

## Speciation of chromium in water by HPLC-ICP-MS

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### Introduction

Chromium exists widely in the earth crust as an oxidized state of divalent to hexavalent species. Although chromium is rare present in surface water, it discharges into the water from plant or mine. Usually, chromium exists in the surface water as trivalent and hexavalent. 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( $\text{CrO}_4^{2-}$ ) or dichromate( $\text{Cr}_2\text{O}_7^{2-}$ ), which is toxic and could cause vomiting, loose vowels, thirst if taken too much. Therefore, the analysis of total chromium does not always provide a true indication of the effects of chromium present in a sample. A more accurate assessment of the true effects of chromium can be obtained by distinguishing trivalent and hexavalent species.

Several methods have been reported on the usage of high performance liquid chromatography-inductively coupled plasma mass spectrometer(HPLC-ICP-MS). However, this separation method is not yet easy for analyzers to use generally because of the insufficient instrumental conditions and analytical information, and they also seem to have paid attention to retention time without considering the separation sensitivity of Cr(VI) and Cr(III).

Therefore, the focus of this work is to establish an accurate and sufficient analytical conditions necessary to separate trivalent and hexavalent species in less than 3 minutes for low concentrations by considering the retention time and the sensitivity of Cr(VI) and Cr(III) at the same time.

### Experimental

**Instrumental parameters.** ELAN DRC II ICP-MS(PerkinElmer-SCIEX) and HPLC(PerkinElmer) used this study. Detection of the chromium species was carried out by operating DRC II ICP-MS.

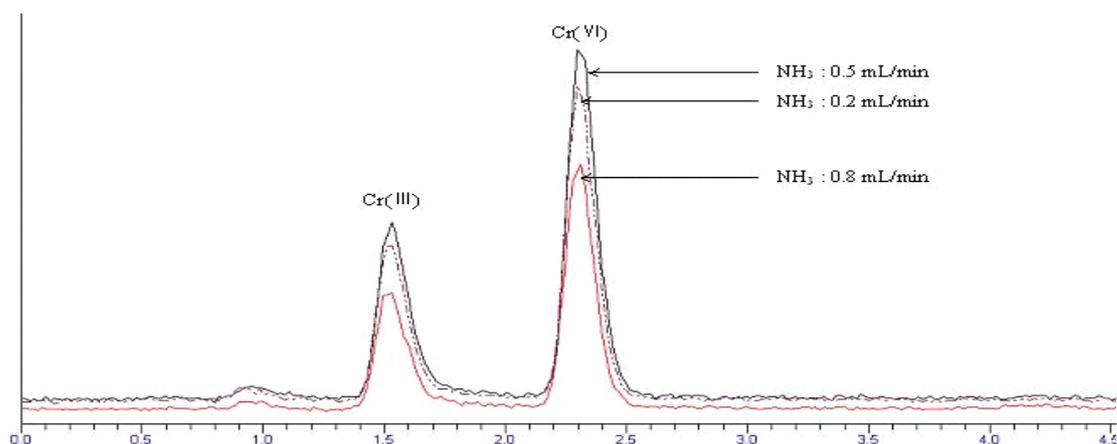
**Reagents.** All reagents were of analytical grade and used without further purification. The disodium salt of ethylenediaminetetraacetic acid(EDTA), tetrabutylammoniumphosphate monobasic(TBAP),

and ammonium hydroxide were purchased from Sigma. HPLC-grade methanol was purchased from Burdick & Jackson. Stock solutions of 1,007 mgL<sup>-1</sup> Cr(III) and 1,009 mgL<sup>-1</sup> Cr(VI) were obtained from Aldrich.

**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 then the pH was adjusted with ammonium hydroxide to 6.8~7.0. Solvent B, 2% v/v methanol was added and diluted with de-ionized water. 5% v/v methanol was used as flushing solvent.

## Results and Discussion

**Elimination of interference.** The main interference in chromium analysis is ArC<sup>+</sup>(argon carbide), this interference would limit the ability to measure chromium of low level. To solve this problem, ammonia was used as a reaction gas in the DRC II ICP/MS. Fig. 1 shows the results of the 3 μg/L standards acquired without and with different amounts of a reaction gas(NH<sub>3</sub>).



**Fig. 1. Overlapped chromatogram for different reaction gas flow rates with 3 μg/L standard solution.**

Fig. 1 displays overlaid chromatogram for different amount of reaction gas. As shown in Fig. 1, 0.5 mL/min of reaction gas flow obtains the most successful result, which means complete removal of interference by the existence of ArC<sup>+</sup>. In contrast, ArC<sup>+</sup> interference was not removed completely when reaction gas flow rate were less than 0.5 mL/min and the peaks became smaller due to the excessive reaction in the reaction cell when reaction gas flow rates were more than 0.5 mL/min. Therefore, 0.5 mL/min of reaction gas was recommended.

**Mobile phase.** To investigate the pH influence of mobile phase on the speciation, a series of tests was performed by changing the pH of solvent A to 6.5~7.2 with ammonium hydroxide. As a result, pH 6.8~7.0 was found to be proper for the peak size and separation. While peaks appeared too broad at pH 6.6, the separation was decreased at pH 7.2. For the study of methanol influence, the mixture of solvent A and B with a ratio of 98 : 2 to 92 : 8 v/v were prepared respectively to

assess the effect of separation on a mobile phase. There were little significant effect on the retention time and the peak size of chromium species with variations in solvent B from 2 % to 8 %. To find the optimal conditions for the separation of chromium species, the flow rate of mobile phase was altered from 0.5 mL/min to 1.5 mL/min. Peaks tended to be narrower, while retention time was shortened as the flow rate increased. When the flow rate decreased, peaks appeared to be broadened and the retention time increased. Therefore, the flow rate of 0.8~1.0 mL/min of mobile phase was founded to be proper for the retention time and the peak size. The 50  $\mu$ L and the 100  $\mu$ L of 3  $\mu$ g/L standard solution were injected separately to find the optimal point of sample injection volume. Though the injection of 50  $\mu$ L led to the half of the concentration when 100  $\mu$ L is injected, the experiment was performed to choice the detection limit and separation.

