An Ion Chromatography Method for Simultaneous Quantification of Chromate, Arsenate, Selenate, Perchlorate, and Other Inorganic Anions in Environmental Media

Srivatsan Mohana Rangan,1–3 Rosa Krajmalnik-Brown,1–3, and Anca G. Delgado1–3,*,†

1School of Sustainable Engineering and the Built Environment, Arizona State University, Tempe, Arizona, USA.
2Biodesign Swette Center for Environmental Biotechnology, Arizona State University, Tempe, Arizona, USA.
3Engineering Research Center for Bio-Mediated and Bio-Inspired Geotechnics (CBBG), Arizona State University, Tempe, Arizona, USA.

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Abstract

Chromium (Cr) (VI) is a toxic, mutagenic, and carcinogenic water pollutant. The standard ion chromatography (IC) method for quantification of Cr (VI) in water samples is Environmental Protection Agency Method 218.7, which requires postcolumn derivatization with 1,5-diphenylcarbazide and UV-Vis spectroscopy detection. Method 218.7 is Cr (VI) specific; thus, it does not allow detection of co-occurring natural and anthropogenic anions in environmental media. In this study, we developed an isocratic IC method with suppressed conductivity detection, a Metrohm Metrosep A Supp 7 column, and sodium carbonate/acetonitrile as mobile phase for simultaneous quantification of Cr (VI), ClO$_4^-$, As (V) as arsenate, Se (VI) as selenate, and the common anions F–, Cl–, NO$_2^-$, NO$_3^-$, and SO$_4^{2-}$. The determination coefficient for every analyte was >0.99 and the method showed good accuracy in quantification. Cr (VI), As (V), Se (VI), and ClO$_4^-$ limit of detection and limit of quantification were 0.1–0.6 µg/L and 0.5–2.1 µg/L, respectively. Recovery of Cr (VI) in various aqueous samples (tap water, surface water, groundwater, and wastewater) was between 97.2% and 102.8%. Overall, most analytes showed acceptable recovery (80–120%) in the environmental samples tested. The IC method was applied to track Cr (VI) and other anion concentrations in laboratory batch microcosms experiments with soil, surface water, and anaerobic medium. The IC method developed in this study should prove useful to environmental practitioners, academic and research organizations, and industries for monitoring low concentrations of multiple anions in environmental media, helping to decrease the sample requirement, time, and cost of analysis.

Keywords: arsenate; chromate; Cr (VI); ion chromatography; perchlorate; selenate; suppressed conductivity

