

## Bromate, chlorate, chlorite and perchlorate in sodium hypochlorite solution used in water supply

Mari Asami, Koji Kosaka and Shoichi Kunikane

### ABSTRACT

A survey was conducted to reveal the concentrations of bromate, chlorite, chlorate and perchlorate as impurities in sodium hypochlorite solutions and those of chlorate and perchlorate in raw and processed waters including a metropolitan area. High concentrations of bromate (max.  $414 \text{ mg l}^{-1}$ ) and chlorate (max.  $260,000 \text{ mg l}^{-1}$ ) were found in purchased sodium hypochlorite solutions for drinking water disinfection that had been stored for a long time, more than two years at a maximum. In the survey of chlorate and perchlorate in raw and processed waters in the Tone River Basin, the highest concentration of chlorate in raw water was  $78 \text{ } \mu\text{g l}^{-1}$  and that of perchlorate was  $40 \text{ } \mu\text{g l}^{-1}$ . Chlorate and perchlorate concentrations in 32 purchased sodium hypochlorite solutions and six on-site-generated hypochlorite solutions were also analysed. In the purchased sodium hypochlorite solutions, perchlorate concentrations ranged from  $0.170$  to  $33.0 \text{ mg l}^{-1}$ . In hypochlorite solutions whose measured FAC (free available chlorine) concentration was lower than the manufacturer-specified FAC concentrations, the chlorate and perchlorate concentrations were higher than those in relatively fresh sodium hypochlorite solutions. In on-site-generated hypochlorite solutions, the maximum concentrations of chlorate and perchlorate were  $1,700 \text{ mg l}^{-1}$  ( $140 \text{ mg g}^{-1}$  of measured FAC) and  $0.660 \text{ mg l}^{-1}$  ( $0.053 \text{ mg g}^{-1}$  of measured FAC), respectively.

**Key words** | bromate, chlorate, chlorite, perchlorate, sodium hypochlorite solution

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### INTRODUCTION

Sodium hypochlorite solution is frequently used as a disinfectant and as an oxidizing agent in waterworks. Since the concentration of residual chlorine should be maintained at more than  $0.1 \text{ mg l}^{-1}$  in distribution systems, sodium hypochlorite solution is commonly used as a residual disinfectant in over 80% of treatment facilities in Japan. It is usually added at the final stage of the treatment process, and sometimes added at the first and/or the middle stage as an oxidizing agent. A 12% (or 6%) stock solution has been widely used in waterworks for the chlorination of water; more recently, on-site generation of hypochlorite has been introduced into 10% of treatment facilities (JWWA 2006).

The duration of storage of stock solutions is sometimes longer, over several months, for example, in small water treatment facilities. In addition, attention should be paid to impurities in hypochlorite solutions, especially in raw waters containing ammonia, which is a chlorine-consuming compound, since the injection ratios of hypochlorite solutions are relatively high in ammonia-contaminated raw water.

For example, in April 2004, bromate concentration in chlorinated drinking water in Hokkaido was found to be  $0.168 \text{ mg l}^{-1}$ , 16.8 times higher than the concentration limit stipulated by Japanese standards (Hokkaido News 2004). Later analysis showed bromate at a concentration of

doi: 10.2166/aqua.2009.014

668 mg l<sup>-1</sup> in the sodium hypochlorite solution used in the water treatment process, illustrating the fact that sodium hypochlorite solution can be a major source of bromate in chlorinated drinking water.

Bromate, known as a carcinogenic ozonation by-product, was introduced in the Japanese drinking water quality standard in 2004 and has been regulated to be less than 0.01 mg l<sup>-1</sup>. Chlorate and chlorite, known by-products of chlorine dioxide disinfection, have also been listed as chemicals to be monitored. The criterion has been set at 0.6 mg l<sup>-1</sup> for both chlorate and chlorite based on their oxidative property for red blood cells in humans (MHLW 2003). In a national survey of monitored items (MHLW 2005), chlorate concentrations exceeded the criterion in 14 of the 598 monitored finished waters. The principal criterion for including a monitored compound in the list of drinking water standards is the detection of the compound in finished water at a concentration near or above one-tenth of its threshold standard. Accordingly, chlorate was introduced into the drinking water standards in April 2008. Perchlorate has only been recently addressed as a contaminant of concern in drinking water, though it is naturally occurring and was identified in Chilean salt caliche in the early 1900s (Dafert 1908). More recently it has been used as a chemical propellant in rocket fuels and an oxidizing agent in many products. Perchlorate is known to interfere with the iodine uptake of the thyroid gland (Greer *et al.* 2002; National Research Council 2005). In 2005, the United States Environmental Protection Agency (US EPA) established an official reference dose (RfD) of 0.7 µg kg<sup>-1</sup> day<sup>-1</sup> of perchlorate and specified its drinking water equivalent level (DWEL) to be 24.5 µg l<sup>-1</sup> (US EPA 2005), based on a report by the National Academy of Sciences (NAS) (National Research Council 2005).

