Application of solid phase extraction (SPE) coupled to dispersive liquid–liquid micro-extraction (DLLME) and sensory evaluation technique for the study of taste and odor active compounds in water

Jian Zou, Chenyi Shi, Jingyi Xu, Shayne Green, Yang Zhou, XiuHan Yang, Tanya Fry and Bill Winniford

ABSTRACT

Short-chain carbonyls could cause taste and odor issues in drinking water due to their very low odour threshold concentrations (OTCs). Several techniques such as 2,4-dinitrophenylhydrazine (DNPH) derivatization-HPLC and solid-phase micro-extraction (SPME) have been applied for trace short-chain aldehydes analysis in water. However, to study the taste and odor contributors in drinking water, it would be helpful to obtain an extract with representative odor from water samples for further studies, such as GC-olfactometry analysis or sensory test. Therefore, the above techniques still have some constraints due to the derivatization process or complex operating procedures. In this work, we developed a solid-phase extraction (SPE) coupled to dispersive liquid–liquid micro-extraction (DLLME) method to study short-chain aldehydes in ozonated water samples (LOQ = 1 ppb, RSD% = 12–45%). This method enables us to obtain an extract with representative odor from water for further volatile components analysis and sensory evaluation. Pair-wise nose clip sensory evaluation on the taste and odor of ozonated water indicated a high correlation between odor and taste of ozonated water. The SPE-DLLME method enabled a reliable study, for the first time, on correlations of volatile carbonyls and taste & odor performance for ozonated water by applying a series of statistical models.

Key words | sensory, short-chain aldehydes, SPE-DLLME, water taste and odor

HIGHLIGHTS

● A sensitive solid-phase extraction (SPE) coupled to dispersive liquid–liquid micro-extraction (DLLME) method was developed in current work. This method enable us to study the trace aldehydes in ozonated water sample (LOQ = 1 ppb, RSD% = 12–45%).

● This method is a cost-effective and green chemistry method. Very small amount of organic solvent is needed to extract the trace aldehydes in water (2 mL of acetonitrile and 0.3 mL of dichloromethane is needed for each water sample).

● By using the SPE-DLLME method, we are able to obtain an extract with representative odor from ozonated water sample. This SPE-DLLME extract enable us not only to study volatile components in water, but also to conduct further GC-olfactometry study and sensory evaluation on the extract.

● By using nose clip sensory evaluation technique, we are able to identify the taste contributors in ozonated water samples.
The SPE-DLLME method and sensory evaluation enabled a reliable study, for the first time, on correlations of volatile carbonyls and taste and odor performance for ozonated water by applying a series of statistical models.

INTRODUCTION

Taste and odor of drinking water are critical issues for the drinking water industry. According to previous studies, the odor and taste of drinking water could be caused by many factors, such as bacteria contamination (Wood et al. 2001), algae (Antonopoulou et al. 2014), ozonation post-treatment process (Antonopoulou et al. 2014), reaction of hypochlorite with amino acids (Hrudey et al. 1988; Bruchet et al. 1992), and other contaminants. Many chemicals, such as inorganic cations and anions (Burlingame et al. 2007), organic chemicals such as halogen-containing compounds (Suffet et al. 1995), sulfur-containing compounds (Antonopoulou et al. 2014) were identified as contributors to the taste and odor of drinking water. Short-chain aldehydes are also well-known odor contributors in drinking water due to their very low odour threshold concentrations (OTCs) (0.1–12 ppb) (http://www.leffingwell.com/ald.htm), especially after ozonation (Antonopoulou et al. 2014). However, due to the low concentration of taste and odor contributors in water, it is challenging to study the trace short-chain aldehydes in water samples. In previous works, various analytical techniques, such as 2,4-dinitrophenylhydrazine (DNPH) derivatization-HPLC (Takeda et al. 1994) and solid phase microextraction (SPME) (Zhang et al. 2015) have been applied to study the trace organic compounds in water. However, there were still several challenges, such as sensitivity and complex operating procedures. Therefore, we would like to develop a more sensitive method for the study of trace organic aldehydes in water. Another important requirement is to get an extract with a representative odor of water, to make sure the major odorants were extracted in the sample for analysis. Dispersive liquid–liquid micro-extraction (DLLME) is a technique to enrich trace hydrophobic organics in water samples (Berijani et al. 2006). Compared with traditional solvent extraction techniques, it has many advantages, such as a high enrichment factor, convenience, and much less solvent used. More important, by using DLLME, we are able to get an extract with enriched odorants for further sensory evaluation, and this will be helpful to understand if the appropriate odorants are extracted in the DLLME extract for further analysis. Therefore in this presented work, it is proposed to use DLLME or the more sensitive solid-phase extraction (SPE)-DLLME (Fattahi et al. 2007) technique for studying trace odorants in water.