Introduction

Chromium (Cr) (VI) is a toxic, mutagenic, and carcinogenic water pollutant (Cohen et al., 1993; Costa, 1997; Salnikow and Zhitkovich, 2008). The World Health Organization (WHO) set a maximum allowable limit of 50 µg/L for Cr (VI) in groundwater and drinking water (WHO, 2003; El-Shahawi et al., 2011). In the United States, the drinking water maximum contaminant level (MCL) set by the Environmental Protection Agency (EPA) is 100 µg/L total Cr (US EPA, 2010). At the state level, the MCL can be even lower (e.g., 50 µg/L as total Cr in California) (California State Water Quality Control Board, 2020). The standard ion chromatography (IC) method for quantification of chromate ion (CrO$_4^{2-}$), the most common Cr (VI) anion, in water samples is EPA Method 218.7 (Zaffiro et al., 2011). Method 218.7 involves the separation of CrO$_4^{2-}$ (referred henceforth as Cr [VI]) using a high-capacity anion exchange separator column, a postcolumn derivatization with Cr (VI)-specific reagent 1,5-diphenylcarbazide, and a UV-Vis detection of the colored complex at 530 nm (Zaffiro et al., 2011). CrO$_4^{2-}$ detection of the colored complex at 530 nm (Zaffiro et al., 2011). The Cr (VI)-specific reagent diphenylcarbazide and UV-Vis detection allow sensitive quantification of Cr (VI) at low microgram per liter concentrations by avoiding interference from other anions like sulfate ion (SO$_4^{2-}$). However, method 218.7 and methods using similar principles are Cr (VI) specific and do not quantify other analytes present in a given samples (Metrohm USA; Thermo Fisher Scientific; Rakhunde et al., 2012; Onchoke and Sasu, 2016).
Cr (VI) often co-occurs with one or more common inorganic anions such as chloride ion (Cl\(^{-}\)), SO\(_4^{2-}\), and nitrate ion (NO\(_3^{-}\)) in drinking water, industrial wastewater, surface waters, groundwater, acid mine drainage, soils, and sediments (Riley, 1992; Gandhi et al., 2002). In groundwater, acid mine drainage and other process waters, Cr (VI) is often a co-contaminant with other regulated anions such as arsenate ion (AsO\(_3^{3-}\)) and selenate ion (SeO\(_4^{2-}\)) (referred hereafter as As (V) and Se (VI), respectively) or perchlorate ion (ClO\(_4^{-}\)) (Pryzyńska, 2002; Urbanbsky, 2002; Parker et al., 2008; Yoon et al., 2009; Zhitkovich, 2011; Wang et al., 2013; Steinmaus, 2016; Khamkhash et al., 2017; WHO, 2018). ClO\(_4^{-}\} and Cr (VI) are frequently co-detected in drinking water systems across the world (Zhitkovich, 2011; Steinmaus, 2016). Most laboratories use IC with conductivity detection to simultaneously quantify Cl\(^{-}\}, SO\(_4^{2-}\), and NO\(_3^{-}\) using EPA Method 9056A (US EPA, 2007; Weiss, 2016). Separate IC methods with conductivity detection have been reported for quantification of ClO\(_4^{-}\} (EPA Method 314.0) (Hautman et al., 1999), As (V) (Lee and Choi, 2002; Ike et al., 2008; Yeo and Choi, 2009; Bhandari et al., 2011), and Se (VI) (Karlson and Frankenberger Jr, 1986; Mehra and Frankenberger, 1988; Pryzyńska, 2002). Thus, analysis of surface water, groundwater, acid mine drainage, and other environmental aqueous samples containing Cr (VI) and co-occurring anions requires multiple IC analytical methods with different anion exchange columns and eluent compositions. This requirement not only increases the sample volume demand but also the time and overall cost of analysis.

A limited numbers of studies achieved separation and detection of Cr (VI), As (V), and Se (VI) in the presence of common inorganic anions using anion exchange columns and conductivity detection (Bruzzoniti et al., 1999; Kończyk et al., 2018). However, linearity, precision, and accuracy of the co-detected analytes were not reported in these studies (Bruzzoniti et al., 1999; Kończyk et al., 2018), limiting the methods’ applicability to environmental samples commonly analyzed in academic or other research-focused laboratories. In this work, we developed an isotropic IC analytical method with suppressed conductivity detection for simultaneous quantification of Cr (VI) and eight other environmentally relevant anions: fluoride ion (F\(^{-}\}), Cl\(^{-}\}, nitrite ion (NO\(_2^{-}\}), NO\(_3^{-}\}, SO\(_4^{2-}\}, Se (VI), As (V), and ClO\(_4^{-}\} (Bruzzoniti et al., 1999; Kończyk et al., 2018). The method was validated by determining the linearity and accuracy (precision and trueness) for all the anion analytes. We used the method to evaluate recovery of Cr (VI) and the other analytes in tap water, surface water, groundwater, and industrial wastewater samples and to analyze Cr (VI), SO\(_4^{2-}\}, NO\(_3^{-}\}, and Cl\(^{-}\} in laboratory microcosm experiments.

Materials and Methods

Instrumentation

All analyses were performed using a Metrohm AG 930 compact IC flex system (Herisau, Switzerland). The IC was equipped with a chemical suppressor (Metrohm suppressor module [MSM]) and a conductivity detector. An 800 dosino regeneration system was used to deliver the chemical suppressor solution to the MSM. The Metrohm CO\(_2\) Suppressor removed the carbonate (as CO\(_2\}) produced during the chemical suppression reaction in the MSM. The anions were separated using a Metrosep A Supp 7 analytical column (250×4 mm; Metrohm) and a Metrosep A Supp 5 Guard column (5×4 mm; Metrohm). A Metrohm AG 919 IC autosampler plus was used for sample injection. The volume of the sample injection loop was 1000 µL. The data acquisition and processing were performed with the MagIC Net 3.2 Metrodata software.

