Determination of Trichloramine and Dichloramine in Drinking Water by a Head-Space Gas Chromatograph Mass Spectrometer

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Abstract
In the water treatment plants(WTPs) of Osaka Municipal Waterworks Bureau(OMWB), ozonation processes before and after sand filtration followed by granular activated carbon bed are employed. The musty odor of tap water caused by geosmin and 2-methlylsoborneol produced by blue-green algae is easily removed if appropriate ozonation processes are applied. Unlike the musty odor, chlorinous odor arisen with break-point chlorination is not completely eliminated by these processes. Thereafter, in Osaka City, the chlorinous flavor has become main grievance among off-flavor problems. While trichloramine is considered as one of the chlorinous odor causing substances, its concentration and behavior in actual WTPs and distribution systems are not well understood due to the analytical difficulties; its conventional determination methods with *N*,*N*-diethyl-*p*-phenylenediamine reagent are interfered by coexisting organic *N*-chloramines and other oxidizing substances. To avoid these interferences, an improved method by head space gas chromatograph mass spectrometry (HS-GC/MS); determination limit is below 0.001mg/L, was developed and applied to the samples collected from a WTP of OMWB.

Keywords
trichloramine; dichloramine; chlorinous odor; HS-GC/MS

INTRODUCTION

In waterworks in Japan, the enforcement regulations of the Waterworks Law stipulate that residual chlorine must be held at the ends of water taps. In contrast, if the concentration of residual chlorine is high, it causes a chlorine odor, which makes the taste of water poor (Suzuki et al., 1985).

From 1998, Osaka City replaced drinking water treatment systems by the advanced water treatment process in turn in which ozone treatment and granular activated carbon treatment are combined and, since 2000, it has been supplying drinking water treated by the advanced water treatment to the entire city areas. After the replacement, the decomposition and removal effects of the advanced water treatment has reduced the amounts of organic matter and disinfection byproducts (Miyata et al., 2005) and has also eliminated instances where 2-methylisoborneol and geosmin are detected, making the musty odor problem a thing of the past in Osaka City. On the other hand, even after switching to the advanced water treatment, chlorine odor in drinking water has not yet been completely eliminated (Wada et al., 2007) .

Free chlorine, inorganic chloramines, organic chloramines, etc. are known as substances causing chlorine odor that are added or formed in drinking water by free chlorine disinfection (Kajino et al., 1999; Frueze et al., 2004). Among these candidate substances, there have been many reports on the mechanism of formation of inorganic chloramines.

Many reports on the chemistry of inorganic chloramine in these breakpoint chlorination processes are measurements on the basis of diethyl-p-phenylenediamine (DPD) methods (titration method, colorimetric method). However, from researches, etc. based on the membrane introduction mass spectrometry (MIMS), it has been reported that the results of measurement of organic chloramine by the DPD method are affected by interfering substances such as organic chloramines, etc. formed by amino acid, protein, etc.(Shang et al., 1999; Shang et al., 2000; Donermair et al., 2003; Lee et al., 2007). Therefore, whether the amount of inorganic chloramines can be properly evaluated by the DPD method has room for study when a water source containing organic nitrogenous compounds,

such as river water, is used. Furthermore, since there is limitation that the low detection limit of free chlorine by the DPD method is approximately 10 μg/L (Standard Method, 2005), it is difficult to say that the existence or behavior of inorganic chloramines in real drinking water has been adequately clarified. In this research, we have improved the measurement method of inorganic chloramines using a headspace gas chromatograph mass spectrometer (HS-GC/MS) that has been reported by Kosaka et al. (2010). as an approach of higher selectivity and compared it with the results of measurement by the DPD method.

METHODS

Glassware and purified water

For glassware used for measurements, those immersed in advance in a sodium hypochlorite solution of approximately 1%, rinsed with purified water on the day of usage. Since the existence of ammonia nitrogen on the surfaces of the hands and fingers and wiper for experiment was verified, we exercised care to prevent the glassware from being contaminated by it. Water purified immediately before use with the ultrapure water system (MilliQ Integral, Millipore) was used.

