

Determination of the Odor Threshold Concentrations Of Iodinated Trihalomethanes in Drinking Water

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Iodinated trihalomethanes (ITHMs) have been usually considered the disinfection byproducts suspected of causing medicinal odor episodes in treated water around the world. The odor threshold concentration (OTC) of mixed ITHMs (bromochloroiodo-, bromodiiodo-, chlorodiiodo-, dibromoiiodo-, and dichloroiodomethane) which were previously synthesized – because commercial standards are not available – were determined by using two sensory techniques: flavor profile analysis (FPA), performed by an experienced panel trained in identifying odors and tastes in water; and gas chromatography coupled with olfactometry (GCO). FPA results gave a theoretical OTCs range from 0.1 to 8.9 $\mu\text{g/L}$ and ITHMs were described as sweet, solvent, and medicinal products. The lowest experimental value (OTC_{exp}) obtained from the six ITHMs, 0.03 $\mu\text{g/L}$, corresponded to iodoform.

Keywords: Flavor profile analysis; gas chromatography coupled with olfactometry; iodinated trihalomethanes; odor; odor threshold concentration; panel; treated water

INTRODUCTION

Despite the benefits of chlorine in drinking water disinfection, halogenated disinfection byproducts (DBPs) are formed from the interaction of aqueous free chlorine with natural organic matter present in the raw water. Trihalomethanes (THMs) were identified as the main DBPs as early as 1974 (1, 2). Iodinated trihalomethanes (ITHMs) can also be formed as a consequence of this interaction when iodide (i.e., from natural sources, seawater infusion, or brines) is present. The kinetics of ITHMs formation has been recently studied (3). ITHMs have been identified in drinking waters worldwide (4–9). Although the six possible ITHMs have been qualitatively identified using different extraction techniques (7, 10–13), the lack of ITHM reference standards has hampered their quantitative determination. Two different analytical methods, liquid microextraction (LLE) and solid phase microextraction (SPME), can be employed to determine them quantitatively in water samples at sub-ppb levels (14, 15).

ITHMs are usually associated with characteristic pharmaceutical or medicinal odors and tastes in drinking water. The odor threshold concentration (OTC) of iodoform obtained by Bruchet et al. (13), 0.02 $\mu\text{g/L}$, is significantly lower than that of chloroform or bromoform, 100 and 300 $\mu\text{g/L}$, respectively. This fact could explain how low ITHM concentrations are able to cause medicinal episodes in drinking water. Complaints from consumers related to iodoform have been reported (7, 8, 13) but there are no data available for the other ITHMs. Recently, Dietrich et al. (16) evaluated the odor properties of phenolic iodinated disinfection byproducts

in drinking water for the U.S. space program. Odor evaluation indicated that iodophenols have much lower OTC values than phenol itself.

Odors and tastes in drinking water are a matter of concern for water suppliers and a frequent source of complaints from consumers who mostly associate the presence of unpleasant odors and tastes with the possibility of health risk. The EEC Drinking Water Directive (European Council Directive 80/778 EE), related to the quality of water intended for human consumption, includes taste and odor parameters. Thus, water companies have to cope with qualitative and quantitative determinations.

In this context, several methods have been adopted by most water utilities such as the Flavor Profile Analysis (FPA) (17, 18) and the sensory GC or GC–olfactometry (GCO) combined with GC–MS. The former is widely used as a sensory technique for the study of tastes and odors in water, but the huge differences among the OTCs of organoleptic compounds in water limit the use of the FPA panel that provides the overall taste and odor characteristics of the sample. On the other hand, the GC–olfactometry method, currently used by the food and perfume industries (19, 20) and increasingly by water companies, (21, 22) combines the odor evaluation of the individual GC peaks eluting from the chromatographic column at an olfactory detector outlet and the chemical identification of the odorous compounds by GC–MS.