Chemicals and reagents

Reagent water, LC-MS Ultra CHROMASOLV (Honeywell, Charlotte, NC), was used to prepare the standards and for the sample dilutions. Cr (VI) standards were prepared using K\(_2\)Cr\(_2\)O\(_7\) (Sigma-Aldrich, St. Louis, MO). As (V) and Se (VI) standards were prepared using Na\(_2\)HAsO\(_4\) • 7H\(_2\)O (J.T. Baker, Phillipsburg, NJ) and Na\(_2\)SeO\(_4\) (ACROS Organics, Geel, Belgium). ClO\(_4^{-}\} standards (Metrohm; cat. no. REAIC1023) and mixed anion standard (Metrohm; cat. no. REAIC1035) were used to generate the calibration curves for ClO\(_4^{-}\}, F\(^{-}\}, Cl\(^{-}\}, NO\(_3^{-}\}, NO\(_2^{-}\}, and SO\(_4^{2-}\}.

The eluent and the MSM suppressor solutions were prepared using deionized and purified water using a PURELAB Ultra (ELGA LabWater, United Kingdom) with a specific resistance ≥18.2 MΩ-cm. The eluent (mobile phase) contained 10.8 mM Na\(_2\)CO\(_3\) (3% [v/v] of Metrohm’s A Supp 7 eluent 100× concentrate) and 35% (v/v) gradient grade acetonitrile (Sigma-Aldrich) in deionized water. The pH of the eluent as prepared was 11.9±0.02. The MSM suppressor solution contained 500 mM H\(_2\)SO\(_4\) in deionized water.

The 10% (v/v) H\(_2\)SO\(_4\) and 10% (v/v) H\(_3\)PO\(_4\) solutions for colorimetric determination of Cr (VI) were prepared from concentrated H\(_2\)SO\(_4\) (95–98% solution; VWR, Randor, PA) and concentrated H\(_3\)PO\(_4\) (85% solution; Alfa Aesar, Haverhill, MA), respectively. The complexing reagent contained 5 g/L of 1,5-diphenylcarbazide (Sigma-Aldrich) in acetonitrile.

Analytical methods

The IC method used a constant eluent flow rate of 0.8 mL/min and a constant column/oven temperature of 55°C. The MSM stepping interval was 10 min and the conductivity detector was set at 2.3% per °C. At these conditions, the back pressure was 12±0.4 MPA. The pump start-up time was at 45–60 min during the equilibration of the instrument. Calibrations for the anion analytes were established by injecting quadruplicates of 1, 5, 10, 25, 50, 100, and 200 µg/L standard mixture. The upper limit of quantification (LOQ) for Cl\(^{-}\}, NO\(_3^{-}\}, SO\(_3^{2-}\}, ClO\(_4^{-}\}, and Cr (VI) was 10,000 µg/L (10 mg/L). For other analytes, the upper LOQ was in the range of 1000–9000 µg/L.

EPA Method 7196A was used to quantify Cr (VI) in a contaminated surface water sample and compare the concentrations obtained by the IC method. Cr (VI) concentration was determined colorimetrically at 540 nm using the diphenylcarbazide method (US EPA, 1992). In brief, 0.1 mL of sample or standard was added to a 10 mL test tube followed by addition of 1 mL each of 10% H\(_2\)SO\(_4\) and 10% H\(_3\)PO\(_4\). Then, 0.1 mL of 5 g/L diphenylcarbazide in acetonitrile was added to the test tube. The mixture was then vortexed and incubated at room temperature for 5 min. Absorbance of the magenta color was analyzed using a Varian Cary 50 UV-Vis spectrophotometer (Agilent, Santa Clara, CA) at 540 nm. The spectrophotometer was calibrated using the standard Cr (VI) solution. The calibration range for the colorimetry method was 0.5–75 mg/L Cr (VI) and the detection limit was 0.25 mg/L.
Resolution, limit of detection, LOQ, and accuracy

Resolution of two peaks (R), defined as the ratio of the difference in retention times between two peaks and the average baseline width of two peaks (Harris, 2010), was determined using Eq. (1):

\[
R = \frac{T_{R2} - T_{R1}}{(w_{b1} + w_{b2})/2}
\]

(1)

where \(T_{R1}\) and \(T_{R2}\) are the retention times of adjacent peaks (analyte 1 elutes before analyte 2) and \(w_{b1}\) and \(w_{b2}\) are the widths of the peaks at baseline.

