

# Preparation of a Reference Material for the Determination of Hexavalent Chromium in Tap Water

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We developed a reference material (RM) for the determination of hexavalent chromium (Cr(VI)) in tap water. The tap water RM was prepared by adding a Cr(VI) standard solution to the raw material without acidification, *i.e.*, under the original pH conditions of 7.6, because the decrease in the concentration of Cr(VI) was observed when the tap water had been adjusted to pH 1 with HNO<sub>3</sub>. The prepared tap-water RM (2 L) was packed in 10 fluororesin (PFA) bottles with an inside plug (200 mL each). Each PFA bottle (Cr(VI)-containing tap water) was sealed in a reclosable poly bag and then stored at 5°C in a refrigerator. The tap water RM had a Cr(VI) concentration of 51 µg L<sup>-1</sup>. The concentration of Cr(VI) was determined by diphenylcarbazide absorptiometry using a 100-mm quartz cell. The detection limit of Cr(VI) in the sample solution corresponding to three-times the standard deviation ( $n = 5$ ) of blank values was 0.51 µg L<sup>-1</sup>. The homogeneity of Cr(VI) in the tap water RM was evaluated by an analysis of the variance after the Cochran test. There was no significant difference between the within-bottle and between-bottle variances of the analytical results, indicating that the tap water RM was sufficiently homogeneous. The stability of Cr(VI) in the tap water RM was investigated by monitoring the Cr(VI) concentration over a period of 6 months. The slope of the regression line of the Cr(VI) concentration *versus* the storage time did not significantly differ from zero, indicating that the tap water RM was stable for 6 months. The concentrations (50 – 51 µg L<sup>-1</sup>) of Cr(VI) in the tap water RM were in good agreement with the total chromium concentrations (50 – 51 µg L<sup>-1</sup>) obtained by atomic absorption spectrometry.

**Keywords** Hexavalent chromium, tap water, reference material, diphenylcarbazide absorptiometry, atomic absorption spectrometry

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## Introduction

Cr is widely used in various industries, such as plating, pigment, stainless steel, and electrically heated wire. Although Cr has several oxidation states, Cr is present as trivalent chromium (Cr(III)) and hexavalent chromium (Cr(VI)) in water. Cr(III) is considered to be one of the essential trace elements in the human body because it is deeply involved in the metabolism of glucose. On the other hand, Cr(VI) is highly toxic and exhibits carcinogenicity. A water quality standard and an environmental quality standard for Cr(VI) in Japan have been established at a concentration of 0.05 mg L<sup>-1</sup>. Therefore, it is important to monitor the Cr(VI) content of tap water and environmental water.

The Japanese Industrial Standard (JIS) K 0102<sup>1</sup> has prescribed diphenylcarbazide (DPC) absorptiometry for the determination of Cr(VI) in water. This method is based on the selective reaction of Cr(VI) with DPC under acidic conditions to form a red-violet colored complex of Cr(III)-diphenylcarbazone, followed by measuring the absorbance at 540 nm using a spectrophotometer. Furusho *et al.*<sup>2</sup> determined Cr(VI) in tap water by DPC absorptiometry with highly selective resin having molecular recognition ability. Ohmori and Saito<sup>3</sup> also

determined Cr(VI) in river water by absorptiometry using a DPC-containing thixotropic gel. Kataoka *et al.*<sup>4</sup> determined Cr(VI) in mineral water by ion chromatography with post-column derivatization and spectrophotometric detection.

Certified reference materials (CRMs) are useful for confirming the validity of analytical results. The Japan Society for Analytical Chemistry (JSAC) developed river water CRMs (JSAC 0301-1, JSAC 0301-2, JSAC 0302).<sup>5</sup> The National Metrology Institute of Japan (NMIJ) has issued a river water CRM (NMIJ CRM 7202-b) and a tap water CRM (NMIJ CRM 7203-a).<sup>6</sup> The certified values of Cr in these CRMs are given as total chromium (T-Cr). In Japan, the water quality standard and the environmental quality standard are set as Cr(VI) (*i.e.*, not T-Cr); therefore, a tap water CRM and an environmental water CRM containing Cr(VI) are necessary for the monitoring of water quality. However, a water-matrix CRM containing Cr(VI) has not yet been developed, because there is little knowledge on the stability of Cr(VI) in solution. For this reason, the development of a water-matrix CRM for the determination of Cr(VI) is required.

