

Behavior of hexavalent chromium in the water supply system by IC-ICP-MS method

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ABSTRACT

The analysis conditions for measuring trace concentration of Cr(VI) based on the ion chromatography-inductively coupled plasma-mass spectrometry (IC-ICP-MS) method was examined. By optimizing the analysis conditions, the measurement of 0.02 $\mu\text{g-Cr(VI)/L}$ was achieved with a high degree of accuracy. The behavior of Cr(VI) through the water treatment process in Osaka city was investigated and it was determined that there was a tendency that the Cr(VI) concentration slightly fluctuated throughout the water treatment process with the highest concentration being observed in finished water. The Cr(VI) concentration at the outlet of Kunijima purification plant was less than 0.02–0.13 $\mu\text{g/L}$, while water taps where retention time from the plant was 4–15 h, were less than 0.02–0.10 $\mu\text{g/L}$. Also, it was found that Cr(III) was oxidized to Cr(VI) by sodium hypochlorite and ozone being used in the water treatment process. Based on this finding, the oxidation reaction of Cr(III) to Cr(VI) was examined. When sodium hypochlorite was added to granular activated carbon (GAC)-treated water and purified water containing Cr(III), the oxidation of Cr(III) to Cr(VI) proceeded and the Cr(VI) production in GAC-treated water was relatively higher. In addition, it was determined that the Cr(III) oxidation reaction rate depended on water temperature and it was faster when the water temperature was higher.

Key words | hexavalent chromium, IC-ICP-MS, oxidation reaction, speciation analysis, water treatment process

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INTRODUCTION

Chromium is a transition element that belongs to the sixth group in the periodic table. It has many oxidation states and stably exists in the environmental water primarily as two oxidation states, i.e. trivalent chromium Cr(III) and hexavalent chromium Cr(VI).

Cr(III) is a naturally-occurring form and an essential element that is necessary for humans because it is related to glucose and protein metabolism. On the other hand, Cr(VI) is a form used by industrial processes such as plating, paint, catalyst, cement, and surface treatment. It is categorized as group 1 (carcinogen for humans) by International Agency for Research on Cancer (IARC) and a maximum contaminant level (MCL) of 0.05 mg/L (provisional value) is set in the Guidelines for Drinking Water Quality, fourth edition (World Health Organization 2011). The water quality

standards for drinking water in Japan also sets 0.05 mg/L as the standard value of Cr(VI) compound. A more stringent standard value may be defined in the future as US Environmental Protection Agency (USEPA 2010) and other organizations have been working on review of the standard value including a more stringent evaluation value.

The analysis of Cr(VI) is generally performed by using diphenylcarbazide spectrophotometry or by using iron coprecipitation that precipitates and removes Cr(III) followed by flame atomic absorption spectrometry, inductively coupled plasma-optical emission spectrometry (ICP-OES) method, or ICP-mass spectrometry (ICP-MS) method. For example, the sensitivity of diphenylcarbazide method is not enough to detect trace level of Cr(VI), while the pre-treatment of the other methods is very complicated.

Therefore, total chromium (hereinafter referred to as T-Cr) concentration has been commonly used instead of Cr(VI) concentration in drinking water test in Japan. However, if a more stringent standard value is adopted, the conventional methods will not be sufficient to determine the actual low concentration of Cr(VI) with appropriate accuracy. It is therefore necessary to conduct a study on an analysis method that enables quantification of Cr(VI) at trace concentration.

We used the ion chromatography-ICP-MS (IC-ICP-MS) system that combined IC which enabled chemical speciation and ICP-MS which enabled measurement of ultralow concentration (Inoue *et al.* 1995; Barnowski *et al.* 1997). Trace level of Cr(VI) can be determined simply, accurately and correctly by this method compared to the other methods. We also investigated the behavior of Cr(VI) in the water purification system and identified properties of oxidative formation from Cr(III).

MATERIAL AND METHOD

Purified water and reagent

Purified water supplied by Milli-QA10 ultrapure water of Millipore was used and chromium standard solution I (Cr(VI) for atomic absorption spectrometry) and chromium standard solution II (Cr(III) for atomic absorption spectrometry) available from Kanto Chemical were used as a standard solution.