Chlorate and perchlorate have been detected in Japanese aquatic environments, especially in the Tone River Basin, which is one of the largest water sources for drinking water supply in the Tokyo metropolitan area (Asami *et al.* 2007; Kosaka *et al.* 2007). The maximum concentration of chlorate and perchlorate in river water affected by industrial effluents was measured at 9,000 µg l<sup>-1</sup> and 15,000 µg l<sup>-1</sup>, respectively. One of the highest concentrations of perchlorate was attributable to unintentional production of perchlorate in an electrolysis process.

All oxyhalides listed here (i.e. bromate, chlorate, chlorite and perchlorate) are industrial chemicals and are also known to exist in chlorinated drinking waters as impurities from sodium hypochlorite solutions. The concentrations of bromate, chlorate, chlorite and perchlorate in hypochlorite solution have been shown to increase during storage (Gordon *et al.* 1995 for chlorate; Weinberg *et al.* 2003 for bromate). However, the quality of the hypochlorite solution used in water treatment plants and the parameters which may contribute to increased rates of production of undesirable oxyhalide species are not well known. In this study, we investigated the concentrations of bromate, chlorate, chlorite and perchlorate in raw, processed and finished waters and hypochlorite solutions collected from various water treatment plants.

## MATERIALS AND METHODS

### Bromate, chlorate and chlorite in stored sodium hypochlorite solutions

The primary study was conducted to detect bromate, chlorate and chlorite concentrations in hypochlorite solutions. Thirty-seven samples were collected from hypochlorite solutions used in water supply facilities from 11 prefectures including Kanto (east), Kansai (west), Hokkaido (north) and Okinawa (south) regions in Japan. The water supply facilities include 28 treatment plants and 9 distribution facilities. Out of 37 facilities, 14 stored the sodium hypochlorite solutions in an air-conditioned environment. Samples were collected and stored in cool and dark conditions and analysed within 2 days. Sodium hypochlorite solutions were diluted 10,000 times by pure water (MilliQ Gradient A10 water purification system, Millipore, Bedford, Massachusetts) and the concentration of free available chlorine (FAC) was analysed by the DPD method. Chlorate was analysed using ion chromatography (IC, DX-500, Dionex, Sunnyvale, California), electric conductivity with an Ion Pac AG19/AS19 (4 mm) column and KOH generator. Bromate and chlorite were analysed by the IC-post-column colouring method using the same eluent reacted with 1.2 mM l<sup>-1</sup> NaNO<sub>2</sub> and 1.5 M KBr 1.0 M l<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> solution, according to the official Japanese notification method (MHLW 2004).

## Chlorate and perchlorate in raw, processed and finished waters and hypochlorite solutions

An intensive survey of chlorate and perchlorate concentrations in source and finished waters was conducted in conjunction with the Ministry of Health, Labour and Welfare, Japan. Raw, processed and finished water and hypochlorite solutions were collected from water treatment plants, especially in the Tone River Basin, to quantify the effect of industrial effluents. The Tone River is the largest water source in the Tokyo Metropolitan area and has been previously found to be contaminated by chlorate and perchlorate (Kosaka *et al.* 2007). More than ten other large cities and water supply bodies previously reporting high concentration of disinfection by-products (DBPs) were selected (MHLW 2006). In addition, 32 purchased and six on-site-generated hypochlorite solutions were collected and analysed. Chlorate and perchlorate concentrations were analysed with IC-tandem mass spectrometry (MS/MS) (Dionex ICS-2000 and API 3200QTrap, Applied Biosystems) as described elsewhere in detail (Kosaka *et al.* 2007).  $^{18}\text{O}$ -enriched  $\text{NaClO}_4$  (Cambridge Isotope Laboratories) was used as an internal standard for perchlorate. The minimum reporting limits (MRLs) for perchlorate and chlorate were set to be 0.05 and 0.05  $\text{mg l}^{-1}$ , respectively, except the MRL for chlorate of the sample waters in several water treatment plants was 0.1  $\text{mg l}^{-1}$ .