No information about the odor parameters of these iodinated compounds was previously found in the literature. The aim of this paper was to determine the OTC values of the six ITHMs as well as their descriptors, using FPA and GCO techniques that can be helpful to water suppliers in the complex task of identifying the cause of odor episodes in water.

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MATERIALS AND METHODS

Glassware. All glassware was washed with soapy water, and rinsed with tap water, Milli-Q purified water, and finally reagent-grade acetone. Then, it was air-dried and baked at 180 °C during 12 h. After this procedure, mouths of the glassware were covered with aluminum foil to prevent the presence of dust or other contaminants.

Reagents. Mixed iodinated trihalomethanes (bromochloro-, bromodiiodo-, chlorodiiodo-, dibromoiodo-, and bromochloroiodomethane) were synthesized as described elsewhere (15). Their purities were CHBr₂I (95%); CHCl₂I (>99.5%); CHBrClI (99%); CHBrI₂ (95%); and CHClI₂ (98%). Iodoform was purchased from Sigma-Aldrich (St. Louis, MO). Other reagents such as methanol (purge-and-trap grade) and methyl-*tert*-butyl ether (MtBE) were from Sigma Aldrich and Merck (Germany), respectively. Ultrapure water was from a Milli-Q water purification system (Millipore, Bedford, MA).

Standard Solutions. Stock standard solutions were prepared in methanol by weighing approximately 0.1 g of analyte into a 10-mL volumetric flask and diluting to volume. Several dilutions were prepared in ultrapure water immediately before the odor evaluation by the FPA, and in MtBE before the analysis by GCO.

Flavor Profile Analysis (FPA). A stock standard solution for each ITHM in methanol was diluted in purified water to different concentrations on the same day that the test was performed. This preliminary stage took place in a different room from the one used for the sensory analysis.

Water samples (200 mL) with different ascending concentrations of each compound were contained in Erlenmeyer flasks (500 mL) with ground-glass stoppers, heated to 45 ± 1 °C for half an hour in a water bath prior to the start the session where they would be presented to the trained panel.

The trained panel consisted at least of five or six panelists (from a group of 18 males and females) who were between 20 and 26 years old. They were carefully selected so that their sensitivities were above average to the basic tastes and odors, and they were trained in product evaluation and description. The panelists had to be free from cold and allergy because of their influence on the odor response. They were not allowed to eat or drink 1 h minimum prior to the tests and were advised not to wear cosmetics or perfumes of any kind.

The panel evaluated the response of odor intensity from the most diluted to the most concentrated water samples, evaluating also some blanks set between the total of ITHM water samples. Each of the panelists had to describe the odor for each ITHM and to indicate its intensity on a 1 (beginning of perception) to 12 (very strong) scale, with intermediate values of 2 (very faint), 4 (faint), and 8 (moderate). The average of intensities for each ITHM were recorded and plotted versus all the concentrations studied as a Weber–Fechner curve, which relates odor intensity to the logarithm of odorant concentration. From the equation obtained for each iodinated compound, the odor threshold concentration (*OTC*) was defined as the value of the log of the concentration corresponding to an intensity average of *I* = 1. The experimental threshold concentration (*OTC*_{exp}) for each ITHM was the lowest concentration smelled by at least one panelist.

Gas Chromatography Coupled with Olfactometry (GCO) Analysis. The commercial sniffer used (SGE International, Ringwood Victoria, Australia) consists of a glass nose cone in which the steam of the GC is mixed with a humidified air stream (installed to prevent the mucous membrane from rapid drying) allowing the identification of individual components as they elute from the chromatographic column. Five people were selected from among people working in the laboratory without any specific sensory experience and no special sensitivity to detect tastes and odors. Assessors were asked to smell the effluent from the column and to move the hand during the whole sensory impression. They were also asked to give a verbal description of each perceived odor as well as the intensity. Assessments of odor intensity were made according to a three-grade scale, with 1 (weak), 2 (medium), and 3 (strong).

