



Fig. 3. Mass spectra of HAAs in NCI modes (a–i) and their selected ion chromatogram (j).

Table 3
Comparison of analytical methods for HAAs in tap water samples.

| Method | Method detection limits ($\mu\text{g L}^{-1}$) | | | | | Extraction solvent | Derivatization reagent | Instrumental method |
|---------------------|--|------|-------|-------|-------|--------------------|------------------------|---------------------|
| | MCAA | DCAA | TCAA | MBAA | DBAA | | | |
| This study | 0.04 | 0.04 | 0.04 | 0.02 | 0.05 | MTBE | PFBBr | GC–NCl-MS |
| US EPA method 552.3 | 0.17 | 0.02 | 0.019 | 0.027 | 0.012 | MTBE | Acidic methanol | GC–ECD ^a |

^a ECD: electron capture detector.

Table 4
HAAs levels in tap water samples collected in 15 cities in Kansai region in Japan.

| Area | City | Point | n | Concentration ($\mu\text{g L}^{-1}$) (mean (range)) | | | | | | | | | | HAA ₅ ^c | HAA ₉ |
|-------------------------------------|------------|-------|------|---|-----------------|--------------|--------------------|--------------|--------------|--------------|--------------|--------------|-------------|-------------------------------|------------------|
| | | | | TCAA | BDCAA | DBCAA | TBAA | DBAA | DCAA | BCAA | MCAA | MBAA | | | |
| Shiga | Otsu | 1 | 3 | 0.57 | ND ^a | ND | Trace ^b | 0.27 | 0.96 | 0.57 | Trace | 0.27 | 2.12 | 2.91 | |
| | | | | (0.31–0.71) | | | (ND–0.26) | (0.23–0.29) | (0.63–1.17) | (0.43–0.65) | (ND–Trace) | (0.24–0.29) | (1.44–2.49) | (2.01–3.48) | |
| Kyoto | Uji | 2 | 3 | 0.39 | ND | ND | ND | 0.20 | 0.37 | 0.24 | ND | 0.21 | 1.19 | 1.57 | |
| | | | | (0.21–0.54) | | | | (0.12–0.35) | (0.24–0.45) | (0.22–0.28) | | (0.18–0.23) | (1.03–1.28) | (1.45–1.64) | |
| | Joyo | 3 | 3 | ND | ND | ND | ND | 0.11 | Trace | 0.06 | ND | 0.11 | 0.34 | 0.54 | |
| | | | | (ND–Trace) | | | | (ND–0.16) | (ND–0.19) | (ND–0.15) | | (0.08–0.14) | (0.15–0.57) | (0.31–0.86) | |
| | Nagaokakyo | 4 | 1 | 0.78 | ND | ND | 0.38 | 0.38 | 1.21 | 0.56 | Trace | 0.45 | 2.90 | 3.93 | |
| | Muko | 5 | 1 | 2.48 | 0.37 | ND | 0.29 | 0.45 | 2.30 | 1.21 | 0.13 | 0.54 | 5.91 | 7.83 | |
| | Otokuni | 6 | 1 | 1.84 | ND | ND | 0.26 | 0.65 | 2.13 | 1.04 | 0.12 | 0.32 | 5.06 | 6.45 | |
| Yawata | 7 | 2 | 2.02 | ND | ND | ND | 0.26 | 2.48 | 0.88 | Trace | 0.57 | 5.41 | 6.44 | | |
| | | | | (1.97–2.08) | | | | (0.23–0.29) | (2.43–2.53) | (0.86–0.90) | (Trace–0.10) | (0.53–0.62) | (5.24–5.58) | (6.25–6.63) | |
| Osaka | Ibaraki | 8 | 3 | 0.59 | ND | ND | Trace | 0.99 | 1.36 | 1.23 | 0.14 | 0.40 | 3.48 | 5.02 | |