It is well known the volatiles will cause an odor issue in water, but we still need to understand the taste contribution to water samples. Technically, taste has a very specific meaning, which refers to the sensation produced when a substance in the mouth reacts chemically with taste receptor cells located on the taste buds in the oral cavity. The sensation of taste includes five established basic tastes: sweetness, sourness, saltiness, bitterness, and umami (Middleton et al. 1956). According to the published literature, taste can be affected by many factors, including cations, anions, pH, temperature, and chemical components (Suffet et al. 1995; Wood et al. 2001). The general concept of ‘taste’ is actually a sum of human sensations caused by three separate sensations, namely taste, odor, and mouthfeel (Burlingame et al. 2007; Haese et al. 2014) (see Figure 1). Apart from the five ‘basic tastes’, the ‘mouthfeel’ is caused by some chemicals in the nose or mouth that result from stimulation of the trigeminal nerves, such as the ‘spicy’, ‘metallic’, and ‘astringent’ taste descriptions when we taste some foods (Burlingame et al. 2007). The ‘flavor’ is a combination of

**Figure 1** | The concept of general ‘taste’.
basic taste, mouthfeel, and odor (Middleton et al. 1956). Actually, in our daily life, the ‘taste’ of water or food is not only the very specific ‘basic taste’ or ‘mouthfeel’, it is a combination of smell (olfaction), trigeminal nerve stimulation (spicy, hot, astringent), and basic taste (sour, bitter, sweet, salty, and umami). Therefore, volatiles could also affect or even dominate the taste (flavor) of water and food. For ozonated drinking water, our hypothesis is that the water taste (flavor) should be dominated by its volatiles due to the very low concentration of inorganic anions and cations in water. To prove our hypothesis, ‘nose clip’ sensory evaluation experiments (Yamamoto et al. 1989) were conducted in this work to identify the taste contributors in ozonated water samples. Statistical modeling was also used to study the correlation of taste and odor performance of ozonated water to total short chain carbonyls concentration.

MATERIALS AND METHODS

Reagent and chemicals

Short chain aldehydes reference compounds were obtained from TCI. Co. Ltd Pentanal (TCI-V0001 > 95.0%), hexanal (TCI-H0135 > 98.0%), heptanal (TCI-H0025 > 95.0%), octanal (TCI-O0044 > 98.0%), nonanal (TCI-N0296 > 95.0%), decanal (TCI-D0032 > 97.0%) and undecanal (TCI-U0009 > 97.0%).

Paper sniffing strips: The smelling strips were ordered from Pin Chuang Co. Ltd in Jinhua, Zhejiang province of China.

The 35 mL glass tubes with a conical bottom were ordered from Shanghai Tao Lun Co. Ltd.

Acetonitrile (ACN) (Cat. No. 4.80448) and dichloromethane (DCM) (Cat. No. DX0838): from Aldrich Co. Ltd.

NaCl (Cat. No. S9888) was obtained from Aldrich Co. Ltd.

