Rapid detection of taste and odor compounds in water using the newly invented chemi-ionization technique coupled with time-of-flight mass spectrometry

Haixu Zhang [a, b], Pengkun Ma [a, b], Jinian Shu [a, b, *], Bo Yang [a, b, **], Jingyun Huang [a, b]

[a] National Engineering Laboratory for VOCs Pollution Control Material & Technology, University of Chinese Academy of Sciences, Beijing, 101408, China
[b] State Key Joint Laboratory of Environment Simulation and Pollution Control, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing, 100085, China

HIGHLIGHTS

- A rapid detection method for taste and odor compounds in water is demonstrated.
- High ionization efficient photo-induced chemi-ionization is utilized.
- The experimental LODs are in the $0.25-50.2$ ng L^{-1} range.
- The new technique is applied to the analysis of city tap water and river samples.

GRAPHICAL ABSTRACT
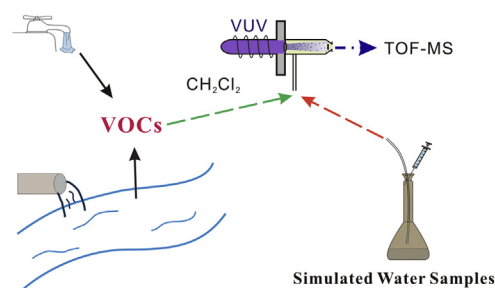
Simulated Water Samples

ABSTRACT

Taste and odor (T&O) compounds are widespread in water environments and have attracted considerable public attention. Nowadays, the standard detections of these chemicals rely mainly on off-line methods such as GC-MS or evaluation by trained analysts' senses. In this study, we report a method for the rapid detection of T&O compounds in water by exploiting a newly invented chemi-ionization source, in combination with headspace vapor measurement at room temperature. The calibrated limits of detection (LODs) of 2-methylbutyraldehyde, methyl tert-butyl ether (MTBE), methyl methacrylate (MMA), 2-isobutyl-3-methyoxypyrazine (IBMP), and 2-isopropyl-3-methoxypyrazine (IPMP) are in the range of $3.5-50.2$ ng L^{-1}, and the estimated LODs of 2-methylisoborneol (2-MIB) and geosmin (GSM) are 0.25 and 0.77 ng L^{-1}, respectively. The calibration results reveal that the instrumental LODs for 2-methylbutyraldehyde, MTBE, MMA, β-cyclocitral, 2-MIB, and GSM are $1-2$ orders of magnitude better than the odor thresholds of humans. The accuracy, precision, recovery, and linearity (R^2) of the method are tested. Water samples from city tap water and three rivers in Beijing are assessed using this technique, and the typical T&O compositions are observed with concentrations ranging from 0.2 to 297 ng L^{-1}. The new ultra-sensitive rapid detection method shows comparable sensitivities to the existing off-line technique and displays great potential for real-time detection of T&O pollution in water environments.

© 2018 Published by Elsevier B.V.

* Corresponding author. Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, 18 Shuangqing Rd, Haidian District, Beijing, 100085, China.
** Corresponding author. Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, 18 Shuangqing Rd, Haidian District, Beijing, 100085, China.
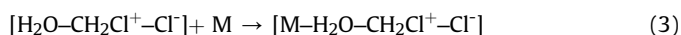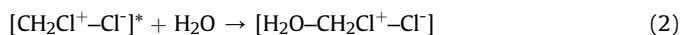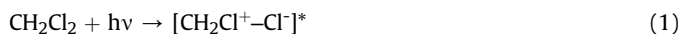E-mail addresses: jshu@rcees.ac.cn (J. Shu), boyang@rcees.ac.cn (B. Yang).

1. Introduction

Taste and odor (T&O) problems that occur in natural and man-made water systems have attracted considerable public and governmental attention. Generally, the T&O compounds brought to the forefront of attention are mainly earthy-musty odorants released by microorganisms [1,2], disinfection by-products (DBPs) of water treatment processes [3], and industrial pollutants emitted during chemical engineering [4]. Major contributors to earthy-musty odors include 2-methylisoborneol (2-MIB), geosmin (GSM), 2-isobutyl-3-methyoxypyrazine (IBMP), 2-isopropyl-3-methoxypyrazine (IPMP), and β-cyclocitral [2,5,6]. The odor threshold concentrations of these compounds are extremely low $(10 \, ng \, L^{-1}$ or less) [7,8], and, as a consequence, they are easily perceptible in drinking water even in trace amounts and have become an important issue for customers when it comes to water quality evaluation [9—11]. Isobutyraldehyde, isovaleraldehyde, and 2-methylbutyraldehyde have long been recognized as important odor agents in the food industry and identified as DBPs formed during the chlorination of amino acids [12]. Methyl *tert*-butyl ether (MTBE) and methyl methacrylate (MMA) are typical industrial pollutants listed in the "Taste and Odor Wheel". These chemicals have been confirmed as harmful to the nervous system. Additionally, they can exert genotoxic activity and cause eye irritation, formation of birth defects, cancer, and even death in both humans and animals [12—16]. Therefore, rapid and effective methods for the detection of T&O compounds are critical for the health security and safety of both humans and animals.