| | | | | (0.51–0.64) | | | (ND–0.33) | (0.86–1.06) | (0.98–1.61) | (0.95–1.38) | (Trace–0.18) | (0.36–0.45) | (2.91–3.93) | (4.29–5.70) | |
| | Takatsuki | 9 | 3 | 0.52 | ND | ND | Trace | 0.87 | 1.19 | 1.11 | Trace | 0.30 | 2.97 | 4.30 | |
| | | | | (0.36–0.71) | | | (ND–0.28) | (0.63–1.07) | (0.88–1.37) | (0.82–1.30) | (Trace–0.12) | (0.26–0.37) | (2.21–3.37) | (3.17–5.04) | |
| | Settsu | 10 | 1 | 0.27 | 0.47 | ND | ND | 0.54 | 0.63 | 0.62 | ND | 0.17 | 1.63 | 2.81 | |
| | Mishima | 11 | 1 | 0.09 | ND | ND | 0.25 | 0.42 | 0.26 | 0.30 | ND | 0.14 | 0.93 | 1.58 | |
| | Moriguchi | 12 | 1 | 0.14 | ND | ND | ND | 0.48 | 0.50 | 0.53 | Trace | 0.28 | 1.48 | 2.15 | |
| | Kadoma | 13 | 2 | 0.14 | ND | ND | ND | 0.21 | 0.23 | 0.22 | ND | 0.20 | 0.79 | 1.16 | |
| | | | | (0.12–0.16) | | | | (ND–0.39) | (Trace–0.40) | (Trace–0.42) | | (0.18–0.22) | (0.44–1.15) | (0.60–1.71) | |
| | Neyagawa | 14 | 2 | 0.11 | ND | ND | ND | 0.38 | 0.50 | 0.44 | Trace | 0.50 | 1.53 | 2.12 | |
| | | | | (0.10–0.12) | | | | (0.30–0.45) | (0.38–0.62) | (0.34–0.55) | (ND–Trace) | (0.41–0.59) | (1.23–1.83) | (1.71–2.52) | |
| | Hirakata | 15 | 3 | 0.12 | ND | ND | ND | 0.33 | 0.40 | 0.41 | ND | 0.40 | 1.28 | 1.83 | |
| | | | | (Trace–0.14) | | | | (0.14–0.60) | (0.19–0.63) | (0.16–0.72) | (ND–Trace) | (0.35–0.49) | (0.84–1.92) | (1.14–2.78) | |
| | Mean (SD) | | | | 0.67 (0.79) | Trace (0.13) | ND | Trace (0.12) | 0.44 (0.25) | 0.97 (0.78) | 0.63 (0.38) | Trace (0.04) | 0.32 (0.15) | 2.47 (1.77) | 3.38 (2.20) |
| | Range | | | | (ND–2.48) | (ND–0.47) | | (ND–0.38) | (ND–1.07) | (ND–2.53) | (ND–1.38) | (ND–0.18) | (0.08–0.62) | (0.17–5.91) | (0.54–7.83) |
| Fraction (%) | | | | 20 | 3 | 1 | 4 | 13 | 29 | 19 | 2 | 9 | 73 | 100 | |
| Standard for HAAs in drinking water | WHO | | | 200 | – | – | – | – | 50 | – | 20 | – | – | – | |
| | USEPA | | | – ^d | – | – | – | – | – | – | – | – | 60 | – | |
| | Japan | | | 200 | – | – | – | – | 40 | – | 20 | – | – | – | |

MDL: method detection limit; MQL: method quantification limit.

^a If concentration levels are under MDL, the levels are described as ND. Concentrations lower than the MDL were given a value of half the MDL for the calculation.

^b If concentration levels are above the MDL and below MQL, the levels are described as trace, and were assigned a value halfway between MDL and MQL for the calculation.

^c HAA₅ = MCAA, DCAA, TCAA, MBAA, DBAA.

^d –: No data.

volume sample is needed to clarify the contribution of BDCAA, DBCAA and TBAA.