The diluted Cr(VI) standard solution (5 µg/L) at approximately pH 7 was confirmed to be stable for a week in purified water, raw water, and finished water of the water purification plant.

Analysis of Cr in the solution

For Cr(VI) under acidic condition, chromate ion (CrO_4^{2-}) is converted to dichromate ion ($\text{Cr}_2\text{O}_7^{2-}$) with high oxidation-reduction potential, which may result in damage to the separation column (Dionex Corporation 1991). For this reason, when the pH value of the sample was less than 5.8, it was adjusted to 6–8 with aqueous ammonia before conducting

the analysis using the IC-ICP-MS method. For T-Cr concentration, concentrated nitric acid solution was added to a sample to become 1% concentration and then the ICP-MS method was used to measure T-Cr concentration. In our study, Cr(VI) was measured using the IC-ICP-MS method, as mentioned above, while Cr(III) concentration was calculated by subtracting Cr(VI) from T-Cr concentration.

The samples were stored using glass bottles and 50 mL polyethylene centrifuge tubes. If the samples contained suspended matters, they were filtered using membrane filters having 0.20 µm pore diameter or glass fiber filters. We confirmed that the filtration did not change the concentration of Cr(VI), since it is an ionic species.

IC-ICP-MS system

IonPac AS19 (anion-exchange column) available from Dionex Corporation was used as a separation column in the IC and the eluent was 60 mM KOH solution. A self-regenerating suppressor was used for improved measurement sensitivity (Gürleyük & Wallschläger 2001). In the ICP-MS section, 8% H_2 -He gas was added as the collision gas to remove molecular interference ions, such as $^{40}\text{Ar}^{12}\text{C}$ and $^{56}\text{Ar}^{16}\text{O}$, that hinder ^{52}Cr measurement (Ogawa *et al.* 2010). Specific analysis conditions are listed in Table 1.

Because Cr(III) exists as cationic hydroxo species and Cr(VI) is present in anionic chromate species in the

Table 1 | IC-ICP-MS analysis conditions

IC parameters	
Column	IonPac AS19
Injection volume	100 µL
Flow rate	0.25 mL/min
Eluent	60 mM KOH
ICP-MS parameters	
Forward power	1400 W
Nebulizer gas flow	0.84 L/min
Auxiliary gas flow	0.80 L/min
Isotope	^{52}Cr ($m/z = 51.94$)
Dwell time	100 msec
Cell gas	8% H_2 in He
Cell gas flow rate	3.0 mL/min

environmental water (Sperling *et al.* 1992), it is impossible to separate Cr(III) and Cr(VI) using a single method. In this method, the minimum limit of determination of Cr(VI) was 0.02 µg/L and the CV value was 7.5% when the sample which contained 0.02 µg/L of Cr(VI) was measured five times. The Cr(VI) standard solution was added 0.02 µg/L to raw water and finished water in Kunijima water purification plant, the recovery rates were obtained by measuring both samples five times. They were 102.8 and 101.6%, respectively.

The example of chromatograph obtained by 0.02 µg-Cr(VI)/L and the calibration curve are shown in Figures 1 and 2, respectively.

Field investigation

The behavior of Cr(VI) in the water treatment process of Kunijima purification plant was researched, and the Cr(VI) concentration was measured in the water tap in Osaka city. The tap water samples were taken from eight points, where finished water of Kunijima purification plant was supplied. The retention time from the purification plant to each tap was assumed 4–15 h. As shown in Figure 3, the water treatment system in Osaka city consists of coagulation, sedimentation, two-stage ozonation, rapid sand filtration, and granular activated carbon (GAC) adsorption. Sodium hypochlorite used as a

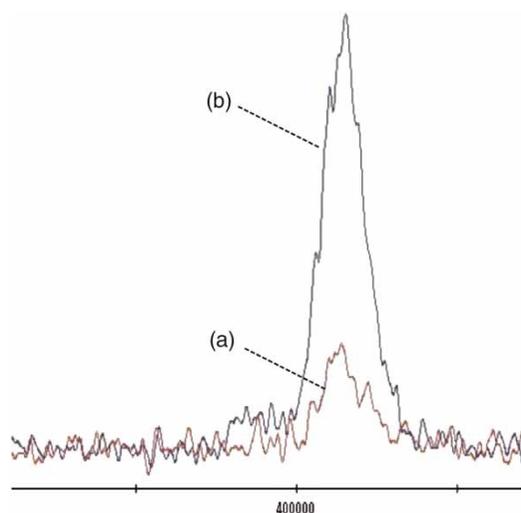


Figure 1 | Chromatograph of 0.02 µg-Cr(VI)/L (a): purified water, (b): 0.02 µg-Cr(VI)/L.

