Determination of Hexavalent Chromium in Drinking Water Using Ion Chromatography

INTRODUCTION

Hexavalent chromium, Cr(VI), is the most toxic form of the metal chromium, a primary drinking water contaminant in the U.S. Dissolved hexavalent chromium can be determined as chromate (CrO_4^{2-}) by ion chromatography in drinking water, groundwater, and industrial wastewater effluents as described in U.S. EPA Method 218.6 and Dionex Technical Note 26.[1,2] Dionex Technical Note 26 uses a 250-µL injection onto a high-capacity IonPac® AS7 anion exchange column to separate Cr(III) from Cr(VI) in four minutes. The product of the postcolumn reaction between Cr(VI) and diphenylcarbazide is detected by absorbance at 530 nm, yielding a method detection limit of 0.4 µg/L in reagent water.

The California Department of Health Services (DHS) recently issued a new Public Health Goal (PHG) of 2.5 µg/L for total chromium and 0.2 µg/L for Cr(VI). In January 2001, California DHS added Cr(VI) to the list of unregulated chemicals that must be monitored. As a result of this regulation, public water systems are now monitoring for Cr(VI) in drinking water.[3]

EPA Method 218.6 does not allow sufficient sensitivity for analysis at the California PHG level of 0.2 µg/L. This application update describes modifications to Method 218.6 that significantly increase sensitivity over the existing method. The modifications include lower eluent and postcolumn reagent (PCR) flow rates, a larger reaction coil, and a larger injection volume. The resulting MDL for Cr(VI) as CrO_4^{2-} of 0.02 µg/L is more than sufficient for determinations at the California PHG level.

EQUIPMENT

A Dionex DX-600 chromatography system consisting of:

- GS50 Gradient Pump with Vacuum Degas Option
- AS50 Automated Sampler with Chromatography Compartment
- AD25 UV/Visible Absorbance Detector
- 1.0 mL sample syringe for AS50 (Dionex PN 55066)
- PC10 Postcolumn Pneumatic Delivery Package, 4-mm (Dionex PN 50601)
- 750-µL knitted reaction coil (Dionex PN 42631)
- PeakNet® 6.1 Chromatography Workstation
- Syringe filters (Gelman IC Acrodisc 0.2-µm, PN 4483)

REAGENTS AND STANDARDS

Prepare all solutions from analytical reagent grade chemicals (when available).

Deionized water, 17.8 MΩ-cm or better

Ammonium sulfate, (Mallinckrodt Gen AR # 7725)

Ammonium hydroxide (Sigma A6899)

1,5-diphenylcarbazide (JT Baker K620-03)

Methanol, HPLC grade (Fisher Optima A454-4)

Sulfuric acid, 95–98% (JT Baker Instra-Analyzed #9673)

Potassium dichromate (JT Baker 4765-01)

CONDITIONS

Guard Column:	IonPac NG1 Guard 4 × 50 mm (Dionex PN 039567)I
Analytical Column:	IonPac AS7 Analytical 4 × 250mm (Dionex PN 035393)
Eluent:	250 mM ammonium sulfate/ 100 mm ammonium hydroxide
Eluent Flow Rate:	1.0 mL/min
Sample Volume:	1000 µL partial loop with 10 µL cut volume from 1100-µL loop
Postcolumn Reagent:	2 mM diphenylcarbazide, 10% methanol, 1 N sulfuric acid
PCR Flow rate:	0.33 mL/min
Detection:	UV/Vis absorbance, 530 nm
Noise:	25–50 µAU peak-to-peak
Backpressure:	1200–1300 psi
Run Time:	10 min (Retention time = 6–7 min)

PREPARATION OF SOLUTIONS AND REAGENTS

Eluent:

250 mM ammonium sulfate

100 mM ammonium hydroxide

Dissolve 66.0 g of ammonium sulfate in about 1 L of reagent water and add 13.0 mL of 29% ammonium hydroxide. Dilute to 2.0 L with water.

Sample Adjustment Buffer:

250 mM ammonium sulfate

1000 mM ammonium hydroxide

Dissolve 3.3 g of ammonium sulfate in about 75 mL of reagent water and add 6.5 mL of 29% ammonium hydroxide. Dilute to 100 mL with water.