## RESULTS AND DISCUSSION

### Bromate, chlorate and chlorite in hypochlorite solutions

In the 37 sodium hypochlorite solutions collected, the concentration of measured free available chlorine (FAC) in the solution ranged from 0.04 to 15%, and the average concentrations of bromate in the solution were 96  $\text{mg l}^{-1}$  (maximum 414  $\text{mg l}^{-1}$ ). When the concentrations were converted into their finished water, bromate concentration was below 0.001  $\text{mg l}^{-1}$ ; chlorate and chlorite concentrations were below 0.20 and 0.003  $\text{mg l}^{-1}$ , respectively, assuming the dose of the hypochlorite solution to be 1  $\text{mg l}^{-1}$ . However, in some cases, chlorate concentration in the hypochlorite solution was extremely high when the measured FAC in the

solution was much lower than its manufacturer-specified FAC at the time of purchase. The concentration of FAC is a critical factor for controlling residual chlorine, chlorate and bromate, because, if the sodium hypochlorite solutions which contain lower FAC than manufacturer-specified are used for disinfection, bromate and chlorate concentration may increase subsequently because of the increased amount of hypochlorite solution used in order to accomplish residual chlorine concentration.

Bromate concentration varied as shown in Figure 1. One factor is that bromate concentration varied among manufacturers. Though the number of samples was limited in this study, the bromate concentrations in sodium hypochlorite solutions of one manufacturer ranged from 5.4 to 49.5  $\text{mg l}^{-1}$  ( $n = 7$ ), while those of another manufacturer ranged from 24.5 to 96.5  $\text{mg l}^{-1}$  ( $n = 7$ ).

The other factor seems to be the timing of the purchase of hypochlorite solutions. It was recently reported that the concentration of bromate is largely dependent upon the salts used to produce hypochlorite solutions and can be controlled by changing the salt to those salts whose concentration of bromide is lower or by refining the salts. It is also reported that the manufacturers have changed the salts to refined types in accordance with the revision of the standard (JWWA 2006). Therefore, the high bromate concentration in older samples may be attributable to the bromide present in salts that were used as a basic ingredient in the production process.

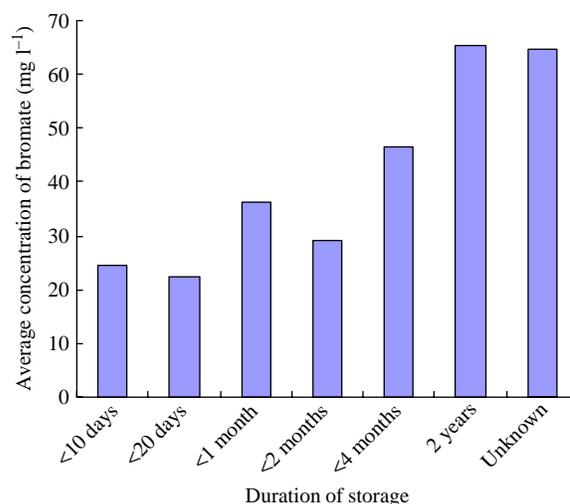
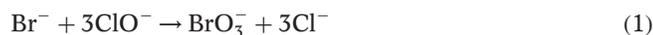


Figure 1 | Concentration of bromate in the hypochlorite solutions in relation to the duration of storage after purchase of each hypochlorite solution.

Weinberg *et al.* (2003) indicated the mechanism of bromate formation in hypochlorite solution as described in Equation (1) below. Since no residual bromide was found in any of the samples, and the reaction has been reported in the literature to occur very rapidly, the majority of bromide in sodium hypochlorite solution was expected to react to produce bromate.



