

## Articles

### A Study of the Potential Interference of $\text{ArC}^+$ on the Direct Determination of Trivalent Chromium and Hexavalent Chromium Using Ion Chromatography Coupled with ICP-MS

Sang-Ho Nam,<sup>\*</sup> Young-Il Park, Jae-Jin Kim, Sun-Ho Han,<sup>†</sup> and Won-Ho Kim<sup>\*</sup>

*Department of Chemistry, Mokpo National University, Muangun, Chonnam 534-729, Korea*

*<sup>†</sup>Nuclear Chemistry Research Division, Korea Atomic Energy Research Institute, Daejeon 305-353, Korea*

*Received August 26, 2003*

Low and high resolution inductively coupled plasma mass spectrometry (ICP-MS) coupled with ion chromatography (IC) has been investigated for speciation of Cr(III) and Cr(VI). In particular, the interference of  $\text{ArC}^-$  formed by the carbon in a sample on the simultaneous determination of Cr(III) and Cr(VI) has been studied. In chemical speciation, this study shows that quadrupole type ICP-MS with low resolution has a limitation of simultaneous determination of chromium species if the sample contains the carbon elements. The interference problems can be solved by high resolution ICP-MS.

**Key Words :** Chromium species, Ion chromatography, ICP-MS

#### Introduction

In various research fields, the chemical speciation of trace elements in a sample has been very important because the effects of elements, especially trace heavy metals, on ecological and environmental systems are generally influenced by the elements' chemical forms.<sup>1-3</sup> Some elements in a sample not only exist in more than one valence state, but also can be present as cationic, anionic, and neutral species. In particular, Cr(III) is an essential element in nutrition, but Cr(VI) is very toxic to human beings.<sup>4</sup> Ion chromatography (IC) has been widely used for the chemical speciation of elements in various samples. The procedure, in general, consists of a separator column, a suppressor column, a conductivity detector (or UV/VIS detector). But, due to the low dissociation characteristics for conductivity detection and the poor complexation ability for UV/VIS absorption detection, some analytes have posed problem for measurement with IC. Thus, IC has been coupled with various detectors to overcome the difficulties.<sup>4,17</sup> The various analytical methods were reviewed for the speciation of Cr(III) and Cr(VI).<sup>2</sup> Direct current plasma atomic emission spectrometry (DCP-AES) has been used as an element selective detection method.<sup>4,5</sup> Inductively coupled plasma atomic emission spectrometry (ICP-AES) has been coupled with chromatography for element speciation. Side-On-View (S-O-V) ICP-AES has been reported as an element selective detection method after chromatographic separation.<sup>6</sup> According to reports, the detection limit can be low for both Cr(III) and Cr(VI) with hollow cathode atomic absorption spectrometry (HC-AAS) coupled with the preconcentration technique.<sup>8</sup> Wavelength modulation diode laser flame atomic absorption

spectrometry (WM-LAAS) was coupled with liquid chromatography for chromium speciation.<sup>9</sup> The speciation of Cr(III) and Cr(VI) has been done with direct-injection nebulization (DIN) and S-O-V ICP-AES.<sup>10</sup> E-O-V ICP-AES could be also used for the detection of chromium species.<sup>18</sup>

Since plasma source mass spectrometry has been used as an element selective detector for IC, inductively coupled plasma mass spectrometry (ICP-MS) has been the most powerful technique for the detection of analytes separated by IC due to high detection power, multi-elemental analysis, minor matrix effect, minor memory effect, high analysis speed and the tolerance to high salt concentration.<sup>7,19-24</sup> The speciation of arsenic in urine has been done using high-performance liquid chromatography with inductively coupled plasma mass spectrometric detection.<sup>19,21</sup> Inductively coupled plasma mass spectrometry was used for micellar liquid chromatography: speciation of alkyltin compounds.<sup>22</sup> Liquid chromatography was combined with an inductively coupled plasma mass spectrometric detector for simultaneous determination of gold drug metabolites and related metals in human blood.<sup>23</sup> ICP-MS was used for the detection of chromium species.<sup>7</sup>

But, in these previous studies, the interferences on the simultaneous determination of chromium species in samples with ICP-MS coupled with chromatographic methods have not been extensively studied. The  $\text{ArC}^-$  formed by the carbon elements can seriously interfere with the accurate analysis of the chromium species in environmental and clinical samples. In the present study, the interference caused by  $\text{ArC}^-$  on the determination of chromium species has been studied with low and high resolution ICP-MS coupled with IC.