Postcolumn reagent:

2 mM diphenylcarbazide

10% methanol

1 N sulfuric acid

Add 28 mL of 98% sulfuric acid to about 500 mL of water in a 1.0 L volumetric flask. (Caution: may get hot.) Mix and allow to cool. Add 0.5 g of 1,5-diphenylcarbazide to about 75 mL of HPLC-grade methanol in a 100 mL volumetric flask, and sonicate to dissolve. Bring to volume with methanol, mix, and add to the cooled sulfuric acid solution. Dilute to 1.0 L with deionized water, mix, and transfer to the pressurized PCR reagent container. The PCR reagent is stable for several days. Prepare fresh as needed.

Standard

Add 0.283 g of potassium dichromate (dried at 100 °C to a constant weight) to about 50 mL of deionized water in a 100 mL volumetric flask. Dissolve and bring to volume with deionized water. Or, prepare a 1000 mg/L stock solution of Cr(VI) as CrO_4^{2-} from a commercially available standard (J. T. Baker, Phillipsburg, NJ). Store the stock standard at 4 °C. Prepare working standards fresh daily. Adjust the pH to 9.0–9.5 by adding 1 mL of sample adjustment buffer per 100 mL of final volume before bringing to final volume.

SAMPLE PREPARATION

Clean all sample collection equipment and containers with 1:1 HNO_3 and rinse well with deionized water before use. Collect samples in amber glass bottles with plastic lined caps. Do not filter the samples at the time of collection, but immediately add the sample adjustment buffer dropwise until the sample pH falls in the range of 9.0–9.5. Be careful not to contaminate the sample while measuring the pH. Most drinking water samples can be adjusted to pH 9.0–9.5 by adding 1 mL or less of the adjustment buffer per 100 mL of sample, which introduces an acceptable 1% dilution error. For more difficult samples, start with a known amount of sample and accurately measure the amount of buffer added so that the amount of Cr(VI) as CrO_4^{2-} determined by IC can be corrected for dilution. Cool to 4 °C and hold at 4 °C during transport and storage. Analyze samples within 24 hr of collection to minimize the potential loss of Cr(VI) through chemical reduction.[4]

Filter drinking water samples through 0.2-µm Acrodisc IC syringe filters (Gelman, Ann Arbor, MI) just prior to injection. Discard the first 300 µL of filtrate and filter the remainder directly into a clean plastic autosampler vial. Qualify filters by analyzing a reagent water blank and a 10-µg/L Cr(VI) as CrO_4^{2-} standard that has been passed through the filter. The blank should be free of peaks within the retention time window of chromate, and the recovery of the 10-µg/L standard should fall between 80% and 120%.

SYSTEM PREPARATION AND SETUP

Verify that the pump flow rate is within specifications and recalibrate if necessary. A GP50 should deliver water at 1.0 ± 0.005 mL/min against a constant backpressure of 2000 psi. Verify that the UV/Vis Absorbance Detector wavelength accuracy is within specifications and recalibrate if necessary. It is a good practice to periodically record the visible lamp output (i.e., the reference cell current in nA) and elapsed time as an aid in troubleshooting. Consult the pump or detector manuals for procedural details.

The precision and accuracy of the AS50 will vary depending on the mode of injection. The most accurate and precise injections are made with a calibrated sample loop in the full-loop injection mode, which aspirates a total of four times the sample volume to flush the sample loop and make the injection. The largest full-loop injection possible with the AS50 is 300 µL. To inject 1000 µL, use the partial-loop injection mode with an 1100-µL sample loop, and a programmed sample loop volume of 1100-µL and cut volume of 10 µL. This injection procedure should provide peak area precision of <1% RSD. Refer to the AutoSelect™ AS50 Autosampler operator's manual (Document No. 31169) for a complete discussion of the different injection modes.

Install a 1-mL sample syringe and set the syringe speed to four or five to make faster large-loop injections. Enter the correct sample loop size and sample syringe volume in the AS50 Plumbing Configuration screen.

Configure the IC with the PCR system as depicted in Figure 3 of Dionex Technical Note 26, and as described in the PC10 Postcolumn Delivery System installation instructions. Pump the eluent at 1.0 mL/min and set the PC10 pneumatic pressure to 70 psi. To measure the PCR flow rate, collect the effluent from the detector *(i.e., the total flow from the IC pump and the PCR module)* in a 10-mL graduated cylinder for 5 min. The PCR flow rate is the difference between the total flow rate and that of the IC pump. Adjust the air pressure of the postcolumn delivery module (PC10) and remeasure the flow rate until the correct PCR flow rate of 0.33 mL/min is established.