**Analytical application.** External calibrations were made from 100  $\mu$ L injections of 1, 3, 5, 7 and 9  $\mu$ g/L of each chromium species in the mobile phase, and peak heights were measured. All of the standards have the same retention time which shows excellent precision and stable separation. The calibration curves of Cr(III) and Cr(VI) are indicated in Fig. 2 and 3, respectively.

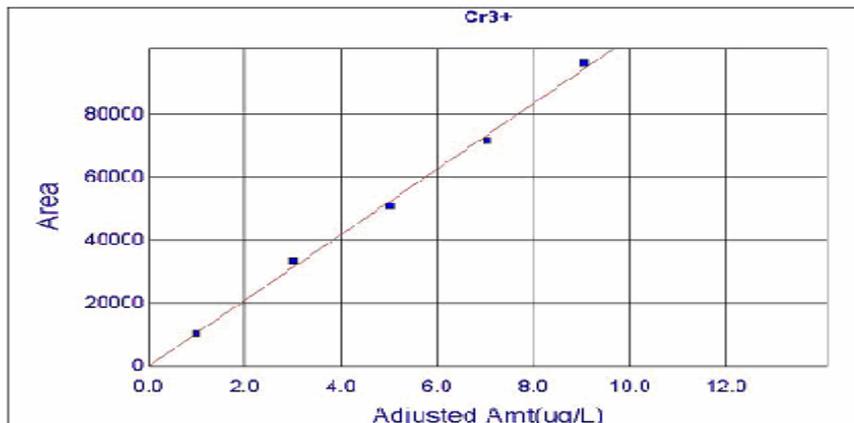


Fig. 2. Chromium calibration curve 「Cr(III)」 .

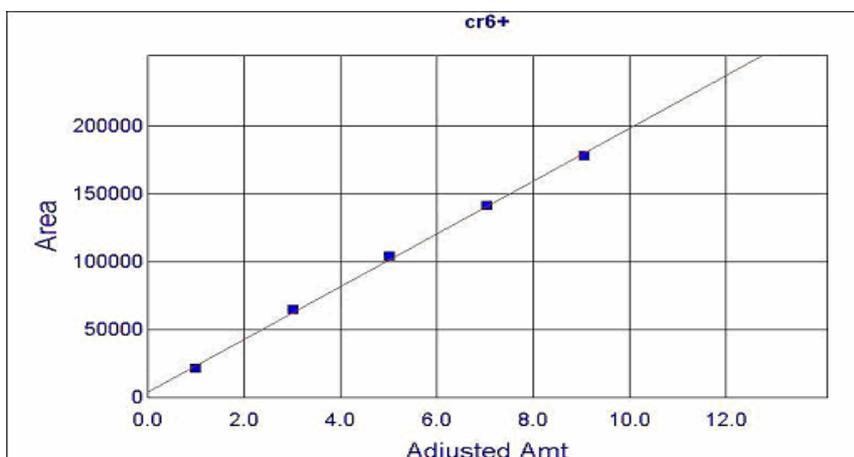


Fig. 3. Chromium calibration curve 「Cr(VI)」 .

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As shown in Fig. 2 and 3, the calibration curves for Cr(III) and Cr(VI) corresponds to the linearity  $r^2=0.998$  and  $r^2=0.997$  respectively. The detection limit is obtained as 70 ng/L for Cr(III) and 50 ng/L for Cr(VI).

The tap water samples were then analyzed after a three times dilution with mobile phase but the resulting chromatogram did not yield any peaks, thereby indicating the absence of or extremely low levels of chromium. For that reason, the same samples was analyzed for total chromium by ICP/MS, and the results showed that 82 ng/L of chromium was present. The tap water was then spiked with 1  $\mu\text{g/L}$  of each chromium species. The results of this analysis show that Cr(III)=57 ng/L and Cr(VI)=22 ng/L. The recovery was 96.3 %.

## Conclusions

In this, trivalent and hexavalent chromium were separated by using HPLC and detected with ICP-MS in less than 3 minutes. Many factors were taken in to consideration and optimized in order to achieve successful separation and reproducibility.

The overall results showed that 0.5 mL/min of the reaction gas, pH 6.8~7.0, the ratio of 95 : 5 for solvent A and B, 0.8~1.0 mL/min of the mobile phase and 100  $\mu\text{L}$  of sample injection volume were appeared to be optimal.

After the optimization of these parameters, low concentrations can be measured with an estimated detection limit of 70 ng/L for Cr(III) and 50 ng/L for Cr(VI). The tap water samples were then analyzed after a three times dilution with mobile phase but the resulting chromatogram did not yield any peaks, thereby indicating the absence of or extremely low levels of chromium. For that reason, the tap water was then spiked with 1  $\mu\text{g/L}$  of each chromium species. The results of this analysis show that Cr(III)=57 ng/L and Cr(VI)=22 ng/L. The recovery was 96.3 %.

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