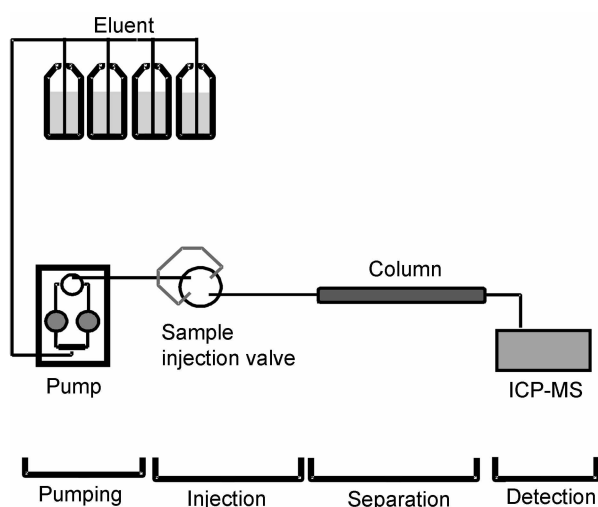


Figure 1. Schematic diagram of ICP-MS with IC.

### Experimental Section

**Instrumentation and operating condition.** The chromatographic system used in the present work was a Dionex (Dionex Corporation, Sunnyvale, CA, 94088-3603, USA) model GP 50 ion chromatography pump. Samples were introduced into the analytical column by direct injection with a sample loop. The sample injection volume was 200  $\mu\text{L}$ . An analytical column ANX4605-Cr (CETAC Technologies INC. 5600 South 42nd street, Omaha, Nebraska 68107, USA) was used. The effluent from the analytical column was introduced directly into HR-ICP-MS (Thermo Finnigan MAT, GmbH Barkhausenstr. 2, D-28197, Bremen, Germany) model Finnigan MAT ELEMENT. The general schematic diagram for this study is shown in Figure 1. Details of the

Table 1. Instrumentals and operating conditions

Ion chromatography	
System	GP50 Gradient Pump (Dionex Corp.)
Flow rate	1.0 mL/min
Analytical column	ANX 4605-Cr anion exchange column (CETAC Technologies)
Sample loop	200
Eluent	0.06 M HNO <sub>3</sub>
ICP-MS	
System	Finnigan MAT ELEMENT
Plasma power	1300W
Outer gas flow	Ar: 13.00 L/min
Auxiliary gas flow	Ar: 0.70 L/min
Nebulizer gas flow	Ar: Low resolution: 0.70 L/min Medium resolution: 0.68 L/min
Resolution	Low resolution: 300 Medium resolution: 4000
Total acquisition time, s	650
Monitoring mass	Low resolution: $m/z$ 51.9400 Medium resolution: Cr: $m/z$ 51.9400 ArC <sup>+</sup> : $m/z$ 51.9618

instrumental and operating condition are described in Table 1.