The limit of detection (LOD), defined as the lowest concentration of analyte in a sample that can be readily distinguished from the absence of that analyte (a blank value) (McNaught and Wilkinson, 1997; Inczedy et al., 1998; Allegrini and Olivieri, 2014), was determined using Eq. (2):

\[
\text{LOD} = \frac{3S_a}{b}
\]

(2)

The LOQ, defined as the smallest concentration of analyte in a sample that can be quantitatively determined with suitable precision and accuracy, was determined using Eq. (3):

\[
\text{LOQ} = \frac{10S_a}{b}
\]

(3)

In Eqs. (2) and (3), \(S_a\) is the standard deviation of the response estimated by the standard error of y-intercepts of the regression lines and \(b\) is the slope of the calibration curve (Shrivastava and Gupta, 2011). A calibration curve with concentrations between 0.3 and 25 \(\mu g/L\) was used to obtain LOD and LOQ of all analytes.

Accuracy, defined as the closeness between a measured value and either a true or accepted value, was evaluated from precision and trueness values of each analyte (Munch et al., 2005). The precision was determined by calculating the relative standard deviation (RSD) using Eq. (4). Trueness was determined by calculating the recovery using Eq. (5).

\[
\text{RSD} (%) = \frac{\text{Standard deviation of measured concentrations}}{\text{Average of measured concentrations (\(\mu g/L\))}} \times 100
\]

(4)

\[
\text{Recovery} (%) = \frac{\text{Average of measured concentration (\(\mu g/L\))}}{\text{Spiked concentration (\(\mu g/L\))}} \times 100
\]

(5)

Environmental samples

Tap water from the city of Tempe and reverse osmosis grade water (US Water Systems, Indianapolis, IN) were collected at the Biosignal Institute, Arizona State University (Tempe, AZ). Tap water from the City of Mesa was collected from a domicile in Mesa, AZ. Three groundwater samples were obtained for testing. One groundwater sample was from Phoenix Goodyear Airport-North Superfund site (AZ) (Rangan et al., 2020). The other samples were collected from two confidential sites in the Southwestern United States. Cr (VI) contaminated surface water was collected from Tamil Nadu Chromates and Chemicals Ltd. (TCCL), an abandoned chromate manufacturing facility in Ranipet, Tamil Nadu, India. The wastewater samples used in this study were received from a power station in the Eastern United States and from the Northwest Water Reclamation Plant (Mesa, AZ).

Laboratory microcosm experiments

The developed IC method was applied to monitor anions in soil and culture-only batch microcosms. Soil laboratory microcosms (Ziv-El et al., 2011; Rangan et al., 2020; Joshi et al., 2021) focused on abiotic and microbiological Cr (VI) reduction were established in 160 mL glass serum bottles with 25 g of Cr (VI)-contaminated soil and 100 mL anaerobic mineral medium as described elsewhere (Delgado et al., 2012, 2017). The soil was collected from 0 to 0.25 m depth at the TCCL site, India, and was homogenized in the anaerobic glove chamber (Coy Laboratory Products, Inc., Grass Lake, MI) under 3.5% \(H_2\) and 96.5% \(N_2\) atmosphere. Two grams per liter yeast extract and 10 mM lactate (870 mg/L) were added to the microcosms as electrons and carbon sources for the microorganisms. The initial Cr (VI) concentration in the soil microcosms was \(\sim 90\) mg/L.

Culture-only microcosms (Delgado et al., 2014, 2016) focused on microbiological Cr (VI) reduction were established in 160 mL serum bottles containing 100 mL anaerobic mineral medium as used in soil microcosms. The inoculum (4% v/v) was a mixed culture grown on Cr (VI) and lactate. The culture-only microcosms were amended with 1 g/L yeast extract and 3 mM lactate (~ 260 mg/L). The initial concentration of Cr (VI) was 15 mg/L. All (soil and culture-only) microcosms were established in triplicates, were incubated in the dark at 30°C, and were shaken on a platform shaker at 125 rpm. Liquid samples from the soil microcosms were collected for IC analysis during the experiment at 0, 2, 3, 7, and 8.2 h. Liquid samples from the culture-only microcosms were collected at 0, 2, 7, 10, 11, 14, and 17 days. The liquid samples were filtered using 0.2 \(\mu m\) syringe filters (mdi Membrane Technologies, Inc., Harrisburg, PA) and analyzed for anions by IC.