Currently, however, there is no real-time method available that would meet the required detection standards, especially for earthy-musty odorants, which are often present in trace quantities. To date, sensory and chemical analyses have been developed to evaluate T&O compounds in water [17]. The American Public Health Association has included three standard methods for evaluating the taste and odor of water and wastewater: (i) the flavor rating scale (FRS), (ii) the threshold odor number (TON), and (iii) the flavor profile analysis (FPA) [18]. FRS and TON are likely to be greatly influenced by the individuals' personal sensitivities to a particular odor, which can make the identification of the source or the cause of a taste-and-odor event extremely challenging [19]. FPA, on the other hand, describes each type of flavor along with its intensity in a procedure that is performed by a panel of trained analysts [20]. GC-MS is a standard analytical method for the detection of T&O compounds in water samples [21]. Generally, the GC-MS methods are mostly run in the electron ionization (EI) and or the chemical ionization (CI) mode, with the ion scans performed in the selected ion monitoring (SIM) mode or using tandem mass spectrometry (MS/MS) techniques [10]. The relationship between the concentration of a chemical in actual water samples and the odor intensity is determined using GC/MS-Olfactometry in combination with FPA [22], which can be described by the Weber—Fechner model [23] or the Stevens' Power model [24].

The sensitivity of GC-MS is usually insufficient for the direct measurement of compounds present at the ng L^{-1} levels [5]. Consequently, a variety of techniques for extraction and enrichment have been established for sensitivity elevation, including the closed-loop stripping analysis (CLSA) [25], the purge and trap (PT) method [26], stir bar sorptive extraction (SBSE) [27], solid phase extraction (SPE) [28], solid phase microextraction (SPME) [29], liquid-liquid extraction (LLE) [30], and liquid-liquid micro-extraction (LLME) [31]. The existing methods can detect earthy-musty odorants at the sub-ng L^{-1} level [5,10,32]. The limits of detection (LODs) of MTBE and MMA are reported as 0.01 $\mu g \, L^{-1}$ and 10 $\mu g \, L^{-1}$ [33,34]. However, the methods capable of highly sensitive detection are also extremely labor-intensive and time-consuming [5,7,32].

Recent studies have shown that dichloromethane doping-assisted photoionization can enhance the ionization efficiencies of oxygenated hydrocarbons by two to three orders of magnitude [35,36]. The mechanism of the phenomenon was proposed as a chemi-ionization induced by excited-state dichloromethane as follows: [37].

$$CH_2Cl_2 + h\nu \rightarrow [CH_2Cl^+–Cl^-]^* \tag{1}$$

$$[CH_2Cl^+–Cl^-]^* + H_2O \rightarrow [H_2O–CH_2Cl^+–Cl^-] \tag{2}$$

$$[H_2O–CH_2Cl^+–Cl^-] + M \rightarrow [M–H_2O–CH_2Cl^+–Cl^-] \tag{3}$$

$$[M–H_2O–CH_2Cl^+–Cl^-] \rightarrow MH^+ + CH_2O + HCl + Cl^- \tag{4}$$

where M represents H_2O or oxygenated organic molecules, $[CH_2Cl^+–Cl^-]^*$ is an ion-pair state. Moreover, this method has been verified effective to amido aromatic hydrocarbons as well [38]. In this study, the chemi-ionization technique is coupled with TOF-MS and used for the rapid detection of T&O compounds, without the need for a pre-enrichment process. The mass spectrometric signatures of 2-methylbutyraldehyde, MTBE, MMA, IBMP, IPMP, β-cyclocitral, GSM, and 2-MIB are investigated and the sensitivities to T&O compounds in the pure gas phase and the headspace vapor of simulated water are measured. City tap water, Xiaoyuehe River, Qinghe River, and Xiaojiahe River are sampled and analyzed utilizing this method.

2. Material and methods

2.1. Chemicals

2-Methylbutyraldehyde (≥98%), MMA (≥99%), IBMP (≥98%), and IPMP (≥98%) were acquired from Adamas Reagent, Ltd. (Shanghai, China). 2-MIB (≥98%) and GSM (≥97%) were purchased from Sigma-Aldrich (St. Louis, MO, USA). MTBE (≥99%), β-cyclocitral (≥95%), and dichloromethane (HPLC grade) were obtained from TCI Development Co., Ltd. (Shanghai, China), New Energy Chemical Co., Ltd. (Hong Kong, China), and Fischer Chemical (Guangzhou, China), respectively. High-purity nitrogen (purity >99.999%) and krypton (5%, v/v in helium) were provided by Hai-keyuanchang Gas Co. Ltd. and Huayuan Gas Co. Ltd. (Beijing, China).

2.2. Sample preparation

The linear calibration was conducted in range of 0.05—125 $\mu g \, L^{-1}$. Prior to the experiments, simulated samples of 2-methylbutyraldehyde, MTBE, MMA, IBMP, IPMP, and β-cyclocitral were prepared separately. Firstly, 125 mg of the target compound was dissolved in 500 mL of deionized water. When the dissolution equilibrium was achieved, the solution was further diluted 1:100 with water. Subsequently, a series of dilutions were performed with deionized water to give different solutions of 25, 50, 75, 100, and 125 $\mu g \, L^{-1}$. In addition, samples with lower concentrations were prepared by adding 25 mg of the target compound initially dissolved in 500 mL of deionized water. After the similar dilution steps, 0.05, 0.2, 0.5, and 1 $\mu g \, L^{-1}$ solutions of MTBE and MMA were obtained. For 2-methylbutyraldehyde, IPMP, and β-cyclocitral, 0.25, 0.5, 1, and 5 $\mu g \, L^{-1}$ solutions were prepared. Because of the lower detection sensitivities, IBMP was calibrated with 0.5, 1, 2, 5 $\mu g \, L^{-1}$ solutions. Besides, all the recovery samples were made by adding 250 ng compounds into 500 mL city tap water. In addition, 2-methylbutyraldehyde, MTBE, MMA, IBMP, IPMP, and β-cyclocitral were separately diluted 348, 313, 352, 222, 242, and 231 times with dichloromethane, resulting in the diluted solutions of 27 mmoL L^{-1}.