Electrochemical decomposition of ppb level trihalomethane in tap water

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Abstract

Continuous decomposition of ppb level halocarbons in tap water using an electrochemical method was attempted. Using a flow cell in which electrical contact with the column-type Ag impregnated activated carbon electrode was improved, the concentration of chloroform in tap water decreased to about 1 ppb. The concentration of other halocarbons also decreased to below ppb levels. Using a two-stage treatment, the concentration of chloroform decreased to below the ppb level.

1. Introduction

Halocarbons in water, represented by trihalomethane, trichloroethylene and tetrachloroethylene, are significant toxic substances in drinking water. It is well known that these compounds are toxic and/or suspected carcinogens [1, 2]. The contamination of tap water and ground water by these compounds has been reported by several investigators [3, 4]. However, the definitive method for the removal of these halocarbons from water has not yet been established. The conventional method for the removal of such chlorinated compounds are air stripping or adsorption onto activated carbon. These methods cause phase transfer rather than decomposition, thus requiring a secondary treatment. On a laboratory scale, decomposition of chlorinated compounds has also been carried out by photocatalytic [5, 6], catalytic [7] and biological methods [8, 9]. Such methods are not appropriate for the treatment of flowing water that contains only ppb levels of chlorinated compounds. The electrochemical method would be one of the most appropriate methods for the treatment of drinking water for the following reasons: (i) the electrochemical reaction proceeds in water at room temperature; (ii) secondary pollution scarcely occurs, because reactive chemical agents are not used in the treatment; (iii) the continuous treatment of flowing water can be achieved using a column type electrode and a flow cell; and (iv) pollutants with very low concentration prion can be decomposed using an electrode with very large surface area.

The electrochemical decomposition of chlorinated compounds in water using a flow system was attempted at a metal plate electrode [10] and a carbon felt electrode [11]. The electrochemical activity of these system was not high and required recirculation of the water. In previous papers, we reported that chloroform in water is electrochemically decomposed to methane and chloride ion, both of which are harmless to human health, at metal plate electrodes [12] and attempted to continuously decompose halocarbons in water (ppm level) using a column-type metal impregnated carbon fibre electrode [13, 14]. This column-type carbon fibre electrode was originally developed for electrochemical analysis of heavy metal ions in water [15] and, therefore, has large surface area and high suitability for electrolysis. Using this electrode, chloroform in water, containing K_2SO_4 as a supporting electrolyte, was decomposed with an efficiency of almost 100%. However, the decomposition efficiency of chloroform in water without a supporting electrolyte decreased with increase in flow rate. This decrease in activity was thought to be caused by defects in the flow cell structure.

In this work, we used a fibrous activated carbon with larger surface area (5.8×10^6 cm^2 in a column; obtained from Osaka Gas Chemical Ltd.) than carbon fibres (2000 cm^2 in a column) [16], as the material for the column-type electrode and developed three new types of column electrodes for the flow cell system. Using these systems, the electrochemical removal of ppb levels of halocarbons in tap water was attempted.

2. Experimental details

2.1. *Electrolysis*

A Hokuto model HX-201 flow cell (*L* 75 mm, *W* 38 mm, *H* 50 mm) was used. [16] The details of the flow cell system were described previously [13]. This flow cell consisted of a working electrode compartment and a counter electrode compartment, separated by an ion permeable Vycor glass tube (Corning Vycor-7930). In the working electrode compartment, 300 carbon strings (about 0.5 mm dia.) (Nihon Carbon GF-20-P7) or