GCO analyses were performed on a Fisons 8180 gas chromatograph equipped with a FID and an olfactometry detector. Injections (2 μL) of the ITHM standards were made on-column into a 50 × 320 μm i.d. CP-Sil 19 CB (0.25 μm film thickness) fused silica column (Chrompack, The Netherlands). A deactivated precolumn (2 m) was used. The chromatographic column was connected to a small T-shaped piece of glass and diverted to two deactivated columns (1 m each) leading on to the flame ionization detector (FID) and the sniff port (SGE, Australia). The flow ratio between the effluents from the chromatographic column to the detector and to the sniffer was 1:1. The GC temperature program was 30 °C (5 min) to 280 °C (10 min) at a rate of 3 °C/min. Helium was the carrier gas and the linear velocity was set to 31 cm/s at 30 °C. Nitrogen was used as makeup gas (125 kPa).

RESULTS AND DISCUSSION

Flavor Profile Analysis. The Weber–Fechner plot for all six ITHMs studied is displayed in Figure 1. This plot includes between five and seven points for each compound and the data obtained were adjusted to a linear regression curve with *r*² values ranging from 0.962 to 0.993 (Table 1). The *OTC* values obtained for the six iodinated trihalomethanes, listed in Table 1, ranged from 8.9 μg/L for the least odorous compound (CHCl₂I) to 0.1 μg/L for the most odorous one (CHI₃). As a general trend, an increase in the iodine atoms in the compound caused a dramatic decrease in the *OTC* value: CHX₂I ≫ CHXI₂ > CHI₃. Those monoiodinated compounds containing bromine atoms (i.e., CHBrClI and CHBr₂I) had lower *OTCs* (8.4 and 6.4 μg/L, respectively) compared to the chlorinated compounds (CHCl₂I, 8.9 μg/L). No significant differences between CHCl₂I and CHBrI₂ *OTC* values (0.2 μg/L both) were observed because of the high decrease in these values originated by the presence of the two iodine atoms in the molecule. Iodoform had an *OTC* value about 64–89 times lower than those obtained for the monoiodinated compounds, and twice lower than those obtained for the diiodinated compounds.

Table 1 also includes the experimental *OTC* values (*OTC*_{exp}) which varied between 1.5 and 2-fold lower for the monoiodinated compounds than those obtained from the extrapolation of the Weber–Fechner plots at *I* = 1. However, it should be noted that there is a considerable margin of error associated with the lowest threshold concentration, because dilution intervals are of factors of about 2.5. No significant differences were observed between the two *OTC* values for the diiodinated compounds, being at the same order. Finally, the *OTC*_{exp} value for CHI₃ was similar to that previously reported by Bruchet et al. (13).

Sweet, perfumed, and solvent were the descriptors reported by panelists for the monoiodinated compounds. On the other hand, medicinal odor was the common descriptor for the most iodinated compounds such as CHCl₂I, CHBrI₂, and CHI₃. These last three compounds presented similar odors and *OTCs* thus making it difficult to identify whether only a single ITHM compound can be considered responsible for causing an odor episode.

Gas Chromatography Coupled with Olfactometry Analysis (GCO). Several standard solutions of a mixture of the six iodinated trihalomethanes were injected into the GC equipped with a FID and olfactory detectors in order to determine the minimal amount of odor perceived for each compound. The odor threshold amount (*OTA*_{sniffing}) of each ITHM is displayed in