Diethyl adipate (Cat. No. 42697) was obtained from Aldrich Co. Ltd.

Ozonated water samples: Obtained from Dow Chemical Co. Ltd, Package & Specialty Plastics business.

SPE-DLLME-TDS GC-MS parameters for aldehydes analysis in water samples

Diethyl adipate (≥99%, FG, SCRC) was added as an internal standard with a concentration of 0.2 ppm in water samples before analysis. An aliquot of 200 mL water sample was passed through a poly-sery HLB SPE cartridge (Anpel Co. Ltd, China. SBEQ-CA3185, lot number H3720120, 200 mg, 6 mL), and then eluted with 2 mL of ACN to obtain the SPE extract. The obtained ACN eluent was diluted with 18 mL deionized water and then placed into a 35 mL screw-cap glass centrifuge tube with a conical bottom. A 2 g NaCl aliquot was added into the centrifuge tube and dissolved in the ACN aqueous solvent. A 300 μL dichloromethane aliquot was injected into the 35 mL screw-cap glass centrifuge tube quickly by a syringe. The mixture was ultra-sonicated at room temperature for 1 min to form a cloudy solution in the centrifuge tube. Then the mixture was centrifuged for 10 min at 3,000 rpm to separate the organic phase (dichloromethane phase) from the water phase. The dichloromethane extract was deposited at the bottom of the centrifuge tube. An aliquot of 20 μL DLLME extract was injected into a Tenax tube (Gerstel Co. Ltd, 60/80 mesh) with a 50 μL syringe for thermal desorption (TDS) coupled to GC-MS analysis. Semi-quantification of various short-chain carbonyls in water samples was conducted by comparing with the peak area of diethyl adipate as equivalent (see Equation 1 of supplemental material).

Sensory evaluation of DLLME extract:

An aliquot of 5 μL DLLME extract was injected on a paper sniffing strip, and the paper sniffing strip was shaken in a fume hood for 10 seconds to remove the DCM solvent in the paper, and then panelists smelled the odor from the sniffing strips and recorded the odor description in a questionnaire.

Pair comparison sensory evaluation on ozonated water samples:

In each test, ~25 trained panelists joined the sensory evaluation, and only one pair of water samples was provided to panelists to compare their taste/odor performance. Panelists used blank water between samples to reduce fatigue and carryover effect. Random three-digit codes were used as blind sample identification. A balanced block design was used to ensure all samples were served equally often and in all positions. The replicate set of samples provided a measure of
test reproducibility. Samples were presented in 8 oz glass jars to use for the sensory test; panelists were allowed to drink from the glass jars, or they could pour the water from the jar into the cup to drink.

For taste/odor intensity comparison, panelists were asked to record which water sample has lower taste/odor intensity in the questionnaire. A two-tailed binomial statistical table was used for the paired comparison data to determine if there were any significant differences among the samples.

For taste/odor hedonic comparison, panelists were asked to record the taste/odor hedonic value of each sample in the questionnaire for further comparison. Taste/odor hedonic value as following: 1. Dislike extremely; 2. Dislike very much; 3. Dislike moderately; 4. Dislike slightly; 5. Neither like nor dislike; 6. Like slightly; 7. Like moderately; 8. Like very much; 9. Like extremely. An F-statistic in analysis of variance (ANOVA) and the hedonic value was used to determine if there were any significant differences among the samples.

For the nose clip sensory experiment, nose clips were used during the evaluation when tasting/drinking the samples to determine the effect of volatiles on taste (flavor) differences, and only water taste intensity and the hedonic value were recorded in the experiment.

**RESULTS AND DISCUSSION**

**Development of SPE-DLLME method to extract trace organics in water**

In a preliminary experiment to study short-chain aldehydes in typical ozonated water samples, we tried DLLME coupled to thermal desorption GC-MS technique. The results indicated that the sensitivity of the method was still not satisfactory. Therefore, an SPE method coupled to the DLLME method was developed to increase the sensitivity for analysis of trace odorants in water samples. The general procedure of SPE-DLLME was shown in Figure 2 below.