This paper describes the preparation of a reference material (RM) for the determination of Cr(VI) in tap water. Because the public water supplier must test the quality of tap water, tap water was selected as the matrix of RM. The tap water RM was prepared by adding a Cr(VI) standard solution to the raw material without acidification. The concentration of Cr(VI) was

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determined by DPC absorptiometry, which can directly determine only Cr(VI) in a mixture of Cr(III) and Cr(VI). Furthermore, the discussion is extended to (1) an enhancement of the sensitivity, (2) the effect of HNO<sub>3</sub> addition, and (3) the homogeneity and stability of the tap water RM. The analytical results of Cr(VI) in the tap water RM were also validated by analyzing T-Cr using atomic absorption spectrometry (AAS).

## Experimental

### Apparatus

A U-1800 spectrophotometer (Hitachi, Ltd., Tokyo, Japan) equipped with a 100-mm quartz cell was used for the determination of Cr(VI). The absorbance of the color-developed solution was measured at 540 nm.

A SpectrAA-220Z atomic absorption spectrometer (Varian, Inc., Australia) equipped with a GTA110 graphite tube atomizer (Varian, Inc.) and an autosampler (Varian, Inc.) was used to determine the T-Cr. A Cr hollow cathode lamp was used as the light source, and the Zeeman effect was employed for a background correction. Ar was used as the carrier gas. A 10- $\mu$ L sample solution was dried at 85–120°C for 55 s, ashed at 1000°C for 8 s, and atomized at 2600°C for 4.8 s. The integrated absorbance (peak area) of Cr was measured at 357.9 nm with a slit width of 0.2 nm. The concentration of T-Cr was determined using a calibration curve with Cr(VI) standard solutions.

An SPS1200VR inductively coupled plasma atomic emission spectrometer (Seiko Instruments Inc., Tokyo, Japan) was used for the determination of Ca and Mg. The operating conditions were as follows: RF power, 1.24 kW; plasma gas flow rate, 16 L Ar min<sup>-1</sup>; auxiliary gas flow rate, 0.5 L Ar min<sup>-1</sup>; carrier gas flow rate, 0.45 L Ar min<sup>-1</sup>; observation height, 11.8 mm; analytical line, 393.366 nm for Ca and 279.553 nm for Mg. The concentrations of Ca and Mg were calculated using calibration curves with respective standard solutions.

An F-72 pH meter (Horiba, Ltd., Kyoto, Japan) was used for pH measurements. The pH meter was calibrated with standard solutions of pH 4 (phthalate), pH 7 (neutral phosphate), and pH 9 (borate). An Aquarius RFD342HA water distillation system (Advantec, Mfs, Inc., Tokyo, Japan) was used to prepare deionized water. An SA310 electric oven (Masuda Corp., Osaka, Japan) was used to dry K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> at 150°C for 1 h. A Sanyo Medicoool refrigerator (Sanyo Electric Co., Ltd., Osaka, Japan) was used to store the samples at 5°C.

### Reagents and samples

A 100 mg L<sup>-1</sup> Cr(VI) stock standard solution was prepared by dissolving the dried K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> (reference material for volumetric analysis, >99.98% purity, Kanto Chemical Co., Inc., Tokyo, Japan) in deionized water. Stock standard solutions (1000 mg L<sup>-1</sup>) of Ca and Mg were purchased from Kanto Chemical Co., Inc. The calibration standards of Cr(VI), Ca, and Mg were prepared by accurate dilution of the stock standard solutions with deionized water. A 10 g L<sup>-1</sup> DPC solution as a coloring agent was prepared by dissolving 1,5-diphenylcarbonohydrazide (guaranteed reagent, Kanto Chemical Co., Inc.) in 100 mL of acetone containing a few drops of acetic acid. All other reagents used were of analytical-reagent grade.