Variations in the PCR flow rate affect the postcolumn reaction time, pH, dilution, mixing rate, and ratio of the reactants. Stable day-to-day results depend on a well-controlled PCR flow rate.

Confirm this flow rate on a daily basis or whenever detector response for a calibration check standard deviates beyond quality control acceptance criteria.

The storage solution that the AS7 is shipped with is 30 mM nitric acid. After equilibrating the column with eluent for 60 min, analyze a system blank of 1000 µL of reagent water. An equilibrated system has a background signal of less than 200 mAU and peak-to-peak noise of less than 50 µAU. There should be no peaks eluting within the retention time window of the chromate anion. The column is equilibrated when two consecutive injections of a standard produce the same retention time for chromate.

RESULTS AND DISCUSSION

Effect of Reaction Coil and Injection Volume

The 375-µL reaction coil and higher flow rates recommended in Dionex Technical Note 26 are adequate for the rapid determination of Cr(VI) as CrO_4^{2-} at the 1-µg/L level, but a standard 375-µL knitted reaction coil does not provide the maximum peak response for chromate.[5] To optimize the sensitivity of this method,

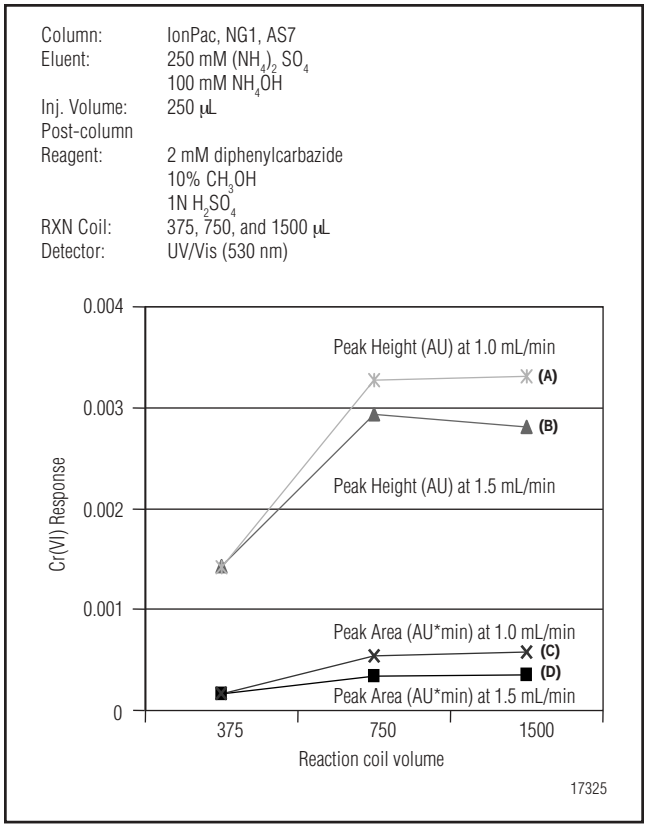

Figure 1. Effect of reaction coil volume on chromate peak response. Conditions: guard column, IonPac NG1; analytical column, IonPac AS7; eluent, 250 mM ammonium sulfate/100 mM ammonium hydroxide; flow rate, 1.0 (A and C) or 1.5 (B and D) mL/min; postcolumn reagent, 2 mM diphenylcarbazide / 10% methanol / 1.0 N sulfuric acid; reaction coil volume, 375–1500 µL as indicated; postcolumn flow rate, 0.33 (A and C) or 0.5 (B and D) mL/min; detection, UV/Vis at 530 nm; injection volume, 250 µL; peaks, chromate (10 µg/L).

the responses obtained with 375-µL, 750-µL, and 1500-µL reaction coils were compared . Figure 1 shows the effect of reaction coil volume on chromate peak height and area at two different flow rates. In both cases, the postcolumn reagent flow rate was adjusted to one-third the eluent flow rate by varying the applied pneumatic pressure. At an eluent flow rate of 1.0 mL/min (A and C) the postcolumn reagent flow rate was 0.33 mL/min. At an eluent flow rate of 1.5 mL/min (B and D) the postcolumn reagent flow rate was 0.50 mL/min.