Thus the authors consider that the high concentration of bromate might depend mainly on the bromide concentration in salts, while bromate concentration was higher in those sodium hypochlorite solutions that had been stored for more than two years or for an unknown period after the purchase of each hypochlorite solution.

Chlorite concentration was rather low in the hypochlorite samples, with an average of 145 mg l<sup>-1</sup> and a maximum of 397 mg l<sup>-1</sup>. Chlorite concentrations in the treated water were below 0.003 mg l<sup>-1</sup> and 0.03 mg l<sup>-1</sup> assuming respective hypochlorite solution doses of 1 mg l<sup>-1</sup> and 10 mg l<sup>-1</sup>. So chlorite concentrations were not expected to be very high in hypochlorite solutions and finished water.

The average concentration of chlorate in the hypochlorite solutions was 15,300 mg l<sup>-1</sup> (maximum 260,000 mg l<sup>-1</sup>), and was largely different between samples and FAC levels. Chlorate concentrations in finished water were estimated to be 0.20 mg l<sup>-1</sup> and 2.0 mg l<sup>-1</sup> when the dose of the sodium hypochlorite solution was assumed to be 1 mg l<sup>-1</sup> and 10 mg l<sup>-1</sup>, respectively. Thus, further study was conducted as described in the next section.

### Chlorate and perchlorate in raw, processed and finished water

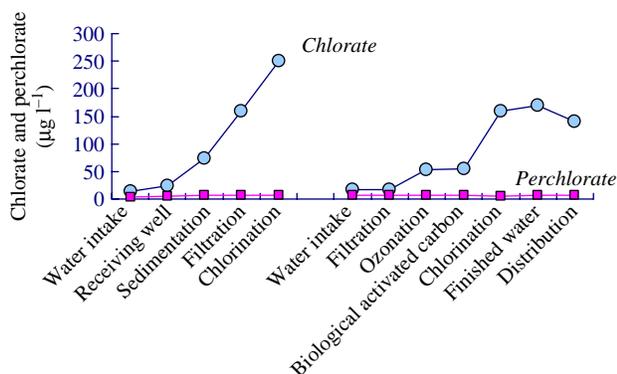
Chlorate and perchlorate concentrations in raw, processed and finished water in water treatment plants are shown in Table 1. Out of the 368 samples, chlorate was detected in 93.2% of the raw water samples and 100% of the processed and finished water samples. Perchlorate was detected in 98.8% of the raw water samples and 94.9% of the processed and finished water samples. The highest concentration of chlorate in raw water (78 µg l<sup>-1</sup>) was found in groundwater apparently affected by the chlorate and perchlorate contamination in the Tone River. The concentrations of chlorate and perchlorate, and the ratio of their concentrations, were higher in the samples taken from the Tone River Basin. Perchlorate concentrations in raw, processed and finished waters at the same treatment plant were almost unchanged during the process. Chlorate concentrations were much higher in processed and finished waters, especially in the smaller facilities located in remote areas. The maximum concentration of chlorate in this study was 2.9 mg l<sup>-1</sup> (2,900 µg l<sup>-1</sup>) due to chlorate in sodium hypochlorite solution used for disinfection.

Figures 2 and 3 show some examples of chlorate and perchlorate concentration through different stages of treatment in water treatment plants using different types of chlorine disinfectant. In Figure 2, the water treatment plant shown on the left-hand side used hypochlorite generated on-site while the plant on the right used manufactured sodium hypochlorite solutions. Chlorate concentrations increased during the treatment process. Both plants showed a large increase in chlorate concentrations. Figure 3 shows

**Table 1** | Chlorate and perchlorate concentrations in raw, processed and finished water in water treatment plants

	Chlorate (µg l <sup>-1</sup> )			Perchlorate (µg l <sup>-1</sup> )		
	Detection rate	Min*	Max	Detection rate	Min*	Max
Raw water of water treatment plants						
Tone River Basin	116/116	0.06	78	114/116	0.09	40
Other than the Tone River Basin	62/75	0.08	53	55/55	0.06	2.5
Processed water and finished water from water treatment plants						
Tone River Basin	178/178	0.17	2,900	168/178	0.05	24

\*The minimum is data detected above LO Q (limits of quantification).