0.28 g of fibrous activated carbon (Osaka Gas Chemical A-20) were packed as the working column electrode (cathode). The counter electrode compartment was filled with 0.5 mol dm^{-3} K$_2$SO$_4$ solution (this solution does not directly contact the flowing water), and the counter electrode (Pt spiral wire) and the reference electrode (Ag/AgCl) were located near the Vycor tube. A graphite carbon rod (original cell), 12 straight Pt wires (12W), 24 straight Pt wires (24W), a spiral Pt wire or a spiral Ag wire (SW) were inserted into the column for electrical contact. The structures of (a) the original cell, (b) a SW ACE cell and (c)12W are illustrated in Figure 1. Water
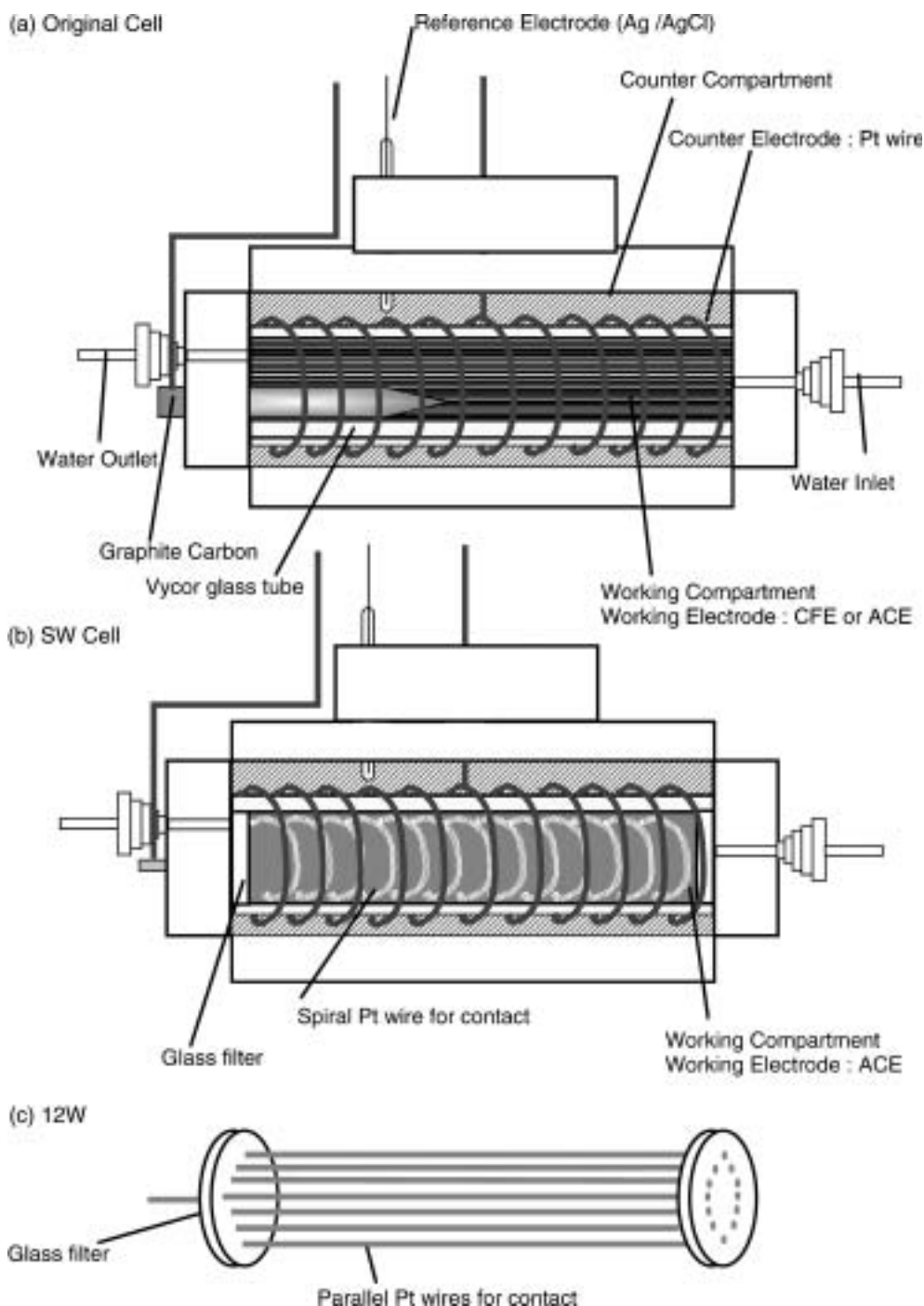

Fig. 1. Structure of (a) original CFE cell, (b) SW ACE cell and (c) 12W.