**Chemicals and reagents.** Analytical stock solution for Cr(III) (ICP-AES of stock solution 1000 ppm, in 2% HNO<sub>3</sub>, cat. # PI.CR2-2Y) was obtained from SPEX Certiprep (203 Norcross Ave. Metuchen, NJ 08840, USA). Cr(VI) (Potassium Chromate K<sub>2</sub>CrO<sub>4</sub>, No. 731692) was obtained from Fisher Laboratory (Fisher Scientific Canada, Ltd, 112ch, Colonnade Road Nepean, Ontario K1E7L6, Canada). The eluent of 0.06 M HNO<sub>3</sub> was prepared from concentrated nitric acid (Merck White House Station NJ 8889-0200, USA). The potassium cyanide and potassium carbonate were obtained from Merck (Merck Ltd, wsiw-53, Germany). All solutions were also prepared with 18 M $\Omega$ -cm distilled deionized water obtained from the aquaMAX<sup>TM</sup> (AQ-MAX-311BASIC(II) MEM) water purification system (Young Lin, 899-6 Hokye 2-dong, Dongan-gu, Anyang-si, Kyonggi-do 431-836, Korea).

### Results and Discussion

Cr(III) is an essential element, but Cr(VI) is very toxic to human beings. Thus, speciation of chromium ions in a sample is very important. Many studies have been done on the chemical speciation of chromium.<sup>1-18</sup> But, the interference effects of other ions on the chemical speciation of chromium have not been investigated. Thus, in this work, a study on the interference effect of CO<sub>3</sub><sup>2-</sup> and CN<sup>-</sup> on the chemical speciation of Cr(III) and Cr(VI) has been done with low and high resolution ICP-MS coupled with IC.

**The effect of CO<sub>3</sub><sup>2-</sup> on the chemical speciation of Cr(III) and Cr(VI).** If the CO<sub>3</sub><sup>2-</sup> exists in a sample, the carbon in the CO<sub>3</sub><sup>2-</sup> ion can form the ArC<sup>-</sup> in the Ar plasma, and then the ArC<sup>-</sup> can interfere with the analysis of Cr (mass 52). In this study, the concentration of carbon in a sample was varied from 5 mg/L to 15 mg/L to investigate the effect of carbon on the chemical speciation of chromium. Figure 2

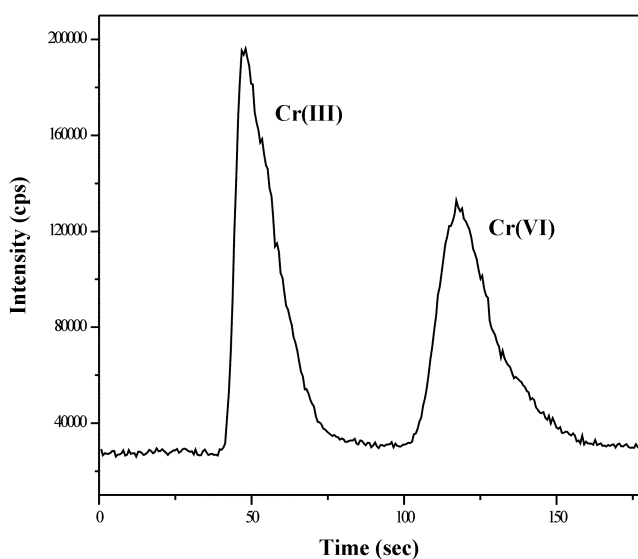
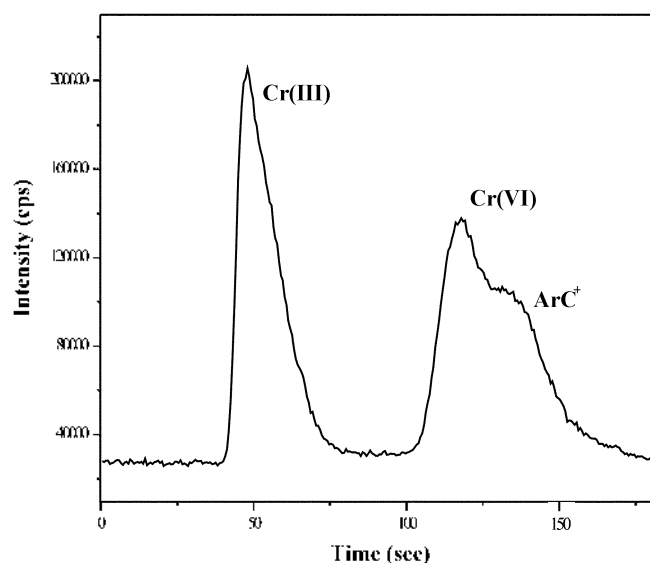
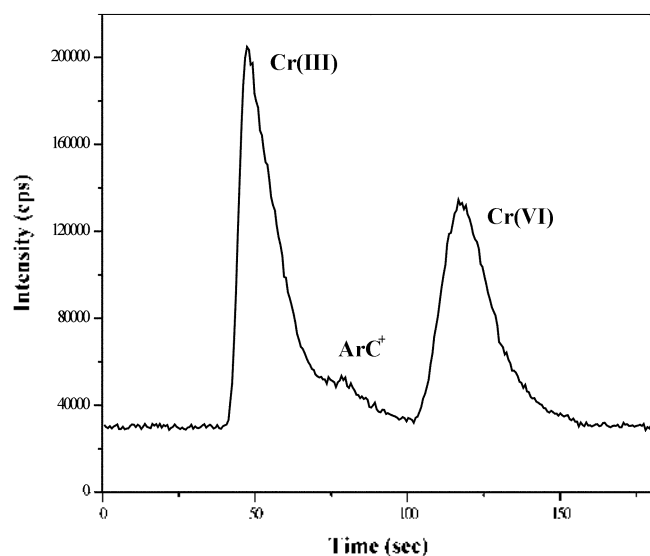