Preparation of mixed chloramine standard solution

Because it is difficult to obtain single standard solution from an aqueous solution system where trichloramine exists metastably(Randtke, 2010), we used a mixed chloramine standard solution. The preparation process is described elsewhere(Tanaka et al., 2011).

DPD Colorimetric method

Measurement of inorganic chloramines by the DPD colorimetric method was conducted using Shimadzu spectrophotometer UV-2400PC or UVmini-1240 fitted with 10 mm cells according to the Standard Method(2003).

Headspace gas chromatograph mass spectrometry

Sample handling. For the mixed chloramine standard solution, 10 mL of it was dispersed into a measurement vial of 22 mL volume using a clean pipette, which was promptly plugged with a crimp cap with septum on which polytetrafluoroethylene was lined. The vial was then light shielded and stored at 10°C up to time immediately before measurements by HS-GC/MS. Drinking water samples were taken in the same way at a water sampling point and measured promptly using the HS-GC/MS.

Table 1. An optimized HS-GC/MS Condition

HSS		GC/MS	
Vial equilibration time	15 min	Injection Mode	Pulsed Split
Vial pressurizing time	0.3 min	Injector temperature	45 °C
Vial shaker	On	Column flow	1 mL/min
Loop fill time	0.3 min	Pulse Pressure	25 psi
Loop eq. time	0.3 min	Split ratio	15:1
Injection time	1.0 min	Ion source temperature	230 °C
Oven temperature	35 °C	Q-pole temperature	150 °C
Loop temperature	35 °C		
Transfer line(HSS->GC) temperature	35 °C	Transfer line(GC->MS) temperature	150 °C

Internal standard solution. 1, 1, 2-Trichloroethane-d_3 (Kanto Chemical) was dissolved by methanol (Kanto Chemical, for phthalate ester test) into a solution of 1 mg/mL, which was then diluted to 40

mg/L with purified water. 2 μL of this solution was dispensed for use into the plugged measurement vial using a micro syringe.

System configuration. The headspace sampler (HSS) used a Hewlett Packard HP7694 and a 3-mL sample loop. For a quadrupole gas chromatograph mass spectrometer (GC/MS), Hewlett Packard HP6890GC/5973MSD was used according to an electron ionization (EI) method. The measurement conditions were optimized as shown in **Table 1**.

Calibration curve. Palin (1957) drew the formula for the trichloramine concentration on the basis of consistency between the residual chlorine concentration obtained by iodometry and that obtained by the DPD method if the recovery rate of trichloramine by the DPD method is 50% in a system where no precursors of organic chloramine such as amino acid are unnecessary to be considered, that is, if a response of 1.5 mol is obtained as Cl_2 with respect to trichloramine of 1 mol. However, the theoretical grounds for the recovery rate of trichloramine have not been demonstrated. In other words, a coefficient that has not been confirmed by stoichiometry is used in the determination of trichloramine by the DPD method. However, in researches on trichloramine that have been reported after the DPD method, the DPD method has been virtually adopted as standard(Shang et al., 2000; Kosaka et al., 2010) and there is no effective method capable of fractionally determining trichloramine in a solution more accurately than the DPD method. Therefore, this research also used the results of determining trichloramine by the DPD colorimetric method as the standard concentration of trichloramine and measured the dilution series of the mixed chrolamine standard solution to examine whether the calibration curve can be created based on the dilution series.