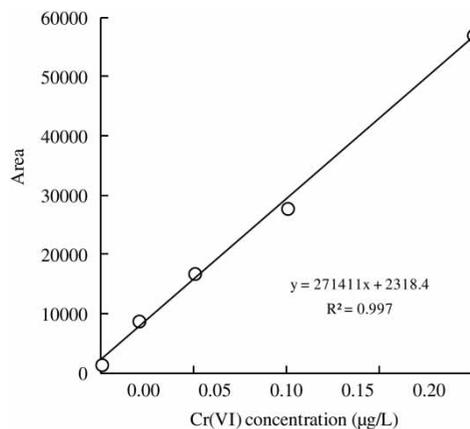


Figure 2 | Calibration curve of Cr(VI).

disinfectant is added after GAC treatment, therefore, GAC-treated water does not contain chlorine.

Oxidation of Cr(III) by sodium hypochlorite

It is known that Cr(III) is oxidized to Cr(VI) by sodium hypochlorite (Ulmer 1986; Clifford & Chau 1988; Brandhuber *et al.* 2004; Lai & McNeill 2006). We examined a relationship between contact time and the Cr(VI) production when sodium hypochlorite was added to the samples that were added 10 µg-Cr(III)/L to purified water and GAC-treated water. The reason of using GAC-treated water was that sodium hypochlorite concentration could be controlled in the experiments and ionic strength was almost equal to finished water. For Cr(VI) measurement, a sample was taken, dechlorinated using sodium thiosulfate, and then used for the analysis.

We investigated the effects of chloride ion, pH value, and water temperature on the oxidation of Cr(III) to Cr(VI). Using test water that was prepared as described below for each investigation, the relationship between the Cr(VI) production by sodium hypochlorite and the contact time were examined. Cr(III) was added 10 µg/L to the samples in advance of each experiment.

Chloride ion

The samples were prepared by adding potassium chloride to purified water so that chloride ion concentration of the

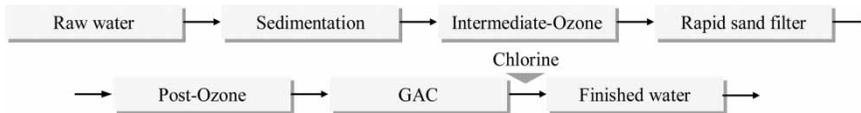


Figure 3 | Water treatment system in Osaka city.

samples was 0, 20, and 180 mg/L. The GAC-treated water was used for comparison.

pH value

The sample prepared by adding 0.2 mM of phosphate buffer solution to purified water was divided into three sub-samples and the pH value of the sub-samples were adjusted to 4.1, 5.8, and 6.9 using nitric acid or aqueous ammonia. Phosphate is reported to precipitate with Cr(III); however, we confirmed that the concentration of our experiment condition did not show any precipitation.

Water temperature

Three samples with different water temperature were prepared using a refrigerator (6.5 °C) and a constant-temperature oven (20.3 and 30.3 °C) to store GAC-treated water for 1 day.

Oxidation of Cr(III) by ozone

The oxidation of Cr(III) to Cr(VI) was also examined by ozone which has higher oxidation–reduction potential than sodium hypochlorite. Rapid sand filtrate and purified water that added 10 µg-Cr(III)/L were applied ozone treatment. The ozone injection rate was set at 0.25 mg-O₃/(L/min). The Cr(VI) measurement samples were deoxygenated by sodium thiosulfate.