Tap water was sampled at Ebina, Kanagawa, Japan. The tap water was filtered through a cellulose filter (1  $\mu$ m pore size, Advantec, Toyo Roshi Kaisha, Ltd., Tokyo, Japan), and the filtrate was used as the raw material of RM. The concentrations of Cr(VI) and T-Cr in the raw material were <0.51  $\mu$ g L<sup>-1</sup> and <0.53  $\mu$ g L<sup>-1</sup>, respectively, whose values are detection limits

corresponding to three-times the standard deviation ( $n = 5$ ) of blank values. The raw material contained 20 mg L<sup>-1</sup> Ca and 5.5 mg L<sup>-1</sup> Mg; that is, the hardness of water was 72 mg L<sup>-1</sup>. The pH of the raw material was 7.6.

### Preparation of tap water RM

The tap water RM was prepared by adding 1 mL of a 100 mg L<sup>-1</sup> Cr(VI) standard solution to a 2-L volumetric flask, and then diluting to 2 L with the raw material without acidification, *i.e.*, under the original pH conditions of 7.6. The prepared tap-water RM (2 L) was packed in 10 fluororesin (PFA) bottles with an inside plug (200 mL each), which were previously washed with HNO<sub>3</sub> and rinsed with deionized water. Each PFA bottle (Cr(VI)-containing tap water) was sealed in a reclosable poly bag and then stored at 5°C in a refrigerator until use.

### Determination of Cr(VI)

The determination of Cr(VI) was carried out using DPC absorptiometry according to JIS K 0102.<sup>1</sup> A 25-mL of sample solution was transferred into a 50-mL volumetric flask, and then 2.5 mL of 1.8 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> and 1 mL of a 10 g L<sup>-1</sup> DPC solution were successively added to the volumetric flask. After shaking for several seconds, the mixture was diluted to 50 mL with deionized water, and allowed to stand for 5 min for color development. The color-developed solution was transferred into a 100-mm quartz cell and introduced into a spectrophotometer. The absorbance of the solution was directly measured at 540 nm. The concentration of Cr(VI) was calculated using a calibration curve, previously constructed with a series of Cr(VI) standard solutions.

## Results and Discussion

### Enhancement of sensitivity

This study aims to prepare a tap water RM with a Cr(VI) concentration of 50  $\mu$ g L<sup>-1</sup>, the water quality standard for Cr(VI) in Japan, using DPC absorptiometry. An enhancement of the sensitivity of DPC absorptiometry is necessary for the precise determination of ppb levels of Cr(VI), because the dynamic range of DPC absorptiometry is from 2 to 50  $\mu$ g for Cr(VI).<sup>1</sup> In the absorptiometric analysis, a cell of 10-mm path length is commonly used to measure the absorbance, although a commercially available cell is 1–100 mm in path length.<sup>7</sup> According to Lambert's law, it is possible to enhance the sensitivity of DPC absorptiometry by using a cell of 100-mm path length.

Figure 1 shows calibration curves of Cr(VI) using a 10-mm quartz cell and a 100-mm quartz cell. A blank (deionized water) and four calibration standards (5, 10, 25, and 50  $\mu$ g L<sup>-1</sup> of Cr(VI)), both of which were prepared through the color development procedure of the DPC method, were used for constructing the calibration curves. The calibration curves of Cr(VI), established using 10-mm and 100-mm quartz cells, showed good linearity in the range of 5–50  $\mu$ g L<sup>-1</sup>. The linear equations of the calibration curves of Cr(VI) were  $Y = 0.00083X + 0.034$  ( $r = 0.9996$ ) for 10-mm quartz cell and  $Y = 0.0083X + 0.040$  ( $r = 0.9999$ ) for 100-mm quartz cell, where  $X$ ,  $Y$ , and  $r$  are the Cr(VI) concentration ( $\mu$ g L<sup>-1</sup>), the absorbance, and the correlation coefficient, respectively. The detection limits of Cr(VI) in the sample solution, corresponding to three-times the standard deviation ( $n = 5$ ) of blank values, were 3.9  $\mu$ g L<sup>-1</sup> for 10-mm quartz cell and 0.51  $\mu$ g L<sup>-1</sup> for 100-mm quartz cell. The relative standard deviations (RSDs) of five independent measurements of 25  $\mu$ g L<sup>-1</sup> of Cr(VI) were 2.1% for 10-mm

quartz cell and 0.2% for 100-mm quartz cell. The sensitivity (*i.e.*, slope of calibration curve of Cr(VI)) of DPC absorptiometry using a 100-mm quartz cell was 10-times higher than that using a 10-mm quartz cell. For this reason, a 100-mm quartz cell was used throughout the study for the determination of ppb levels of Cr(VI).