Increasing the reaction coil volume from 375 µL to 750 µL significantly increases the peak response, while the change from 750 µL to 1500 µL only marginally increases the response. Larger coil sizes require greater pneumatic pressure to deliver the necessary PCR flow rate. Also, higher eluent flow rates require greater pneumatic pressure to deliver the necessary PCR flow

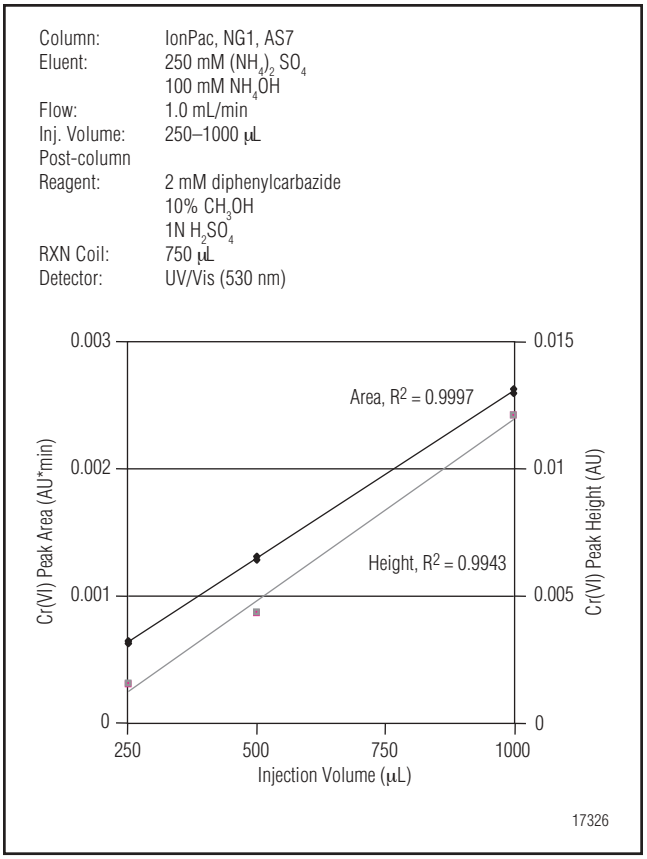

Figure 2. Effect of injection volume on chromate peak response. Conditions: as for Fig. 1, except; flow rate, 1.0 mL/min; postcolumn flow rate, 0.33 mL/min; reaction coil volume, 750 µL; injection volume, 250–1000 µL as indicated.

rate. For example, a pneumatic pressure of over 100 psi was required to deliver the PCR reagent at a flow rate of 0.5 mL/min against an eluent flow rate of 1.5 mL/min through a 1500-µL reaction coil. We recommend using a 750-µL reaction coil with an eluent flow rate of 1.0 mL/min and a PCR flow rate of 0.33 mL/min. This combination provides nearly the maximum peak response while requiring a modest pneumatic pressure of about 70 psi to deliver the postcolumn reagent at the necessary flow rate.

Greater sensitivity can be gained by increasing the volume of sample injected, but too large a sample can cause retention time shifts or loss of efficiency when column overloading leads to excessive peak distortion. The effect of injection volume on chromate peak response was studied using the conditions described above. Figure 2 shows a linear increase in both chromate peak height and area as the injection volume is increased from 250 µL to 1000 µL. We did not test larger injection volumes because a 1000 µL injection volume is the largest that can be made with the AS50 Autosampler.