RESULTS AND DISCUSSIONS

Field investigation

Figure 4 shows the behavior of Cr(VI) through the water treatment process of Kunijima purification plant. The

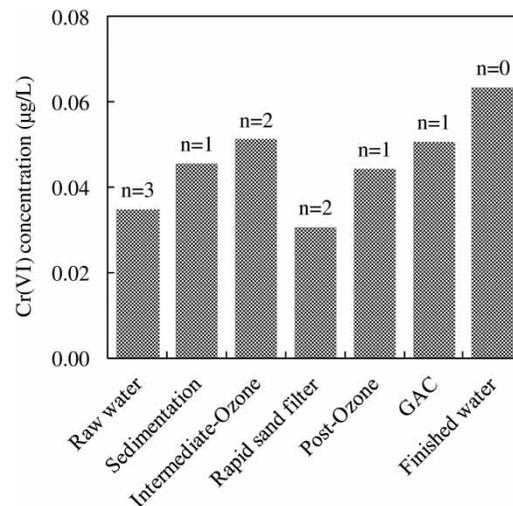


Figure 4 | Average concentration of Cr(VI) in the water treatment process (August–December 2010, N = 11).

process was examined 11 times and some results were less than the minimum limit of determination which was 0.02 µg/L. Their frequencies were indicated by the form ‘n = x’ in Figure 4 when x times were observed less than 0.02 µg/L. We detected Cr(VI) in more than 70% of raw waters, therefore, we have concluded that Cr(VI) has been contained in natural river water. The average concentration of Cr(VI) in raw water was 0.03 µg/L. The concentration increased slightly, as shown in Figure 4, and finished water contained around 0.06 µg/L on average. Cr(VI) was found to decrease at rapid sand filtration, because of the reduction of Cr(VI) to Cr(III) by biological activity in the filter (Wang & Xiao 1995; Han *et al.* 2010; Dogan *et al.* 2011). The reason of the increase of Cr(VI) through the treatment process was considered the oxidation of Cr(III) by ozone and chlorine (Ulmer 1986; Clifford & Chau 1988; Brandhuber *et al.* 2004; Lai & McNeill 2006).

The concentration change of Cr(VI) in the distribution process was observed by comparing the concentration of

finished water and tap water. The Cr(VI) concentrations less than 0.02 µg/L were observed nine times in raw water, four times in finished water, and once in tap water. Figure 5 shows the result on which Cr(VI) in finished water and tap water were 0.06 and 0.05 µg/L, respectively. The reason that the average concentration in taps is lower than that of finished water is assumed due to the difference of sample number, 50 samples at finished water instead of 18 samples at tap water.

Figure 5 also shows Cr(VI) in raw water. When these results were considered, it was concluded that Cr(VI) had increased by oxidants, such as ozone and chlorine in the purification process, while it had not increased in the distribution process despite tap water had always contained free residual chlorine. The reason that the oxidation to Cr(VI) was not observed in the distribution process was assumed to be due to lack of chromium species which could be oxidized, since most of them had been oxidized in the purification process.

Oxidation of Cr(III) by sodium hypochlorite

Figure 6 shows the change in T-Cr concentration and Cr(VI) production over time after sodium hypochlorite was added. During this investigation, free residual chlorine concentration was kept at 0.70 mg/L in purified water. In GAC-treated water (chloride ion: 17.5 mg/L), although it was reduced from 0.70 to 0.14 mg/L, sufficient free residual

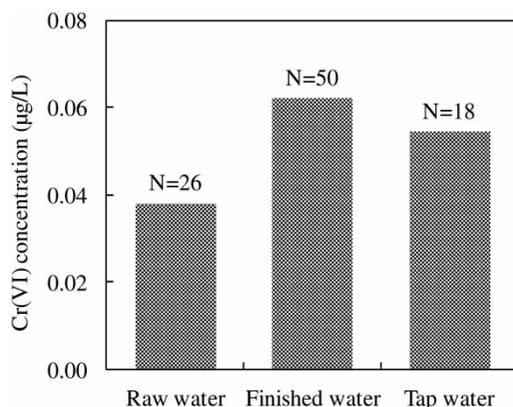


Figure 5 | Average concentration of Cr(VI) in the water distribution system (August 2010 to March 2011).