Table 1. Concentration of halocarbons before and after the electrochemical treatment at an Ag impregnated CFE and ACE

Column	Concentration of K_2SO_4/mol l^{-1}	*Concentration of halocarbons in water/ppb						
		$CHCl_3$	$CHBrCl_2$	$CHBr_2Cl$	$CHBr_3$	CH_3CCl_3	$CHClCCl_2$	CCl_2CCl_2
No treatment	0	11.08	3.29	1.37	ND	ND	ND	ND
Carbon fibre	0	3.46	ND	ND	ND	ND	ND	ND
Carbon fibre	0.01	0.58	ND	ND	ND	ND	ND	ND
Activated carbon	0	2.57	ND	ND	ND	ND	ND	ND
Activated carbon	0.01	0.79	ND	ND	ND	ND	ND	ND

* Tap water was sampled at Tokyo Institute of Technology at Midori-ku, Yokohama in Japan.
 ND = not detected.

flowed through the column electrode and drained from the water outlet. The flow rate was controlled by a minichemical pump (Nihon Seimitsu Kagaku model NP-KX-120 or Shimazu model LC-10AT). Microparticles of metal were impregnated on the carbon fibres and the fibrous activated carbon by an impregnation method [17]. Water was sampled from the tap water of Tokyo Institute of Technology at Midori-ku, Yokohama or the Osaki factory of Meidensha Corporation at Shinagawa-ku, Tokyo, Japan. The concentration of halocarbons in the tap water largely depended on the location and season of sampling. In the experiment for comparison of the carbon fibre electrode (CFE) and the activated carbon electrode (ACE), the stored tap water sampled at the same time was used in the experiment. In subsequent experiments, 4 dm³ of tap water was sampled in every run and was stored in a refrigerator. Before electrolysis, a negative potential (−1.2 V vs Ag/AgCl) was imposed on the working electrode overnight to decompose and remove adsorbates on the electrode surface (pre-electrolysis). When the ACE was used as the working electrode, tap water was pumped through the column electrode during the pre-electrolysis. Electrolysis was carried out potentiostatically at −1.2 V vs Ag/AgCl using a potentiostat–galvanostat (Hokuto model HABF-501) and at a tap water flow rate of 10 ml min⁻¹, unless otherwise noted.

2.2. *Analytical methods*

Analysis of the volatile organic compounds (VOC), including halocarbons, was carried out by a head space sampler (Perkin–Elmer HS-40) equipped GC-MS (Shimazu QP5000). The column was CP. Silica Plot (0.32 mm × 30 m, $df = 40$ μm) (GL Science). A mixed standard solution for the analysis of tap water (GL Science Inc.) was used as the standard for VOC. The ion analysis in the solution was carried out using an ion chromatograph (Toha Denpa model ICA-3000) equipped with an anion exchange column PCI-201S (Toha Denpa) and a electrical conductivity detector, using a phthalic acid eluent (2.5×10^{-3} mol dm⁻³) and tris-buffer. K_2SO_4 (GR Wako Pure Chemical) was used for the supporting electrolyte without further purification.

3. Results and discussion

3.1. *Effect of adding electrolyte*

In Table 1, the concentration of halocarbons before and after the electrochemical treatment at Ag impregnated CFE and ACE in the original flow cell are summarized. In all electrolyses, the current efficiency for decomposition was not high; the base current was higher than the current for pollutant decomposition, because the concentration of the pollutants is very low (ppb level). The concentration of chloroform in the solution without a supporting electrolyte decreased to 2–3 ppb at the CFE and ACE. Other halocarbons were not detected. By adding 0.01 mol dm⁻³ of K_2SO_4, the conductivity of the solution increased from 0.15 mS to 1.53 mS and the concentration of chloroform in treated water decreased to below 1 ppb. This increase in activity caused by addition of supporting electrolyte may be explained as follows. Without addition of electrolyte, the potential is not homogeneously distributed over the entire electrode because of its high electrical resistance. In the original flow cell (Hokuto model HX-201 flow cell) that we are using for the continuous treatment of water, electrical contact to the column-type working electrode is obtained by inserting a graphite carbon rod in the column. [13] This partial contact to the large column electrode seems to cause an uneven distribution of potential.

