane protection. In the direct extraction mode, the coated fiber is inserted into the sample matrix directly to extract organic analytes. This works well for gaseous sample and relatively clean water sample. In the headspace extraction mode, sampling analytes from gas phase equilibrated with the sample matrix, are necessary if volatile compounds in solid or complex samples such as samples with grease, oil, and protein are going to be analyzed. In the SPME with membrane protection, the fiber is separated from the sample with a selective membrane which protects the fiber against adverse effects from some high-molecular compounds. This mode is suitable for analyzing less volatile compounds from very dirty samples. However the membrane barrier may delay the extraction time.

Selected ions of MIB, geosmin and haloanisoles and chromatorams

Excellent separation could be achieved both on LVI-PTV-GC/MS and SPME-PTV-GC/MS, as indicated in Figure 1. GC/MS was running at the selective ion mode (SIM) to achieve the best sensitivity, fragment ions with m/e of 95, 108, 110 were chosen for MIB, 112 and 125 for geosmin, 210, 167 or 195 for the other three chloroanisoles, and 346 and 331 for the 2,4,6-tribormoanisole.

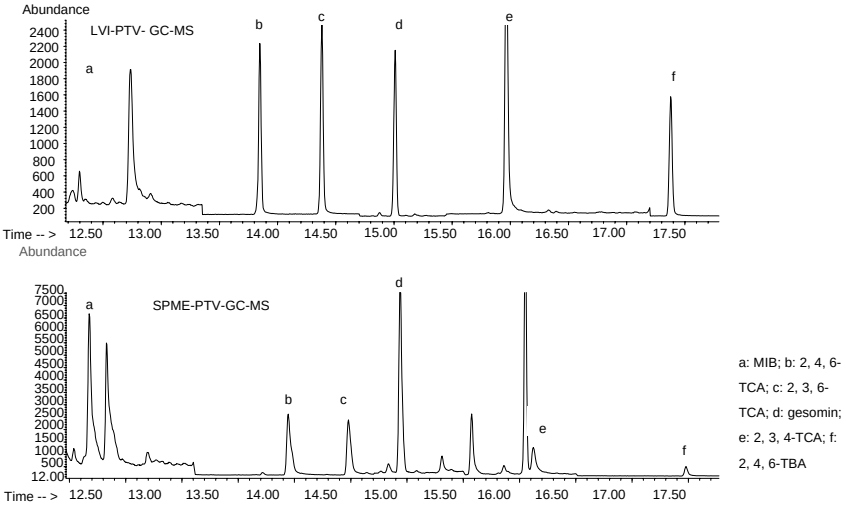

Figure 1 Chromatogram of off-flavor compounds on PTV-GC-MS and SPME-PTV-GC-MS

Influence of injection volume on LVI-PTV-GC/MS

Theoretically, increase of injection volume will increase the relative response peak area. Although the system PTV control software allows up to 99 injections, a practically reasonable upper limit is about 20 times with 25 μL per injection. Our experimental results indicate that with the increase of injection volume, the response peak intensity also increases stably. However, after an injection volume over 100 μL, the increasing rate of response intensity will be no longer proportional to the injection volume, which means that the effect of injection volume is much less than that in small injection volume (Figure 2). In current study, the optimal injection volume is 100 μL.

Column pressure

Column pressure only affects retention time on the normal split/splitless inlet. But on PTV inlet, column pressure not only affects the retention time of analytes but also affects the response of analytes. According to an earlier report, when using PTV multiple injection mode, the column head pressure should be set to 0 psi followed by a pressure ramp program during solvent elimination process (Philip, 1997). It would help to prevent analytes going into the column, which would possibly cause sample diffusion and peak

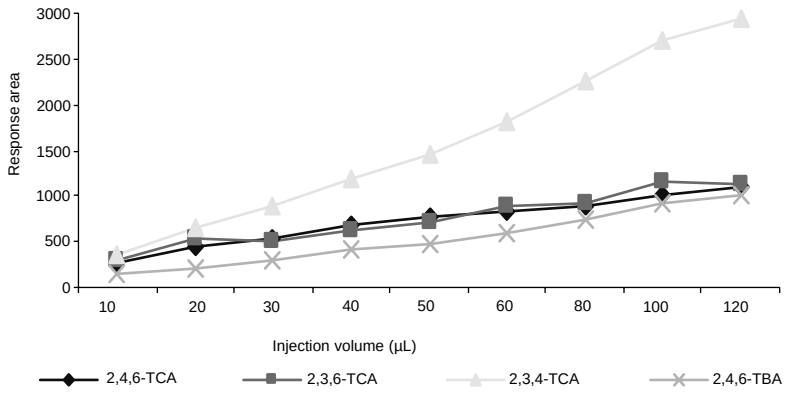

Figure 2 Influence of injection volume on the response of off-flavor

broadening and tailing. However, our study indicates that operation under constant column pressure is better than ramp pressure for off-flavor compounds. Increasing initial pressure will increase the response intensity of analyte in solvent vent large volume injection mode. It could be understood that, during large volume injection process, increase of the initial pressure will increase the amount of analyte going into the column, thus reducing the possibility of the amount of analyte being vented out of the system, and increasing the response of analytes. However, if the column pressure is higher than 14 psi, the analyte response intensity starts to drop. It is because an overly high gas pressure in PTV inlet would drive the analyte to the vent and thus cause a loss of the analytes. Therefore, the best column pressure should be 14 psi.

