

of NCl_3 may rarely be affected by that of NH_2Cl in HS-GC/MS. In fact, the peak of NCl_3 in tap water was unaffected by that of NH_2Cl (Figure 8).

Comparison of NCl_3 concentration determined by HS-GC/MS and DPD/FAS titration

Figure 7 shows a comparison of NCl_3 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 NCl_3 concentrations in samples determined using both methods were similar. These observations confirmed that HS-GC/MS was applicable for determination of NCl_3 concentrations in water samples. In addition, the effects of dilution in drawing the calibration curve of NCl_3 on its decomposition were not highly significant. On the other hand, at pH 8, NCl_3 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

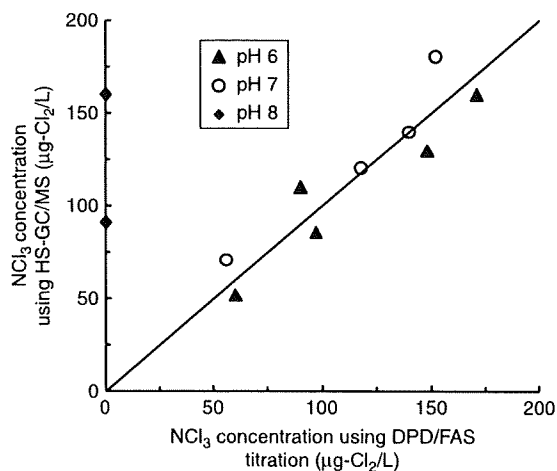


Figure 7 | Comparison NCl_3 concentrations in chlorinated ammonium solution determined using HS-GC/MS and DPD/FAS titration: reaction time, 30 min; temperature, 30°C; pH 6–8 (5 mM phosphate buffer).

Table 2 | NCl_3 concentration in tap water using HS-GC/MS

| Sample | NCl_3 concentration ($\mu\text{g-Cl}_2/\text{L}$) |
|--------|--------------------------------------------------------------|
| A | 29 |
| B | 42 |
| B* | < 15 |
| C | 46 |
| D | 27 |
| E | 27 |
| F | 27 |
| G | 21 |
| H | 31 |
| I | < 15 |

*After passage through point-of-use treatment device.

(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 NCl_3 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.

NCl_3 concentrations in tap water samples

Table 2 shows the concentrations of NCl_3 in nine tap water samples. Figure 8 shows the SIM chromatogram of NCl_3 in tap water determined by HS-GC/MS. The NCl_3

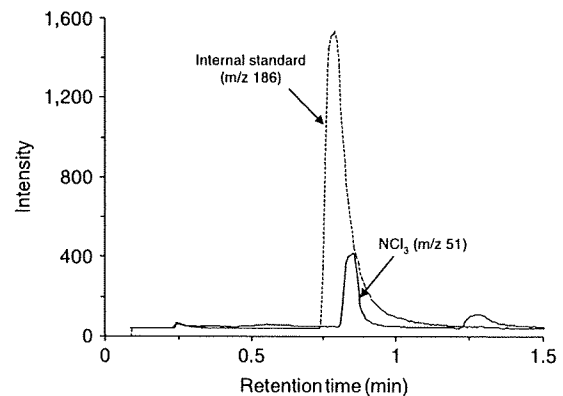


Figure 8 | SIM chromatogram of NCl_3 in tap water determined by HS-GC/MS.

concentrations ranged from < 15 to 46 $\mu\text{g-Cl}_2/\text{L}$, and those in eight of nine tap water samples exceeded the LOQ of 15 $\mu\text{g-Cl}_2/\text{L}$. NCl_3 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 NCl_3 in tap water samples. The remaining one tap water sample (I) in which NCl_3 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 NCl_3 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 NCl_3 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 NCl_3 concentration in one tap water sample (B) were investigated. NCl_3 was detected in the untreated tap water sample, but was not detected after passage through the treatment device. As it has been reported that NCl_3 is reactive with powdered activated carbon (Matsui *et al.* 2008), the NCl_3 may have been removed by activated carbon treatment in the device.

CONCLUSIONS

- (1) The calibration curve of NCl_3 was expressed by a quadratic curve. This was considered to be due to partial decomposition of NCl_3 at least in the column. The LOQ of NCl_3 was 15 $\mu\text{g-Cl}_2/\text{L}$.
- (2) NCl_3 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, NCl_3 was detected by HS-GC/MS but was not detected by DPD/FAS titration.
- (3) NCl_3 concentrations in nine tap water samples using HS-GC/MS ranged from < 15 to 46 $\mu\text{g-Cl}_2/\text{L}$. NCl_3 was detected in eight of the nine tap water samples.

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