Results and Discussion

In this study, we report an isocratic IC method with suppressed conductivity detection for simultaneous quantification of Cr (VI), \(F^-\), \(Cl^-\), \(NO_2^-\), \(NO_3^-\), \(SO_4^{2-}\), Se (VI), As (V), and \(ClO_3^-\). A typical chromatogram of the analytes (50 \(\mu g/L\) each in DI water) is given in Fig. 1. Most analytes showed good separation (defined as \(R > 1.5\) (Harris, 2010)). All analytes were eluted within 20 min of sample injection (Fig. 1). Table 1 compiles the resolution of the peaks, linear regression equation, determination coefficient, LOD, and LOQ for the analytes. The determination coefficient of every analyte was >0.99 and the LOD was in the range of 0.1–7.5 \(\mu g/L\) (Table 1). These data demonstrate the capability of the method to quantify trace concentrations of the analytes. For Cr (VI), the LOD and LOQ were 0.2 and 0.6 \(\mu g/L\), respectively, which are three orders of magnitude lower than EPA’s current MCL of 100 \(\mu g/L\) Cr.

A comparison of published IC methods for measurement of Cr (VI) in aqueous samples is given in Table 2. The
A contribution of our method over previously published IC methods for Cr (VI) quantification is that ClO\(_4^-\) can also be quantified. We validated our method by demonstrating linearity, precision, and accuracy for simultaneous quantification of all the anion analytes, which was not reported previously by other IC methods (Bruzoniti et al., 1999; Kończyk et al., 2013). The LOD and LOQ for Cr (VI) determined in this study was lowest among IC methods with suppressed conductivity detection (Table 2). We were able to achieve this low LOD and LOQ for Cr (VI) using a 1000 \(\mu\)L injection loop, which is used in the EPA Method for trace analysis of ClO\(_4^-\) in drinking water (Hautman et al., 1999). Methods that use UV-Vis spectroscopy, chemiluminescence, and thermal lens spectroscopy detection systems can achieve lower LOD for Cr (VI) but cannot quantify other anions.

SO\(_4^{2-}\) is among the most abundant anions in many environmental media (Miao et al., 2012). In our analytical method, As (V) and Se (VI) elute within 3 min after SO\(_4^{2-}\) (Fig. 1). Thus, high SO\(_4^{2-}\) concentrations could potentially interfere with quantification of As (V) and Se (VI) through this method. In such cases, samples would require dilution, making it challenging for trace analysis of the analytes using a conductivity detector. Alternatively, pretreatment of the sample matrix to remove SO\(_4^{2-}\) can be employed using pretreatment cartridges, but these can severely affect the recovery of other analytes like Cr (VI) (Thermo Scientific, 2013). To elucidate SO\(_4^{2-}\) interference, we evaluated the effect of SO\(_4^{2-}\) concentration (up to 500 mg/L) on recovery of co-analytes. SO\(_4^{2-}\) concentration had no effect on recovery of F\(^-\), Cl\(^-\), NO\(_2^-\), and NO\(_3^-\) as these analytes eluted before SO\(_4^{2-}\) in our method (Fig. 1). Se (VI) and As (V) recovery was <80% when SO\(_4^{2-}\) concentration was >10 mg/L (data not shown). A recovery of 80% or greater is an acceptable criterion for quantification of chemical analytes (Hautman et al., 1999; US EPA, 2007). Hence, Se (VI) and As (V) cannot be quantified with accuracy in samples containing SO\(_4^{2-}\) at concentrations >10 mg/L. Cr (VI) and ClO\(_4^-\) recovery was ≥85% in the presence of up to 500 mg/L SO\(_4^{2-}\) (Fig. 2). These data demonstrate that the method can be used to quantify low concentrations of Cr (VI) and ClO\(_4^-\) in matrices with a high concentration of SO\(_4^{2-}\) without requiring pretreatment or dilution of the sample.

We evaluated the analytical accuracy (precision and trueness) for quantification of the anions at three concentration levels (2, 10, and 100 mg/L) using the developed IC method. In reagent water or DI water, US EPA’s acceptance criterion for RSD is ≤10%. The acceptance criterion for recovery is 80–120% for mid-level check standards (US EPA, 1996; Hautman et al., 1999). The acceptance criterion for recovery is 50–150% at concentrations close to the LOD of the analyte (low-level check standard) (US EPA, 1996). Table 3 documents the recovery of all anion analytes. At

