Flow injection analysis of trace chromium (VI) in drinking water with a liquid waveguide capillary cell and spectrophotometric detection

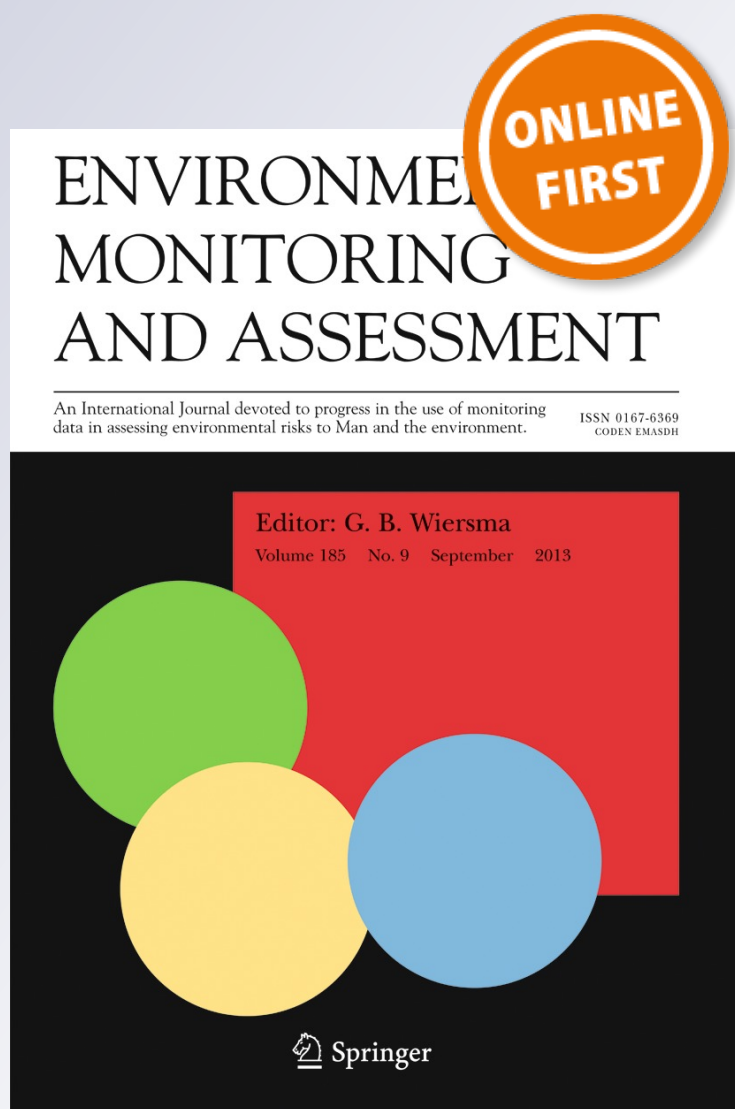## Jian Ma, Dongxing Yuan & Robert H. Byrne

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Flow injection analysis of trace chromium (VI) in drinking water with a liquid waveguide capillary cell and spectrophotometric detection

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Abstract Hexavalent chromium (Cr(VI)) is an acknowledged hazardous material in drinking waters. As such, effective monitoring and assessment of the risks posed by Cr(VI) are important analytical objectives for both human health and environmental science. However, because of the lack of highly sensitive, rapid, and simple procedures, a relatively limited number of studies have been carried out in this field. Here we report a simple and sensitive analytical procedure of flow injection analysis (FIA) for sub-nanomolar Cr(VI) in drinking water samples with a liquid core waveguide capillary cell (LWCC). The procedure is based on a highly selective reaction between 1, 5-diphenylcarbazide and Cr(VI) under acidic conditions. The optimized experimental parameters included reagent concentrations, injection volume, length of mixing coil, and flow rate. Measurements at 540 nm, and a 650-nm reference wavelength, produced a 0.12-nM detection limit. Relative standard deviations for 1, 2, and 10 nM samples were 5.6, 3.6, and 0.72 % (n=9), and the analysis time was <2 min sample^{-1}. The effects of salinity and interfering ions, especially Fe(III), were evaluated. Using the FIA-LWCC method, different sources of bottled waters and tap waters were examined. The Cr(VI) concentrations of the bottled waters ranged from the detection limit to ∼20 nM, and tap waters collected from the same community supply had Cr(VI) concentration around 14 nM.