The highest mean HAA levels ($5.27 \pm 1.72 \mu\text{g L}^{-1}$) were obtained in drinking water samples 1 and 4–9 (Table 1), which were treated by oxidation with sodium hypochlorite. By comparison, the drinking water samples that were treated by oxidation with ozone contained significantly lower levels of HAAs ($1.72 \pm 0.64 \mu\text{g L}^{-1}$) ($p < 0.001$, t -test). Chlorine-containing HAAs showed a significant

difference between ozonation and chlorination processes (TCAA: $0.16 \pm 0.14 \mu\text{g L}^{-1}$ and $1.01 \pm 0.73 \mu\text{g L}^{-1}$; DCAA: $0.34 \pm 0.21 \mu\text{g L}^{-1}$ and $1.51 \pm 0.61 \mu\text{g L}^{-1}$; BCAA: $0.31 \pm 0.22 \mu\text{g L}^{-1}$ and $0.95 \pm 0.31 \mu\text{g L}^{-1}$; MCAA: $0.029 \pm 0.016 \mu\text{g L}^{-1}$ and $0.098 \pm 0.041 \mu\text{g L}^{-1}$, respectively; $p < 0.0001$). In contrast, decrease in MBAA and DBAA levels were moderate in ozonation process ($0.26 \pm 0.15 \mu\text{g L}^{-1}$ and $0.27 \pm 0.19 \mu\text{g L}^{-1}$, respectively) compared with chlorination process ($0.38 \pm 0.12 \mu\text{g L}^{-1}$ and $0.60 \pm 0.33 \mu\text{g L}^{-1}$, respectively).

Table 5
Comparison of tap water analysis in the present study with reported data.

| Location | n | Concentration ($\mu\text{g L}^{-1}$) (mean (range)) | | | | | | | References |
|---------------|-----|---|----------------------|----------------------|----------------------|------------------------------------|---------------------|---------------------|----------------------|
| | | TCAA | DBAA | DCAA | BAA | MCAA | MBAA | HAA ₅ | |
| Seoul, Korea | 770 | 10.7 (ND–34.9) | ND ^a | 6.3 (ND–21.6) | – ^b | ND | ND | 16 (ND–49.5) | Lee et al. (2013) |
| China | 7 | 20.7 (8.4–31.2) | 6.36 (0.8–20.9) | 4.36 (0.3–10.9) | 16.5 (ND–39.5) | 17.5 (ND–55.3) | 5.96 (0.4–35.5) | 53.6 (29.6–86.8) | Zhang et al., 2009 |
| Netherlands | 20 | 0.40 (<0.1–1.4) | 0.99 (<0.1–6.5) | 0.63 (<0.2–3.0) | 0.69 (<0.1–2.5) | – | 0.11 (<0.1–3.0) | 2.82 (<0.3–10.4) | Peters et al. (1991) |
| Kansai, Japan | 30 | 0.67 (<0.04–2.48) | 0.44 (<0.05–1.07) | 0.97 (<0.04–2.53) | 0.63 (<0.01–1.38) | Trace ^c (<0.04–0.18) | 0.32 (0.08–0.62) | 2.47 (0.17–5.91) | This study |

^a If concentration levels are under MDL, the levels are described as ND.

^b –: No data.

^c If concentration levels are above the MDL and below the MQL, the levels are described as trace.

Bromide ion in water reacts with ozone and forms hypobromous acid, which causes brominated organic by-products (Glaze et al., 1993). Followed by ozonation, water was further treated with activated carbon while the levels of MBAA and DBAA remained comparable to those in chlorination process.