Injection mode and initial inlet temperature

Both splitless and pulsed splitless modes for PTV inlet were evaluated for trace level odorous compounds analyses. Peak tailing was found in the pulsed splitless mode and the response area was also smaller than that obtained in splitless mode. Therefore, in the following work, the PTV inlet was always set at splitless mode.

One of the major differences between PTV inlet and normal split/splitless inlet is that PTV is designed to have the capability of holding the sample in the cool inlet liner until the entire sample (usually a large volume) is injected. The PTV is then heated rapidly via a temperature ramp to sweep the injected samples to the column. Here in the initial cool inlet could help to reduce the evaporation of analytes during injection period, and thus avoid loss of target components. Initial cool inlet could also help to minimize the thermal decomposition of the labile analytes. In principle, these advantages of PTV inlet could also help SPME process by keeping the absorbed analytes in the fiber at cool temperature during injection period to improve its sensitivity. However, there is no report so far on the combination of SPME process with such an initial cool inlet.

In our experiments, fritted deactivated glass PTV liner (Part No. 5183-2041, 1.5 mm i.d., 150 μL) for LVI method and multi baffle deactivated borosilicated glass PTV liner (Part No. 5183-2037, 1.5 mm i.d., 150 μL) was employed for SPME method. These liners have a small internal diameter and small volume than a normal liner, which allows sharp peaks to be generated after column separation to improve separation and enhance sensitivity.

Experiments were performed on the same SPME extraction process and GC/MS conditions, except that the PTV initial inlet temperature is different. Cool PTV inlet means the initial PTV inlet temperature was set at 40 °C, followed with a temperature program as: hold at 40°C for 2 minutes followed by raising the temperature to 265°C with ramp rate of 500°C/min; hold at 265°C for 5 minutes to recondition the fiber. The hot inlet means the inlet temperature was held at 265 °C constantly. The results indicated that the response intensities will increase 20–300% via cool inlet than that for hot inlet. For MIB and geosmin, their response areas increase 300% and 80% respectively (Figure 3). The response intensities for haloanisoles increased 20–60%. Obviously, towards the parameters of MIB with relative better volatility, much more improvement on the response intensity could be achieved by cool PTV inlet than that towards haloanisoles. This could be easily clarified as that the cool PTV inlet helped to retain the absorbed analytes on the SPME fiber before they are swept into GC column, thus avoid the loss of analytes during desorption process. This experiment clearly indicated for the first time, that the application of initial cool PTV inlet can greatly improve the sensitivity of SPME analysis, especially towards the analyte with high volatility, such as MIB. Our other studies have also proven that injection sample in cool inlet would achieve much better response than in hot inlet under splitless mode.

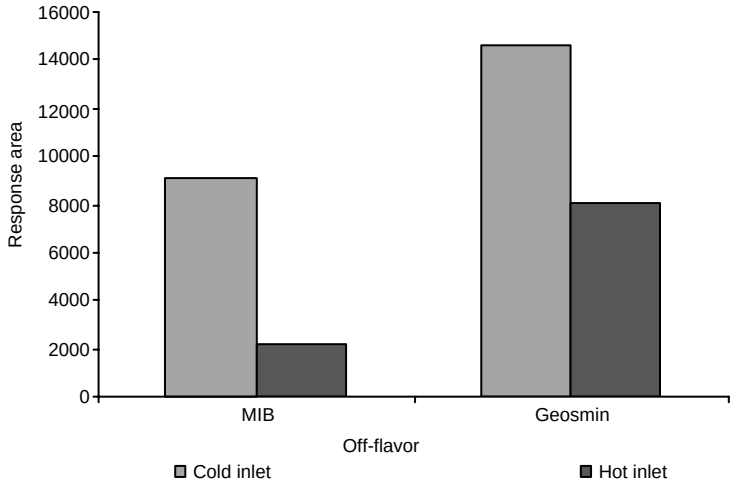

Figure 3 Influence of initial inlet temperature on the response of off-flavor

Optimized method

The optimized PTV condition and SPME condition are as follows:

- LVI-PTV-GC/MS: Dichloromethane was used as the solvent for sample and chemical standard preparation. PTV inlet temperature ramp rate was set at 300°C/min. The total injection volume was 100 μL. Column pressure was set as 14 psi. Sample extraction was conducted using continuous liquid–liquid extraction by dichloromethane for 5 hours at pH = 7.
- SPME-PTV-GC/MS: DVB/CAR/PDMS fiber was used for SPME process. All analyses were conducted at HS-SPME mode, with water bath temperature set at 60°C. The SPME fiber adsorption time was 30 minutes. PTV injector was set at splitless mode with initial temperature at 40°C followed with a increasing temperature program with ramp rate of 500°C/min to a final temperature of 265°C. The PTV constant column pressure was set at 14 psi.