Introduction

Chromium can be released to the environment from a variety of industrial activities such as iron and steel production, leather tanning, photographic processing, and chromium plating (Richard and Bourg, 1991). The principal oxidation states of chromium in the natural environment are hexavalent chromium (Cr(VI)) and trivalent chromium (Cr(III)) (Gomez and Callao 2006). Although Cr(III) is essential for the metabolic processes of some organisms (Agency for Toxic Substances and Disease Registry ATSDR 2000), Cr(VI) is toxic to humans, animals, plants, and microorganisms and is classified as a group I human carcinogen by the International Agency of Research on Cancer (IARC) (International Agency of Research on Cancer 1999). With a relatively high mobility, Cr(VI) can move through sediments into aquifers and groundwater (Buerge and Hug 1998). While chromium contamination is mostly observed in waste

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water, recent research has shown that chromium contamination at trace levels can also enter drinking water supplies (Divrikli et al. 2008) and surface and ground waters (Yilmaz et al. 2010). Zhitkovitch (2011) has recently reviewed the metabolism of chromium and the risks of cancer created by chromium in drinking water. In July 2011, the Office of Environmental Health Hazard Assessment (OEHHA) of the California EPA proposed a 0.02-μg/L (~0.4 nM) Public Health Goal (PHG) for Cr(VI) in drinking water (California Environmental Protection Agency 2011), substantially lower than the 0.06 μg/L (~1.1 nM) level established in 2009 (California Environmental Protection Agency 2009). Both of these limits are much lower than the provisional guideline value for total chromium set by the World Health Organization (WHO; 50 μg/L, ~0.96 μM) (World Health Organization and Guidelines for drinking-water quality 2006), as well as the 100 μg/L (~1.92 μM) maximum contaminant level for total chromium set by the United States Environmental Protection Agency (2010). As additional research on Cr(VI) toxicity has become available, the US EPA has begun to re-evaluate this standard (100 μg/L) and has recommended enhancing the monitoring of Cr(VI) in drinking water (United States Environmental Protection Agency 2010).

Most published methods for determining chromium concentrations and speciation (Gomez and Callao 2006; Ressalan et al. 1997; Kotas and Stasicka 2000; Parks et al. 2004; Bobrowski et al., 2009; Pakhunde et al. 2012) suffer from one or more shortcomings including slow sample throughput, high cost of instrumentation, and necessity of substantial operator expertise (Ma et al. 2012). A sensitive, simple, and low-cost method for analysis of Cr(VI) at nanomolar levels in drinking water was recently reported based on a commercially available solid phase extraction cartridge and a portable spectrometer (Ma et al. 2012). However, the 3-nM detection limit (DL) of the method was approximately one order of magnitude higher than that of the strictest California EPA standard (0.4 nM).

The study described below is directed at development of a fast, automated method for measuring Cr(VI) at levels consistent with the strictest California EPA concentration limit. The measurement chemistry is based on a reaction with 1, 5-diphenylcarbazide (DPC) under acidic conditions, and highly selective for Cr(VI) from other metals (Public Health Association) et al. 1995). Flow injection analysis (FIA) was chosen due to its simplicity, amenability to automation, high sample-throughput, and

low risk of contamination (Ma et al. 2009). The liquid waveguide capillary cell (LWCC) was adapted to enhance method sensitivity by substantially increasing spectrophotometric path length (Dallas and Dasgupta 2004; Gimbert and Worsfold 2007; Páscoa et al. 2012). Subsequent to development of the FIA-LWCC method, different brands of bottled water and tap waters samples were analyzed in order to demonstrate the utility of the method for discriminating between samples that clearly meet recommended concentration levels and those that do not. Compared with previous work (Yao and Byrne, 1999; Li et al. 2003), the protocol described in the present study exhibits higher rates of sample throughput and unsurpassed sensitivity.

