Determination of trichloramine in drinking water using headspace gas chromatography/mass spectrometry

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ABSTRACT

Trichloramine (NCl₃) is one of the major causes of the chlorine odor in drinking water. In the present study, a method was developed for analysis of NCl₃ concentration in water using headspace gas chromatography/mass spectrometry (HS–GC/MS). For quantification of NCl₃, m/z of 51 was selected because other major m/z of NCl₃ were also observed as fragments of trichloromethane (CHCl₃) and the peaks of NCl₃ and CHCl₃ overlapped on the chromatogram. The limit of quantification for NCl₃ was set to 15 μg-Cl₂/L. The calibration curve of NCl₃ was expressed as a quadratic curve because of the partial NCl₃ decomposition. NCl₃ concentrations in chlorinated ammonium solution were determined by HS–GC/MS and titration using N,N-diethyl-p-phenylenediamine and ferrous ammonium sulfate (DPD/FAS), and the results using the two methods were similar at pH 6 and 7. However, at pH 8, NCl₃ was detected using HS–GC/MS, but not using DPD/FAS titration. NCl₃ concentrations in nine tap water samples were determined using HS–GC/MS and ranged from < 15 to 46 μg-Cl₂/L. The results of the present study indicated that HS–GC/MS is applicable to determination of NCl₃ in drinking water.

Key words | chlorination, drinking water, headspace gas chromatography/mass spectrometry, trichloramine

INTRODUCTION

Trichloramine (NCl₃) is an inorganic chloramine formed by chlorination of ammonia (Jafvert & Valentine 1992; Schurter et al. 1995; Shang & Blatchley III 1999), and also by chlorination of some nitrogen-containing organic compounds (Shang & Blatchley III 1999; Shang et al. 2000; Li & Blatchley III 2007).

There is increasing consumer interest in Japan regarding not only the safety of drinking water but also in improving both its taste and odor. The major complaints regarding the odor of drinking water are related to its chlorine and musty odors. With regard to musty odors, the drinking water standards in Japan list target values of 10 ng/L for both 2-methylisoborneol and geosmin (Water Supply Division, Health Bureau, Ministry of Health, Labour and Welfare). However, the drinking water standards include no regulations regarding the chlorine odor. Recently, several programs to produce high-quality drinking water taking into consideration both taste and odor have been conducted by some water utilities in Japan, and they have set their own drinking water quality goals surpassing the national drinking water quality standards (Bureau of Waterworks, Tokyo Metropolitan Government; Chiba Prefectural Waterworks Bureau). In some cases, these drinking water quality goals include NCl₃ as a target item because this component is known to be one of the major causes of the chlorine odor in drinking water. For example, the target value of NCl₃ is currently under consideration in the standards of the Bureau of Waterworks, Tokyo Metropolitan Government, and its specified goal is for most people to not notice a chlorine odor in the drinking water.
Titration using \( N,N \)-diethyl-\( p \)-phenylenediamine and ferrous ammonium sulfate (DPD/FAS), and colorimetric methods using DPD have conventionally been applied to determine the concentrations of inorganic chloramines, i.e. monochloramine (\( \text{NH}_2\text{Cl} \)), dichloramine (\( \text{NHCl}_2 \)), and \( \text{NCl}_3 \), in water (APHA, AWWA, and WEF 2005). Recently, several groups made use of membrane inlet mass spectrometry (MIMS) as an alternative method for analysis of inorganic chloramines in water. Shang & Blatchley III (1999) reported that the concentrations of inorganic chloramines in chlorinated ammonium solution determined by MIMS were similar to those determined by DPD/FAS titration. However, they also reported that the concentrations of inorganic chloramines in chlorinated glycine solution determined by DPD/FAS titration were higher than those determined by MIMS. Shang et al. (2000) reported similar results regarding the concentrations of inorganic chloramines in chlorinated amino acid solutions. In addition, Lee et al. (2007) reported that the concentrations of inorganic chloramines were overestimated by the colorimetric method using DPD in the presence of natural organic matter containing organic nitrogen. These results suggested that in the case of DPD/FAS titration or the colorimetric method using DPD, organic chloramines were detected as inorganic chloramines, including \( \text{NCl}_3 \), when some organic compounds containing nitrogen were chlorinated. Therefore, analytical methods with higher accuracy, such as MIMS, were considered suitable for determination of \( \text{NCl}_3 \) in drinking water containing many organic compounds. The reported method detection limit (MDL) of \( \text{NCl}_3 \) by MIMS is 60 \( \mu \text{g-Cl}_2/\text{L} \) (Shang & Blatchley III 1999). \( \text{NCl}_3 \) concentration in finished water was reported to be around 20 \( \mu \text{g-Cl}_2/\text{L} \) when chlorine injection points and its dose were changed in a rapid sand filtration system to reduce the \( \text{NCl}_3 \) concentration (Hosoda et al. 2009). In this previous study (i.e. Hosoda et al. 2009), \( \text{NCl}_3 \) concentration was determined by a colorimetric method using DPD, and therefore the accuracy of the results may have been poor. However, the required MDL of \( \text{NCl}_3 \) is lower than that by MIMS when the goal is reduction of \( \text{NCl}_3 \) concentration in drinking water. In the present study, headspace gas chromatography/mass spectrometry (HS–GC/MS) was applied to tap water samples for determination of \( \text{NCl}_3 \) in drinking water.