Comparison between HS-GC/MS method and DPD colorimetric method. The Osaka Municipal Waterworks Bureau uses the main stream of Yodo River as the water source and has been performing the advanced water treatment consisting of coagulating sedimentation, intermediate ozone treatment, sand filtration, post-ozone treatment, granular activated carbon (GAC) treatment, and breakpoint chlorination. To study whether fractional determination of inorganic chloramines by the DPD – colorimetric method is possible, in August 2, 2010, GAC-treated water of Niwakubo Water Treatment Plant, Osaka Municipal Waterworks Bureau that was sampled was dispensed into 100-mL color comparison tubes by 100 mL each. Then chlorine was added to the comparison tubes so that the injection rate of sodium hypochlorite was 1 mg/L (as Cl_2) and they were left still at room temperature (approx. 25°C) to measure the concentrations of trichloramine and dichloramine at each elapsing time by the DPD colorimetric method and HS-GC/MS method.

Survey of actual conditions of trichloramine and dichloramine in drinking water. From January to March 2009, we surveyed the concentrations of trichloramine and dichloramine in drinking water of Niwakubo Water Treatment Plant located in Moriguchi City.

RESULTS AND DISCUSSION

Separation and mass spectrum

The chromatogram of samples of the raw water of Niwakubo Water Treatment Plant, Osaka Municipal Waterworks Bureau that was chlorinated is shown in **Figure 1**. Although the peaks of trichloramine and chloroform and those of dichloramine and bromodichloromethane are respectively close to each other under these conditions, it was verified that they are sufficiently separated by the retention time. This report adopted m/z = 84 and m/z = 85, largest intensities as the quantification ions of trichloramine and dichloramine, respectively. The mass spectra of the trichloramine and dichloramine agreed with the report of Kosaka et al.(2010) and also agreed with

the report based on MIMS(Shang et al., 1999) with the exception that the peak of m/z = 44 based on CO_2 cannot be observed. Immediately after use of a new column, no peaks of the trichloramine and dichloramine were detected, but only the peak of monochloramine was observed. However, repetitive injection of the standard solution enabled the peaks of the dichloramine and trichloramine to be observed in this order, allowing us to verify that the trichloramine and dichloramine were separated on selected ion monitoring (SIM) chromatogram (**Figure 2**). The reason why the peak of trichloramine was not detected at the beginning of use of the new column is not clear. However, because it was revealed that repetitive injection of the standard solution enables the peak area value to be stabilized, the standard solution was repeatedly injected prior to measurements afterward to make the peak area value stabilized. Apart from the column concerned, we also tried to perform separation using VOCOL (60 m, inner diameter of 0.25 mm, film thickness of 1.5 μm, SUPELUCO), but no peak of inorganic chloramines was observed even after repetitive injection of the standard solution.

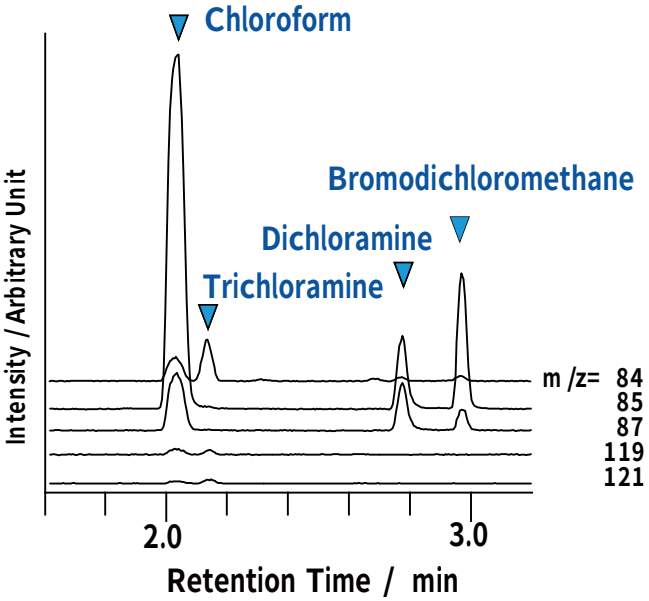

Figure 1. SIM chromatogram of a chlorinated sample of the raw water of Niwakubo Water Treatment Plant