Experimental

Reagents

All chemicals were reagent grade or better, purchased from Sinopharm Chemical Reagent Co., China and used without further purification. Milli-Q water (Millipore, USA), 18.2 MΩ cm, was used for making all solutions. A stock Cr(VI) solution (10 mM) was prepared by dissolving K_2CrO_4 in water, and a 2-μM Cr(VI) working solution was prepared by stepwise dilution of the stock solution daily. H_2SO_4 (2.5 M) was prepared from ultrapure grade sulfuric acid. A 0.5 % (m/v, ~20.6 mM) DPC stock solution, prepared by dissolving 0.25 g of DPC in 50 mL of acetone, was stored in a brown bottle at 4 °C while not in use. Based on optimization studies, a working colorimetric solution for the FIA system was prepared by 20-fold dilution of the stock DPC solution with 0.125 M H_2SO_4 (the final DPC working solution concentration was 0.025 % (m/v))

Analytical system

The FIA system utilized one two-channel peristaltic pump (BT-100-1L, Baoding Longer Precision Pump Co., China) equipped with 1.30 mm i.d. PharMed BPT tubing (Cole-Parmer, USA). With identical tubing size, the working colorimetric solution and the carrier solution were delivered at the same rate, reducing flow pulses and generally simplifying the system (Ma and Byrne, 2012). Samples from the standard solution container and sample bottles were withdrawn with a syringe through a six-port injection valve (Cheminert C22-3186D, VICI, USA).

This reduced sample cross-contamination and carryover effects (vide infra). When the valve was switched from "load" position to "injection" position, the injected sample was mixed with DPC reagent in a 75-cm knotted mixing coil (MC) made from 1/16 PTFE tubing (i.d. 0.75 mm, VICI, USA). Subsequent formation of the colored Cr-DPC complex was monitored with the LWCC-based detection system. The system consisted of one 500-cm capillary flow cell (550 μm i.d., WPI Inc., USA). The light source (tungsten halogen lamp LS-1-LL), two fiber-optic cables (QP600-2-SR), a miniature charge coupled device (CCD) spectrometer (USB 2000+), and data-collecting software (Spectrasuite) were purchased from Ocean Optics Inc., USA. Light absorption of the Cr-DPC complex was monitored at 540 nm, and 650 nm was used as a correction wavelength to compensate for variations in the intensity of the light source and refractive index difference between carrier and sample. A detailed description of experiment setup, data processing, and the LWCC cleaning protocol can be found in our previous publications (Ma and Byrne, 2012).

Sample collection and analysis

Twenty-nine bottled drinking water samples from different vendors were purchased from local markets and kept sealed until analysis. Most of them were collected in duplicate for comparisons of sample differences in the same batch. Bottled waters were classified as purified water, mineralized water, and natural spring/mineral water. Five tap water samples from different laboratories in Xiamen University were stored in clean plastic bottles and analyzed within 1 h.

Results and discussion

The FIA system was optimized via univariate experimental design with investigated parameters including reagent concentrations, injection volume, length of mixing coil, and flow rate. Optimization of flow rate balanced two factors: higher flow rate shortens reaction time and can result in incomplete Cr-DPC product formation; low flow rates causes higher dispersion and peak broadening. Therefore, the effects of variable injection volume and MC length were evaluated over a wide range of flow rate. A low concentration Cr(VI) standard solution (20 nM) was used throughout the parameter-optimization experiments. Each sample

was quantified at least three times, and the results were shown as an average ± the standard deviation (SD, $n \geq 3$). Sensitivity, analysis time, and peak shape were central concerns for parameter optimization.

Influence of H_2SO_4 and DPC concentrations

At a total Cr(VI) concentration of 1 μM, the kinetic of Cr-DPC formation was found to be dependent on the concentrations of DPC and H_2SO_4 (Ma et al. 2012). For FIA measurements at nanomolar concentration levels (Fig. 1), no significant absorbance increases were found when the H_2SO_4 concentration was higher than 0.1 M and the DPC concentration was higher than 0.025 %. Since this is consistent with our previous study (Ma et al. 2012) at much higher Cr(VI) concentrations, the respective concentrations of sulfuric acid and DPC used in all subsequent experiments were 0.125 M and 0.025 %.