Method validation

This developed method was validated according to USP/ICH guideline (Michael and Ira, 1997).

Calibration and linearity. Linearity is the ability of the method of elicited test results to be directly proportional to analytes concentration within a given range. The calibration curve linear range for the six off-flavor compounds was determined over seven to nine concentration levels. For LVI- PTV-GC-MS method, the linear range is 0.5–20 μg/L for MIB and 0.05–20 μg/L for the others. The linear regression r^2 is from 0.993–0.999, with RSD 4.7–15.1%. For SPME-PTV-GC-MS method, the linear range is 0.5 ng/L to 50 ng/L, with the linear regression r^2 being from 0.993–0.999, as indicated in Table 1.

Precision. Precision (repeatability) is the measure of the degree of the repeatability of an analytical method under normal operation and is normally expressed as the relative standard deviation (RSD) for a statistically significant number of samples. It is the degree of agreement among individual test results when the procedure is carried out repeatedly.

Instrument precision was measured by comparing standard deviation of the response from the injection in triplicate of different standard solutions within different batches.

Table 1 Protocols for method validation

		MIB	2,4,6-TCA	2,3,6-TCA	Gesomin	2,3,4-TCA	2,4,6-TBA
Linear range	LVI-PTV-GC/MS (μg/L)	0.5 ~ 20	0.1 ~ 20	0.1 ~ 20	0.1 ~ 20	0.1 ~ 20	0.1 ~ 20
	SPME-PTV-GC/MS (ng/L)	0.5 ~ 50	0.5 ~ 50	0.5 ~ 50	0.5 ~ 50	0.5 ~ 50	0.5 ~ 50
Linear regression (r^2)	LVI-PTV-GC/MS	0.993	0.997	0.998	0.994	0.999	0.996
	SPME-PTV-GC/MS	0.993	0.997	0.998	0.994	0.999	0.996
RSD	LVI-PTV-GC/MS	15.1%	6.7%	11.7%	9.4%	4.7%	8.4%
	SPME-PTV-GC/MS	3.3%	6.9%	4.7%	5.5%	8.1%	6.3%
Recovery	LVI-PTV-GC/MS	58%	71%	78%	69%	96%	94%
	SPME-PTV-GC/MS	88%	66%	63%	92%	66%	86%
MDL (ng/L)	LVI- PTV-GC/MS	0.34	0.056	0.035	0.05	0.07	0.07
	SPME-PTV-GC/MS	0.15	0.32	0.14	0.16	0.16	0.38

Accuracy. Accuracy is a measure of the closeness of a result to the true value and should be established across the specified range of the analytical procedure. Accuracy is usually expressed as the recovery of the analyte.

$$\text{Recovery}\,(\%) = (C_{\text{spiked sample}} - C_{\text{sample}})/(C_{\text{spiking standard}}) \times 100$$

The accuracy of six off-flavor compounds was determined by analysis of DI water spiked with 10 ng/L of off-flavor standard mixtures for both SPME and LVI method. The recovery of each off-flavor standard is listed in Table 1. The recovery of haloanisole was greater than 70%, and the recovery of geosmin and MIB were relatively low due to their high polarity for LVI method. Interestingly, towards MIB and geosmin, the recovery on SPME-PTV-GC/MS is much higher than that of LVI-PTV-GC/MS method; this could result from the high volatility of MIB and geosmin.

Method detection limit (MDL). The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.

MDL $= t_{(n-1,1-\alpha=0.99)}$ (S), $t_{(n-1,1-\alpha=0.99)}$ is the students t-value appropriate for a 99% confidence level and a standard deviation estimate with $n - 1$ degrees of freedom. S is the standard deviation of the replicate analyses. When the number of replicates $= 7$, $t_{(n-1,1-\alpha=0.99)} = 3.14$ (USEPA SW-846, 1992).

Method detection limits of these six off-flavor compounds are indicated in Table 1. It was found that in general, towards five of these six off-flavor compounds, LVI-PTV-GC/MS method will have better sensitivity than SPME-PTV-GC/MS. However, towards MIB, which has the highest volatility, SPME-PTV-GC/MS demonstrated the best sensitivity, which is ten times more sensitive than that of previous reported one (Zimmerman *et al.*, 2002).

Conclusions

LVI-PTV-GC/MS and SPME-PTV-GC/MS have been proven to be efficient technologies for analyses of off-flavor compounds in water at sub part per trillion level. LVI via PTV could greatly improve system sensitivity towards the detection of off-flavor compounds with low volatility such as haloanisoles. Among the six off-flavor compounds, five of them could be analyzed by LVI-PTV-GC/MS with better sensitivity. However, to analyze off-flavor compounds with high volatility, eg MIB, SPME coupled with PTV-GC-MS with cool initial temperature has always demonstrated the best sensitivity.

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