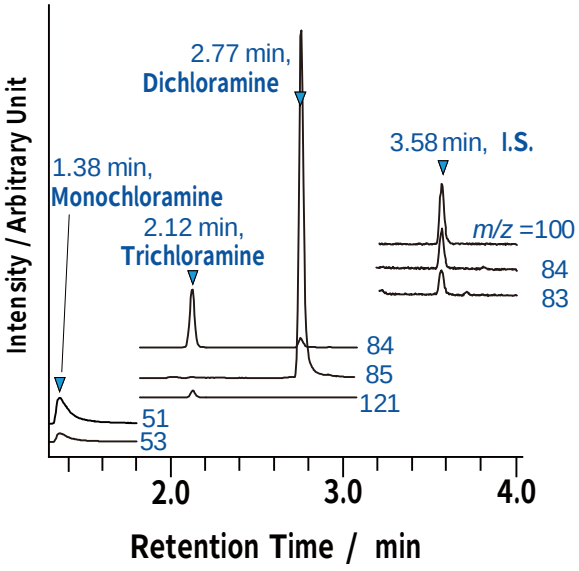

Figure 2. SIM chromatogram of standard solution

Calibration curves

The results of examination of the relationship between the concentration obtained from the dilution factor by preparing the dilution series of the standard solution and the area ratio (relative peal area) of internal standard substances are shown in **Figure 3**. Trichloramine showed a smaller relative area value than that expected from the dilution factor(**Figure 3a**). In contrast, in the case of dichloramine, there was a tendency for the relative area value to get greater than expected from the dilution factor(**Figure 3b**). To verify if the tendency shown in **Figure 3** is attributable to GC/MS such as decomposition in the analysis column, the mixed chloramine standard solution was dispensed into multiple vials by the same volume to measure the area values of the trichloramine and dichloramine. The area values were measured by changing the split ratio of GC to change the sample volumes that were introduced into the capillary column. Since the response of 1, 1, 2-trichloroethane-d_3 has linearity and its area value is proportional to the volume of the sample introduced into the capillary column, the sample volume introduced into the column in each injection is proportional to the area value of the 1, 1, 2-trichloroethane-d_3. The horizontal axis of **Figure 4** shows the volume of the

sample flowed into the column that was calculated and converted into concentration on the basis of the area value of the 1, 1, 2-trichloroethane-d_3. Unlike the case of measuring the dilution series, a good linearity was observed between the converted concentration value of the introduced volume and the area value for both the types of chloramines (r^2 > 0.999 for each). Therefore, it is conceivable that the main cause of degrading the linearity of response in the dilution series method is not decomposition in the GC/MS, but it is in the phase before introduction into the GC/MS such as dilution operation or contamination. In other words, it is considered that degraded linearity of the response is caused by a deviation in equilibrium resulting from dilution operation or by sampling. Therefore, no dilution series was used for creation of a calibration curve, but the concentration of trichloramine in the chloramine-mixed solution that had been prepared so that the trichloramine shows approx. 0.2 mg/L was determined by repetitive measurements by the DPD – colorimetric method immediately before measurement by HS-GC/MS. Then, the area value of this solution was quantified by comparing it with the area value of an unknown sample. When the concentration where the S/N of the peak of determined ion becomes 10 was taken as the low limit of determination, the concentration was 0.0003 mg/L for the trichloramine and 0.003 mg/L for the dichloramine.