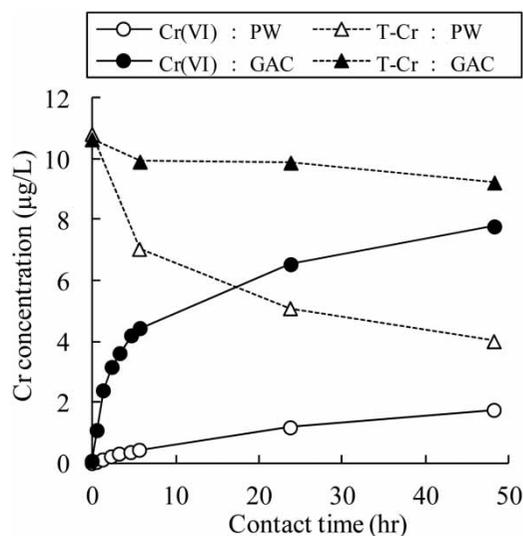


Figure 6 | Change in T-Cr concentration and Cr(VI) production over time after sodium hypochlorite was added. Condition: pH 5.8 (purified water, PW), 6.9 (GAC-treated water); water temperature 20 °C.

chlorine concentration relative to Cr concentration was maintained.

In purified water, T-Cr concentration reduced over time and it was approximately 40% of Cr(III) concentration 2 days after sodium hypochlorite was added. From the fact that no precipitate was confirmed in the sample of purified water and only slight reduction of T-Cr was confirmed in the sample of GAC-treated water, it was assumed that the adsorption of Cr(III) on the apparatus surface was the reason for the T-Cr reduction. To confirm this, nitric acid solution was poured to some glass beaker which was used to the Cr oxidation experiment and showed the reduction of T-Cr concentration. Around 30% of the decreased amount of chromium was detected, therefore, we concluded that glass apparatus adsorbs some chromium species under certain conditions.

The Cr(VI) production gradually increased after sodium hypochlorite was added, and it was 1.75 µg/L after 48 h in purified water. In GAC-treated water, T-Cr concentration reduced by approximately 10% while the Cr(VI) production was higher compared with that in purified water reaching 7.79 µg/L after 48 h. Based on the result, it was determined that Cr(III) was oxidized to Cr(VI) largely in finished water by sodium hypochlorite that being used in the water treatment process, while not in purified water.

Chloride ion

Figure 7 shows the change in Cr(VI) production over time for different chloride ion concentration in the samples. The concentration of chloride ion in GAC-treated water was 13.0 mg/L. Free residual chlorine concentration was maintained at 0.48–0.80 mg/L.

It was found that the coexistence of chloride ion in the sample enhanced the oxidation of Cr(III) to Cr(VI), and the Cr(VI) production increased when chloride ion concentration was higher. By coexistence of 20 mg/L chloride ion, the production of Cr(VI) increased to four times compared to that in purified water. Clifford reported that chromium forms complex with chloride ion and it was assuming that the complex was easier to oxidize than the hydrated one. While the chloride ion in GAC-treated water is almost equal to that of purified water which was added 20 mg/L chloride ion, the production of Cr(VI) in GAC-treated water was more than that in purified water. On the other hand, the result that when chloride ion concentration was higher, the adsorption of T-Cr on the apparatus surface was less, was obtained. It was observed that chloride ion might not only depress the adsorption of T-Cr but also enhance the oxidation of Cr(III) to Cr(VI).

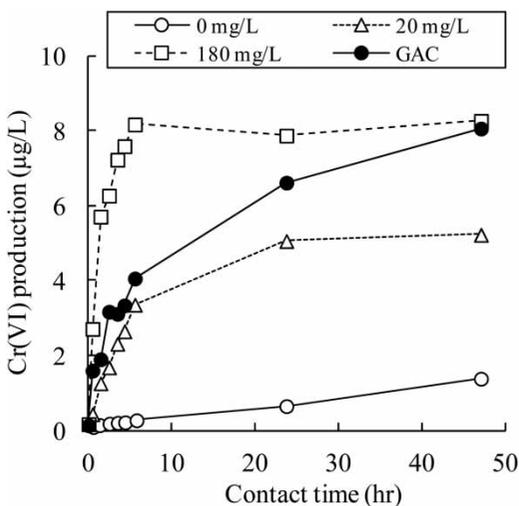


Figure 7 | Change in Cr(VI) production over time for different chloride ion concentrations in the sample. **Condition:** pH 5.8 (purified water, PW), 6.8 (GAC-treated water); water temperature 20 °C.