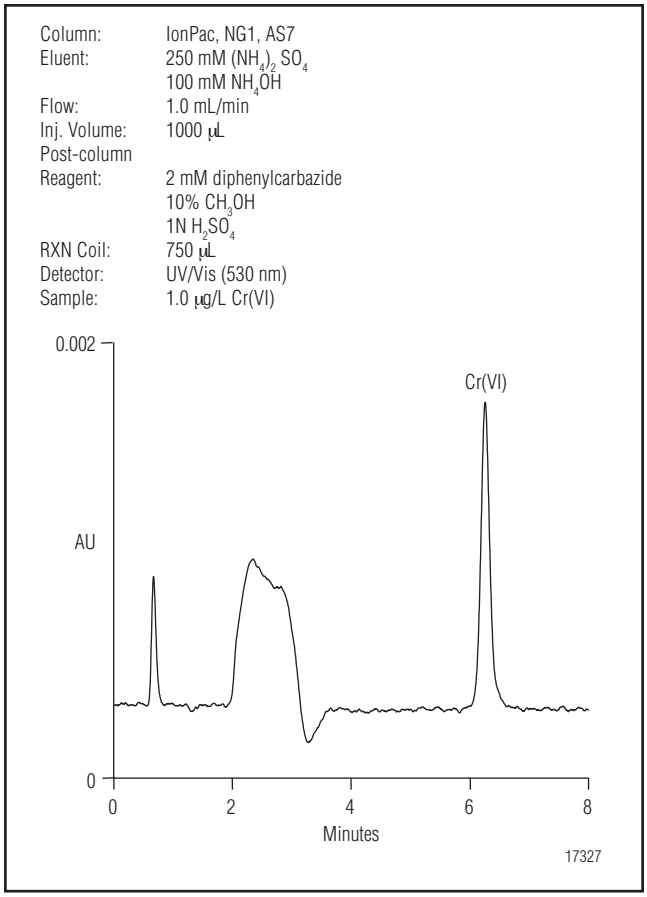

Figure 3. Determination of chromate using optimized EPA Method 218.6. Conditions: as for Fig. 2, except injection volume, 1000 µL; peaks, chromate (1.0 µg/L).

Sample Adjustment Buffer

Method 218.6 requires a solution consisting of 330 g/L ammonium sulfate and 65 mL/L ammonium hydroxide to adjust the sample pH. However, the large-loop injection used in this application update increases the possibility of overloading the analytical column if the sample ionic strength is too high. A solution consisting of 33 g/L ammonium sulfate and 65 mL/L ammonium hydroxide is a suitable substitute to adjust the sample pH and provides results comparable to those obtained by using the Method 218.6 buffer (data not shown).

Optimized Method Performance

By using a larger volume reaction coil, lower eluent flow rate and increased injection volume, this updated method provides greater than a 10-fold increase in the chromate peak area compared to the response obtained by using the standard conditions specified in Method 218.6. Figure 3 shows a chromatogram of a 1.0-µg/L

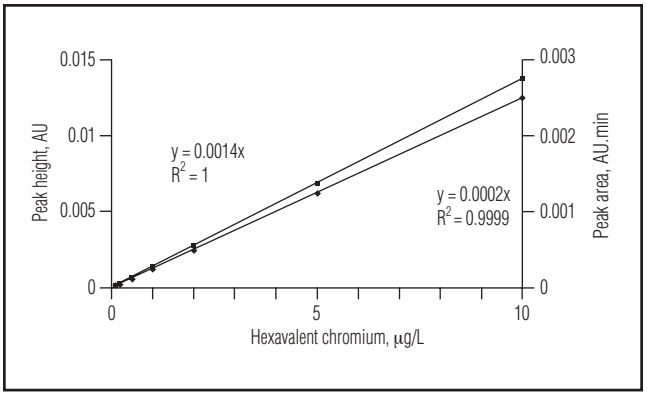

Figure 4. Calibration curve for Cr(VI) as chromate.

Cr(VI) as CrO_4^{2-} standard obtained by using the optimized conditions described above.

Figure 4 summarizes the calibration data for chromate anion obtained by using the partial-loop injection mode to make 1000-µL injections of Cr(VI) as CrO_4^{2-} standards at 0, 0.04, 0.1, 0.2, 0.5, 1, 2, 5, 10, and 20 µg/L. The calibration curve is linear over the calibration range of 0.1–10 µg/L for Cr(VI) as CrO_4^{2-} with a coefficient of determination of 0.9999.

Table I. Method Detection Limits for Chromate Based on a 1000-µL Injection

Chromate Conc. (µg/L)	Std. Dev. (µg/L)	RSD (%)	MDL* (µg/L)
0.1	0.0060	6.986	0.018
0.2	0.0056	3.193	0.018

* MDL = (Std. Dev.) x ($t_{s, 99}$), where $t_{s, 99}$ = 3.14 for n = 7.