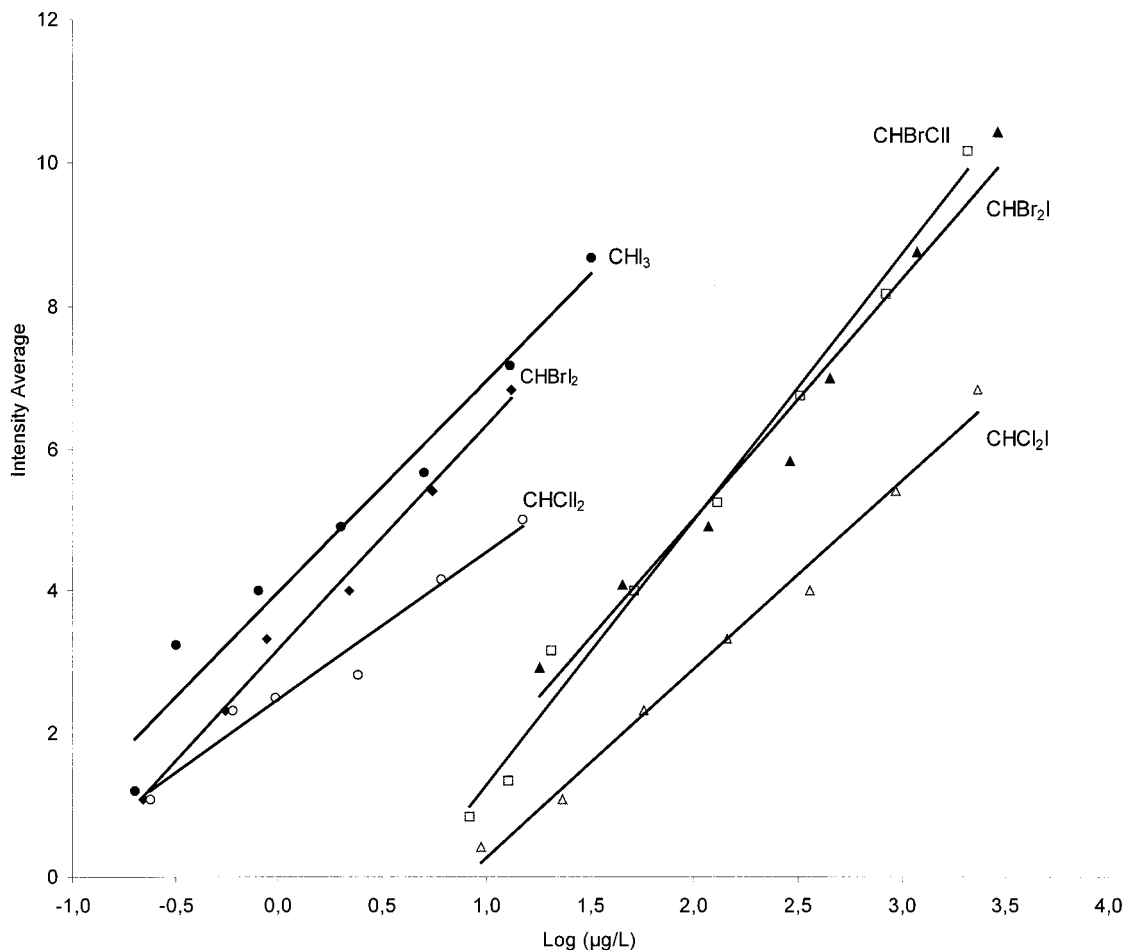


Figure 1. Weber–Fechner plots of individual iodinated trihalomethanes obtained by FPA analysis

Table 1. Odor Descriptors and Odor Threshold Concentrations for Iodinated Trihalomethanes^a

	descriptors	equation WF plot	r^2 WF plot	OTC ($\mu\text{g/L}$)	OTC _{exp} ($\mu\text{g/L}$)	OTA (ng)	OTC _{sniffing} ($\mu\text{g/L}$)
dichloriodomethane (CHCl ₂ I)	sweet, syrup	$I = 2.70 \log \text{conc} - 1.56$	0.993	8.9	5.8	140	5.5
bromochloriodomethane (CHBrClI)	sweet, feesh grass, perfumed, alcoholic	$I = 3.72 \log \text{conc} - 2.43$	0.989	8.4	5.1	185	5.2
dibromiodomethane (CHBr ₂ I)	sweet, solvent, perfumed, bitumen	$I = 3.36 \log \text{conc} - 1.70$	0.971	6.4	2.9	80	1.7
chlorodiodomethane (CHClI ₂)	medicinal, sweet, solvent, candy	$I = 2.07 \log \text{conc} + 2.48$	0.968	0.2	0.2	77	< 1.7
bromodiodomethane (CHBrI ₂)	medicinal, sweet, solvent, perfumed	$I = 3.10 \log \text{conc} + 3.21$	0.984	0.2	0.1	52	< 1.5
iodoform (CHI ₃)	medicinal, sweet, perfumed, gum	$I = 2.97 \log \text{conc} + 3.99$	0.964	0.1	0.03	< 14	< 0.7