**METHODS**

**Reagents and solutions**

Ultrapure water obtained using a Gradient A10 ultrapure water system (Millipore, Bedford, MA) was used for preparation and dilution of stock solutions. Hexafluorobenzene (HFB) was purchased from Acros Organics (Geel, Belgium). In the present study, quenching agents for chlorine and chloramines could not be added to the samples. Therefore, HFB was selected as an internal standard for \( \text{NCl}_3 \) because its structure appears to be unreactive with chlorine and chloramines. In fact, addition of HFB had no effect on \( \text{NCl}_3 \) concentrations in the samples (data not shown). Sodium hypochlorite (\( \text{NaOCl} \)) solution was prepared by diluting commercially available \( \text{NaOCl} \) solution (Wako Pure Chemicals, Osaka, Japan). Standard \( \text{NCl}_3 \) solution was prepared by mixing \( \text{NaOCl} \) solution with ammonium chloride (\( \text{NH}_4\text{Cl} \); Aldrich, St. Louis, MO) solution at a chlorine to ammonia molar ratio of 3.15:1 at pH 6 (5 mM phosphate buffer) at 30°C with reference to a previous study by Shang & Blatchley III (1999). After mixing for 30 min at 30°C, the standard \( \text{NCl}_3 \) solution was stored for about 1.5 h at 30°C and used for the experiments. The \( \text{NCl}_3 \) concentration in the standard solution was determined by DPD/FAS titration (APHA, AWWA, and WEF 2005), and ranged from 200 to 300 \( \mu \text{g-Cl}_2/\text{L} \). Note that the \( \text{FAS} \) concentration used in this study was set to 1/10 (or 1/5) that in the FAS solution described previously (APHA, AWWA, and WEF 2005). Fresh standard \( \text{NCl}_3 \) solution was prepared on each experimental day. Other reagents used were of analytical grade.

**Comparison of \( \text{NCl}_3 \) concentrations in chlorinated ammonium solution determined by HS–GC/MS and DPD/FAS titration**

To compare the \( \text{NCl}_3 \) concentrations determined by HS–GC/MS and DPD/FAS titration (APHA, AWWA, and WEF 2005), \( \text{NH}_4\text{Cl} \) solution was chlorinated at pH 6–8 (5 mM phosphate buffer) at 30°C. After 30 min, \( \text{NCl}_3 \) concentrations in the solutions were determined by the two methods. As described above, the FAS concentration in the solution was set to 1/10 (or 1/5) that in the FAS solution.
described previously. The yield of NCl₃ at pH 8 was lower than those at pH 6 and 7. Therefore, higher chlorine and NH₄Cl concentrations were required to produce similar NCl₃ concentrations to those at pH 6 and 7.

**Sampling of tap water**

Nine tap water samples (A–I) were collected from four prefectures in Japan (i.e., Tokyo, Saitama, Chiba, and Kanagawa) in January 2009. The source waters of these water purification plants were surface water from several basins and ground water combined with surface water in some cases. Six tap water samples were produced by rapid sand filtration systems. Three tap water samples were blended waters produced by rapid sand filtration systems and ozone/biological treatment systems in the distribution reservoir or distribution network. Tap water samples before and after passage through a point-of-use treatment device were collected from one area (B). The treatment device involved activated carbon treatment followed by filtration. The tap water samples were collected in glass bottles covered with aluminium foil without a headspace. After sampling, they were transported to the laboratory under cool conditions and analyzed.

**Analytical method of NCl₃ by HS–GC/MS**

Standard NCl₃ solution was diluted to 5 mM in phosphate buffer (pH 6) at 30°C. Samples of 20 mL of NCl₃ solution at the desired concentration were prepared. Samples of 10 mL of NCl₃ solution were poured into 20-mL headspace vials, HFB solution was added as an internal standard (final concentration, 2 μg/L), and the vials were capped. The vials were shaken vigorously by hand for about 5 s and incubated for 3 min at 35°C. Then, 1.5 mL of gas phase in the vial was sampled with a gas-tight syringe and analyzed by GC/MS. To draw the calibration curve, the same procedures were repeated by changing the desired NCl₃ concentration in the solution. In the case of tap water, the bottle containing the tap water sample was initially warmed at 30°C, and then the same procedures as described for the NCl₃ solution were performed.