3.2. *New column electrode*

To overcome this uneven potential distribution, we developed a new type of column electrode. We made three types of column electrode. To distribute the potential all over the column electrode, we inserted (a) a spiral Pt wire (SW), (b) 24 parallel Pt wires (24W) and (c) 12 parallel Pt wires (12W). The structure of the original cell, a SW ACE cell and 12W are illustrated in Figure 1. In subsequent experiments, we used activated carbon as the electrode material in the column due to its large surface area and packing flexibility. Both sides of the column were capped with glass filters.

In Table 2, the concentration of halocarbons before and after the electrochemical treatment at a Ag impregnated ACE are summarized. The initial concentration of halocarbons in tap water largely depended on the

Table 2. Concentratibn of halocarbons before and after electrochemical treatment at an original Ag impregnated CFE and SW, 12W and 24W Ag impregnated ACEs

*RN	Type of electrode	†Concentration of halocarbons in water/ppb							
			$CHCl_3$	$CHBrCl_2$	$CHBr_2Cl$	$CHBr_3$	CH_3CCl_3	$CHClCCl_2$	CCl_2CCl_2
1	Original CFE	Before electrolysis	26.33	15.39	6.96	0.75	ND	0.06	0.03
		After electrolysis	5.43	ND	ND	0.07	ND	ND	ND
	SW ACE	Before electrolysis	25.43	13.16	5.56	0.46	ND	0.08	0.05
		After electrolysis	1.42	ND	0.02	ND	ND	0.05	0.03
	12W ACE	Before electrolysis	30.40	16.30	6.87	0.54	ND	0.07	0.05
		After electrolysis	2.91	0.15	0.05	ND	ND	0.02	ND
	24W ACE	Before electrolysis	26.60	13.94	6.07	0.55	ND	0.05	0.04
		After electrolysis	1.80	0.11	0.05	ND	ND	ND	ND
2	Original CFE	Before electrolysis	91.99	37.06	9.62	ND	0.19	0.45	0.37
		After electrolysis	22.06	0.11	ND	ND	0.03	ND	0.61
	SW ACE	Before electrolysis	97.55	38.23	10.10	0.72	0.15	0.40	0.31
		After electrolysis	1.64	ND	0.05	ND	ND	11.83	0.07
	12W ACE	Before electrolysis	72.38	30.72	8.76	ND	ND	0.25	0.23
		After electrolysis	19.09	1.73	0.21	ND	ND	0.05	0.03
	24W ACE	Before electrolysis	72.38	30.72	8.76	ND	ND	0.25	0.23
		After electrolysis	10.05	0.31	0.11	ND	0.05	0.17	0.06

* Run number.

† Tap water was sampled at Osaki factory of Meidensha Corporation in Shinagawa-ku, Tokyo.

ND = not detected.

location and the season of sampling. That of water sampled from the Osaki factory in the summer season (the second run in Table 2) was especially high. This high concentration of halocarbons would be caused by the environment of the factory where tap water is hardly used. The general concentration of halocarbons in tap water in this area cannot be estimated from this result. The SW ACE, 12W ACE and 24W ACE cells showed a higher efficiency for the decomposition of halocarbons than the original CFE cell. This result demonstrates that the above assumption is correct. The SW ACE cell showed the highest activity for both the first and second runs. For the second run, an increase in the trichloro-ethylene concentration (from 0.40 to 11.83 ppb) was observed in the SW ACE cell, whereas this was not observed for the first run. This increase in the concen-tration of trichloroethylene was not observed in experi-ments other than the SW ACE system for the second run in Table 2.