Figure 2. A chromatogram for 10  $\mu\text{g/L}$  Cr(III) and Cr(VI) in 0.001 M HNO<sub>3</sub> including carbonate ion (CO<sub>3</sub><sup>2-</sup>) with ICP-MS and IC. (Concentration of carbon: 5 mg/L. Eluent: 0.06 M HNO<sub>3</sub>. Resolution: 300.

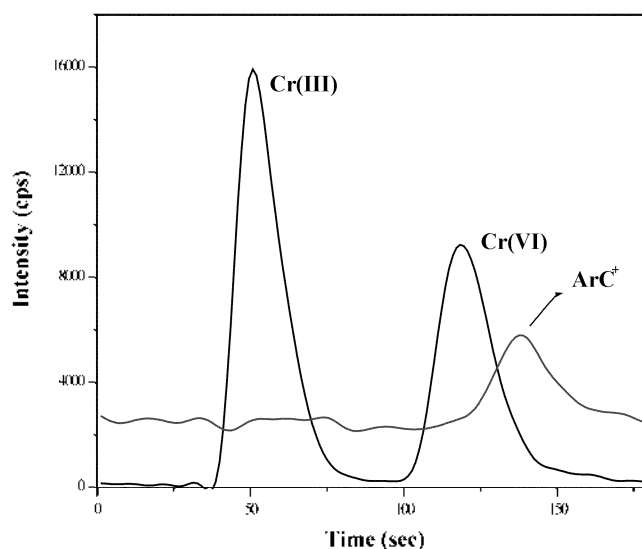


**Figure 3.** A chromatogram for 10 µg/L Cr(III) and Cr(VI) in 0.001 M HNO<sub>3</sub> including carbonate ion (CO<sub>3</sub><sup>2-</sup>) with ICP-MS and IC. (Concentration of carbon: 15 mg/L). Eluent: 0.06 M HNO<sub>3</sub>. Resolution: 300.

shows the chromatogram for 10 µg/L Cr(III) and Cr(VI) in 0.001 M HNO<sub>3</sub> including carbonate ion (CO<sub>3</sub><sup>2-</sup>). The concentration of carbon was 5 mg/L. The employed mass resolution was 300, which is typically used for quadrupole ICP-MS. As the results show, the carbon concentration of 5 mg/L did not have a serious effect on the speciation of Cr(III) and Cr(VI). Figure 3 shows the chromatogram for 10 µg/L Cr(III) and Cr(VI) in 0.001 M HNO<sub>3</sub> including carbonate ion (CO<sub>3</sub><sup>2-</sup>). The concentration of carbon was 15 mg/L. The result showed that the ArC<sup>+</sup> did seriously interfere with the determination of Cr(VI). As the concentration of carbon in a sample was increased, the determination