#### Effect of HNO<sub>3</sub> addition

In general, water-matrix CRMs for elemental analysis are acidified to *ca.* pH 1 with HNO<sub>3</sub> to prevent the hydrolysis of metal ions and the adsorption of metallic elements on the container walls during storage. However, Cr(VI) is present as HCrO<sub>4</sub><sup>-</sup> in an acidic solution, and HCrO<sub>4</sub><sup>-</sup> is unstable because of its high oxidizing power.<sup>8</sup> Archundia *et al.*<sup>9</sup> and Pezzin *et al.*<sup>10</sup> reported that low concentrations of Cr(VI) in diluted HNO<sub>3</sub>, HCl, and HClO<sub>4</sub> were reduced to Cr(III). Therefore, it is not desirable to preserve Cr(VI) under acidic conditions. On the other hand, Cr(VI) is present as CrO<sub>4</sub><sup>2-</sup> in solution above pH 7, and CrO<sub>4</sub><sup>2-</sup> has a low oxidizing power compared with HCrO<sub>4</sub><sup>-</sup>.

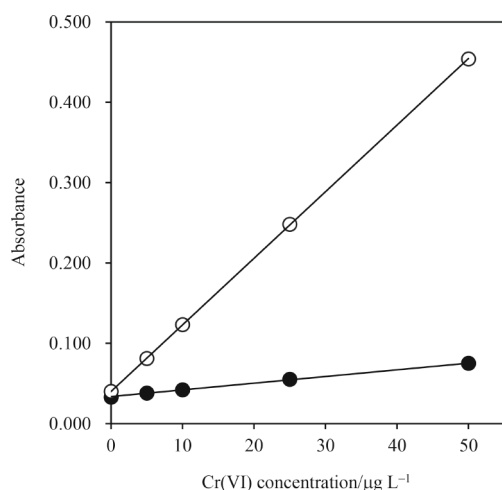


Fig. 1 Calibration curves of Cr(VI) using a 10-mm quartz cell (●) and a 100-mm quartz cell (○).

Tap water is usually pH 7 – 8; therefore, Cr(VI) may be stable in the tap water. In other words, a RM for the determination of Cr(VI) in tap water may be able to be prepared without acidification.

We first investigated the effect of HNO<sub>3</sub> addition on the stability of Cr(VI) in tap water. Four tap water samples, each containing an initial Cr(VI) concentration of 50 μg L<sup>-1</sup> in a PFA bottle with inside plug, were prepared with and without the addition of HNO<sub>3</sub>. They were stored at 5°C in a refrigerator and at room temperature in the dark. After preservation for 0, 3, 7, 14, 35, and 90 days, the concentrations of Cr(VI) in the tap water were determined by DPC absorptiometry after 2-fold dilution of the water samples. Figure 2 shows the variations in the concentration of Cr(VI) in the tap water with and without the addition of HNO<sub>3</sub> with the storage time. The concentration of Cr(VI) in the tap water of pH 1 (*i.e.*, with HNO<sub>3</sub> addition) gradually decreased with an increase in the storage time at both 5°C and room temperature. After 90 days of storage at pH 1, the concentrations of Cr(VI) in the tap water decreased by 20% at 5°C and by 29% at room temperature. The decreases in the concentrations of Cr(VI) in the tap water are due to the reduction of Cr(VI) to Cr(III), caused by the acidification of tap water, as reported by Archundia *et al.*<sup>9</sup> and Pezzin *et al.*<sup>10</sup> Furthermore, the reduction rate of Cr(VI) at room temperature (*ca.* 20°C) was slightly higher than that at 5°C, suggesting that the reduction reaction of Cr(VI) was accelerated by a temperature increase. In contrast, the concentration of Cr(VI) in the tap water of pH 7.6 (*i.e.*, without HNO<sub>3</sub> addition) did not decrease at both 5°C and room temperature during 90 days of storage. This result may be attributed to the difference in the oxidizing power of Cr(VI) between pH 1 (*i.e.*, HCrO<sub>4</sub><sup>-</sup>) and pH 7.6 (*i.e.*, CrO<sub>4</sub><sup>2-</sup>). The results indicated that Cr(VI) in the tap water was stable at the original pH of 7.6. In this study, therefore, a RM for the determination of Cr(VI) in tap water was decided to be prepared by adding a Cr(VI) standard solution to the raw material without acidification.