Figure 2 shows the relationship between flow rate of the tap water and the concentration of halocarbons in the treated water at the SW ACE for the second run. The concentration of halocarbons other than chloro-form and trichloroethylene was independent of flow rate and was almost zero. The concentration of trichloro-ethylene increased with increase in flow rate, whereas the dependence of chloroform concentration on flow rate was not very high. These results suggest that trichloro-ethylene is produced from electrochemical reduction of chloroform at the SW ACE. For the first run, no formation of trichloroethylene was observed. This indicates that formation of trichloroethylene occurs only when the concentration of chloroform in tap water is very high. If the concentration of chloroform in the
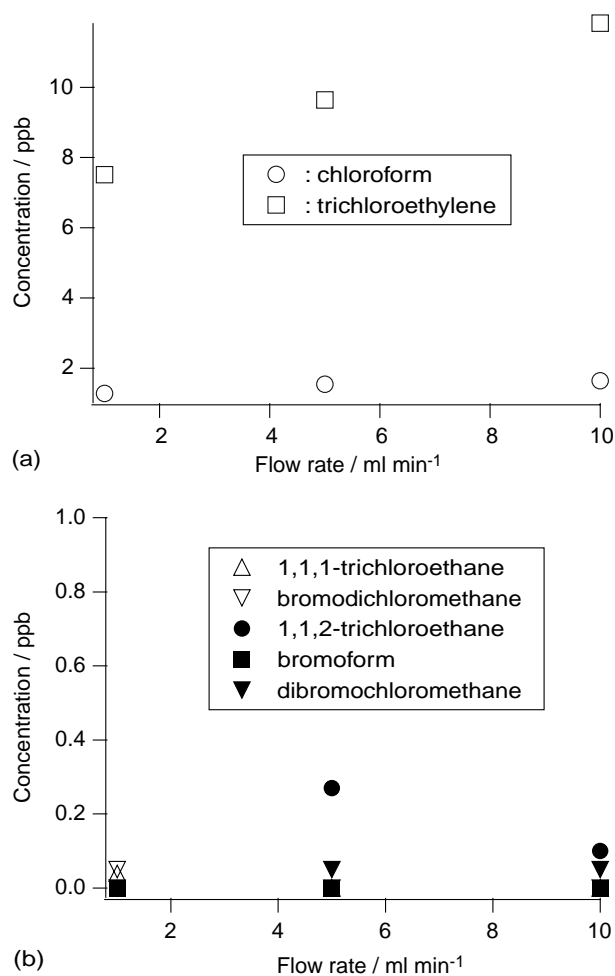

(a)

(b)

Fig. 2. Relationship between tap water flow rate and concentration of (a) chloroform and trichloroethylene and (b) other halocarbons after electrochemical treatment.

tap water is not high, the produced trichloroethylene is electrochemically decomposed before it is drained. In the case that the concentration of chloroform is high, the trichloroethylene produced is drained before it is fully decomposed. Therefore, formation of trichloroethylene will be prevented by using a longer column electrode.

3.3. *Effect of the length of column electrode*

As discussed previously [13], the efficiency for decomposition of the chlorinated compounds decreases with increase in water flow rate. However, a low flow rate will prevent a stable supply of drinking water. This dilemma can be solved using a flow cell with a longer column-type electrode. To investigate the effect of the column length, we used a two-stage electrolysis system. The cell structure, the electrode material and the electrolysis conditions for each stage were the same. For the two-stage treatment, we used a Ag spiral wire instead of a Pt spiral wire in order to reduce the cost. The concentration of halocarbons in water before and after the treatment at the double SW ACEs at a flow rate of 10 ml min^{-1} and a single 24W ACE, which showed the highest activity at lower flow rate among the electrodes we used in this study, at flow rates of 1, 5 and 10 ml min^{-1} are summarized in Table 3. For the single stage treatment system, the concentration of residual halocarbons increased with increase in flow rate. By the two-stage treatment system, the efficiency of treatment was improved compared with that of the single stage system, though the time necessary for treatment by the single treatment system at 1 ml min^{-1} is much longer than the time by the double treatment system at 10 ml min^{-1}. This suggests that the treatment efficiency is largely dependent on the number of encounter times with Ag particles.