**Figure 4.** A chromatogram for 10 µg/L Cr(III) and Cr(VI) in 0.001 M HNO<sub>3</sub> including carbonate ion (CN<sup>-</sup>) with ICP-MS and IC. (Concentration of carbon: 5 mg/L). Eluent: 0.06 M HNO<sub>3</sub>. Resolution: 300.

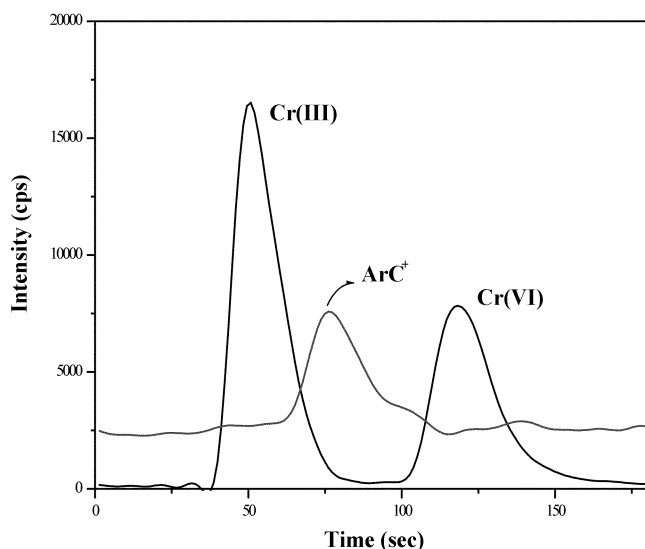


**Figure 5.** A chromatogram for 10 µg/L Cr(III) and Cr(VI) in 0.001 M HNO<sub>3</sub> including carbonate ion (CO<sub>3</sub><sup>2-</sup>) with ICP-MS and IC. (Concentration of carbon: 15 mg/L). Eluent: 0.06 M HNO<sub>3</sub>. Resolution: 4000.

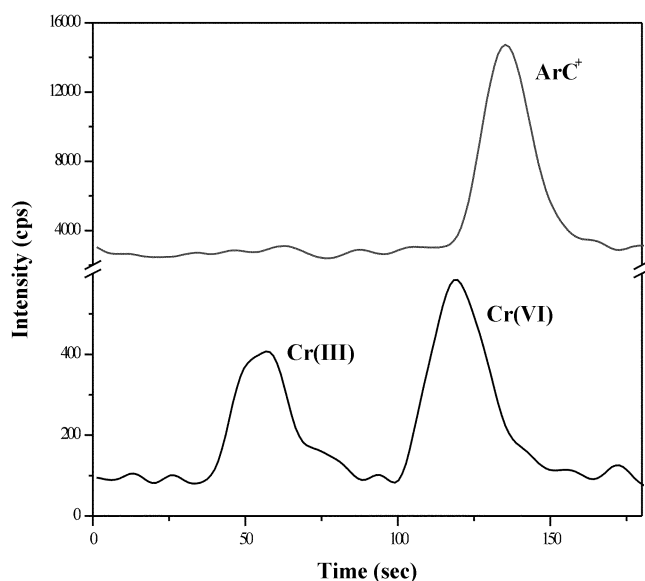
of Cr(VI) was not possible. This study shows that the determination of Cr(VI) can not be done with IC-ICP-MS (mass resolution: 300) when the concentration of carbon in a sample is above the 15 mg/L.

