Analytical method to identify chromium species with HPLC-ICP-MS and application of the method to identify chromium species in the Han River, Korea

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ABSTRACT

Methods to identify chromium species, Cr( ) and Cr( ), in water samples were studied using High Performance Liquid Chromatography(HPLC) coupled with Inductively Coupled Plasma Mass Spectrometer(ICP-MS) equipped with Dynamic Reaction Cell(DRC). The characteristic distribution of Cr( ) and Cr( ) in the raw waters from the six water intake stations of Seoul, was analyzed with the method developed by the authors.

Separation of chromium species by HPLC was conducted isocratically by using tetrabutylammonium phosphate monobasic(1.0 mM TBAP), ethylenediaminetetraacetic acid(0.6 mM EDTA) and 2 % v/v methanol as the mobile phase. 5 % v/v methanol was used as flushing solvent. Reactive ammonia(NH_3) gas was used to eliminate potential interference by ArC^+. Several parameters such as solvent ratio, pH, flow rate and injected volume of sample were optimized for the separation and reproducibility.

Although it has been reported that the separation sensitivity of Cr( ) is superior to that of Cr( ), the authors observed Cr( ) was more sensitive than Cr( ) when the reaction gas was ammonia(NH_3). It took less than 3 minutes to analyze chromium species with this method and the detection limits were estimated to be 0.061 and 0.052   /L for Cr( ) and Cr( ), respectively.

According to the results from the analyses on chromium species in the raw waters from the six intake stations, the concentrations of Cr( ) ranged from 0.048 to 0.064   /L (ave. 0.054   /L) while those of Cr( ) ranged from 0.014 to 0.023   /L (ave. 0.019   /L). Recovery ratio was very high (90.1~94.1 %). The concentration of Cr(III) in the raw water was two or three times higher than Cr(VI).

KEY WORDS

Chromium, Speciation, DRC ICP-MS, HPLC

INTRODUCTION

Chromium exists as trivalent and hexavalent species in the surface water. Trivalent chromium, an essential nutrient, is present in cationic form of hydroxide and other chemical compounds. On the other hand, hexavalent chromium exists as an anion, such as chromate (CrO_4^{2-}) or dichromate ($Cr_2O_7^{2-}$), which are toxic and can cause vomiting, loose bowels, and thirst, when taken too much. The analysis of total chromium can not provide true indication of the effects by chromium present in a sample. More accurate assessment on true effects of chromium can be obtained by distinguishing trivalent and hexavalent species.

Although the usage of high performance liquid chromatography-inductively coupled plasma mass spectrometer (HPLC-ICP-MS) has increased recently, most studies used retention time to separate Cr(III) from Cr(VI) with ICP-MS (intensity/count vs. time/s). Without the functions of HPLC such as offset and full scale, it was very hard to analyze size, sharpness, and broadness of peaks of samples at the same time even when the same chromium species was analyzed. In addition, the optimized condition for the analysis could hardly be found as the conditions were determined only by the retention time.

The authors studied the distribution and the characteristics of Cr(III) and Cr(VI) in the raw water from the Han River with the conditions determined considering not only retention time but also size, sharpness and broadness of peak. The conditions were also determined with considerations on solvent ratio, pH, flow rate, and amount of sample injection of mobile phase with the offset and full scale functions of HPLC.

METHODS

Instrumental parameters. The operating conditions of the ICP-MS (PerkinElmer-SCIEX, Canada) were listed in Table 1. The chromium species were separated by HPLC (PerkinElmer, USA) and detected by ICP-MS

Table 1.Conditions and parameters used for ICP-MS operation

Parameter	Setting/Type

Nebulizer	Meinhard® Type A Quartz
Spray Chamber	Quartz Cyclonic
Nebulizer Ar Gas Flow	1.01 L/min
Auxiliary Ar Gas Flow	1.2 L/min
Plasma Ar Gas Flow	16 L/min
Lens Voltage	5.75 V
RF Power	1500 W
Monitored Ion m/z	$^{52}Cr^+$
Dwelling Time	1,000 ms
Integration Time	180,000 ms(3 min)
RPq	0.7 N/A
Cell Gas(NH$_3$) Flow	0.5 mL/min

Reagents. All reagents were analytical grade and used without further purification. All glassware was soaked in 5 % v/v nitric acid(Aldrich, USA) for 24 hours and then rinsed with de-ionized water. The disodium salt of ethylenediaminetetraacetic acid(EDTA), tetrabutylammonium phosphate monobasic(TBAP), and ammonium hydroxide were purchased from Sigma (Steinheim, Germany). HPLC-grade methanol was purchased from Burdick & Jackson (Muskegon, USA). Stock solutions of 1007 μg L^{-1} Cr(Ⅲ) and 1009 μg L^{-1} Cr(Ⅵ) were obtained from Aldrich (Milwaukee, USA).