Influence of injection volume

Analyte concentrations in reagent–sample mixtures, as well as the absorbance of the Cr-DPC complex, are strongly influenced by the sample injection volume. As
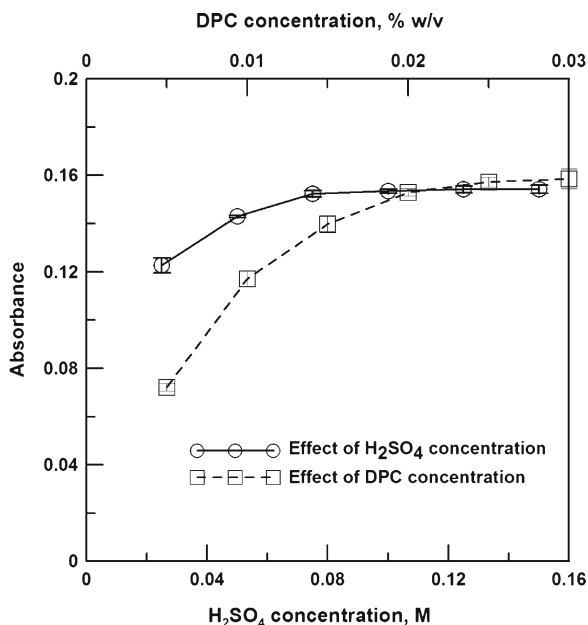

Fig. 1 The effect of H_2SO_4 and DPC concentrations on absorbance with injection volume of 350 μL, mixing coil of 75 cm, and flow rate of 1.75 mL/min. Results are shown as an average ± the standard deviation (SD, $n=3$)

shown in Fig. 2, absorbance increases were observed for injection volumes up to 350 μL, and no further increases were observed for injection volumes at 400 μL. In our previous investigations (Ma et al. 2009), excessive injection volumes can create peak broadening and reduce reproducibility. As such, the injection volume used for all subsequent measurements was 350 μL. With an injection volume of 350 μL, Fig. 2 shows that no significant absorbance variations are observed for flow rates between 1.25 and 2.50 mL/min.

Influence of MC length

The influence of mixing coil length on absorbance is shown in Fig. 3. In contrast with the results in Fig. 2, flow rate had a large influence on observed absorbances, especially for shorter MC lengths (e.g., 25 cm). The effect was substantially reduced for longer MC lengths. Based on the results in Fig. 3, an MC length of 75 cm and a flow rate of 1.75 mL/min were chosen in order to enhance reaction time (promoting absorbance) and minimize dispersion (reducing absorbance).

Refractive index changes between sample and carrier can lead to two types of errors/anomalies in absorbance measurements. One is the physical influence referred to as the Schlieren effect. Another type of problem can be created by the influence of ionic strength or solution composition variations. Samples
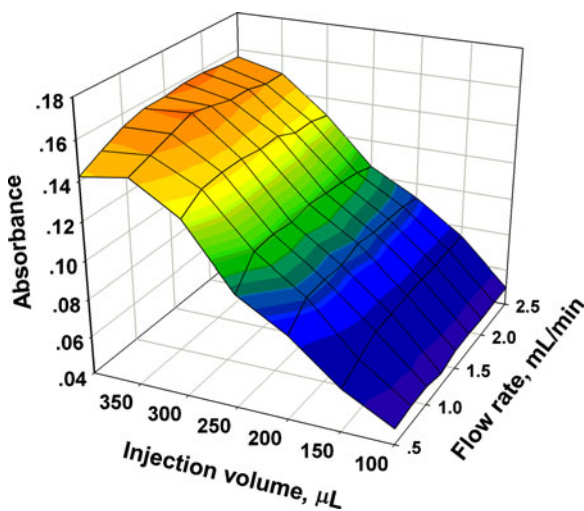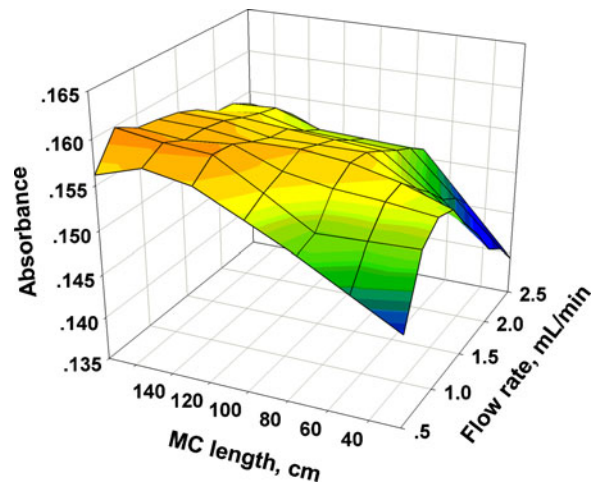