Method Detection Limits (MDLs) for Cr(VI) as CrO_4^{2-} are summarized in Table 1. The MDL is a measure of the precision of replicate injections of a low-level solution and is defined as the minimum concentration of an analyte that can be identified, measured, and reported with 99% confidence that the analyte concentration is greater than zero.[6] We determined the MDL for Cr(VI) as CrO_4^{2-} by analyzing seven replicates of reagent water fortified with Cr(VI) as CrO_4^{2-} at two concentrations levels of 0.1 and 0.2 µg/L (i.e., about 3–5 times the estimated instrument detection limit). Both levels produced a calculated MDL value of 0.018 µg/L. This permits a minimum limit (ML) for quantitation of 0.06 µg/L for Cr(VI) as CrO_4^{2-}, which is

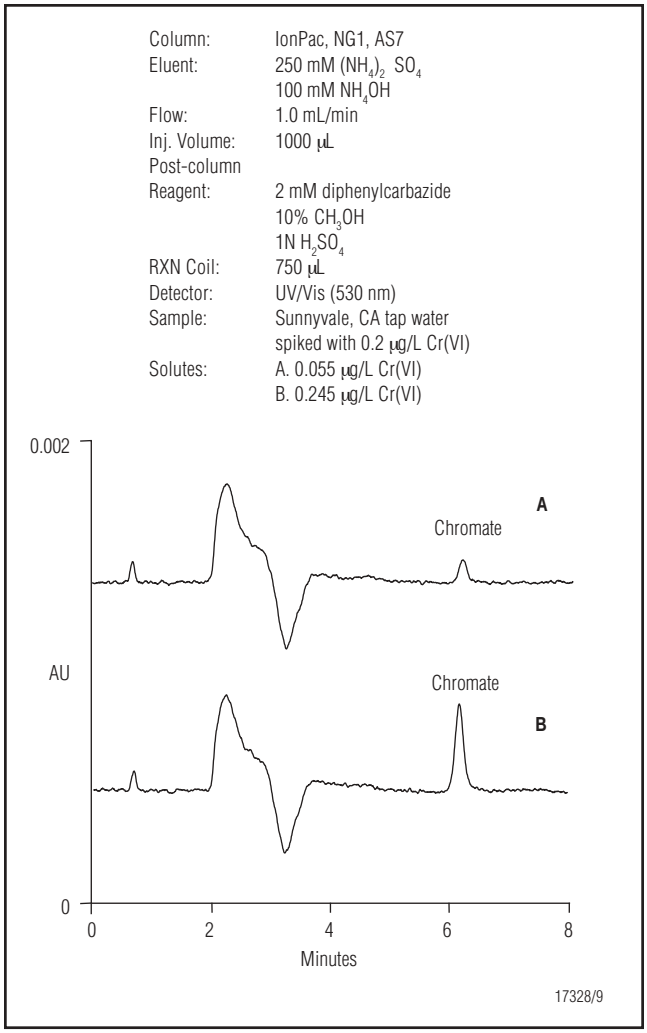

Figure 5. Determination of chromate in drinking water. Conditions: as for Fig. 3, except sample, buffered Sunnyvale, CA drinking water (A) and drinking water spiked with 0.2 µg/L chromate (B); peaks, (A) chromate (0.055 µg/L) and (B) chromate (0.245 µg/L)

