

Behavior of Hexavalent Chromium in 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 IC-ICP-MS method was examined. By optimizing the analysis conditions, the measurement of 0.02 µg-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 increased and decreased throughout the water treatment process with the highest concentration being observed in finished water. The Cr(VI) concentration was 0.06 µg/L at the outlet of the water purification plant and 0.05 µg/L at the water tap. 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 founding, the oxidation reaction of Cr(III) to Cr(VI) was examined. When sodium hypochlorite was added to 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.

Keywords

Hexavalent chromium; speciation analysis; IC-ICP-MS; water treatment process; oxidation reaction

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 with glucose and protein metabolism. On the other hand, Cr(VI) is a form generated 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 specified in the Guidelines for Drinking Water Quality, Third Edition (World Health Organization, 2004). The water quality standards for drinking water in Japan also specifies 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 (EPA, 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, ICP-OES method, or ICP-MS method. Because each of these measurements has problems with sensitivity and accuracy at low concentration and requires a complicated analytical

procedure, total chromium (hereinafter referred to as T-Cr) concentration has been commonly used instead of Cr(VI) concentration in drinking water in Japan. However, if a more stringent standard value is adopted, the common method will be unable to determine the actual low concentration of Cr(VI) with an 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 IC-ICP-MS system that combined IC that enabled chemical speciation and ICP-MS that enabled measurement of ultralow concentration to examine a separated determination method of Cr(VI). We also investigated the behavior of Cr(VI) in the water supply system and identified properties of oxidative formation from Cr(III).

MATERIAL AND METHOD

Test water and Reagent

Purified water supplied by Milli-QA10 ultrapure water production system from Nihon 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 existed stably for a week in purified water, raw water, and finished water of the water purification plant.

Analysis sample

For Cr(VI) at pH 6 or less, 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 a damage to the separation column (Dionex Corporation, 1991). For this reason, when the pH value of the sample was 6 or less, 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% and then the ICP-MS method was used to measure 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.

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 *et al.* 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 $^{36}\text{Ar}^{16}\text{O}$, 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 environmental water (Sperling *et al.* 1992), it is impossible to separate Cr(III) and Cr(VI) using a

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

single method. In our study, Cr(VI) was measured using the IC-ICP-MS method while Cr(III) concentration was calculated by subtracting Cr(VI) from T-Cr concentration.

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.

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 seven points, where finished water of Kunijima purification plant was supplied. The retention time from the purification plant to each taps were assumed 4 to 15 hours. As shown in Figure 1, the water treatment system in Osaka city consists of coagulation, sedimentation, two-stage ozonation, rapid sand filtration, and GAC.

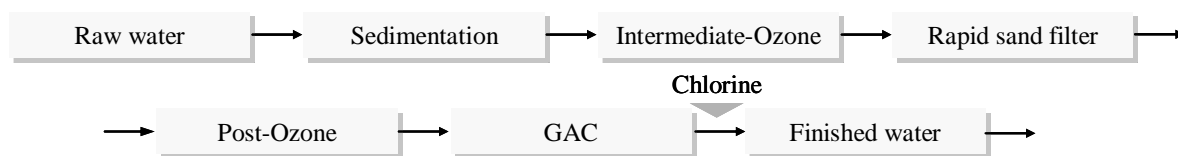


Figure 1. Water treatment system in Osaka city

Oxidation of Cr(III) by sodium hypochlorite

It is known that Cr(III) is oxidized to Cr(VI) by sodium hypochlorite (Brandhuber *et al.* 2004; Lai *et al.* 2006). We examined a relationship between the 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 conducted the investigations on possible effects: 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 10µg/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 samples was 0 mg/L, 20 mg/L, and 180 mg/L. The GAC-treated water was used for comparison. It is known that, under the presence of chloride ion, Cr(III) forms chloro-complexes that are soluble in water (Clifford *et al.* 1988).

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, 6, and 7 using nitric acid or aqueous ammonia. Based on the solubility product ($6.3 \times 10^{-31} \text{ M}^4$) for chromium hydroxide, Cr(III) exists in a dissolved state in the sample at pH 4 while in the sample at pH 6 and 7, hydrolysis takes place gradually and insoluble chromium hydroxides are formed.

water temperature: Three samples with different water temperature were prepared using a refrigerator (6.5°C) and a constant-temperature oven (20.3°C and 30.3°C) to store GAC-treated water for one 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 μ g-Cr(III)/L were applied ozone treatment. The ozone injection rate was settled 0.25 mg-O₃/(L/min). The Cr(VI) measurement samples were deoxygenated by sodium thiosulfate. The reason of using rapid sand filtrate was that ozone treatment was executed to rapid sand filtrate.