**Figure 2** | Chlorate and perchlorate in water treatment plants using hypochlorite solutions (left-hand side, hypochlorite generated on-site; right-hand side, manufactured sodium hypochlorite solutions).

an example of two treatment plants where liquid chlorine was used in the disinfection processes. As such, concentrations of chlorate and perchlorate through the stages of treatment were not noticeably increased when liquid chlorine was used.

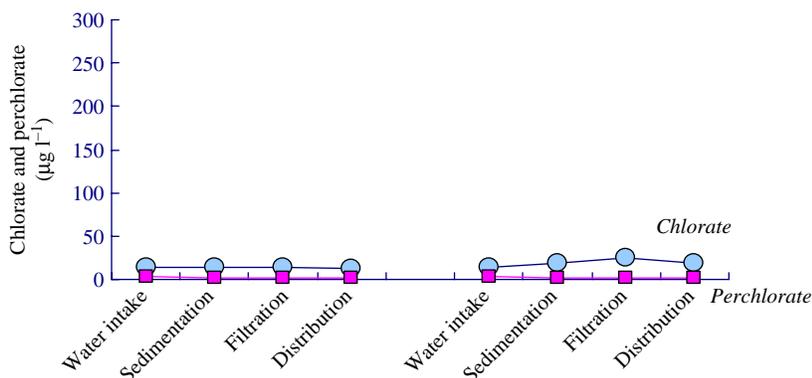
### Chlorate and perchlorate in hypochlorite solutions

For the analysis of chlorate and perchlorate concentrations, hypochlorite solutions were collected mainly from the water treatment plants investigated in the previous section. Of these, 32 sodium hypochlorite solutions were purchased and 6 hypochlorite solutions were generated on site. Measured FAC concentrations in the purchased sodium hypochlorite solutions ranged from 8.0 to 16.4%, while the FAC in on-site-generated hypochlorite solutions ranged from 1.0 to 7.2%. Chlorate concentration in the purchased sodium

hypochlorite ranged from 1,200  $\text{mg l}^{-1}$  to 26,000  $\text{mg l}^{-1}$ . The chlorate concentration varied and was above 10,000  $\text{mg l}^{-1}$  in 10 samples. Perchlorate concentrations in the purchased hypochlorite solutions ranged from 170 to 33,000  $\mu\text{g l}^{-1}$ , as shown in Table 2.

### FAC and concentration of chlorate and perchlorate

Figure 4 shows the relationship between the measured FAC concentration and the concentrations of chlorate and perchlorate per measured FAC in the hypochlorite solutions. The concentrations of chlorate and perchlorate in purchased hypochlorite solutions were higher in instances when the measured FAC was low. The maximum chlorate concentration was 26,000  $\text{mg l}^{-1}$  (320  $\text{mg g}^{-1}$  of measured FAC). The maximum concentration of perchlorate was 33,000  $\mu\text{g l}^{-1}$  (0.420  $\text{mg g}^{-1}$  of measured FAC) with the hypochlorite solution whose FAC was 8.0% while the manufacturer-specified FAC concentrations was '12.0% or above'. The manufacturer-specified FAC concentrations in the hypochlorite solutions were similar in range, from 12 to 13.2%, except for four samples for which information could not be obtained. However, the FAC concentrations ranged from 8.0 to 16.4% for purchased hypochlorite solutions. The chlorate and perchlorate concentrations were higher in hypochlorite solutions in which the FAC was lower than the manufacturer-specified FAC concentrations, while no difference was observed among nine different manufacturers. Thus, it was considered that the concentrations of chlorate and perchlorate increased with the decay of FAC in the hypochlorite solutions.



**Figure 3** | Chlorate and perchlorate in water treatment plants using liquid chlorine.

**Table 2** | Chlorate and perchlorate concentrations in hypochlorite solutions

	Chlorate (mg l <sup>-1</sup> )			Perchlorate (µg l <sup>-1</sup> )		
	Detection rate	Min*	Max	Detection rate	Min*	Max
Sodium hypochlorite (Purchased)	32/32	1,200	26,000	32/32	170	33,000
Sodium hypochlorite (On-site generation)	6/6	160	1,700	6/6	13	660

\*The minimum is data detected above LO Q (limits of quantification).