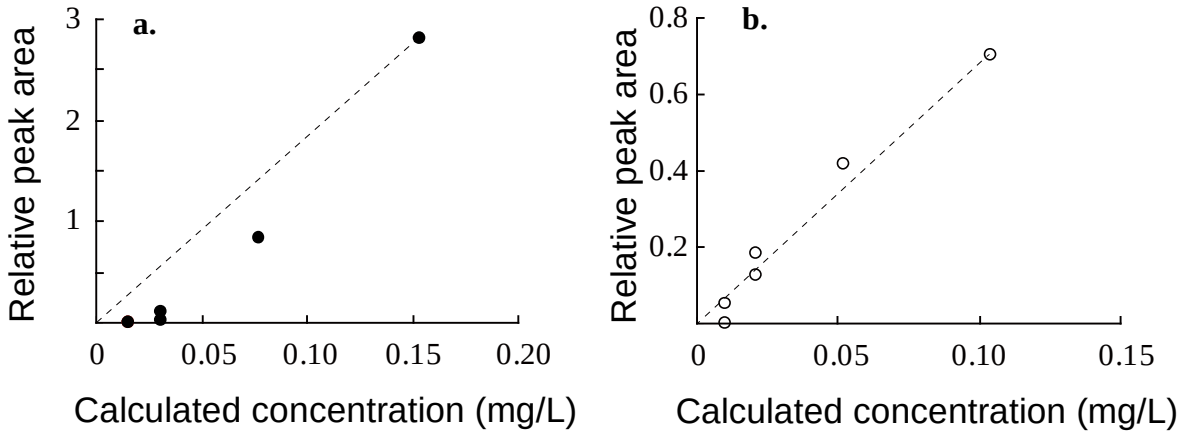

Figure 3. Relationship between the dilution factor of standard solution and the relative peak area (**a**. trichloramine, **b**. dichloramine). Dashed line represents relative peak area simply calculated by dilution factor.

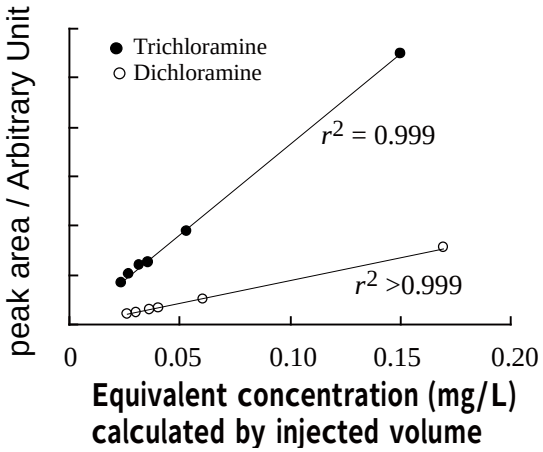

Figure 4. Relationship between the injected sample volume and the peak area.

Comparison between HS-GC/MS and DPD colorimetric methods

GAC-treated water was chlorinated so that the injection ratio of sodium hypochlorite became 1 mg/L (as Cl_2) and the trichloramine and dichloramine concentrations were measured by the DPD – absorptiometric and HS-GC/MS methods for every elapsed time. The results of the measurements are shown in **Figure 5**. The concentration of free residual chlorine was 0.64 mg/L an hour after addition of chlorine and 0.53 mg/L 54 hours after the addition. In measurements using the HS-GC/MS method, when the concentrations reached an hour and 54 hours after chlorine addition were compared, the trichloramine and dichloramine concentrations were decreased to 21% and 32%, respectively. On the other hand, the determined values by the DPD – absorptiometric method were stable and 86% or more of trichloramine and 97% or more of dichloramine remained even 54 hours after chlorine addition. Therefore, it is conceivable that considerable proportions of the determined values of the trichloramine and dichloramine by the DPD – colorimetric method were in reality attributable to color development caused by interfering substances such as organic nitrogen. Thus, it is inappropriate to apply fractional determination of inorganic chloramines by the DPD – colorimetric method to drinking water of Osaka Municipal Waterworks Bureau.