*Table 1* shows the analytical conditions of GC/MS. Separation was performed using an Agilent 6890 gas chromatograph equipped with an Agilent 5975C mass spectrometer. The chromatographic conditions are as follows:

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The injection temperature was 40°C and flow rate was 1.0 mL/min (helium). Injection mode was pulsed split and the split ratio was 1:2. The temperature program was as follows: 30°C (1.5 min), 60°C at 30°C/min, and 0.5 min hold. Detection was performed using an Agilent 5975C mass spectrometer (Agilent Technologies) in selected ion monitoring (SIM) mode. The m/z values of NCl₃ were 51 (quantification), 119 (identification), 121 (identification), and 123 (identification), and those of HFB were 186 (quantification) and 117 (identification). Aux temperature was 150°C, quadrupole temperature was 110°C, and ion source temperature was 150°C. Note that the sensitivities of NCl₃ for several of the initial samples were lower and varied on each experimental day. Thus, on each experimental day, samples containing NCl₃ were initially injected into the GC/MS system at several time points for preconditioning to stabilize the sensitivity for NCl₃. It should also be noted that samples were warmed and incubated in HS–GC/MS. Thus, to minimize the production or decomposition of NCl₃ during warming and incubation, water samples the reactivity of which with chlorine had become stable (e.g. tap water) were considered suitable. Note that in some cases (e.g. in winter), the stability of tap water may be insufficient and the NCl₃ concentration in the tap water may be changed to some degree by the increase in water temperature.

RESULTS AND DISCUSSION

Analytical conditions of NCl₃ by HS–GC/MS

Figure 1 shows the SIM chromatogram of NCl₃ in chlorinated ammonia solution determined by HS–GC/MS. The mass spectrum of NCl₃ obtained in this study (Figure 2) was the same as that reported by Shang & Blatchley III (1999). Thus, the peak shown in Figure 1 was confirmed to be that of NCl₃.

Figures 3 and 4 show the SIM chromatogram and the mass spectrum of trichloromethane (CHCl₃) determined by HS–GC/MS, respectively. The main fragment of CHCl₃ was m/z 83, but m/z 119, 121, and 123 were also observed as minor fragments. These three m/z values corresponded to those of the molecular ion of NCl₃. In Figures 3 and 4, the intensities of the three fragments increased in the order 119, 121, and 123. Other major fragments of NCl₃ were also observed in the fragment of CHCl₃, except for m/z 51. Figures 1 and 3 show that the peak of NCl₃ overlapped with that of CHCl₃. CHCl₃ is known to be one of the major disinfection by-products of chlorination. Thus, in this study, m/z 51 was selected for quantification of NCl₃.

The NCl₃ peak areas decreased with decreasing concentrations of NCl₃ in the solution. The peak area per amount of NCl₃ injected was significantly lower at lower NCl₃ concentrations. Thus, the calibration curve of NCl₃ was not linear and was expressed by a quadratic curve (Figure 5). When a longer column (60 m) was used for separation, NCl₃ was not detected regardless of its concentration.
concentration. That is, NCl₃ was considered to be partially decomposed at least in the column, and it was also suggested that NCl₃ may have been decomposed during incubation. Thus, the calibration curve of NCl₃ was expressed by a quadratic curve because of the partial NCl₃ decomposition. The relative standard deviation (number of repetitions = 5) at 15 μg-Cl₂/L of NCl₃ was less than 10%. Thus, the limit of quantification (LOQ) of NCl₃ was set to 15 μg-Cl₂/L in this study. Moreover, the peak of NCl₃ overlapped with that of HFB (Figure 8). However, the peak of HFB did not affect determination of NCl₃ in the present study because HFB did not have a fragment at m/z 51.