Figure 5 shows the relationship between chlorate and perchlorate concentration in purchased hypochlorite solution. Across the concentration range tested, the concentration of perchlorate was approximately three orders of magnitude lower than chlorate, though the ratio increased with the chlorate concentration, especially when the chlorate concentration was higher than 10,000 mg l<sup>-1</sup>. Therefore, their relationship was expressed as an approximate equation of the second order.

#### Hypothesized mechanism of generation of chlorate and perchlorate in hypochlorite solutions

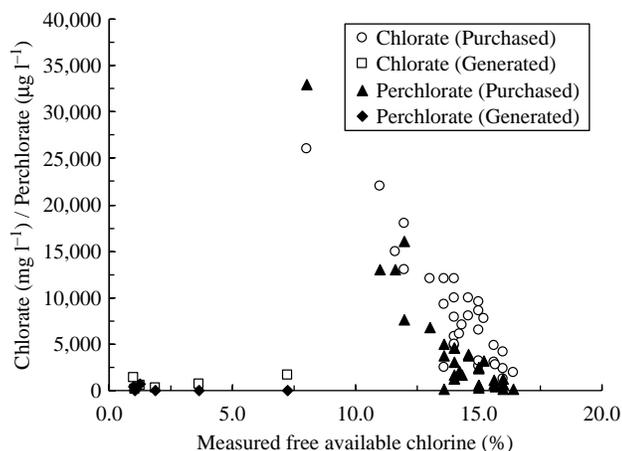
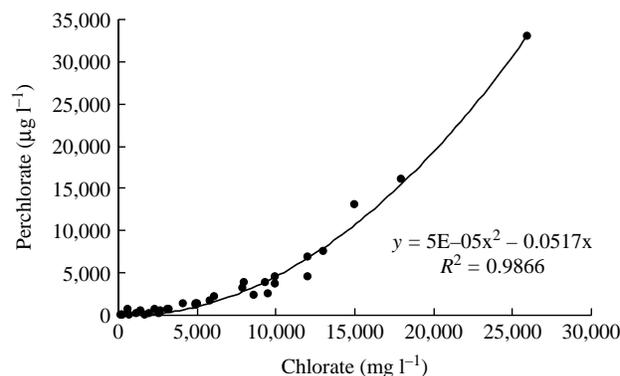
It is reported that, in hypochlorite solution, chlorate is generated from a disproportionation reaction of hypochlorous acid (HOCl) expressed by Equations (2) and (3), or a decomposition reaction of hypochlorite ion (ClO<sup>-</sup>) through chlorite ion (ClO<sub>2</sub><sup>-</sup>). It is of note that the reaction rate in Equation (2) is much faster than that in Equation (3)

(Gordon *et al.* 1995).



As shown in Figure 5, chlorate concentrations in the hypochlorite solutions were almost 1,000 times higher than perchlorate concentrations. The ratio of perchlorate to chlorate concentration was elevated under conditions where there was a corresponding increase in chlorate concentration from the decay of FAC in the hypochlorite solution. In addition, perchlorate was not found in stored chlorate standard solutions (data not shown). Considering these results, a hypothetical explanation for the presence of perchlorate in hypochlorite solution is from the reaction between chlorate and hypochlorite.

The manufacturer-specified FAC concentrations in the purchased sodium hypochlorite solutions normally ranged from 12 to 13.2%. Therefore, from the higher FAC samples (i.e. above 14%), chlorate and perchlorate concentrations in relatively fresh purchased hypochlorite solutions could be obtained. Chlorate concentrations in the solutions ranged from 1,200 to 12,000 mg l<sup>-1</sup> (average 5,900 mg l<sup>-1</sup>)

**Figure 4** | Relationship between the measured FAC concentration and the concentrations of chlorate and perchlorate per measured FAC in the hypochlorite solution.**Figure 5** | Relationship between chlorate and perchlorate concentration in purchased hypochlorite solution.

and perchlorate concentrations ranged from 170 to 4,400  $\mu\text{g l}^{-1}$  (average 1,800  $\mu\text{g l}^{-1}$ ). The ratios of perchlorate to chlorate concentration ranged from  $7.9 \times 10^{-5}$  to  $5.0 \times 10^{-4}$  (average  $2.7 \times 10^{-4}$ ), rather lower compared with the average of all solutions.