Mobile phase preparation. The mobile phase, solvent A (0.6 mM EDTA and 1.0 mM TBAP) was prepared by dissolving EDTA and TBAP in de-ionized water, and the pH was adjusted to 6.8 with ammonium hydroxide. Solvent B, 2 % v/v methanol, was added and diluted with de-ionized water. 5 % v/v methanol was used as flushing solvent.

Standards and sample preparation. Chromium standards were prepared from stock solutions of Cr(Ⅲ) and Cr(Ⅵ). Chromium standards were diluted with mobile phase to 1, 3, 5, 7 and 9 μg/L. The water samples were analyzed after diluted three times with mobile phase.

HPLC column. The column used for this application is a high-speed, reversed-phase, C$_8$ cartridge column (PerkinElmer, USA). It is 3.3 cm long and packed with 3-μm particles.

RESULTS AND DISCUSSION

Elimination of interference. The main interference in chromium analysis is caused by ArC$^+$ (argon carbide), which forms at m/z 52, the same m/z as that of major chromium isotope. This interference would limit the ability to measure chromium of low level concentration. Ammonia was used as a reaction gas in the ICP-MS to solve this problem. Ammonia gas reacts with ArC$^+$ and eliminates it, leaving $^{52}Cr^+$ free from interference.

$$ArC^+ \ + \ NH_3 \ \rightarrow \ ArC \ + \ NH_3^+$$
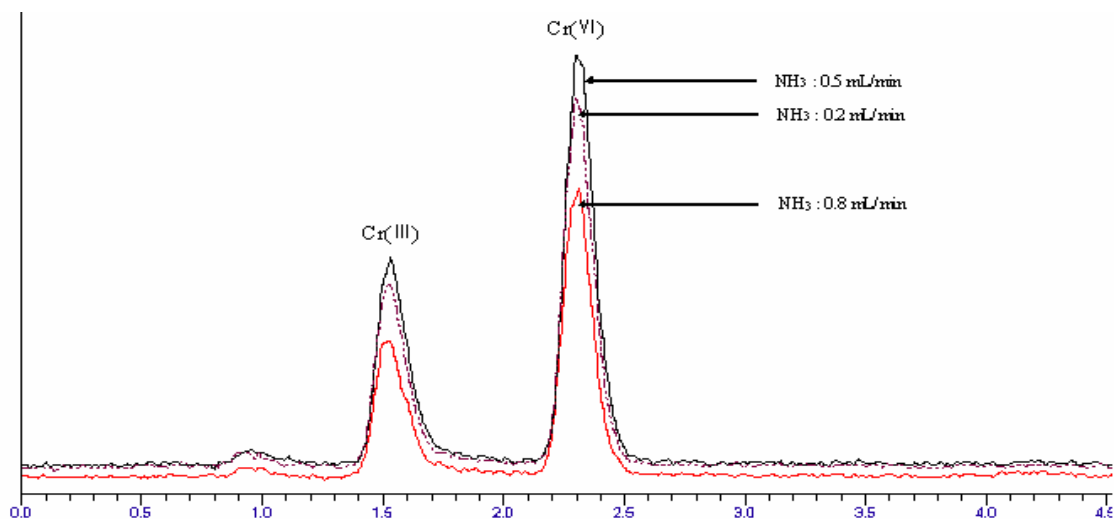
Fig. 1. Chromatograms of chromium speciation with different flow rates of reaction gas.

As presented in Fig. 1, the most successful results were obtained with the flow rate of 0.5 mL/min as the interference by ArC^+ was completely removed under this condition. On the other hand, ArC^+ interference was not removed completely when reaction gas flow rates were lower than 0.5 mL/min. The peaks became smaller due to the excessive reactions in the reaction cell when reaction gas flow rates were higher than 0.5 mL/min. It is recommended to use 0.5 mL/min of reaction gas flow to analyze chromium in the range of the experiment.