Several studies have investigated HAAs levels around the world (Table 5). The mean concentration of the HAA₅ in drinking water in Seoul has been reported as $16.0 \mu\text{g L}^{-1}$ (range of not detected to $49.5 \mu\text{g L}^{-1}$) in 770 samples (Lee et al., 2013). A survey of drinking water in China reported a range of 29.6 – $86.8 \mu\text{g L}^{-1}$ for the HAA₅ (Liu et al., 2011). The mean level of $2.47 \mu\text{g L}^{-1}$ for the HAA₅ in this study appears low compared with these earlier results in Asian countries. Levels and composition of HAA₅ in Netherlands seemed a comparable to current study (Peters et al., 1991).

4. Conclusion

In conclusion, a safe, simple and sensitive method for the determination of HAAs in tap water was developed for GC–NCI–MS with pentafluorobenzyl esterification. The method has a low detection limit (8 – 94 ng L^{-1}) and good recovery rates (99–89%). This method could be used for routine monitoring of HAAs in drinking water without exposure of workers to occupational hazards.

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References

- Alaee, M., Scott, B.F., 1998. Determination of haloacetic acids from aqueous samples collected from the Canadian environment using an in situ derivatization technique. *Water Qual. Res. J. Can.* 33, 279–293.
- American Public Health Association, 2012. *Standard Methods for the Examination of Water and Wastewater*. American Public Health Association, Washington, DC.
- Badawy, M.I., 1992. Trihalomethane in drinking water supplies and reused water. *Bull. Environ. Contam. Toxicol.* 48, 157–162.
- Chang, H.H., Tung, H.H., Chao, C.C., Wang, G.S., 2010. Occurrence of haloacetic acids (HAAs) and trihalomethanes (THMs) in drinking water of Taiwan. *Environ. Monit. Assess.* 162, 237–250.
- Domino, M.M., Pepich, B.V., Munch, D.J., Fair, P.S., 2004. Optimizing the determination of haloacetic acids in drinking waters. *J. Chromatogr. A* 1035, 9–16.
- Galdiga, C.U., Greibrokk, T., 1998. Ultra trace determination of fluorinated aromatic carboxylic acids in aqueous reservoir fluids by solid phase extraction in combination with negative ion chemical ionisation mass spectrometry after derivatization with pentafluorobenzyl bromide. *Fresenius' J. Anal. Chem.* 361, 797–802.