From these results, perchlorate concentrations in new hypochlorite solutions are normally low, but increase during storage. This might be controlled by controlling chlorate formation during storage.

### Chlorate and perchlorate concentrations in the on-site-generated hypochlorite solutions

The on-site-generated hypochlorite solutions had concentrations of chlorate ranging from 160 to 1,700  $\text{mg l}^{-1}$  and perchlorate from 0.013 to 0.660  $\text{mg l}^{-1}$ . Their concentrations per measured FAC are shown in Figure 4. Maximum ratios of chlorate and perchlorate were 140 and 0.053  $\text{mg g}^{-1}$  of measured FAC, respectively. The apparatus used to generate hypochlorite solutions was different in each of the companies, although the electrodes used in the apparatus were the same (titanium oxide). Thus, the reason for the difference of the chlorate and perchlorate concentrations between the on-site-generated hypochlorite solutions does not seem to be related to the material of the electrode. In addition, although the storage conditions of each on-site-generated hypochlorite solution were unknown, these conditions may have affected chlorate and perchlorate concentrations as in the case of the purchased hypochlorite solutions.

There were no reports of investigations on perchlorate generation in on-site-generated hypochlorite solutions. However, Tock *et al.* (2004) reported generation of perchlorate in water storage tanks that employed the electron voltage technique to prevent corrosion. In that study, perchlorate was generated in proportion to the contact time. It was thought that the same phenomenon might occur in on-site generation tanks.

### Estimation of chlorate and perchlorate concentration due to hypochlorite solutions

Using the manufacturer-specified FAC, chlorate and perchlorate concentrations in hypochlorite solution, maximum

chlorate and perchlorate load concentrations in hypochlorite solution were calculated. Chlorine dosage was assumed to be 10  $\text{mg l}^{-1}$ . As in the case shown in Figure 5, the manufacturer-specified FAC concentration was taken as 12.5% for purchased and 1.0% for on-site-generated hypochlorite solutions when no data were available. For the purchased hypochlorite solutions, calculated load concentrations of chlorate ranged from 92 to 2,100  $\mu\text{g l}^{-1}$ ; most of the measured values ranged from 100 to 1,000  $\mu\text{g l}^{-1}$ . The chlorate concentrations in four hypochlorite solutions exceeded 1,000  $\mu\text{g l}^{-1}$ . For on-site-generated hypochlorite solutions, the load concentrations of chlorate ranged from 160 to 1,400  $\mu\text{g l}^{-1}$ . It was shown that the load concentrations of chlorate in on-site-generated hypochlorite solutions were usually lower, but not necessarily lower than those in the purchased hypochlorite solutions.

For perchlorate, the calculated load concentrations in purchased hypochlorite solutions ranged from <0.05 to 2.8  $\mu\text{g l}^{-1}$ , with most values falling below 0.5  $\mu\text{g l}^{-1}$ . The load concentration of perchlorate in four hypochlorite solutions exceeded 1.0  $\mu\text{g l}^{-1}$ . The load concentrations in on-site-generated hypochlorite solutions ranged from <0.05 to 0.67  $\mu\text{g l}^{-1}$ . These values were much lower than those for purchased hypochlorite solutions.

### Distribution channel of sodium hypochlorite solutions

Interviews were conducted with the manufacturers, distributors and users (waterworks) involved with the distribution channel of sodium hypochlorite solutions to identify the duration of time in each distribution process. One route is direct delivery of the products from manufacturer to large facilities by trucks. The other is indirect delivery of solutions distributed by trucks to packaging facilities followed by distribution in small packages to rather small facilities. The two main routes of distribution are shown in Figure 6. Normal distribution from manufacturer to the large treatment plants and distributors is accomplished 0–7 days after production. On the other hand, indirect delivery of small packages takes longer than direct distribution. It takes 0–7 days to deliver from manufacturer to distributors and more days to deliver to the smaller water treatment facilities, though the number of interviews was limited.