Mobile phase. To investigate the influence of pH changes in mobile phase on chromium speciation, series of tests were carried out with different pH of solvent A from 6.6 to 7.2 with ammonium hydroxide. pH 6.8 was found to be the best condition in terms of the peak size and separation. The separation was decreased at pH 7.2 and the peaks appeared to be too broad at pH 6.6. The results and chromatograms are illustrated in Fig. 2.
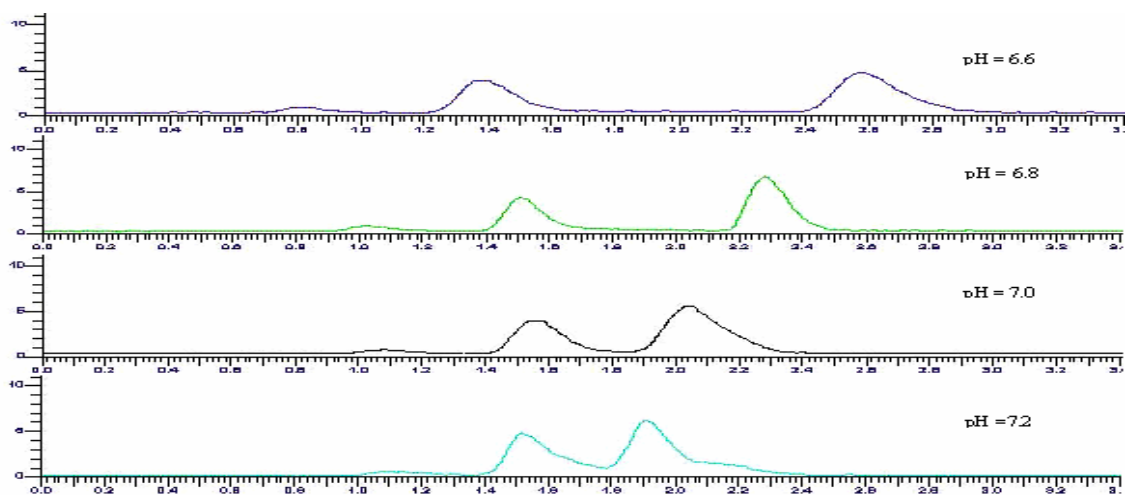
Fig. 2. Effect of pH on chromium speciation (0.6 mM EDTA and 1.0 mM TBAH, 3   /L standard solution).

The mixtures of solvent A and B with the ratios of 98:2 (v/v) and 92:8 (v/v) were used to investigate the influence of methanol on the chromium speciation. The variation of ratio in solvent B from 2%

to 8% did not change the retention time and the peak size of chromium species significantly. The mixture of solvent A and B with the ratio of 95 : 5 (v/v) was used for the further study.

The flow rate of mobile phase was altered from 0.5 to 1.5 mL/min to find out the optimal conditions to separate chromium species. As the flow rate increased, the peaks tended to be narrower and retention time decreased, and vice versa. The flow rate of 0.8 mL/min for mobile phase was determined to be the best condition in terms of the retention time and the peak size.

Sample injection volume. The 50 µL and the 100 µL of 3   /L standard solution were injected separately to find the optimal point. As the injection volumes did not affect the separation of the species, 100 µL was selected considering detection limit and separation.