#### Homogeneity of the tap water RM

RMs are required to be sufficiently homogeneous. The homogeneity of Cr(VI) in the tap water RM was evaluated by the analysis of variance after the Cochran test.<sup>11</sup> For the

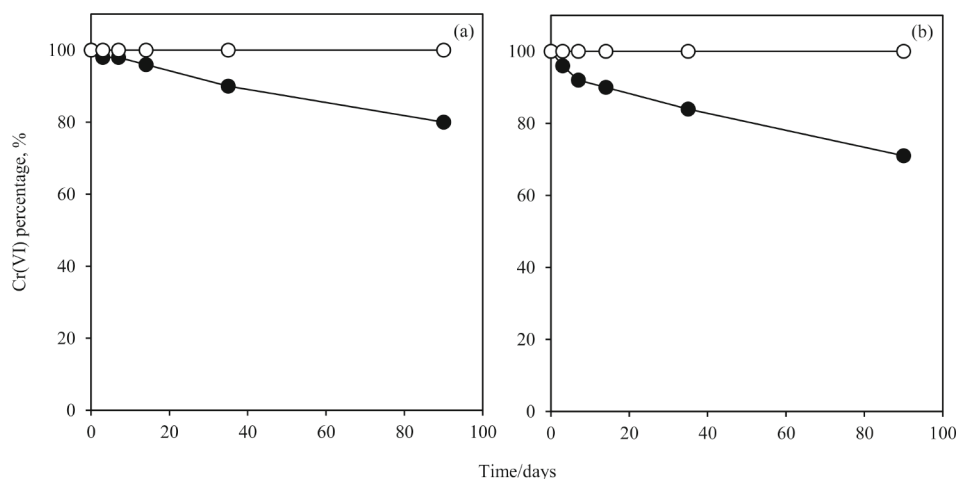


Fig. 2 Variations in the Cr(VI) concentration (initial concentration = 50 μg L<sup>-1</sup>) in the tap water with (●) and without (○) the addition of HNO<sub>3</sub> with the storage time: (a) 5°C in the refrigerator and (b) room temperature in the dark. The tap water samples with and without the addition of HNO<sub>3</sub> were pH 1 and pH 7.6, respectively.

Table 1 Results of a homogeneity test for Cr(VI) in tap water reference material by the analysis of variance after the Cochran test

Cr(VI) concentration <sup>a</sup> /μg L <sup>-1</sup>	RSD <sup>b</sup> , %	Cochran test		Analysis of variance	
		Cochran's value	Critical value <sup>c</sup>	F-value	Critical value <sup>d</sup>
51	0.4	0.440	0.684	2.04	3.49

a. Determined by diphenylcarbazide absorptiometry. b. Relative standard deviation, % ( $n = 16$ ). c. Level of significance,  $\alpha = 0.05$ ; number of groups,  $k = 4$ ; degree of freedom,  $\nu_x = 3$ . d. Level of significance,  $\alpha = 0.05$ ; degree of freedom for between-bottle,  $\nu_1 = 3$ ; degree of freedom for within-bottle,  $\nu_2 = 12$ .

homogeneity test, 4 bottles were randomly selected from 10 bottles, and four independent measurements of the concentration of Cr(VI) were carried out for each bottle. The concentrations of Cr(VI) were determined by DPC absorptiometry after a 2-fold dilution. The results of the homogeneity test for Cr(VI) in the tap water RM are given in Table 1. The average concentration of Cr(VI) was 51 μg L<sup>-1</sup>, and the RSD ( $n = 16$ ) of the concentration was 0.4%.