### Table 1: Resolution, Regression Equation, Determination Coefficient, Quantification Range, Limit of Quantification, and Limit of Detection of Nine Analytes Using the Method from This Study

| Elution order | Analyte | Resolution (R) | Regression equation | \(R^2\) | Quantification range (µg/L) | LOD (µg/L) | LOQ (µg/L) |
|---------------|---------|----------------|---------------------|---------|-----------------------------|-------------|-------------|
| 1             | F\(^-\) | 3.05           | \(Y=0.0071X+0.1517\) | 0.9986  | 24.9–1000                   | 7.5         | 24.9        |
| 2             | Cl\(^-\) | 1.03           | \(Y=0.0083X+0.0541\) | 0.9984  | 14.4–10,000                 | 4.3         | 14.4        |
| 3             | NO\(_2^-\) | 2.92          | \(Y=0.002X+0.0082\)  | 0.9979  | 1.5–5000                    | 0.4         | 1.5         |
| 4             | NO\(_3^-\) | 5.51          | \(Y=0.0122X+0.0009\) | 0.9981  | 1.9–10,000                  | 0.6         | 1.9         |
| 5             | SO\(_4^{2-}\) | 2.45          | \(Y=0.0067X+0.0903\) | 0.9983  | 9.5–10,000                  | 2.9         | 9.5         |
| 6             | Se (VI) | 1.55           | \(Y=0.0066X+0.0024\) | 0.9999  | 0.5–9000                    | 0.5         | 0.5         |
| 7             | As (V)  | 2.51           | \(Y=0.0023X–0.009\)  | 0.9988  | 2.1–7000                    | 0.6         | 2.1         |
| 8             | ClO\(_4^-\) | 3.71          | \(Y=0.0025X–0.0045\) | 0.9992  | 0.5–10,000                  | 0.1         | 0.5         |
| 9             | Cr (VI) | NA             | \(Y=0.0041X+0.0046\) | 0.9998  | 0.6–10,000                  | 0.2         | 0.6         |

\(R\) values >1.5 are baseline resolutions.

Cr, chromium; LOD, limit of detection; LOQ, limit of quantification; NA, not applicable (Cr [VI] was the last analyte in the method run; \(X\), concentration (µg/L); \(Y\), peak area (\(\mu\)S/cm) × min).
100 μg/L, all analytes were quantified with RSD <2.3% and
the recovery was in the range of 96.2–107.9%, showing
precision and trueness (accuracy) for quantification (Ta-
ble 3). At 10 μg/L, the RSD and recovery for F– and Cl– were
substantially affected (RSD values >10% and recovery of
47.5–90.6% [Table 3]). These results are expected as 10
μg/L is within a factor of 3 from the LOD of F– and Cl– (US
EPA, 1996). All other analytes were quantified with RSD
<7.4% and recovery of 92.6–105.3% using 10 μg/L standard (Ta-
ble 3). At 2 μg/L concentration, all analytes except NO
were quantified with RSD <6% and recovery in the range
of 95.8–106.4% (Table 3). Overall, the method accomplished
accuracy in quantification of NO2–, Se (VI), As (V), ClO4–,
and Cr (VI) at concentrations as low as 2 μg/L. At 100 μg/L,
the RSD and recovery for all analytes are well within the
acceptance accuracy criteria (Hautman et al., 1999; Munch
et al., 2005).

To test the applicability of the developed IC method on
environmental aqueous samples, we evaluated the recovery
of all analytes in deionized water, tap water, surface water,
groundwater, and wastewater. The US EPA’s acceptance
criteria for recovery of analytes in environmental samples is
80–120% (Hautman et al., 1999). As given in Table 4, the
recovery of Cr (VI) in all environmental samples tested was
in the range of 97.2–102.8%. The recovery of the other
analytes was within the acceptable recovery criterion in most
environmental samples (Table 4). These data support the
applicability of this method for simultaneous quantification
of the analytes in environmental aqueous samples.

We evaluated the trueness of Cr (VI) concentration in the
surface water sample measured with our IC method by
comparing it with the measured value using the EPA method
7196A (diphenylcarbazide-based colorimetry method). The
concentration of Cr (VI) in the surface water was
20.6 ± 0.2 mg/L using the diphenylcarbazide method (EPA
Method 7196A). Assuming this was the true Cr (VI) con-
centration, the recovery of Cr (VI) concentration using the IC
method was 100.2 ± 3.4% (data not shown), demonstrating
trueness for Cr (VI) quantification in the surface water
sample. For Cr (VI) quantification using the IC method, the
surface water was diluted 1000 times with reagent water to fit
the Cr (VI) concentration within the calibration range.