Before the DLLME procedure, an SPE experiment was conducted on a water sample to extract the organic compounds in water and then elute the compounds absorbed in an SPE cartridge with ACN. The ACN eluent was used as a dispersive solvent for further DLLME and added to a deionized water sample in a centrifuge tube. A small amount of extractant was then injected into the mixture of ACN and water by a syringe to extract the trace organic compounds. The organic compounds in water can be first enriched by SPE experiment and then further enriched by DLLME; therefore higher enrichment factors can be achieved by SPE-DLLME than by just DLLME. In this work, we selected dichloromethane as DLLME extractant due to its low boiling point (b.p. 39.8 °C) and less toxicity than traditional DLLME extractant such as CHCl₃ (b.p. 61.2 °C) and chlorobenzene (b.p. 131 °C). Therefore, the solvent in DLLME extractant can be easily removed for further odor study such as sensory evaluation and GC-olfactometry analysis.

**Optimize DLLME parameters by CCD (central composite design)**

A CCD design was used to study the experimental parameters of DLLME: dispersive solvent content (ACN%), volume of extractant (dichloromethane), and salt content (NaCl %). An aldehydes mixture standard solution (C5-C11 aliphatic linear aldehydes) was prepared in a 25% ACN aqueous solution as a model solution to evaluate the effect of various DLLME parameters. Although 19 experiments were designed with three repeats together, five of those did not result in the dichloromethane layer at the centrifuge tube bottom because
either the dichloromethane remained dispersed in the water or did not go to the bottom of the centrifuge tube. The enrichment factor of DLLME experiments were measured using Equation 3 of supplemental material. All of the models for peak areas of C5-C11 are with $R^2$ higher than 0.99 and $p$-value from 0.0023 to 0.001, which indicated these are significant models.

Thus dichloromethane and NaCl content are the most critical factors; increasing either will decrease the volatiles enrichment factor. Since there is an interaction between the variables, altering one variable can change the response curve for the other variables. When dichloromethane at low volume (Figure 3), increasing NaCl content hurts the enrichment more significantly versus when dichloromethane volume increases, the influence of NaCl content will drop. When NaCl is at low concentration, dichloromethane volume has more effect than when NaCl content is at a high level. Dichloromethane/NaCl has a similar impact on the enrichment for all the aldehydes tested. ACN has more influence on the short-chain than the long-chain aldehydes. The concentration of ACN can only be in a small range (10–12%), because higher content of dispersive solvent (ACN) will increase the solubility of dichloromethane in the aqueous solution, thus preventing the separation of the dichloromethane layer in the bottom of the centrifuge tube. By addition of NaCl, the additional solubility of DCM in the ACN-water phase is offset. The finalized parameters were determined as a balance of the enrichment factor and

---

**Figure 3** | Predict profiler for aldehydes in DLLME DOE experiment.
DLLME extract volume: 20.0 mL of ACN aqueous solvent (10%), NaCl (10%), and 500 μL of dichloromethane.

The recovery of the SPE-DLLME method was measured using an aqueous solution with the aldehyde standard mixtures (C5–C11 aliphatic linear aldehydes, 0.1 ppm), see Equation 4 in supplemental material. The aqueous solution was analyzed with the optimized SPE-DLLME procedure coupled to the TDS GC-MS method, and the results showed that the recovery of aldehydes of C6 to C9 aldehyde ranged from 60 to 80%, while C5, C10, and C11 aldehydes ranged from 18 to 46% (Table 1). The lower recovery of C5 aldehyde could be due to their higher solubility in the water compared with other aldehydes, thus it was harder to be extracted by DCM in the DLLME process. While the lower recovery of C10 and C11 aldehyde could be due to their longer alkyl chain in structure, which made it more difficult for them to be eluted in SPE cartridge. Although the recoveries of several aldehydes were not ideal, we considered it sufficient to make a comprehensive analysis of the odorants in the ozonated water samples.