3.4. *VOCs in tap water*

In Table 4, the VOC concentrations before and after the first and the second electrochemical treatment at the Ag impregnated SW ACE are summarized. Halocarbons,

Table 4. Concentration of VOC before and after electrochemical treatment by a single column treatment and double columns treatment

Compound	*Concentration/ppb		
	Before electrolysis	Single column treatment	Double columns treatment
Chloroform	17.45	1.17	0.09
Bromodichloromethane	10.25	ND	ND
Dibromochloromethane	4.55	ND	ND
Bromoform	0.53	ND	ND
1,1,1-trichloroethane	0.23	ND	ND
Trichloroethylene	0.11	ND	ND
Tetrachloroethylene	0.15	ND	ND
Dichloromethane	ND	1.30	2.49
Benzene	0.04	0.05	0.09
Toluene	0.65	0.41	0.44
m, p-Xylene	0.04	0.03	0.03
o-Xylene	0.04	0.02	ND
1,4-Dichlorobenzene	0.04	0.02	ND
Total	34.1	3.0	3.1

*Tap water was sampled at Osaki factory of Meidensha Corporation in Shinagawa-ku, Tokyo.
ND = not detected.

except for dichloromethane, could not be detected from the treated water, whereas the concentration of dichloromethane increased with treatment. No increase in dichloromethane concentration was observed using the flow cell so far. This formation of dichloromethane seems to be caused by the Ag spiral wire used for electrical contact; some chloroform reacting on the surface of a Ag wire would be converted to dichloromethane. In previous studies, we have reported that dichloromethane was produced by electrolysis of chloroform at a Ag plate electrode with a current efficiency of 6.2% [12], whereas a Ag impregnated CFE hardly produces dichloromethane during electrolysis of chloroform [13]. Dichloromethane produced at a Ag wire would be drained from the column electrodes before it is electrochemically decomposed, due to the low activity of a Ag impregnated electrode for the decomposition of dichloromethane [13]. These results suggest that the

Table 3. Concentration of halocarbons before and after electrochemical treatment at a single Ag impregnated 24W Ag impregnated ACE and double SP Ag impregnated ACE

*FR	Type of electrode	†Concentration of halocarbons in water/ppb						
			CHCl$_3$	CHBrCl$_2$	CHBr$_2$Cl	CHBr$_3$	CH$_3$CCl$_3$	CHClCCl$_2$	CCl$_2$CCl$_2$
1	Single 24W	Before electrolysis	26.60	13.94	6.07	0.55	ND	0.05	0.04
		After electrolysis	0.14	ND	ND	0.12	ND	0.02	ND
5	Single 24W	Before electrolysis	26.60	13.94	6.07	0.55	ND	0.05	0.04
		After electrolysis	1.36	0.11	ND	ND	ND	ND	ND
10	Single 24W	Before electrolysis	26.60	13.94	6.07	0.54	ND	0.05	0.04
		After electrolysis	1.80	0.11	0.05	ND	ND	ND	ND
10	Double SP	Before electrolysis	17.45	10.25	4.55	0.53	0.23	0.11	0.15
		After electrolysis	0.09	ND	ND	ND	ND	ND	ND

*Flow rate.
†Tap water was sampled at Osaki factry of Meidensha Corporation in Shinagawa-ku, Tokyo.
ND = not detected.

structure of the metal surface affects the electrolysis products; at a metal plate electrode, electrochemical reaction proceeds on the surface of the Ag polycrystal, whereas reaction occurs on fine grains of Ag at an Ag impregnated electrode. Hoshi et al. also reported that the structure of the electrode surface influences electrocatalytic activity in carbon dioxide reduction using various single crystal metal electrodes. [18, 19] Changing the Ag spiral wire to Zn, which selectively produces methane from chloroform [12], will prevent formation of dichloromethane.