Effect of pH with or without chloride ion

Figure 8 shows the change in Cr(VI) production over time for different pH values for the sample water without chloride ion. Free residual chlorine concentration was maintained at 0.40–0.64 mg/L.

Almost no effect of pH on the oxidation of Cr(III) to Cr(VI) was observed in this experiment. The produced amount of Cr(VI) was the same in the three pH condition, which show that less than 10% of T-Cr was oxidized to Cr(VI). On the other hand, it was confirmed that the adsorption of T-Cr was depressed by lowering pH value. T-Cr concentration for the sample at pH 4.1 showed little change even after 48 h. Concentration of T-Cr in the samples at pH 5.8 and 6.9 decreased, the reduction amount of T-Cr at pH 6.9 was larger than that at pH 5.8. This implied that the reduction was due to the adsorption of chromium hydroxide complexes.

The investigation of the effect of pH value on Cr(VI) production in the solution of which chloride ion concentration were 180 mg/L was done (data not shown). It was found that the Cr(VI) production of the sample at pH 4 was approximately one third that of the pH 5.8 sample at 48 h after sodium hypochlorite was added, while T-Cr

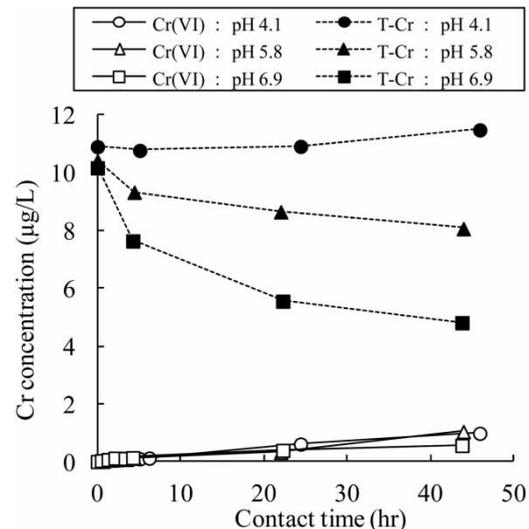


Figure 8 | Change in Cr(VI) production over time when sodium hypochlorite was added. **Condition:** water temperature 20 °C.

concentration did not decrease. Compared to the results at around pH 4 with or without chloride ion, however, Cr(VI) production with chloride ion increased 2.5 times more than the result without chloride ion. We concluded that chloride ion could enhance the oxidation of Cr(III) even under the condition of low pH value, in which the oxidation of Cr(III) was depressed.

Water temperature

Figure 9 shows the change in Cr(VI) production over time for different water temperature. During this investigation, free residual chlorine concentration was reduced from 0.66 to 0.26 mg/L in the sample at 6.5 °C, from 0.64 to 0.14 mg/L at 20.3 °C and from 0.60 to 0.04 mg/L at 30.3 °C.

It was observed that the Cr(VI) production was higher when water temperature was higher. Assuming that the oxidation reaction follows a pseudo-first-order reaction, the reaction rate constants were calculated as $k_{6.5\text{ }^{\circ}\text{C}} = 4.83 \times 10^{-4} \text{ (min}^{-1}\text{)}$, $k_{20.3\text{ }^{\circ}\text{C}} = 1.43 \times 10^{-3} \text{ (min}^{-1}\text{)}$, and $k_{30.3\text{ }^{\circ}\text{C}} = 3.96 \times 10^{-3} \text{ (min}^{-1}\text{)}$. In Figure 10, these constants were plotted against the sample water temperature according to Arrhenius equation. As the Arrhenius plot with a coefficient of determination of $R^2 = 0.991$ showed a good linear relationship, it was identified that the Cr(III) oxidation reaction depended on water temperature.