- Glaze, W.H., Weinberg, H.S., Cavanagh, J.E., 1993. Evaluating the formation of brominated DBPs during ozonation. *J. Am. Water Works Assoc.* 85, 96–103.
- International Programme on Chemical Safety, 1995. *International Chemical Safety Cards No1256*, <http://www.ilo.org/dyn/icsc/showcard.display?p_lang=en&p_card_id=1256> (access date: 13.02.14).
- Jia, M., Wu, W.W., Yost, R.A., Chadik, P.A., Stacpoole, P.W., Henderson, G.N., 2003. Simultaneous determination of trace levels of nine haloacetic acids in biological samples as their pentafluorobenzyl derivatives by gas chromatography/tandem mass spectrometry in electron capture negative ion chemical ionization mode. *Anal. Chem.* 75, 4065–4080.
- Kawamoto, T., Makihata, N., 2004. Distribution of bromine/chlorine-containing disinfection by-products in tap water from different water sources in the Hyogo prefecture. *J. Health Sci.* 50, 235–247.
- Knapp, D.R., 1979. *Handbook of Analytical Derivatization Reactions*. John Wiley & Sons Inc, New York.
- Lee, J., Kim, E.S., Roh, B.S., Eom, S.W., Zoh, K.D., 2013. Occurrence of disinfection by-products in tap water distribution systems and their associated health risk. *Environ. Monit. Assess.* 185, 7675–7691.
- Linder, R.E., Klinefelter, G.R., Strader, L.F., Suarez, J.D., Dyer, C.J., 1994. Acute spermatogenic effects of bromoacetic acids. *Fundam. Appl. Toxicol.* 22, 422–430.
- Liu, W., Zhao, Y., Chow, C.W., Wang, D., 2011. Formation of disinfection byproducts in typical Chinese drinking water. *J. Environ. Sci. (China)* 23, 897–903.
- Magnuson, M.L., Kelty, C.A., 2000. Microextraction of nine haloacetic acids in drinking water at microgram per liter levels with electrospray-mass spectrometry of stable association complexes. *Anal. Chem.* 72, 2308–2312.
- Mather, G.G., Exon, J.H., Koller, L.D., 1990. Subchronic 90 day toxicity of dichloroacetic and trichloroacetic acid in rats. *Toxicology* 64, 71–80.
- Michler, C.H., Lineberger, R.D., Chism, G.W., 1986. A highly sensitive method for quantitative determination of abscisic acid. *Plant Physiol.* 82, 600–603.
- Morris, R.D., Levin, R., 1995. Estimating the incidence of waterborne infectious disease related to drinking water in the United States. *Int. Assoc. Sci. Hydrol.* 233, 75–88.
- Munch, D., Munch, J., Pawlecki, A., 1995. METHOD 552.2 Determination of haloacetic acids and dalapon in drinking water by liquid-liquid extraction, derivatization and gas chromatography with electron capture detection. *Methods for the Determination of Organic Compounds in Drinking Water, Supplement III, US Environmental Protection Agency, Cincinnati, OH*.
- Nikolaou, A.D., Goulinopoulos, S.K., Kostopoulou, M.N., Lekkas, T.D., 2002. Determination of haloacetic acids in water by acidic methanol esterification–GC–ECD method. *Water Res.* 36, 1089–1094.
- Pepich, B.V., Domino, M.M., Dattilio, T.A., Fair, P.S., Munch, D.J., 2004. Validating sample preservation techniques and holding times for the approved compliance monitoring methods for haloacetic acids under the US EPA's stage 1 D/DBP rule. *Water Res.* 38, 895–902.
- Peters, R.J.B., Erkelens, C., de Leer, E.W.B., de Galan, L., 1991. The analysis of halogenated acetic acids in dutch drinking water. *Water Res.* 25, 473–477.
- Rahman, M.B., Driscoll, T., Cowie, C., Armstrong, B.K., 2010. Disinfection by-products in drinking water and colorectal cancer: a meta-analysis. *Int. J. Epidemiol.* 39, 733–745.
- United States Environmental Protection Agency, 1999. *Disinfection, Profiling and Benchmarking Guidance Manual*. United States Environmental Protection Agency (EPA) Office of Water, EPA 815-R-99-013.
- United States Environmental Protection Agency, 2001. *National Primary Drinking Water Standards*. United States Environmental Protection Agency (EPA) Office of Water, EPA 816-F-01-007.
- Villanueva, C.M., Cantor, K.P., Cordier, S., Jaakkola, J.J., King, W.D., Lynch, C.F., Porru, S., Kogevinas, M., 2004. Disinfection byproducts and bladder cancer: a pooled analysis. *Epidemiology* 15, 357–367.

- Wakayama, H., 2003. Revision of Drinking Water Quality Standards and QA/QC for Drinking Water Quality Analysis in Japan. Ministry of Health, Labour and Welfare, Japan. <<http://www.nilim.go.jp/lab/bcg/siryou/tnn/tnn0264pdf/ks0264011.pdf>> (access date: 13.02.14).
- World Health Organization, 1993. Guidelines for drinking-water quality.
- Xie, Y., 2001. Analyzing haloacetic acids using gas chromatography/mass spectrometry. *Water Res.* 35, 1599–1602.
- Xie, Y., Reckhow, D.A., Springborg, D.C., 1998. Analyzing HAAs and ketoacids without diazomethane. *J. Am. Water Works Assoc.* 90, 131–138.
- Xie, Y., Inni, R., Zhou, H., Leslie, G., 2002. Acidic methanol methylation for HAA analysis: limitations and possible solutions. *J. Am. Water Works Assoc.* 94, 115–122.