Fig. 3 The effect of mixing coil length (20 to 100 cm) and flow rate (0.5 to 2.5 mL/min) on absorbance with an injection volume of 400 μL

containing 20 nM Cr(VI) were prepared in artificial seawater over a range of salinities and analyzed with the FIA-LWCC system using Milli-Q water as the carrier. The net absorbance exhibits no significant salinity effect. This result is, in part, attributable to the use of the reference wavelength at 650 nm where the Cr-DPC complex is non-absorbing. In addition, it is notable that calibration curves obtained using Milli-Q water and seawater at salinity of 35 had very similar slopes: 0.00752 ± 0.00005 Abs/nM (Milli-Q water, $n=12$) vs. 0.00768 ± 0.00005 Abs/nM (seawater, $n=12$). This less salinity interference result is consistent with our previous study (Yao and Byrne, 1999).

Analytical figures of merit

Using the optimized conditions tabulated in Table 1, a calibration curve was obtained over a concentration range between 0 and 160 nM. The regression equation,

Fig. 2 The effect of injection volume (100 to 400 μL) and flow rate (0.5 to 2.5 mL/min) on absorbance with mixing coil length of 75 cm

Table 1 Recommended analytical parameters

Parameters	Range of tested values	Selected value
H_2SO_4 concentration, M	0.025–0.15	0.125
DPC concentration, %, w/v	0.005–0.03	0.025
Injection volume, μL	100–400	350
Length of mixing coil, cm	25–175	75
Flow rate, mL/min	0.5–2.5	1.75

Table 2 Summary of Cr(VI) concentrations and recoveries in bottled and tap water samples

Sample type	Sample no.	Concentration, nM	Added, nM	Recovery, %
Bottled purified water	7	Below DL–1.5	10 or 20	95.7–103.8
Bottled mineralized water	7	0.3–4.0	10	95.4–101.7
Bottled natural mineral water	15	0.4–19.4	10 or 20	95.1–102.3
Tap water	5	13.5–14.2	20	96.8–101.8

given as Absorbance$=(0.00747\pm0.00010)\times C_{Cr}$ (nM)$+$ (-0.004 ± 0.005), with $R^2=0.9998$ ($n=104$), was created on data obtained over several days. The slope the calibration curve for concentrations between 0 and 10 nM was 0.00741 ± 0.00006 Abs/nM ($R^2=0.9983$, $n=28$), which had excellent agreement with the slope that obtained over the much broader range of concentrations, showing that the analytical system was capable of accurate measurements over a wide range of conditions. Notably, the sample throughput for the optimized conditions was >30 h^{-1}.

The detection limit of the system was calculated as three times the SD of nine measurements of 1 nM Cr(VI) divided by the calibration slope. The result, 0.12 nM, is equivalent to an absorbance uncertainty of ±0.001. The relative standard deviations (RSDs) for repetitive determinations ($n=9$) of 1, 2, and 10 nM Cr(VI) solutions were 5.6, 3.6, and 0.72 %. It should be noted that these results were obtained at concentrations lower than the operating range of most published methods.

Carryover effects were investigated using the following scheme (Zhang 1997): A 2-nM Cr(VI) sample was analyzed three times, with an average observed absorbance 0.0159 ± 0.0004. Next, a 100-nM Cr(VI) sample was analyzed twice and the average absorbance was 0.7766 ± 0.0002. Subsequently, a 2-nM Cr(VI) sample was analyzed again, and the observed absorbance was 0.0160 ± 0.0003. The difference between the

two measurements of the 2 nM sample was insignificant, indicating that sample carry-over is negligible. During the experiment, samples were withdrawn from the sample bottle with only inserted PTFE tubing. This sampling method appears to reduce contamination relative to other sampling methods such as injection with a syringe or use of a pump, where the sample had contact with syringe or pump tubing.

Interferences

The effect of major ions in seawater and drinking water on determinations of Cr(VI) was examined with the optimized parameters shown in Table 1. Based on the criteria of ≤5 % bias for analysis of 10 nM Cr(VI), tolerable molar ratios (analyte/Cr) were 5.2×10^7 for Na$^+$ and Cl$^-$, 4.1×10^6 for Mg^{2+} and SO$_4^{2-}$, 1.0×10^6 for HCO$_3^-$, 1.6×10^5 for Ca^{2+}, 9.0×10^4 for HSiO$_3^-$, 2.5×10^4 for K$^+$, 1.2×10^4 for Li$^+$, and 570 for Sr^{2+}. Dissolved oxygen as high as 100 mg/L had no effect on the analysis of 20 nM Cr(VI). It was found that there was little interference from these foreign ions because the Cr-DPC reaction was highly specific to Cr(VI) (Public Health Association) et al. 1995).