RESULTS AND DISCUSSIONS

Field investigation

Figure 2 shows the behavior of Cr(VI) through the water treatment process of Kunijima purification plant. We examined raw water 13 times and 10 determination results were at or more than the minimum limit of determination which was 0.02 μ g/L. The average concentration of Cr(VI) in raw water was 0.03 μ g/L (0.026 μ g/L), therefore, we have concluded that Cr(VI) has been contained in natural river water. The concentration increased slightly, as shown in Figure 2, and finished water contained around 0.07 μ g/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 *et al.* 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 (Brandhuber *et al.* 2004; Lai *et al.* 2006).

The concentration change of Cr(VI) in the distribution process was observed by comparing the concentration of finished water and tap water. Figure 3 shows the result on which Cr(VI) in finished water and tap water were 0.06 μ g/L and 0.05 μ g/L, respectively. Figure 3 also shows Cr(VI) in raw water. Considering these results together, it was concluded that Cr(VI) has 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 being lack of chromium species which would oxidized all in the purification process.

Oxidation of Cr(III) by sodium hypochlorite

Figure 4 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

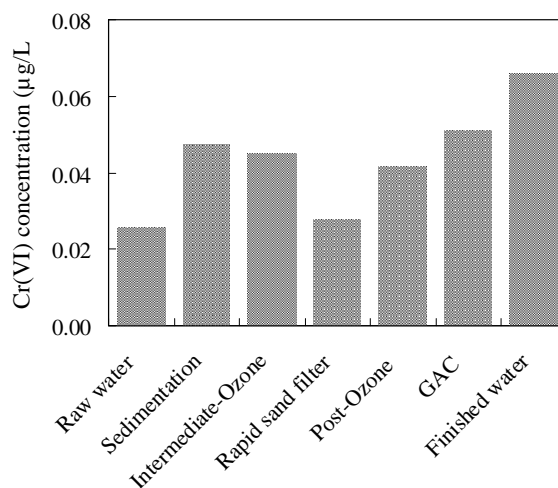


Figure 2. Average concentration of Cr(VI) in the water treatment process (August to December 2010, N=13)

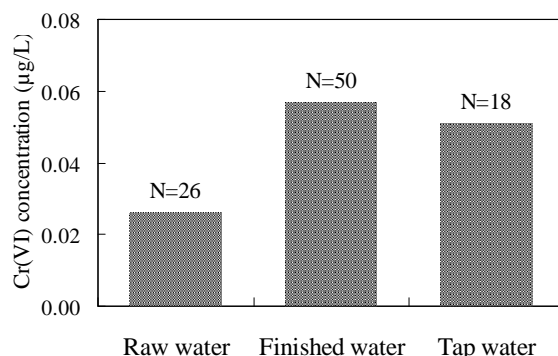


Figure 3. Average concentration of Cr(VI) in the water distribution system (August 2010 to March 2011)

0.70 mg/L in purified water. In GAC-treated water (chloride: 17.5 mg/L), although it was reduced from 0.70 mg/L to 0.14 mg/L, sufficient free residual 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 two days after sodium hypochlorite was added. The Cr(VI) production gradually increased after sodium hypochlorite was added, and it was 2.01 $\mu\text{g/L}$ 48 hours later. In GAC-treated water, T-Cr concentration reduced by approximately 10% while the Cr(VI) production was higher compared with that in purified water system reaching 7.79 $\mu\text{g/L}$ 48 hours later. Based on the result, it was determined that Cr(III) was oxidized to Cr(VI) by sodium hypochlorite that being used in the water treatment process.

Chloride ion

Figure 5 shows the change in Cr(VI) production over time for different chloride ion concentration in the samples. Free residual chlorine concentration was maintained at 0.48–0.80 mg/L.

It was found that the existence of chloride ion in the sample enhanced the oxidation of Cr(III) to Cr(VI), and the Cr(VI) production was increased when chloride ion concentration was higher. This was due to the fact that one or more H_2O molecules that were ligands of chromium hydroxide having a regular octahedron structure were replaced with one or more chloride ions to form easy-to-oxidize chloro-complexes. Though chloride ion concentration in GAC-treated water was 13 mg-Cl/L which was almost equal to the 20 mg-Cl/L sample, the Cr(VI) production was much higher in GAC-treated water than that of the 20 mg-Cl/L sample. This result suggested that there might be one or more factors to enhance the oxidation of Cr(III) to Cr(VI).