**The effect of CN<sup>-</sup> on the chemical speciation of Cr(III) and Cr(VI).** The carbon in the CN<sup>-</sup> ion can also form the ArC<sup>+</sup> in the Ar plasma, then it can possibly interfere with the determination of chromium species. The carbon concentration was varied from 5 mg/L to 15 mg/L to investigate the effect of CN<sup>-</sup> on chemical speciation of chromium. The carbon was originally from the CN<sup>-</sup> ion in the sample. Figure 4 shows the chromatogram for 10 µg/L Cr(III) and Cr(VI) in 0.001 M HNO<sub>3</sub> including cyanide ion (CN<sup>-</sup>) with IC-ICP-MS (mass resolution: 300). The concentration of carbon was 5 mg/L. As the results are shown, the formed ArC<sup>+</sup> from CN<sup>-</sup> ion interfered with the determination of Cr(III). This study shows that the CN<sup>-</sup> ion in a sample can have an interference effect on the determination of Cr(III) with IC-ICP-MS (mass resolution: 300) when the concentration of carbon from the CN<sup>-</sup> ion is above 5 mg/L.

**The chemical speciation of Cr(III) and Cr(VI) with IC-ICP-MS (mass resolution: 4000).** In this study, the mass resolution of ICP-MS was increased to reduce or remove the interference by ArC<sup>+</sup>. Figure 5 shows the chromatogram for 10 mg/L Cr(III) and Cr(VI) in 0.001 M HNO<sub>3</sub> including carbonate ions with IC-ICP-MS (mass resolution: 4000). The concentration of carbon was 15 mg/L. The chromium species (mass 51.9400) could be separated from ArC<sup>+</sup> (mass 51.9618) with IC-ICP-MS (mass resolution: 4000). Thus, the interference of ArC<sup>+</sup> could be eliminated. This study shows that the chromium speciation can be successfully performed with IC-ICP-MS (mass resolution: 4000) even though the CO<sub>3</sub><sup>2-</sup> ions co-exist in samples. Figure 6 shows the chromatogram for 10 µg/L Cr(III) and Cr(VI) in 0.001 M HNO<sub>3</sub> including cyanide ion (CN<sup>-</sup>). The concentration of carbon



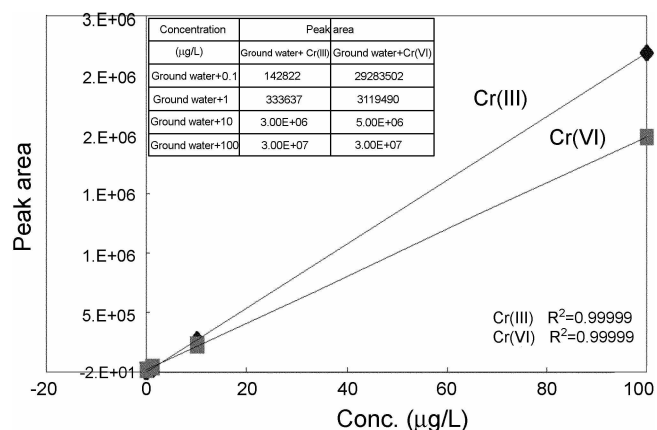
**Figure 6.** A chromatogram for 10  $\mu\text{g/L}$  Cr(III) and Cr(VI) in 0.001 M  $\text{HNO}_3$  including carbonate ion ( $\text{CN}^-$ ) with ICP-MS and IC. (Concentration of carbon: 15 mg/L). Eluent: 0.06 M  $\text{HNO}_3$ , Resolution: 4000.