We further applied the IC analytical method to simulta-
nously track concentrations of anions in typical batch mi-
crocosms used commonly in laboratory settings. The
microcosms in this study were focused on abiotic and mi-
crobiological Cr (VI) reduction. Figure 3 shows the time
course concentrations of Cr (VI) (naturally present and
spiked) and SO42–, NO3–, and Cl– (naturally present anions
in the soil matrix). The concentration of Cr (VI) decreased from

| Detection system | Postcolumn derivatization | LOD (µg/L) | LOQ (µg/L) | Sample injection volume (µL) | Simultaneous detection of other anions | Reference |
|------------------|---------------------------|------------|------------|----------------------------|---------------------------------------|-----------|
| UV-Vis spectroscopy | Yes | a0.01 | a0.036 | 1250 | No | U.S. EPA method 218.7 |
| Chemiluminescence detection | Yes | 0.09 | NR | 50 | No | Zaffiro et al. (2011) |
| Thermal lens spectrometry | Yes | 0.1 | NR | 200 | No | Gammelgaard et al. (1997) |
| Direct UV detection | No | 0.2 | 1.2 | 100 | No | Michalski (2003) |
| Suppressed conductivity | No | 13.5 | 44.7 | 10 | No | (Destanoğlu and Gümüş Yılmaz (2016) |
| Suppressed conductivity | No | 2 | NR | 200 | 20 Cl–, NO3–, SO42–, Se (IV), ClO4–, W (VI), As (V), Mo (VI) | bBruzzoniti et al. (1999) |
| Suppressed conductivity | No | NR | NR | 100 | F–, Cl–, Br–, NO2–, NO3–, PO43–, SO42– | bKonczyk et al. (2018) |

FIG. 2. Effect of SO42– concentration on recovery of Cr (VI) and ClO4–.
90 mg/L to below detection limit in ~8 h, likely from abiotic reduction by reducing agents in the soil such as sulfide and iron bearing minerals and/or microbial reduction to Cr (III) (Chen and Hao, 1998; Kim et al., 2001; Joe-Wong et al., 2017). The concentrations of SO$_2^–$/C0$_2^–$ and Cl$^–$ did not change significantly during the incubation time in the soil microcosms (Fig. 3).

Figure 4 tracks concentrations of Cr (VI) in culture-only microcosms focused on microbial reduction of Cr (VI) using a mixed culture. Cr (VI) concentration was reduced from ~15 to <1 mg/L in ~18 days. Data from Figs. 3 and 4 highlight the applicability of the IC method in laboratory experiments using both complex matrices containing multiple analytes and simple matrices focused only on Cr (VI).

Owing to the capability of quantifying several anions simultaneously, the IC method developed in this study is useful to environmental practitioners, academic and research organizations, and other industries that routinely measure Cr (VI) and co-occurring anions. An ion chromatograph equipped

| Elution order | Analyte       | Spiked concentration, 2 µg/L (n=6) | Spiked concentration, 10 µg/L (n=6) | Spiked concentration, 100 µg/L (n=6) |
|---------------|---------------|-------------------------------------|-------------------------------------|-------------------------------------|
|               | Precision (RSD [%]) | Trueness (recovery [%]) | Precision (RSD [%]) | Trueness (recovery [%]) | Precision (RSD [%]) | Trueness (recovery [%]) |
| 1             | F$^–$         | NA                                  | 20.3                               | 47.5                               | 2.2                   | 99.5                   |
| 2             | Cl$^–$        | NA                                  | 12.2                               | 90.6                               | 0.9                   | 96.2                   |
| 3             | NO$_2^–$      | 0.0                                 | 95.8                               | 2.4                                | 97.2                               | 1.3                    | 97.6                   |
| 4             | NO$_3^–$      | 60.7                                | 42.6                               | 3.1                                | 99.1                               | 0.9                    | 96.3                   |
| 5             | SO$_2^–$/C0$_4^–$ | NA                                  | 7.3                                | 92.6                               | 1.5                    | 101.0                  |
| 6             | Se (VI)       | 3.2                                 | 100.4                              | 1.6                                | 105.3                              | 0.7                    | 103.1                  |
| 7             | As (V)        | 0.0                                 | 102.2                              | 0.0                                | 101.7                              | 0.7                    | 107.9                  |
| 8             | ClO$_4^–$     | 0.0                                 | 104.6                              | 1.6                                | 103.2                              | 0.7                    | 98.7                   |
| 9             | Cr (VI)       | 5.2                                 | 98.3                               | 1.7                                 | 100.1                              | 0.7                    | 98.7                   |