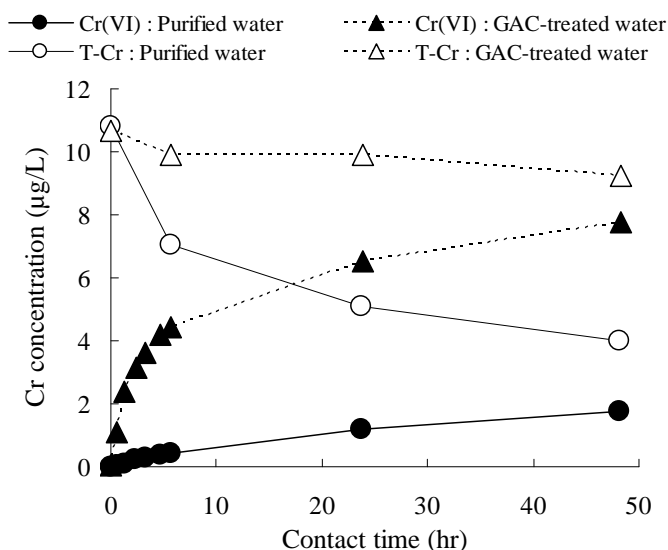


Figure 4. Change in T-Cr concentration and Cr(VI) production over time after sodium hypochlorite was added

Condition: pH 6.5 (purified water), 6.9 (GAC-treated water); water temperature 20°C

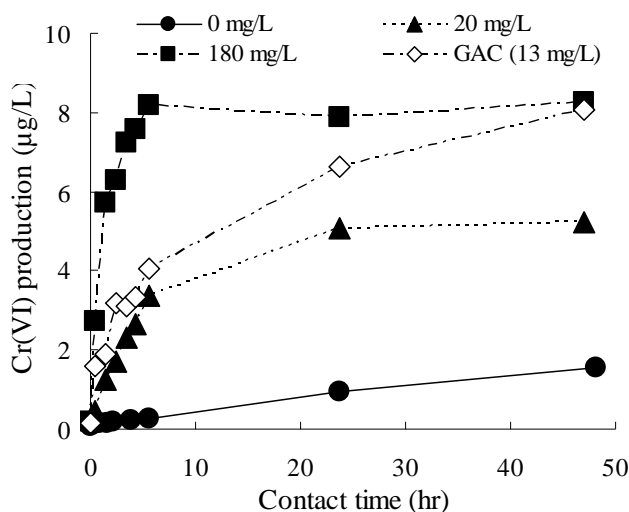


Figure 5. Change in Cr(VI) production over time for different chloride ion concentrations in the sample

Condition: pH 6.5 (purified water), 6.8 (GAC-treated water); water temperature 20°C

Effect of pH

Figure 6 shows the change in Cr(VI) production over time for different pH values for the sample water. Free residual chlorine concentration was maintained at 0.40–0.64 mg/L.

T-Cr concentration for the sample at pH 4.1 showed little change. But, we found the reduction of T-Cr concentration in the samples at pH 5.8 and 6.9. 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 formation chromium hydroxides which were insoluble complexes.

As to Cr(VI) production, there was little change. It was assumed that the little production of Cr(VI) in purified water was inhibited by the formation of Cr(III)-hydroxide complexes which were hard-to-oxidize (Clifford *et al.* 1988).

The investigation of the effect of pH value on Cr(VI) production both 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 one fourth times than that of the sample at pH 6.5 48hours later after sodium hypochlorite was added, while there was the same trend in T-Cr concentration.

Water temperature

Figure 7 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 mg/L to 0.26 mg/L in the sample at 6.5°C, from 0.64 mg/L to 0.14 mg/L at 20.3°C and from 0.60 mg/L 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 $k_{6.5^{\circ}\text{C}} = 3.30 \times 10^{-4} (\text{min}^{-1})$, $k_{20.3^{\circ}\text{C}} = 8.81 \times 10^{-4} (\text{min}^{-1})$, and $k_{30.3^{\circ}\text{C}} = 2.84 \times 10^{-3} (\text{min}^{-1})$. In Figure 8, these constants were plotted against the