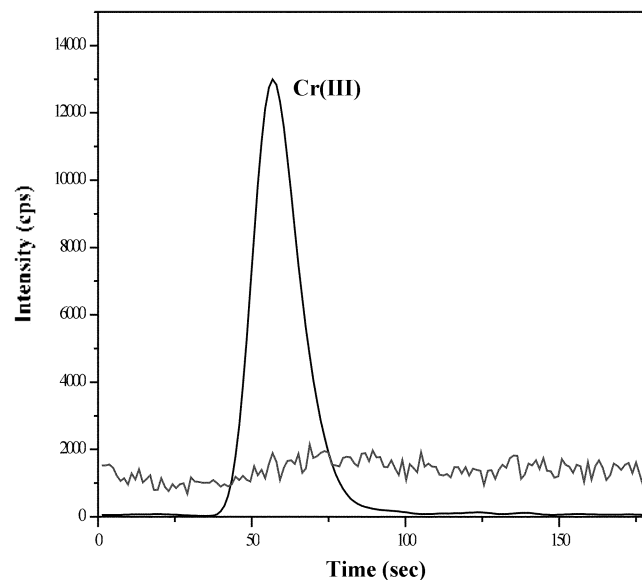
**Figure 7.** A chromatogram for Cr(III) and Cr(VI) in groundwater with ICP-MS and IC. Eluent: 0.06 M  $\text{HNO}_3$ , Resolution: 4000.

was 15 mg/L. The result shows that the mass spectral interference of  $\text{ArC}^+$  formed from  $\text{CN}^-$  could be eliminated with IC-ICP-MS (mass resolution: 4000). The chemical speciation of Cr(III) and Cr(VI) could be performed with IC-ICP-MS even if  $\text{CN}^-$  ions exists in the sample.

**The determination of Cr(III) and Cr(VI) in ground water.** The above results show that IC-ICP-MS (mass resolution: 300) could not quantitatively determine the Cr(III) and Cr(VI) due to the mass spectral interference of  $\text{ArC}^+$  formed from  $\text{CO}_3^{2-}$ . The ground water, in general, contained the  $\text{CO}_3^{2-}$  ions. Thus, IC-ICP-MS (mass resolution: 4000) was used for the determination of Cr(III) and Cr(VI) in a ground water sample. The ground water was



**Figure 8.** Calibration curve for Cr(III) and Cr(VI) in groundwater with IC-ICP-MS. Eluent: 0.06 M  $\text{HNO}_3$ , Resolution: 4000.



**Figure 9.** A chromatogram for Cr(III) in NIST SRM 1643d with ICP-MS and IC. Eluent: 0.06 M  $\text{HNO}_3$ , Resolution: 4000.

obtained from a site at the Korea Atomic Energy Research Institute, Daejeon, South Korea. Figure 7 shows the chromatogram for the speciation of Cr(III) and Cr(VI) in a ground water with IC-ICP-MS (mass resolution: 4000). The quantitative determination of Cr(III) and Cr(VI) was done by the standard addition method. The calibration curves of standard addition method were obtained with IC-ICP-MS (mass resolution: 4000). The results are shown in Figure 8. The measured concentration of Cr(III) and Cr(VI) were 0.17  $\mu\text{g/L}$  and 0.87  $\mu\text{g/L}$ , respectively.

**The determination of Cr(III) and Cr(VI) in a NIST SRM 1643d water sample.** IC-ICP-MS (mass resolution: 4000) was used to quantitatively determine the Cr(III) and Cr(VI) in a NIST SRM 1643d. As the results show in Figure 9, the Cr(III) was detected only in the SRM 1643d. The Cr(VI) and  $\text{ArC}^+$  were not detected in the SRM 1643d. The measured value is  $19.43 \pm 0.41 \mu\text{g/L}$ , which closely matches with the certified value of  $19.05 \pm 0.57 \mu\text{g/L}$  (total chromium).

### Conclusion

This study shows that the  $\text{CO}_3^{2-}$  and  $\text{CN}^-$  ions can interfere with the simultaneous determination of Cr(III) and Cr(VI) in a sample with IC-ICP-MS. In particular, IC-ICP-MS with low resolution (resolution of 300) is limited for the chemical speciation of Cr(III) and Cr(VI) due to the mass spectral interference of  $\text{ArC}^-$  formed by  $\text{CO}_3^{2-}$  and  $\text{CN}^-$ . Thus, interference problems can be solved by IC-ICP-MS with high resolution (resolution of 4000). The method was applied to a ground water sample and an NIST SRM 1643d water sample. The measured concentrations of Cr(III) and Cr(VI) were  $0.17 \mu\text{g/L}$  and  $0.87 \mu\text{g/L}$ , respectively, in the ground water samples. The Cr(III) was detected only in a NIST 1643d water sample. The measured value of Cr(III) agrees well with the certified value of total chromium.