^a C = concentration in $\mu\text{g/L}$; OTC, odor threshold concentration obtained by Weber–Fechner plot; OTC_{exp}, odor threshold concentration smelled directly by the trained panel; OTA, Odor threshold amount smelled directly from the olfactory detector by panelists; OTC_{sniffing}, odor threshold concentration obtained by GCO, considering the ITHM recoveries by CLSA (15).

Table 1, and they ranged from 185 ng (CHBrClI) to < 14 ng (CHI₃). These values were the lowest amounts perceived by at least 60% of the panelists. As a general trend, and similarly with the behavior observed by the panel, the monoiodinated compounds were the least odorous.

GCO is usually employed in our company as a tool to identify organic compounds causing taste and odor problems in water. Panelists smell in the olfactory port the organic extracts obtained by the closed loop stripping analysis (CLSA) technique (23), which is often the most suitable method for detecting volatile organic compounds (VOCs) present in water at very low trace levels (ng/L). The following analytical conditions were

employed: a 1-L water sample was stripped for 1 h at 45 °C and VOCs were trapped in the carbon filter which was eluted with carbon disulfide (20 μL) (22).

Applying these experimental conditions and considering the recovery values for ITHMs using the CLSA technique, which are 51% (CHCl₂I); 92.5% (CHBr₂I); 71% (CHClBrI); 89% (CHClI₂); 68.5% (CHBrI₂); and 38.5% for CHI₃ (15), we can calculate the minimal amount sniffed by a panelist at the olfactory port using the formula:

$$A = C \times R \times V_s \times V_i \times 1000 \quad (1)$$

where A = lowest amount smelled, ng; C = lowest

spiked concentration in water smelled by panelists, $\mu\text{g/L}$; R = recovery; V_s = volume of sample, 1 L; V_i = injection volume, 1 μL ; and 1000 is a conversion unit.

From eq 1 we can calculate the OTC_{sniffing} of a particular ITHM:

$$OTC_{\text{sniffing}} = A \times V_e/R \times V_s \times V_i \times 1000 \quad (2)$$

where V_e = volume of extract, 20 μL . This approach gave theoretical OTC_{sniffing} values ranging from 5.5 $\mu\text{g/L}$ (CHCl_2I) to <0.7 $\mu\text{g/L}$ (CHI_3), as can be seen in Table 1. These OTC_{sniffing} values correlated well with those OTC values obtained from the FPA panel.

CONCLUSIONS

The OTCs of ITHMs in water were established in the low $\mu\text{g/L}$ level, the same range of the most odorous compounds commonly identified in treated water. The FPA and GCO analyses indicated that an increase of iodine atoms in the molecule causes a decrease in the odor threshold concentration following the trend $\text{CHI}_3 < \text{CHXI}_2 \ll \text{CHX}_2\text{I}$ (0.1 < 0.2 \ll 6.4–8.9 $\mu\text{g/L}$, respectively). At the same time, a reasonable agreement between the calculated OTCs with the two sensory techniques was obtained for each compound.

Medicinal and sweet were the common descriptors described by panelists for diiodinated and monoiodinated compounds, respectively. However, the similarity of descriptors and OTC values among the diiodinated compounds makes it difficult to unequivocally identify the compound responsible for the event if iodoform is not present. On the other hand, the relatively high OTC levels of the monoiodinated derivatives compared to the current values found in treated water allows us to discard these compounds as causing medicinal odor problems.

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