As reported previously (Shang & Blatchley III 1999), other inorganic chloramines (i.e. NH₂Cl and NHCl₂) also have a fragment at m/z 51. Figure 6 shows the SIM chromatograms of NH₂Cl, NHCl₂, and NCl₃ at m/z 51 as determined by HS–GC/MS. The SIM chromatogram at m/z 53 is also shown in the figure because it was reported that NH₂Cl has a fragment at m/z 53 (Shang & Blatchley III 1999). The mass spectra of NH₂Cl and NHCl₂ in the present study (data not shown) were the same as those reported previously (Shang & Blatchley III 1999). The peaks of three inorganic chloramines were separated in the chromatogram. However, it was possible that the peak of NCl₃ may be affected by that of NH₂Cl at higher concentrations of NH₂Cl. NCl₃ is more volatile than NH₂Cl, so the sensitivity of NH₂Cl was much lower under the conditions used in the present study. In addition, NH₂Cl is the dominant chlorine species at chlorine doses less than that required for breakpoint chlorination, while NCl₃ is frequently detected when the chlorine dose is higher than this level (Shang & Blatchley III 1999). Thus, the peak
of NCl₃ may rarely be affected by that of NH₂Cl in HS–GC/MS. In fact, the peak of NCl₃ in tap water was unaffected by that of NH₂Cl (Figure 8).

**Comparison of NCl₃ concentration determined by HS–GC/MS and DPD/FAS titration**

Figure 7 shows a comparison of NCl₃ concentrations in chlorinated ammonium solution determined using HS–GC/MS and DPD/FAS titration. In DPD/FAS titration (APHA, AWWA, and WEF 2005), the DPD solution and phosphate buffer were initially mixed, the sample was then added, and the mixture was titrated with FAS solution. On the other hand, in the case of HS–GC/MS, no pH adjustment of the sample was performed before analysis. At pH 6 and 7, the NCl₃ concentrations in samples determined using both methods were similar. These observations confirmed that HS–GC/MS was applicable for determination of NCl₃ concentrations in water samples. In addition, the effects of dilution in drawing the calibration curve of NCl₃ on its decomposition were not highly significant. On the other hand, at pH 8, NCl₃ was detected using HS–GC/MS but not using DPD/FAS titration. Chlorine odor was noted in the samples at pH 8. For DPD/FAS titration, the appropriate pH range of the solution after addition of the sample to the DPD and phosphate buffer solutions was in the range from 6.2 to 6.5 (APHA, AWWA, and WEF 2005). The pH ranges after addition of chlorinated ammonium solutions in the DPD and phosphate buffer solutions at pH 8 were from 6.2 to 6.5. These pH ranges were also from 6.2 to 6.5 after titration by FAS. These results indicated that NCl₃ was actually present in the solution at pH 8 but was not detected by DPD/FAS titration because of its decomposition in the DPD/FAS analytical process or due to limitations of the analytical method. Further studies are needed to clarify the reasons for these observations.

**NCl₃ concentrations in tap water samples**

Table 2 shows the concentrations of NCl₃ in nine tap water samples. Figure 8 shows the SIM chromatogram of NCl₃ in tap water determined by HS–GC/MS. The NCl₃
concentrations ranged from <15 to 46 µg.Cl₂/L, and those in eight of nine tap water samples exceeded the LOQ of 15 µg.Cl₂/L. NCl₃ was shown to be widely present in tap water samples regardless of the source and water treatment systems used. The results also indicated that HS–GC/MS was applicable for determination of NCl₃ in tap water samples. The remaining one tap water sample (I) in which NCl₃ concentration was below the LOQ was produced by a rapid sand filtration system, but its pH was higher than the other tap water samples (i.e. pH 8.0 vs. pH 7.0–7.5). The yield of NCl₃ is known to be lower at higher pH for the same chlorine dose. Therefore, the higher pH of this sample was thought to explain why the NCl₃ concentration in this one tap water sample was below its LOQ.

The effects of a point-of-use treatment device, in which the sample is treated with activated carbon followed by filtration, on NCl₃ concentration in one tap water sample (B) were investigated. NCl₃ was detected in the untreated tap water sample, but was not detected after passage through the treatment device. As it has been reported that NCl₃ is reactive with powdered activated carbon (Matsui et al. 2008), the NCl₃ may have been removed by activated carbon treatment in the device.

CONCLUSIONS

(1) The calibration curve of NCl₃ was expressed by a quadratic curve. This was considered to be due to partial decomposition of NCl₃ at least in the column. The LOQ of NCl₃ was 15 µg.Cl₂/L.

(2) NCl₃ concentrations in chlorinated ammonium solution at pH 6 and 7 determined by HS–GC/MS and DPD/FAS titration were similar. However, at pH 8, NCl₃ was detected by HS–GC/MS but was not detected by DPD/FAS titration.

(3) NCl₃ concentrations in nine tap water samples using HS–GC/MS ranged from <15 to 46 µg.Cl₂/L. NCl₃ was detected in eight of the nine tap water samples.

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REFERENCES

APHA, AWWA, and WEF 2005 Standard Methods for the Examination of Water & Wastewater, 21st edition. APHA, AWWA and WEF, Washington DC, USA.