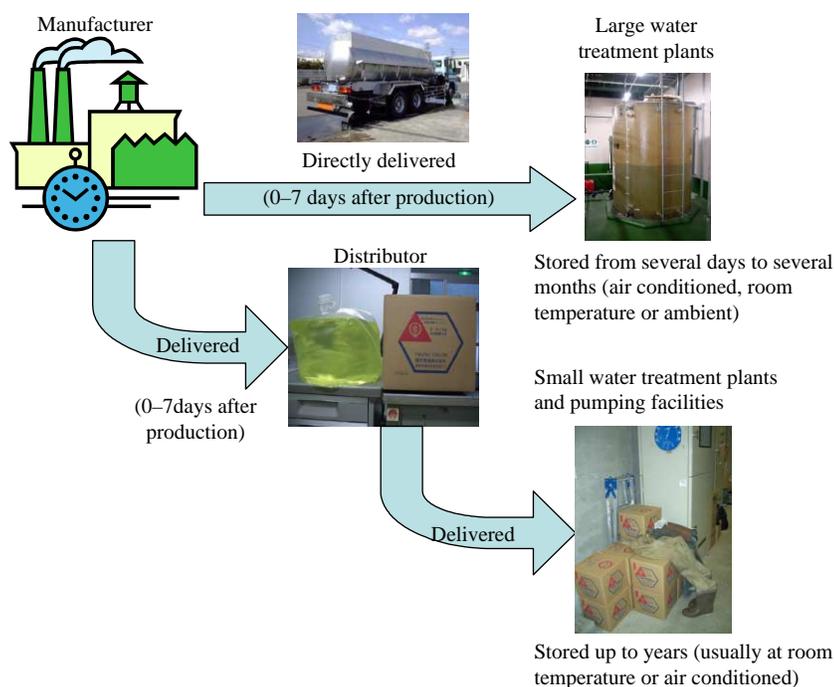


Figure 6 | Distribution channels for sodium hypochlorite.

In this study, initial concentrations of chlorate and perchlorate in hypochlorite solutions at the manufacturers were not studied; however, the concentrations of chlorate and perchlorate are not noticeably high in relatively fresh solutions. Control of the distribution process and storage is the key factor to control chlorate and perchlorate as far as this study is concerned. Since the temperature of storage and the impurities in the sodium hypochlorite solutions have been pointed out to affect the decay of hypochlorite (JWWA 2006), further study is needed to prove the factors affecting degradation of hypochlorite in sodium hypochlorite solutions. In addition, further research is required on the relationship between concentrations of chlorate and perchlorate and their generation conditions in on-site generation facilities for hypochlorite.

## CONCLUSIONS

- Higher concentrations of bromate and chlorate were found in hypochlorite solutions stored for longer periods of time, more than two years at a maximum; their maximum concentrations were 414 and 260,000  $\text{mg l}^{-1}$ , respectively.
- A survey was conducted to reveal the concentrations of chlorate and perchlorate in raw, processed and finished water and hypochlorite solutions. The highest concentration of chlorate in raw water was 78  $\mu\text{g l}^{-1}$  and that of perchlorate was 40  $\mu\text{g l}^{-1}$ .
- In purchased hypochlorite solutions tested, perchlorate concentrations ranged from 0.170 to 33.0  $\text{mg l}^{-1}$ .
- In hypochlorite solutions whose measured FAC concentration was lower than the manufacturer-specified FAC concentration, the chlorate and perchlorate concentrations were higher than those in the relatively fresh hypochlorite solutions. The ratio of perchlorate to chlorate concentration in the relatively fresh hypochlorite solutions was around  $10^{-3}$ .
- In on-site-generated hypochlorite solutions, the maximum concentrations of chlorate and perchlorate were 1,700  $\text{mg l}^{-1}$  (140  $\text{mg g}^{-1}$  of measured FAC) and 0.660  $\text{mg l}^{-1}$  (0.053  $\text{mg g}^{-1}$  of measured FAC), respectively.
- Perchlorate in hypochlorite solutions was considered to be produced by degradation of hypochlorite and reaction with chlorate.

## ACKNOWLEDGEMENTS

The authors express special thanks to the water supply bodies for providing samples and information for this research. This study was financially supported by the grant-in-aid for Basic Science Research (C)-19560557. The authors also thank Dr Shane Snyder and Dr Benjamin Stanford, Southern Nevada Water Authority, for their advice in preparing this manuscript.

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First received 7 February 2008; accepted in revised form 28 July 2008. Available online January 2009