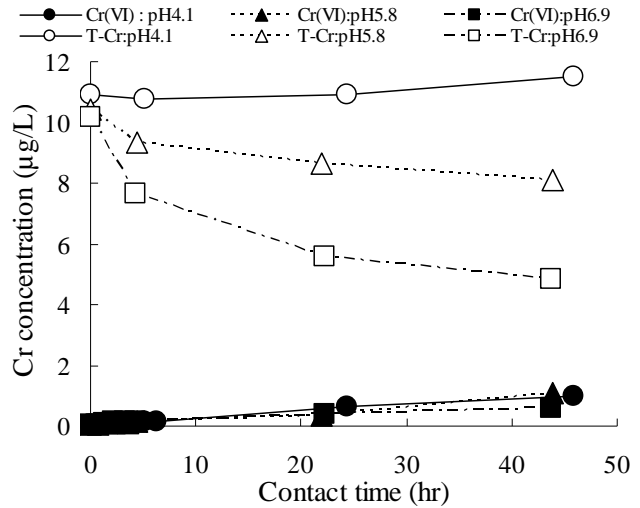


Figure 6. Change in Cr(VI) production over time when sodium hypochlorite was added
Condition: water temperature 20°C

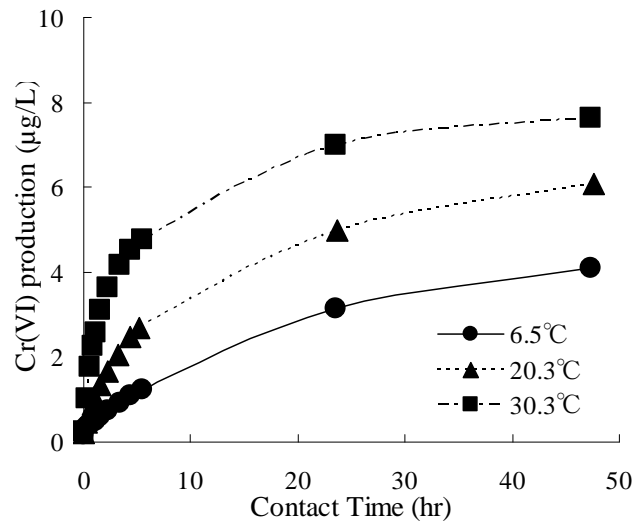


Figure 7. Change in Cr(VI) production for different water temperature
Condition: pH 6.8

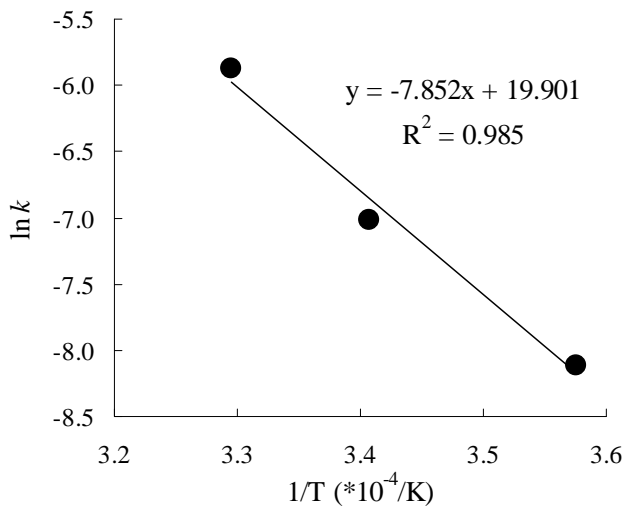


Figure 8. Arrhenius plot

sample water temperature according to Arrhenius equation. As the Arrhenius plot with a coefficient of determination of $R^2=0.985$ showed a good linear relationship, it was identified that the Cr(III) oxidation reaction depended on water temperature.

Oxidation of Cr(III) by ozone

Figure 9 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 minute 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. Chloride ion concentration in rapid sand filtrate was approximately equal to that in the GAC-treated water.

When considering from the results of the oxidation of Cr(III) to Cr(VI) in purified water by sodium hypochlorite and ozone, it was obvious that detectable amount of Cr(VI) wasn't formed unless the substances such as chloride ion coexisted.