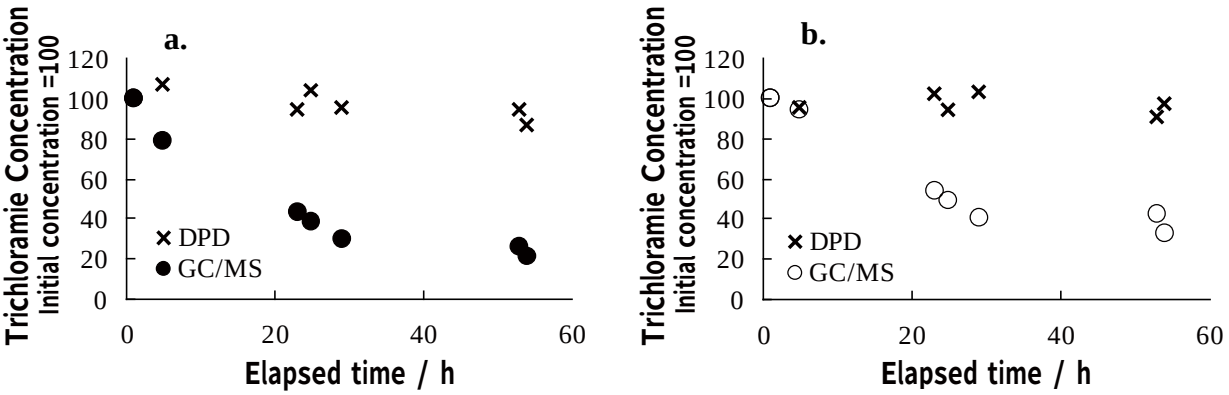

Figure 5. Secular changes in the chloramine concentration by the DPD colorimetric and HS-GC/MS methods (**a**. trichloramine and **b**. dichloramine).

Table 2. Results of measurement of inorganic chloramines at the outlet of Niwakubo Water Treatment Plant in 2009. (NH_3-N; Ammonia nitrogen in gac-filterd water(before chlorination), T; Trichloramine as Cl_2 in milligrams per litre, D; Dichloramine as Cl_2, in milligrams per litre F; Free Chlorine in milligrams per litre, Hyphens denote "not measured")

Date	Temperature	NH_3-N	HS-GC/MS		DPD		
	(°C)	(mg/L)	T	D	F	T	D
Jan 29	8.1	0.05	-	-	0.49	<0.02	0.06
Feb 9	8.2	0.03	-	-	0.52	0.022	0.07
Feb 10	9.3	0.03	0.0025	0.011	0.59	-	-
Feb 16	10.8	<0.02	-	-	0.55	<0.02	0.06
Feb 26	9.5	0.09	0.0021	0.021	0.47	0.04	0.06
Mar 13	10.0	<0.02	-	-	0.58	<0.02	0.04
Mar 16	10.6	<0.02	<0.0003	0.005	0.59	-	-
Mar 17	11.6	<0.02	<0.0003	0.005	0.59	-	-

Survey of actual conditions of inorganic chloramine in drinking water by HS-GC/MS

The results of measurement of inorganic chloramines at the outlet of Niwakubo Water Treatment Plant, Osaka Municipal Waterworks Bureau (approximately three hours elapsed after addition of chlorine at the water sampling point) are shown in Table 3. Trichloramine was detected twice out of four measurements by HS-GC/MS. On the other hand, dichloramine was detected in all measurements by the HS-GC/MS. The results of determination of the trichloramine and dichloramine by the HS-GC/MS method were 1/18 and 1/3 of the results obtained by the DPD – absorptiometric method, respectively.

CONCLUSIONS

The analysis method of inorganic chloramines by the HS-GC/MS have been improved. and optimized the measuring conditions. To improve separation and the peak shape, the analysis column of 30 m long was used and the split ratio was taken as 15. As a result, it was possible to separate the inorganic chloramines and trihalomethanes completely according to the retention time, enabling fragment ions with good sensitivity to be used for quantification. The limits of determination of trichoramine and dichloramine are 0.0003 mg/L and 0.003 mg/L, respectively. For drinking water of Osaka City whose water source is surface water, it has been proved that the inorganic chloramine concentration cannot be appropriately evaluated by the DPD – colorimetric method. It is assumed that the cause of it is interference by organic nitrogen compounds, etc.

At the survey of actual conditions of the trichloramine concentration at the outlet of Niwakubo Water Treatment Plant, Osaka Municipal Waterworks Bureau, trichloramine and dichloramine were detected.

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