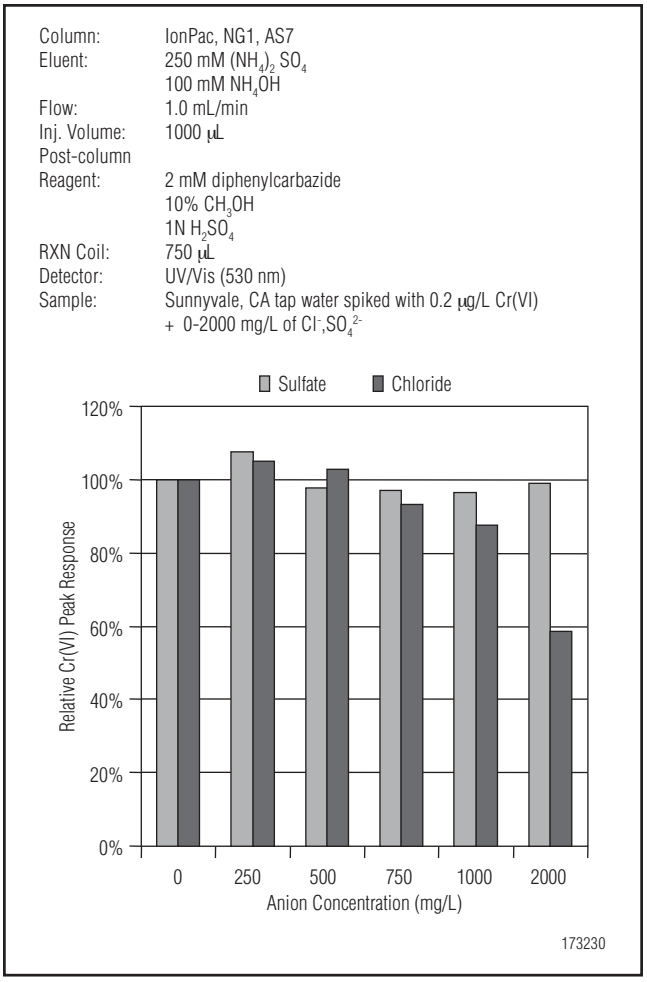

Figure 6. Effect of common anions on chromate peak response. Conditions: as for Fig.3, except sample, buffered Sunnyvale, CA drinking water spiked with 0.2 µg/L chromate to which 0–2000 mg/L of sulfate or chloride was added, as indicated.

adequate for routine analysis at the California PHG level of 0.2 µg/L.

Fig. 5 shows chromatograms obtained by using the optimized conditions of a Sunnyvale, CA, tap water blank (A) and tap water sample spiked with Cr(VI) as CrO_4^{2-} at the PHG level of 0.2 µg/L (B). In both cases, the sample was adjusted to pH 9 by using the solution consisting of 33 g/L ammonium sulfate and 65 mL/L ammonium hydroxide. The presence of the ammonium sulfate and ammonium hydroxide in the sample did not adversely affect the chromate peak shape and a recovery of 96% was obtained for the Cr(VI) as CrO_4^{2-} spike at this level. The tap water blank contained a background level of 0.06 µg/L chromate.

Although the IonPac AS7 column specified in Method 218.6 has a relatively high capacity of 100 µequivalents/column, the large injection volume used in this application update increases the possibility of interference from other anions in the sample. Hence, the effect of chloride and sulfate on Cr(VI) as CrO_4^{2-} response was investigated, as some drinking and ground waters can contain elevated levels of these common anions. Increasing concentrations of sulfate or chloride were added to a series of tap water samples that had been adjusted to pH 9 with the recommended buffer and spiked with 0.2 µg/L Cr(VI) as CrO_4^{2-}. Figure 6 shows the effect of common anions on chromate peak response, relative to the peak area for 0.2 µg/L Cr(VI) as CrO_4^{2-} spiked in tap water containing no added sulfate or chloride. This method provides acceptable performance, for example greater than 80% recovery in the presence of up to 1000 mg/L chloride or 2000 mg/L sulfate. Typical ground and drinking waters are not expected to contain more than 200 mg/L chloride or 500 mg/L sulfate.

CONCLUSIONS

U.S. EPA Method 218.6, as published, does not allow sufficient sensitivity to determine hexavalent chromium (i.e., Cr(VI) as CrO_4^{2-}) at the California PHG level of 0.2 µg/L. Modifications to the method, including the use of a lower eluent flow rate and larger reaction coil (to increase reaction time) and a larger injection volume, significantly increase the sensitivity of Method 218.6, resulting in an MDL for Cr(VI) as CrO_4^{2-} of 0.02 µg/L. These modifications allow a minimum limit (ML) of quantitation for Cr(VI) as CrO_4^{2-} of 0.06 µg/L, which is more than sufficient for analysis at the California PHG level. Calibration was linear over the range of 0.1–10 µg/L, and quantitative recoveries were obtained for Cr(VI) as CrO_4^{2-} spiked at 0.2 µg/L in drinking water. The modified method provides acceptable performance, in terms of peak shape and recovery, in the presence of up to 1000 mg/L chloride or 2000 mg/L sulfate.

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6. *The Determination of Inorganic Anions in Water by Ion Chromatography;* U.S. Environmental Protection Agency, Method 300.0; Cincinnati, Ohio (1993).

SUPPLIERS

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Fisher Scientific, 711 Forbes Ave., Pittsburgh, PA 15219 USA, Tel. 800-766-7000, www.fishersci.com.

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LPN 1495 pdf 1/03