First, the Cochran test was performed to verify the homoscedasticity of the within-bottle variance of the analytical results. Cochran's value ( $C_0$ ) was calculated using the following equation:

$$C_0 = S_H^2 / \sum_i S_i^2, \quad (1)$$

where  $S_H$  is the maximum standard deviation of the within-bottle, and  $S_i$  is the standard deviation of the within-bottle. The calculated Cochran's value was then compared with the critical value obtained from the statistical table under the following conditions: level of significance,  $\alpha = 0.05$ ; number of groups,  $k = 4$ ; degree of freedom,  $\nu_x = 3$ . When Cochran's value is lower than the critical value, the within-bottle variance is homoscedastic.

Next, the analysis of variance was performed to compare the between-bottle variance and the within-bottle variance of the analytical results. The between-bottle sum of square ( $S_{sam}^2$ ), within-bottle sum of square ( $S_{an}^2$ ), and  $F$ -value ( $F$ ) were calculated using the following equation:

$$S_{sam}^2 = n \sum_i (\bar{x}_i - \bar{x})^2 / (m - 1), \quad (2)$$

$$S_{an}^2 = \sum_i \sum_j (x_{ij} - \bar{x}_i)^2 / m(n - 1), \quad (3)$$

$$F = S_{sam}^2 / S_{an}^2, \quad (4)$$

where  $\bar{x}_i$  is an average value of bottle  $i$ ,  $\bar{x}$  is an average of the whole value,  $x_{ij}$  is a  $j$ th analytical value of bottle  $i$ ,  $m$  is the number of bottles, and  $n$  is the number of measurements. The calculated  $F$ -value was then compared with the critical value obtained from table of the  $F$ -distribution under the following conditions: level of significance,  $\alpha = 0.05$ ; degree of freedom for between-bottle,  $\nu_1 = 3$ ; degree of freedom for within-bottle,  $\nu_2 = 12$ . When  $F$ -value is lower than the critical value, there is no significant difference between the within-bottle variance and the between-bottle variance of the analytical results.

As a result, both Cochran's value and  $F$ -value were lower than the critical values (Table 1). In other words, the within-bottle variance was homoscedastic, and there was no significant difference between the within-bottle and between-bottle variances of the analytical results. From these results, we concluded that the tap water RM was sufficiently homogeneous.

Table 2 Results of a stability study for Cr(VI) in tap water reference material over a period of 6 months

Time/month	Cr(VI) concentration <sup>a</sup> /μg L <sup>-1</sup>	T-Cr concentration <sup>b</sup> /μg L <sup>-1</sup>	pH
0	50	51	7.6
1	51	50	7.6
3	50	51	7.6
6	50	51	7.6

a. Determined by diphenylcarbazide absorptiometry. b. Determined by atomic absorption spectrometry.

#### Stability of the tap water RM

RMs are also required to be sufficiently stable. The stability of Cr(VI) in the tap water RM was investigated by monitoring the Cr(VI) concentration over a period of 6 months. For the stability study, 4 bottles were selected from the remaining 6 bottles, and Cr(VI), T-Cr, and pH were determined after preservation for 0, 1, 3, and 6 months. The concentrations of Cr(VI) were determined by DPC absorptiometry after a 2-fold dilution. The results of the stability study for Cr(VI) in the tap water RM are given in Table 2. The concentrations (50 - 51 μg L<sup>-1</sup>) of Cr(VI) in the tap water RM were in good agreement with those (50 - 51 μg L<sup>-1</sup>) of T-Cr obtained by AAS, suggesting that Cr(VI) in the tap water RM was not reduced to Cr(III). In addition, the tap water RM showed a constant pH value of 7.6, indicating that Cr(VI) was present as CrO<sub>4</sub><sup>2-</sup> in the tap water RM. Furthermore, precipitates and algae were not visually observed in the tap water RM during 6 months of storage.