The repeatability of the method was studied by four parallel ozonated water samples. The repeatability (n = 4) of the major carbonyl species varied from 12 to 45%. For total carbonyls, the RSD (%) is 13.2%. The LOQ of the method decreased from ~10 ppb (DLLME) to ~1 ppb (SPE-DLLME) in water, based on s/n value. In some previous techniques, such as o-(2, 3, 4, 5, 6-pentafluorobenzylhydroxylamine (PFBHA) derivatization-SPME-GC method, we are able to obtain a low boiling point extract, which enables us to conduct further odor studies such as sensory evaluation or GC-olfactometry study. The theoretical enrichment factor is ~1,000–2,000 (condensed from 200 g of water to ~100 μL of SPE-DLLME extract, see Equation 5 in supplemental material).

A series of ozonated water samples were analyzed. The results indicated that the major VOCs in water were short-chain and middle-chain carboxyls. More than 40 carbonyls (C5 to C11) were identified, and their concentrations ranged from 1 ppb to 100 ppb in ozonated water. The SPE-DLLME extracts were also evaluated using a paper sniffing strip, and we found that the extracts have a typical odor of ozonated water described as ‘plastic’, ‘green’, which was very close to the odor of the ozonated water samples. This indicated that the major odorants were extracted in the SPE-DLLME extract.

**Identifcation of taste contributors in ozonated water**

Nose clip sensory evaluation means that when tasting samples, a nose clip is worn on the nose in order to remove the effect of volatiles on the perception of sample taste. The principle of the nose clip technique is as follows: Generally, there are two ways for a panelist to perceive sample odor during the eating or drinking process. The first way is by orthonasal olfaction, by which the odor is detected through the nostrils by sniffing or inhalation. The second way is to detect the odorant when it is released from food in the mouth during chewing, exhalation, or swallowing process. During this process, the odorant released by food will pass through the posterior nares of the nasopharynx (Figure 4(a)). However, when using a nose clip to do the sensory evaluation, the odorant is prevented from passing through the nostrils by sniffing, or inhalation, and also retronasal olfaction is affected (see Figure 4(b)). Therefore, by wearing a nose clip, the effect of volatiles on the taste of the sample is decoupled. Previous work showed that for some samples such as soy sauce (Hayase et al. 2013), wine (Yamamoto & Totsuka 1990), and sake (Yamamoto et al. 1989), volatiles are the key to taste. While for several samples, such as oyster soup flavor, it was found that some sensory attributes, such as ‘oyster’, ‘fishy’, and ‘fried pork’ odors were highly affected by volatiles, while ‘sweet’ and ‘salty’ tastes were highly correlated to amino

<p>| Table 1 | The recovery of SPE-DLLME method |
|----------------------------------|</p>
<table>
<thead>
<tr>
<th>Aldehyde name</th>
<th>Aldehydes spiked weight in 100 g of water (μg)</th>
<th>Measured aldehyde weight in SPE-DLLME extract (μg)</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C5</td>
<td>10</td>
<td>2.4</td>
<td>23.8</td>
</tr>
<tr>
<td>C6</td>
<td>10</td>
<td>6.1</td>
<td>61.1</td>
</tr>
<tr>
<td>C7</td>
<td>10</td>
<td>8.0</td>
<td>80.4</td>
</tr>
<tr>
<td>C8</td>
<td>10</td>
<td>8.0</td>
<td>80.0</td>
</tr>
<tr>
<td>C9</td>
<td>10</td>
<td>7.1</td>
<td>70.8</td>
</tr>
<tr>
<td>C10</td>
<td>10</td>
<td>4.6</td>
<td>46.4</td>
</tr>
<tr>
<td>C11</td>
<td>10</td>
<td>1.9</td>
<td>18.5</td>
</tr>
</tbody>
</table>
acids and inorganic cations/anions in the samples (Nguyen & Wang 2012). This indicated that the five basic tastes (sour, bitter, sweet, salty, and umami) were mainly affected by non-volatiles, while other taste perceptions (oily, metallic, fishy, fullness, etc.) are mainly affected by volatiles.