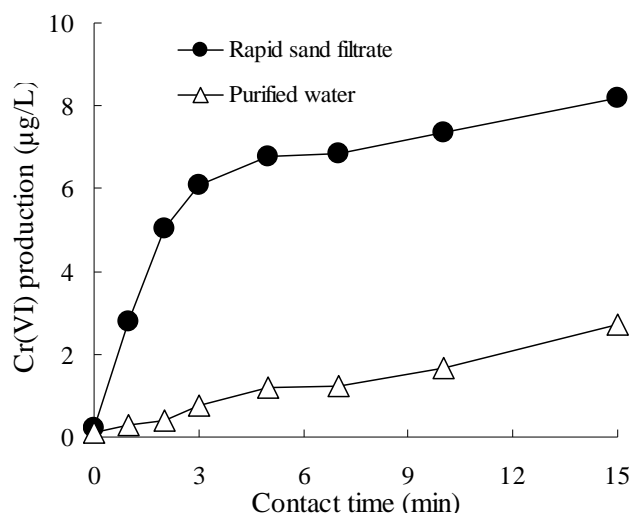


Figure 9. Change in Cr(VI) production over time when ozone treatment was applied

Condition: pH 6.5 (purified water), 6.9 (rapid sand filtrate); water temperature 21°C

CONCLUSION

(1) With regard to the behavior of Cr(VI) through the water treatment process in Osaka city, there is a tendency that Cr(VI) concentration slightly increases and decreases throughout the water treatment process with the highest concentration being observed in finished water. Cr(VI) concentration during the water distribution system is 0.06 µg/L at the outlet of the water purification plant and 0.05 µg/L at the water tap, representing approximately 1/1000 of the current water quality standard for drinking water.

(2) The Cr(III) oxidation reaction was examined and we could find the following:

- Cr(III) is oxidized to Cr(VI) with sodium hypochlorite and ozone.
- The Cr(VI) production in purified water is proportional to chloride concentration ion in the samples.
- There are one or more factors other than chloride ion that improves Cr(VI) production.
- The Cr(III) oxidation reaction depends on water temperature and the rate of production is faster when the water temperature is higher.

REFERENCE

Brandhuber, P., Frey, M., McGuire, M. J., Chao, P., Seidel, C., Amy, G., Yoon, J., McNeill, L. & Banerjee, K. 2004 Low-level hexavalent chromium treatment options: Bench-scale evaluation. *American Water Works Association Research Foundation(AWWARF) Rep.*

No.91042F, Denver

- Clifford, D. & Chau, J. M. 1988 The fate of chromium(III) in chlorinated water. *Project Summary*. EPA /600/S2-87/100, Environmental Protection Agency, Cincinnati
- Dionex Corporation. 1991 Determination of chromium by ion chromatography. Technical note 24
- Dogan, N. M., Kantar, C., Gulcan, S., Dodge, C. J., Yilmaz, B. C. & Mazmanci, M. A. 2011 Chromium(VI) bioremoval by *Pseudomonas* bacteria: Role of microbial exudates for natural attenuation and biotreatment of Cr(VI) contamination. *Environ. Sci. Technol.* **45**, 2278-2285
- Gürleyük, H. & Wallschläger, D. 2001 Determination of chromium(III) and chromium(VI) using suppressed ion chromatography inductively coupled plasma mass spectrometry. *J. Anal. At. Spectrom.* **16**, 926-930
- Han, R., Geller, J. T., Yang, L., Brodie, E. L., Chakraborty, R., Larsen, J. T. & Beller, H. R. 2010 Physiological and transcriptional studies of Cr(VI) reduction under aerobic and denitrifying Conditions by an aquifer-derived *Pseudomonas*. *Environ. Sci. Technol.* **44**, 7491-7497
- Lai, H. & McNeill, L. S. 2006 Chromium redox chemistry in drinking water systems. *J. Environ. Eng.* **132**(8), 842-851
- Ogawa, Y., Yamasaki, & Tsuchiya, N. 2010 Application of a dynamic cell(DRC) ICP-MS in chromium and iron determinations in rock, soil and terrestrial water samples. *Analytical Sciences.* **26**, 867-872
- Sperling, M., Xu, S. & Welz, B. 1992 Determination of chromium(III) and chromium(VI) in water using flow injection on-line preconcentration with selective adsorption on activated alumina and flame atomic absorption spectrometric detection. *Anal. Chem.* **64**, 3101-3108
- United States Environmental Protection Agency.
<http://yosemite.epa.gov/opa/admpress.nsf/d0cf6618525a9efb85257359003fb69d/5876c7ed5950679385257801006be6bc!OpenDocument>
- Wang, Y. & Xiao, C. 1995 Factors affecting hexavalent chromium reduction in pure cultures of bacteria. *Wat. Res.* **29**(11), 2467-2474
- World Health Organization. 2004 WHO Guidelines for Drinking-water Quality. THIRD EDITION. Volume 1 Recommendations.