Analytical application. External calibrations were carried out with 100 µL injections of solutions and 1, 3, 5, 7 and 9   /L of each chromium species in the mobile phase, and the heights of the peaks were measured. All of the standards have the same retention time that shows excellent precision and stable separation. The calibration curves of Cr( ) and Cr( ) are presented in Fig. 3 and 4, respectively.
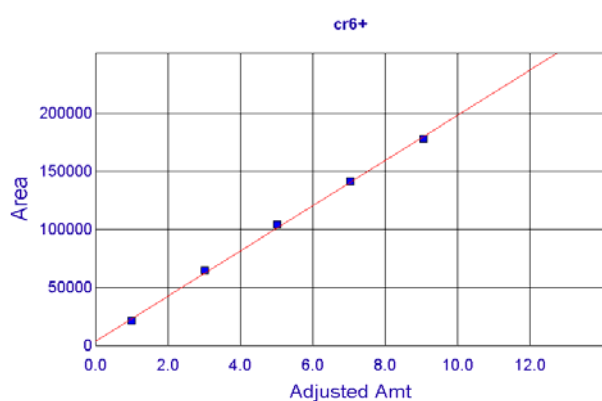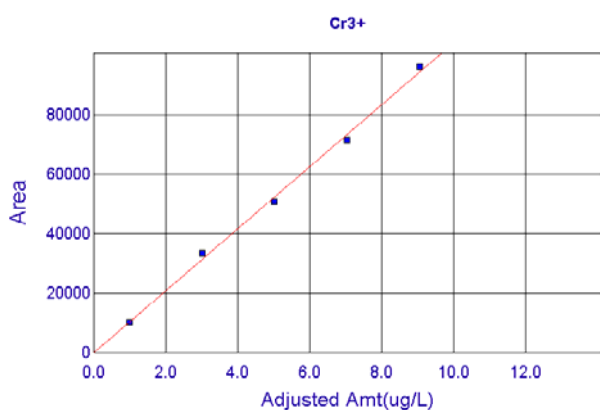
Fig. 3. Chromium calibration curve Cr( )   **Fig. 4**. Chromium calibration curve Cr( )

As shown in Fig. 3 and 4, both the calibration curves for Cr( ) and Cr( ) were quite linear with r^2 values of 0.998 and 0.997, respectively. Although it has been reported that the separation sensitivity of Cr( ) is superior to that of Cr( ), the authors observed Cr( ) was more sensitive than Cr( ) when ammonia(NH_3) gas was used as the reaction gas. It took less than 3 minutes to analyze chromium species with this method and the estimated detection limits were 0.061 and 0.052   /L for Cr( ) and Cr( ), respectively.

The water samples were then analyzed after diluted three times with mobile phase. As the resulting chromatogram did not yield any peaks, it could be said that there was no or little chromium in the water samples. The same samples were analyzed to determine total chromium by ICP/MS. According to the results, the concentrations of chromium were 0.066~0.089   /L in the water samples. According to the results from the analyses on chromium species in the raw waters after spiked with 1   /L of each chromium species, the concentrations of Cr( ) ranged from 0.048 to 0.064   /L(ave. 0.054   /L) while those of Cr( ) ranged from 0.014 to 0.023   /L(ave. 0.019   /L). Recovery ratio was very high (90.1~94.1 %). There were two or three times more Cr( ) than Cr( ) in the raw water.

Table 2. Results of chromium separation in finished water in Seoul

Results		Cr	Cr( )	Cr( )	Recovery(%)
Intake stations (Raw water)	Paldang	0.086	0.059	0.022	94.1
	Amsa	0.078	0.056	0.016	92.3
	Guui	0.089	0.064	0.019	93.2
	Jayang	0.074	0.049	0.019	91.8
	Pungnap	0.066	0.048	0.014	93.9
	Gangbuk	0.081	0.050	0.023	90.1
	Average	0.079	0.054	0.019	92.5

CONCLUSION

In this study, trivalent and hexavalent chromium species were separated by HPLC and detected with ICP-MS. Many factors were taken into account and optimized in order to achieve successful separation and reproducibility. The factors considered include solvent ratio, pH, flow rate of mobile phase, sample injection volume, flow rate of the reaction gas and detection mode. Retention time and sensitivity were considered at the same time.

The overall results showed that 0.5 mL/min of the reaction gas, pH 6.8, the ratio of 95:5 for solvent A and B, 0.8 mL/min of the mobile phase and 100 µL of sample injection volume could make an optimal condition. Although it has been reported that the separation sensitivity of Cr( ) is superior to that of Cr( ), the authors observed Cr( ) was more sensitive than Cr( ) when ammonia(NH_3) gas was used as the reaction gas. It took less than 3 minutes to analyze chromium species with this method and the estimated detection limits were 0.061 /L for Cr( ) and 0.052 /L for Cr( ).

According to the results from the analyses on chromium species in the raw waters from the six intake stations, the concentrations of Cr( ) ranged from 0.048 to 0.064 /L(ave. 0.054 /L) while that of Cr( ) ranged from 0.014 to 0.023 /L(ave. 0.019 /L)

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