To understand the effect of volatiles on taste in ozonated water, we selected two ozonated water samples with a significant difference in taste performance. First, the two water samples were submitted for tasting by the panel without a nose clip. Then in a second experiment within 2 weeks, the two water samples were evaluated using a nose clip technique by the same panel under the same conditions. If the nose clip sensory evaluation experiment showed no taste difference, while the sensory experiment without the nose clip did observe a significant taste difference, then it indicated that volatiles in the ozonated water were major contributors to the water taste.

The nose clip sensory evaluation results are shown in Table 2. In Test 1, we have compared the odor/taste intensity and hedonic value of water samples A and B without a nose clip. The results show that sample A has a significantly higher odor/taste intensity and a worse odor/taste hedonic value than sample B. We also compared the total carbonyls concentration in samples A and B, the results show that the total carbonyls in sample A are much higher than in sample B. Then in a separate sensory evaluation test, we re-prepared water samples A and B, and conducted the taste evaluation with a nose clip by the same panel. With a nose clip, the panelists could not identify any taste intensity/hedonic difference between the two samples. To confirm our results, we made a similar Test 2 on another pair of water samples, C and D. The results were similar to Test 1. When tasted without a nose clip, the panelists found that both the taste and odor difference between the two samples was significant; however, in the sensory test with a nose clip by the same panel, no taste difference could be observed, even though the total carbonyls concentration in the two water samples was quite different.

Another interesting finding is that when using a nose clip, 40 out of 127 panelists wrote ‘no taste’ in the

Table 2 | Comparison of taste intensity/hedonic response of water samples evaluated with and without a nose clip

<table>
<thead>
<tr>
<th>Sensory test without nose clip</th>
<th>Sensory test with nose clip</th>
</tr>
</thead>
<tbody>
<tr>
<td>Taste hedonic value</td>
<td>Taste intensity</td>
</tr>
<tr>
<td>Test 1 sample A</td>
<td>3.38 b</td>
</tr>
<tr>
<td>sample B</td>
<td>4.33 a</td>
</tr>
<tr>
<td>Test 2 sample C</td>
<td>2.88 b</td>
</tr>
<tr>
<td>sample D</td>
<td>3.50 a</td>
</tr>
</tbody>
</table>

Remark:
1. Letters that are different indicate that the samples are statistically different. Letters that are the same indicate that there is no statistical difference (for example, ‘a’ and ‘a’ means there was no statistical difference, while ‘a’ and ‘b’ means there was a significant difference between the two samples).
questionnaire, while testing without a nose clip, only 10 out of 120 panelists wrote ‘no taste’ in the questionnaire (Table 3). This indicated that when decoupling the effect of volatiles, more panelists cannot perceive the taste (flavor) of the water samples. This result also confirmed our hypothesis that ozonated water taste (flavor) in the current samples was dominated by volatiles.

A series of ozonated water samples was obtained from different customers, and sensory evaluation was conducted to record odor and taste hedonic values, and total volatile carbonyls. In total, ~30 data points were obtained. We used correlation coefficient to investigate the relationship between hedonic taste and odor, and it was calculated based on data variance and covariance. The value of the correlation coefficient ranges between −1.0 and 1.0. A correlation of −1.0 shows a perfect negative correlation, while a correlation of 1.0 shows a perfect positive correlation. A correlation of 0.0 shows no relationship between the movements of the two variables. In our case, we obtained a correlation coefficient of 0.8113 based on 30 samples. We also used standard least squares, and the R² of the linear regression is 0.6582 (see Figure 5). This indicated 65.8% of the variance in the hedonic taste value could be explained by the hedonic odor value. Therefore, the odor and taste of the water sample are highly correlated, and this was consistent with our nose clip sensory evaluation experiment.