The stability of the tap water RM was evaluated using a linear regression model ( $y = b_1x + b_0$ ) according to JIS Q 0035.<sup>12</sup> If  $|b_1| < t_{0.95, n-2} \times s(b_1)$ , the slope does not significantly differ from zero; that is, there is no instability. Here,  $b_1$  is the slope,  $b_0$  is the intercept,  $t_{0.95, n-2}$  is the Student's  $t$ -factor for  $n - 2$  degrees of freedom and  $p = 0.95$  (95% confidence level), and  $s(b_1)$  is the uncertainty associated with the slope. In Table 2, the concentration of Cr(VI) and the storage time are plotted as the  $y$ -axis (μg L<sup>-1</sup>) and  $x$ -axis (months), respectively. When the regression analysis was performed,  $b_1$  was  $-0.0714$  and  $s(b_1)$  was  $0.1237$ . In this case, the Student's  $t$ -factor is equal to 4.30. As a result, the slope of the regression line of the Cr(VI) concentration *versus* the storage time did not significantly differ from zero, and hence, no instability was observed. Consequently, we concluded that the tap water RM was stable for 6 months. In the future, the stability of Cr(VI) in the tap water RM will be continuously monitored.

## Conclusions

A RM for the determination of Cr(VI) in tap water was developed using DPC absorptiometry. The tap water RM was prepared by adding a Cr(VI) standard solution to the raw material without acidification. A 100-mm quartz cell was used to enhance the sensitivity of DPC absorptiometry. The concentration of Cr(VI) in the tap water (pH 1) with the addition of HNO<sub>3</sub> decreased, whereas that of Cr(VI) in the tap water (pH 7.6) without the addition of HNO<sub>3</sub> did not decrease. This study revealed that Cr(VI) in tap water is stable at the original pH of 7.6. The results of the analysis of variance after the Cochran test indicated that the tap water RM was sufficiently homogeneous. In addition, the results of the regression analysis indicated that the tap water RM was stable for 6 months. The tap water RM with a Cr(VI) concentration of 51 µg L<sup>-1</sup>, nearly equal to the water quality standard (50 µg L<sup>-1</sup>) for Cr(VI) in Japan, can be used for confirming the validity of analytical results of Cr(VI) in tap water.

## References

1. JIS K 0102, "Testing Method for Industrial Wastewater", 2016, Japanese Industrial Standards Committee, Tokyo.
2. Y. Furusho, M. Ono, M. Yamada, T. Kitade, and S. Motomizu, *Bunseki Kagaku*, **2009**, 58, 147.
3. K. Ohmori and T. Saito, *Bunseki Kagaku*, **2009**, 58, 801.
4. Y. Kataoka, T. Watanabe, K. Hayashi, R. Ozawa, K. Takizawa, and H. Akiyama, *Shokuhin Eiseigaku Zasshi*, **2017**, 58, 275.
5. A. Kawase, K. Ohashi, I. Akabane, T. Kuroiwa, M. Murayama, H. Yoshimura, J. Yoshinaga, M. Uemoto, A. Ono, K. Kakita, and M. Sakata, *Bunseki Kagaku*, **2006**, 55, 875.
6. Y. Zhu, T. Narukawa, K. Inagaki, S. Miyashita, T. Kuroiwa, T. Ariga, I. Kudo, M. Koguchi, S. W. Heo, J. K. Suh, K. S. Lee, Y. H. Yim, and Y. Lim, *Anal. Sci.*, **2017**, 33, 403.
7. M. Kamaya, *Bunseki*, **2008**, 4, 158.
8. J. Kotaš and Z. Stasicka, *Environ. Pollut.*, **2000**, 107, 263.
9. C. Archundia, P. S. Bonato, J. F. Lugo Rivera, L. C. Mascioli, K. E. Collins, and C. H. Collins, *Sci. Total. Environ.*, **1993**, 130, 231.
10. S. H. Pezzin, J. F. Lugo Rivera, C. H. Collins, and K. E. Collins, *J. Braz. Chem. Soc.*, **2004**, 15, 58.
11. H. Tanaka, *Bunseki*, **2010**, 4, 168.
12. JIS Q 0035, "Reference Materials—General and Statistical Principles for Certification", **2008**, Japanese Industrial Standards Committee, Tokyo.