Since Fe^{3+} is a highly reactive ion, high concentrations of iron have the potential to create interferences. As this potential interference has not been evaluated previously, samples containing Fe^{3+}, but Cr(VI) free,

Table 3 Comparison of main parameters for different LWCC-based Cr(VI) analysis methods

Reference	Operation mode	LWCC length, cm	DL, nM	Sample type
Yao and Byrne 1999	Manual	500	0.2	Spring, rain, and sea water
Li et al. 2003	FIA	50	4.8	No application
Pressman and Aldstadt 2005	CFA[b]	1	411	Spiked river water
Xin et al. 2009[a]	Manual	37.6	13.5	No application
This work	FIA	500	0.15	Tap and bottled water

[a]Based on the color of Cr(VI) itself, not DPC chemistry
[b]Continual flow analysis

were analyzed using the optimized FIA system described in Table 1. The relationship between absorbance and iron concentration (C_{Fe}) in this analysis was Absorbance=$(0.00258\pm0.00008)\times C_{Fe}$ (μM)+(0.002 ± 0.001), with R^2=0.9902 (n=12). This result demonstrates that the sensitivity of the analysis to Fe^{3+} is more than three orders of magnitude lower than the sensitivity of the analysis to Cr(VI). As such, considering that the normal concentration of iron in tap water was ~0.3 μM (measured by inductively coupled plasma mass spectrometry, unpublished data), the increase in absorbance due to the presence of Fe^{3+} in such a sample would be less than 0.001, and thus ignored.

Application

The FIA-LWCC system described above was used to determine the concentrations of Cr(VI) in various brands of bottled drinking water and tap water. The samples were also spiked with 10 or 20 nM Cr(VI) to examine recoveries, and duplicate samples were collected and analyzed to assess whether there were significant differences between nominally identical batches of the products. A summary of the results of these analyses is given in Table 2, and a detailed description of the different samples can be found in the Supplementary Materials.

The bottled water samples included three classifications: purified drinking waters (n=7 brands), waters artificially mineralized/oxidized by addition of electrolytes (e.g., KCl, $MgSO_4$, etc.) or oxygen (n=7 brands), and natural mineral/spring waters (n=15 brands). The results in Table 2 show that waters produced using purification techniques such as reverse osmosis and distillation had Cr(VI) concentrations as low as the detection limit to as much as 1.5 nM. Cr(VI) concentrations in artificially mineralized/oxidized waters ranged from 0.4–4.0 nM, only slightly higher than the purified water. As such, waters with added electrolytes had Cr(VI) concentrations that were only slightly in excess of the levels in purified waters. Natural waters, with Cr(VI) concentrations between 0.4 and 19.4 nM, had the highest levels of hexavalent chromium. Results obtained for duplicate samples indicated that Cr(VI) concentrations were very similar for samples obtained from the same source (brand). A high degree of consistency was also seen in the concentrations of Cr(VI) in tap water collected from the same community water supply. Recoveries for spiked tap

water and mineral water samples varied from 95–104 %. Although the Cr(VI) concentrations determined in the tap waters and bottled drinking waters (Table 2) were much lower than most current standards for drinking water (World Health Organization and Guidelines for drinking-water quality 2006), many of the concentrations shown in Table 2 were significantly higher than the PHG of California EPA (0.4 nM).

Conclusions

A fast, sensitive FIA-LWCC method was developed and applied to determination of trace Cr(VI) in drinking water samples. As summarized in Table 3, relative to other LWCC methods for Cr(VI) analysis (Yao and Byrne 1999; Li et al. 2003; Pressman and Aldstadt 2005; Xin et al. 2009), the procedures developed in this work exhibit enhanced performance with respect to sensitivity, sample throughput, and automation. It was shown that natural mineral water had substantially higher Cr(VI) concentrations than purified or artificially mineralized water. The low detection limit, good RSDs, and high recoveries demonstrated in this work show that the FIA-LWCC protocol is an excellent analytical tool for trace Cr(VI) determinations in drinking water. This technique has the potential for long-term online monitoring of water quality for enforcement of strict Cr(VI) limits.

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