NA, not applicable (concentration below limit of detection); RSD, relative standard deviation.

| Samples                  | Cr (VI) recovery (%) | F$^–$ recovery (%) | Cl$^–$ recovery (%) | NO$_2^–$ recovery (%) | NO$_3^–$ recovery (%) | SO$_2^–$/C0$_4^–$ recovery (%) | Se (VI) recovery (%) | As (V) recovery (%) | ClO$_4^–$ recovery (%) |
|--------------------------|----------------------|--------------------|---------------------|-----------------------|-----------------------|-------------------------------|---------------------|----------------------|----------------------|
| DI water                 | 100.9±0.5            | 94.5±1.2           | 93.5±0.8            | 98.1±1.3              | 96.5±0.6              | 102.1±1.5                     | 104.3±0.9           | 103.2±0.7           | 103.3±0.6           |
| RO water (Tempe, AZ)     | 100.1±0.3            | ND                 | ND                  | ND                    | ND                    | ND                            | ND                  | ND                   | ND                   |
| Tap water (Tempe, AZ)    | 102.1±0.3            | ND                 | ND                  | ND                    | ND                    | ND                            | ND                  | ND                   | ND                   |
| Tap water (Mesa, AZ)     | 100.5±0.6            | ND                 | ND                  | ND                    | ND                    | ND                            | ND                  | ND                   | ND                   |
| Groundwater (Goodyear, AZ)| 97.6±0.3            | ND                 | ND                  | ND                    | ND                    | ND                            | ND                  | ND                   | ND                   |
| Groundwater (confidential site 1) | 100.2±0.0            | 107.8±7.0         | 101.5±3.0           | 92.7±2.3              | 90.2±6.1              | 104.2±2.8                     | 94.3±2.6            | 84.9±4.9             | 95.9±0.5             |
| Groundwater (confidential site 2) | 99.7±0.6            | 82.6±3.6           | 100.3±2.5           | 85.0±0.7              | 109.7±1.9             | 111.8±3.1                     | 89.1±0.2            | 71.0±4.9             | 93.2±0.4             |
| Surface water (Tamil Nadu, India) | 102.8±0.6            | 86.1±4.6           | 95.5±0.4            | 92.5±2.1              | 90.7±2.7              | 89.5±1.4                     | 108.8±0.2           | 98.7±7.2             | 92.3±0.6             |
| Wastewater (confidential site 3, Eastern United States) | 99.5±0.3            | ND                 | ND                  | ND                    | ND                    | ND                            | ND                  | ND                   | ND                   |
| Wastewater (Water Reclamation Plant, Mesa, AZ) | 97.2±0.2            | 107.8±3.7         | 108.8±5.2           | 76.1±2.4              | 103.7±2.9             | 84.2±0.3                     | 97.0±0.8            | 97.0±0.5             | 101.2±0.4            |

The data are averages with standard deviation of triplicates. The spiking concentration for all anions was 100 µg/L. ND, not determined; RO, reverse osmosis.
with a suppressed conductivity detector is a common instrumentation that many laboratories possess for quantification of common inorganic anions (e.g., Cl\(^{-}\), NO\(_3\)/C\(_3\)O\(_2\), and SO\(_2\)/C\(_3\)O\(_4\)) by EPA Method 9056A. Thus, the method developed can be easily adapted by laboratories that use the most common IC instrument. Our study shows that Cr (VI), As (V), Se (VI), and ClO\(_4\) in the low microgram per liter concentration range can be measured without pretreatment of the sample or postcolumn derivatization. The IC method from this work was shown to be reliable, precise, accurate, and suitable for monitoring important anions in environmental aqueous media, industrial wastewaters, and laboratory experiments.

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No competing financial interests exist.

FIG. 3. Concentrations of Cr (VI), SO\(_4^{2-}\), NO\(_3^{-}\) and Cl\(^{-}\) during incubation in replicate soil microcosms. Note that Cl\(^{-}\) is plotted on the secondary y-axis.

FIG. 4. Concentrations of Cr (VI) during incubation in replicate culture-only microcosms.

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