The concentration of benzene was also increased by the treatment. Considering the result that the concentration of toluene was hardly changed by the electrochemical treatment, this method seems to have low activity for decomposition of aromatic hydrocarbons. On the other hand, the concentration of 1,4-dichlorobenzene decreased under electrochemical treatment to below the detection limit. These results suggest that 1,4-dichlorobenzene was electrochemically dechlorinated and was converted to benzene, as reported by Rusling et al. [20]. The increase in the concentration of benzene is not very high compared to the concentration of toluene in the tap water. For the actual removal of these aromatic hydrocarbons in tap water, an adsorption process will have to be simultaneously used.

3.5. Concentration of ions before and after electrochemical treatment

Results of the ion analysis in water before and after the electrochemical treatment for the first run in Table 2 are summarized in Table 5. The result of the second run showed the same tendency. The concentration of Na^+, Cl^-, SO_4^{2-} ions hardly changed with electrolysis. During the electrolysis, halocarbons were decomposed to Cl^- ion and hydrocarbons, as previously reported [13]. In tap water, the electrochemically produced Cl^- ion is negligible, because the concentration of halocarbons is at the ppb level. NO_2^-, that was not detected in the raw water, was detected from all electrochemically treated water in this study. On the other hand, the concentration of NO_3^- decreased with electrolysis and the total of

concentration of NO_2^- and NO_3^- before and after the electrochemical treatment was almost the same for all the four cell types. In the two stage treatment, the concentration of NO_2^- ions was increased from below the detection limit to 0.90 ppm by the first treatment then to 1.05 ppm by the second treatment. These results suggest that NO_2^- was produced from reduction of NO_3^- ion in the tap water. Formation of NO_2^- ion by electrochemical reduction of NO_3^- ion was reported by Kvaratskheliya [21]. A high level of nitrate in drinking water (excess 10 mg dm^{-3} of NO_2^- and NO_3^-) is reported to cause infant methemoglobinemia [22]. The concentration of NO_2^- after electrolysis is above the WHO guideline (0.2 mg l^{-1}). Therefore, formation of NO_2^- is a problem that needs to be solved in order to develop this method for a practical use.

One of the NO_2^- treatment methods is reoxidation to NO_3^- by the column-type electrode. This method is very simple and reformation of halocarbons by oxidation will scarcely occur because hydrocarbons produced from halocarbons are electrochemically stable. However, NO_3^- ion is said to be reduced to NO_2^- in the human body and exhibits toxicity [22]. Considering this, it is desirable that NO_3^- should also be removed from drinking water. Generally, the removal of NO_3^- from water is very difficult due to its high solubility in water. At the present time, only the distillation method, the ion exchange method and the reverse osmosis method can remove NO_3^- ion from water. The reverse osmosis method removes ions in water by passing through the semipermeable membrane to the reverse direction applying pressure on the water. Such methods require a long treatment time and also remove useful ions from water. Bouzek et al. reported that NO_3^- ion can be finally reduced to ammonia at a Cu electrode [23]. If the selective electrochemical reduction of NO_3^- to ammonia is possible, NO_3^- may be removed from water by reduction at the column-type electrode and the following adsorption process. This needs further investigation in order to develop this method.

For practical use, improvement in current efficiency will be needed. To improve the current efficiency, decreasing the base current is necessary. At the CFE,

Table 5. Concentration of ions in water before and after the electrochemical treatment at various type electrodes

*RN	Type of electrode		†Concentration of ions in water/ppm							
			Na^+	K^+	Cl^-	NO_2^-	NO_3^-	SO_4^{2-}	NH_4^+	Br^-
1	Original CFE	Before electrolysis	17.99	2.50	28.30	ND	9.36	33.86	ND	ND
		After electrolysis	18.45	37.31	28.10	2.55	5.91	36.21	ND	ND
	SW ACE	Before electrolysis	18.02	2.74	28.42	ND	9.39	34.03	ND	ND
		After electrolysis	18.22	32.58	28.26	2.51	6.01	36.14	ND	ND
	12W ACE	Before electrolysis	17.90	2.81	28.60	ND	9.46	34.07	ND	ND
		After electrolysis	18.15	32.89	28.60	1.14	7.91	35.55	ND	ND
	24W ACE	Before electrolysis	17.80	2.64	28.49	ND	9.50	33.99	ND	ND
		After electrolysis	15.52	29.34	28.16	1.31	7.63	33.79	ND	ND