### References

1. Trace Metal Analysis and Speciation in *Journal of Chromatography Library*; Krull, I. S., Ed.; Elsevier: Amsterdam, 1991; Vol. 47.
2. Trace Metal Analysis and Speciation in *Journal of Chromatography Library*; Gjerde, D. T.; Mechra, H.; Krull, I. S., Eds.; Elsevier: Amsterdam, 1991; Vol. 47, pp 213-239.
3. Makata, F.; Hara, S.; Matsuo, H.; Kumamaru, T.; Matsushita, S. *Anal. Sci.* **1985**, *1*, 157.
4. Urasa, I. T.; Nam, S. *J. Chromatogr. Sci.* **1989**, *127*, 30.
5. Urasa, I. T.; Ferede, F. *Anal. Chem.* **1987**, *59*, 1563.
6. Posta, J.; Berndt, H.; Luo, S. K.; Schaldach, G. *Anal. Chem.* **1993**, *65*, 2590.
7. Jakubowski, N.; Jepkens, B.; Stuver, D.; Berndt, H. *J. Anal. Spectrom.* **1994**, *9*, 193.
8. Vidal, J. C.; Sanz, J. M.; Castillo, J. R.; Fresenius, J. *Anal. Chem.* **1992**, *344*, 234.
9. Groll, H.; Schaldach, G.; Berndt, H.; Niemax, K. *Spectrochim. Acta Part B* **1995**, *50*, 1293.
10. Gjerde, D. T.; Wiederin, D. R.; Smith, F. G.; Mattson, B. M. *J. Chromatogr.* **1993**, *640*, 73.
11. Cox, A. G.; Cook, I. G.; McLeod, C. W. *Analyst* **1985**, *110*, 332.
12. LaFreniere, K. E.; Fassel, V. A.; Eckels, D. E. *Anal. Chem.* **1987**, *62*, 879.
13. Roychowdhury, S. B.; Koropchak, J. A. *Anal. Chem.* **1990**, *62*, 484.
14. Lou, S. K.; Berndt, H.; Posta, J. *J. Anal. Spectrom.* in press.
15. Rochl, R.; Alforque, M. M. *At. Spectrosc.* **1990**, *11*, 210.
16. Niemax, K.; Groll, H.; Schnurer-Patschan, C. *Spectrochim. Acta Rev.* **1993**, *15*, 349.
17. Jakubowski, N.; Feldmann, I.; Stuver, D.; Berndt, H. *Spectrochim. Acta Part B* **1992**, *47*, 119.
18. Nam, S. H.; Kim, M. J.; Oh, S. W.; Lee, J. H.; Pak, Y. N. *American Laboratory* **2001**, *33*(8), 40.
19. Heitkemper, D.; Creed, J.; Caruso, J.; Fricke, F. L. *J. Anal. At. Spectrom.* **1989**, *4*, 279.
20. Beauchemin, D.; Siu, K. W. M.; McLaren, J. W.; Berman, S. S. *J. Anal. At. Spectrom.* **1989**, *4*, 285.
21. Branch, S.; Bancroft, K. C. C.; Ebdon, L.; O'Neill, P. *Anal. Proc.* **1989**, *26*, 73.
22. Suyani, H.; Heitkemper, D.; Creed, J.; Caruso, J. A. *Appl. Spectrosc.* **1989**, *43*, 962.
23. Matz, S. G.; Elder, R. C.; Tepperman, K. *J. Anal. At. Spectrom.* **1989**, *4*, 767.
24. Nam, S.-H.; Kim, J.-J.; Han, S.-S. *Bull. Korean Chem. Soc.* **2003**, *24*, 12.