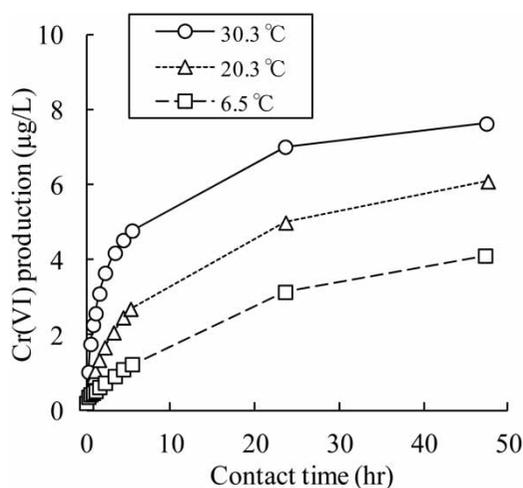


Figure 9 | Change in Cr(VI) production for different water temperature. Condition: pH 6.8.

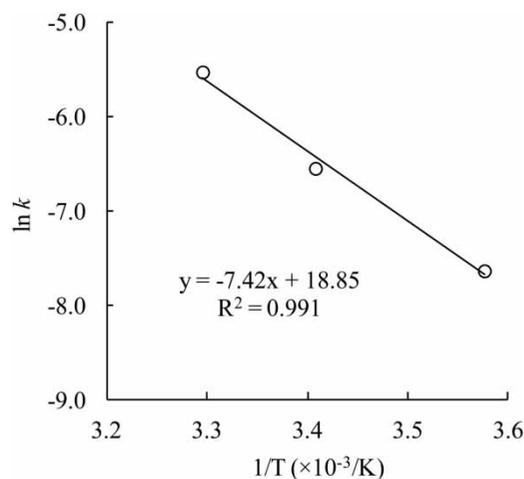


Figure 10 | Arrhenius plot.

Oxidation of Cr(III) by ozone

Figure 11 shows the change in Cr(VI) production over time when ozone treatment was applied. Dissolved ozone concentration was 0.4 mg/L in rapid sand filtrate and 0.3 mg/L in purified water after 15 min ozone treatment.

The Cr(VI) production in rapid sand filtrate water was higher than that of purified water. This implied there might exist one or more factors, such as chloride ion, that promoted the oxidation of Cr(III) to Cr(VI) in rapid sand filtrate, as observed in the experiment of Cr(III) oxidation by sodium

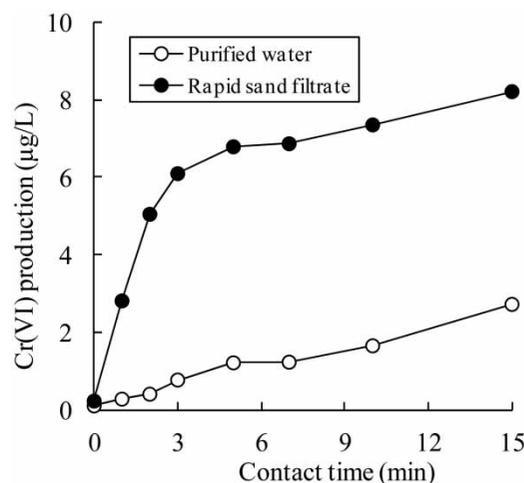


Figure 11 | Change in Cr(VI) production over time when ozone treatment was applied. Condition: pH 5.8 (purified water), 6.9 (rapid sand filtrate); water temperature 21 °C.

hypochlorite. Chloride ion concentration in rapid sand filtrate was approximately equal to that in the GAC-treated water.

Considering the results of the oxidation of Cr(III) to Cr(VI) in purified water by sodium hypochlorite and ozone, it was obvious that Cr(III) oxidation might have occurred under the drinking water treatment condition because certain amount of chloride ion was included in the water.

CONCLUSIONS

- (1) With regard to the behavior of Cr(VI) during the water treatment process in Osaka city, there was a tendency that Cr(VI) concentration slightly fluctuated throughout the water treatment process with the highest concentration being observed in finished water. Cr(VI) concentration during the water distribution system was 0.06 µg/L at finished water and 0.05 µg/L at the water tap, representing approximately 1/900 of the current water quality standard for drinking water.
- (2) The Cr(III) oxidation reaction was examined and the following results were obtained.
 - Cr(III) is oxidized to Cr(VI) by sodium hypochlorite or ozone.
 - The Cr(VI) oxidation in water was increased by the coexistence of chloride ion concentration.
 - The Cr(III) oxidation reaction depends on water temperature, and the rate of Cr(VI) production grows faster when the water temperature becomes higher.

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