**Study on correlations of volatiles and T&O performance**

We used several statistical models to help fit the chemical composition concentrations with the hedonic value of the water odor to understand further the key chemicals or series of chemicals that influence the human sense of odor. In our study, we applied partial least squares, boosted tree, decision tree and generalized regression. Comparing the results from the four algorithms, we concluded the first key factor that highly correlated with odor hedonic value is total volatile carbonyls (TVC). We fit TVC with the hedonic value on odor by simplex linear regression (Figure 6) with R² of 0.7714, which indicated around 77% of the hedonic value variance could be explained by this model with TVC as a variable. And we obtained a correlation coefficient of 0.8783.

---

### Table 3 | Summary of panelists who wrote ‘no taste’ in questionnaires

<table>
<thead>
<tr>
<th></th>
<th>Panelist wrote ‘no taste’</th>
<th>% of panelists wrote ‘no taste’</th>
<th>Panelists can describe the taste of water</th>
<th>% of panelists can describe the taste of water</th>
<th>Panelists total number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Test with nose clip</td>
<td>40</td>
<td>31%</td>
<td>87</td>
<td>69%</td>
<td>127</td>
</tr>
<tr>
<td>Test without nose clip</td>
<td>10</td>
<td>8%</td>
<td>110</td>
<td>92%</td>
<td>120</td>
</tr>
</tbody>
</table>

---

![Figure 5](image1.png) **Figure 5** | The correlation between the hedonic value on water odor and water taste.

![Figure 6](image2.png) **Figure 6** | The correlation between the hedonic value on water odor and total volatile carbonyls.
Similar algorithms were applied to the hedonic value of taste versus the chemical compositions. We also found TVC as a key contributor, shown in Figure 7, can explain more than 66% of hedonic taste variance. And we obtained a correlation coefficient of 0.8164. This result indicated that both water taste and odor hedonic are highly correlated with TVC in ozonated water.

**CONCLUSION**

In this presented work, we have developed an SPE-DLLME method coupled to TDS GC-MS for the analysis of trace odorants in ozonated water samples. Based on this work, the theoretical enrichment factor could be ~1,000–2,000. The extract of SPE-DLLME was successfully used for sensory evaluation and analysis of trace carbonyls in ozonated water samples. The LOQ of the method was ~1.0 ppb based on s/n value. We also conducted a fundamental study in order to understand taste contributors in ozonated water using a nose clip sensory evaluation technique. When tasting water samples with a nose clip, the taste difference between the water samples disappeared. This result indicated that the taste (flavor) of ozonated water was dominated by their volatiles. Further study on correlations between the water taste hedonic and water odor hedonic values also confirmed this conclusion. By using a statistical model analysis, we found that total volatile carbonyls have a significant correlation with water taste and water odor, which indicated that total volatile carbonyls in water are a key factor to affect water taste and odor.

**ACKNOWLEDGEMENTS**

The authors would like to thank Dr Yi-dong Lu, Dr Yan Luo, and Dr Xuemei Zhai for their great support. The authors would like to thank Dr Shaoguang Feng, Dr Cuilan Chang, and Dr Haiying Li for their fruitful discussion. The authors would like to thank Mr Chang Wu, Dr Lei Ying, Dr Thomas Allgeuer, Dr Jim Luong, Dr Greg Meyers, Dr Hongyu Chen, Mr Xiaobing Yun, and Dr Jian Wang for their help. Special thanks to Prof. Helene Hopfer from Penn State University for her fruitful discussion and suggestions.

**DATA AVAILABILITY STATEMENT**

All relevant data are included in the paper or its Supplementary Information.

**REFERENCES**


First received 17 December 2019; accepted in revised form 15 July 2020. Available online 27 July 2020.