* Run number.
† Tap water was sampled at Osaki factry of Meidensha Corporation in Shinagawa-ku, Tokyo.
ND = not detected.

which has a more homogeneous and clean surface, the base current was lower than at the ACE. Therefore, development of homogeneous and clean material for large surface area electrodes is necessary.

4. Conclusion

Using metal-impregnated ACEs with a spiral metal wire contact in a flow cell, halocarbons in tap water, as well as trihalomethanes, were decomposed to below the ppb level. However, at the same time, NO_2^- was produced at a ppm order by electrochemical reduction of NO_3^-. This study demonstrated that almost all the toxic halocarbons in tap water can be continuously decomposed by the electrochemical method.

Acknowledgements

References

1. J.W. Lloyd, R.M. Jr. Moore and P. Breslin, *J. Occup. Med.* **17** (1975) 603.
2. M.P. Strier, *Environ. Sci. Technol.* **14** (1980) 28.
3. J.J. Rook, *Water Treat. Exam.* **23** (1974) 234.
4. S.W.J. Lagakos, B. Wessen and M. Zelen, *J. Am. Statist. Assoc.* **81** (1986) 583.
5. A.L. Pruden and D.F. Ollis, *Environ. Sci. Technol.* **17** (1983) 628.
6. W.H. Glaze, J.F. Kenneke and J.L. Ferry, *Environ. Sci. Technol.* **27** (1993) 177.
7. M. Martino, R. Rosal, H. Sastre and F.V. Díez, *Appl. Catal. B-Environ.* **20** (1999) 301.
8. L.P. Wackett and D.T. Gibson, *Appl. Environ. Microbiol.* **54** (1988) 1703.
9. R.B. Winter, K-M. Yen and B.D. Ensley, *Biotechnol.* **7** (1989) 282.
10. S. Nishimoto, H. Hatta, H. Fu, T. Atsumi and T. Kagiya, *Jpn. J. Water Pollut. Res.* **11** (1988) 107.
11. A.M. Polcaro and S. Palmas, *Ind. Eng. Chem. Res.* **36** (1997) 1791.
12. N. Sonoyama, K. Hara and T. Sakata, *Chem. Lett.* (1997) 131.
13. N. Sonoyama and T. Sakata, *Environ. Sci. Technol.* **33** (1999) 3438.
14. N. Sonoyama, K. Ezaki and T. Sakata, *Adv. Environ. Res.* **6** (2001) 1.
15. H. Aoyagi, Z. Yoshida and S. Kihara, *Anal. Chem.* **59** (1987) 400.
16. F. Kusu, H. Tamanouchi, T. Sato, K. Arai, K. Takamura and T. Sueoka, *Denki Kagaku* **65** (1997) 51.
17. K. Hara and T. Sakata, *Bull. Chem. Soc. Jpn.* **70** (1997) 571.
18. N. Hoshi, M. Kato and Y. Hori, *J. Electroanal. Chem.* **440** (1997) 283.
19. N. Hoshi, T. Suzuki and Y. Hori, *J. Phys. Chem. B* **101** (1997) 8520.
20. M.O. Iwunze and J.F. Rusling, *J. Electroanal. Chem.* **266** (1989) 197.
21. R.K. Kvaratskheliya, *Seriya Khimicheskaya* **2** (1976) 140.
22. A. Terblanche, *Water SA* **17** (1991) 77.
23. K. Bouzek, M. Paidar, A. Sadílková and H. Bergmann, *J. Appl. Electrohem.* **31** (2001) 1185.