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Determination of hexavalent chromium at the level of the California Public Health Goal by ion chromatography

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Abstract

Chromium is a primary drinking water contaminant in the USA with hexavalent chromium, Cr(VI), being the most toxic form of the metal. As a required step in developing a revised state drinking water standard for chromium, the California Department of Health Services recently issued a new Public Health Goal (PHG) of 2.5 μg/l for total chromium and 0.2 μg/l for Cr(VI). Hexavalent chromium can be determined (as chromate) by ion chromatography, as described in US Evironmental Protection Agency Method 218.6; however, the method as originally published does not allow sufficient sensitivity for analysis at the California PHG level of 0.2 μg/l. Modification of the conditions described in Method 218.6, including the use of a lower eluent flow-rate, larger reaction coil, and larger injection volume, significantly increases the method sensitivity. The modified method, which uses IonPac NG1 and AS7 guard and analytical columns, an eluent of 250 m*M* ammonium sulfate–100 m*M* ammonium hydroxide operated at 1.0 ml/min, a 1000 μl injection volume, and postcolumn reaction with 2 m*M* diphenylcarbazide–10% methanol–0.5 *M* sulfuric acid (using a 750 μl reaction coil) followed by UV–Vis detection at 530 nm, permits a method detection limit for chromate of 0.02 μg/l. This results in a quantitation limit of 0.06 μg/l, which is more than sufficient for analysis at the California PHG level. Calibration is linear over the range of 0.1–10 μg/l and quantitative recoveries (>80%) are obtained for chromate spiked at 0.2 μg/l in drinking water. The modified method provides acceptable performance, in terms of chromate peak shape and recovery, in the presence of up to 1000 mg/l chloride or 2000 mg/l sulfate.

Keywords: Water analysis; Optimization; Chromium; Chromate; Inorganic anions; Metals

1. Introduction

Chromium (total) is a primary drinking water contaminant in the USA with a maximum contaminant level (MCL) of 100 μg/l, while the World Health Organization recommends 50 μg/l as a guideline [1]. Hexavalent chromium, Cr(VI), is the most toxic form of the metal and is a known carcinogen when inhaled. While there is no clear evidence that Cr(VI) is a carcinogen when ingested, the California Office of Environmental Health Hazard Assessment (OEHHA) recently listed Cr(VI) as a carcinogen for the purposes of developing a revised drinking water standard. In 1999, based on the review by OEHHA, the California Department of Health Services issued a Public Health Goal (PHG) of 2.5 μg/l for total chromium and 0.2 μg/l for hexavalent chromium [1].

The publication of a new PHG for Cr(VI) created some degree of local concern and regional newspapers have since published several articles on chromium contamination in southern California

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groundwaters (e.g., Refs. [2,3]). Hexavalent chromium has been detected at levels above the PHG in numerous groundwaters in California, including 24 wells in the San Fernando Valley, which supplies drinking water to the Los Angeles area [4]. In January 2001, the California Department of Health Services (DHS) adopted a regulation adding Cr(VI) to the list of unregulated chemicals that require monitoring. As a result of this regulation, public water systems are now monitoring for Cr(VI) in drinking water [1]. The recent media and regulatory attention has created a renewed interest in analytical methods for low level chromium analysis.

Hexavalent chromium can be determined (as chromate) by ion chromatography (IC), as described in US Environmental Protection Agency (EPA) Method 218.6 [5]. This method specifies the use of a high-capacity IonPac AS7 anion-exchange column and UV–Vis detection after postcolumn reaction with diphenylcarbazide for the analysis of chromate in drinking water, groundwater and industrial wastewater effluents. This method permits a detection limit of 0.4 μg/l in reagent water when using a 250 μl injection, hence modifications are required for analysis at the California PHG level of 0.2 μg/l. This paper will describe the results of investigations to improve the performance of Method 218.6 in order to allow quantitation of Cr(VI) at the level of the California PHG.

2. Experimental

2.1. Ion chromatography system

A Dionex (Sunnyvale, CA, USA) DX-600 ion chromatography system was used for this work. The system consisted of a GS50 gradient pump, an AS50 automated sampler with chromatography compartment and an AD25 UV–Vis absorbance detector. A Dionex PeakNet chromatography workstation was used for system control and data collection. The postcolumn reagent was delivered pneumatically using a PC10 pneumatic controller. An IonPac NG1 guard column and IonPac AS7 analytical column, as specified in EPA Method 218.6, were used for all separations.

2.2. Reagents and procedures

All solutions were prepared from analytical-reagent grade chemicals (when available) in 18 MΩ water, obtained from a Water Pro PS purification system (Labconco, Kansas City, MO, USA). A 1000 mg/l stock solution of chromate was prepared from a commercially available standard (J.T. Baker, Phillipsburgh, NJ, USA). The stock standard was stored at 4 °C and working standards were prepared fresh daily. Ammonium sulfate and ammonium hydroxide, both ACS grade, were purchased from Fisher Scientific (Fair Lawn, NJ, USA) and Sigma (St. Louis, MO, USA), respectively. ACS-grade 1,5-diphenylcarbazide was obtained from J.T. Baker, while HPLC-grade methanol and 98% sulfuric acid were obtained from Fisher Scientific. Drinking water samples were filtered through 0.45 μm Acrodisc syringe filters (Gelman, Ann Arbor, MI, USA) prior to injection.

3. Results and discussion

3.1. EPA method 218.6 performance

EPA Method 218.6 was originally devised to be applicable to a broad range of aqueous samples, most specifically industrial wastewaters, rather than drinking water samples. The method provides some flexibility in sample preservation and pretreatment, depending on the type of data required. For drinking water analysis, the California DHS recommends not filtering the samples at time of collection, although the samples should be filtered prior to analysis. Immediately on collection, the sample pH should be adjusted to the range 9.0–9.5 in order to minimize the potential loss of Cr(VI) through chemical reduction [1]. Method 218.6 requires a buffer solution consisting of 330 g/l ammonium sulfate and 65 ml/l ammonium hydroxide to adjust sample pH. However, the buffer solution recommended by California DHS (consisting of 33 g/l ammonium sulfate and 65 ml/l ammonium hydroxide) was used for this work to reduce the possibility of overloading the analytical column. Samples must also be cooled to 4 °C during transport and storage and analyzed within 24 h of collection [1].

The performance of the IC system was first verified using the standard conditions described in Method 218.6. Method detection limits (MDLs) were derived by calculating the standard deviation of seven replicates of a low-level standard, as described in the method protocol [5]. Fig. 1 shows a chromatogram of a 1.0 μg/l Cr(VI) standard, as the chromate anion, obtained using the conditions described in Method 218.6. Replicate injections at this level resulted in a calculated MDL of 0.34 μg/l for chromate, compared to the published MDL of 0.4 μg/l.

3.2. Effect of reaction coil and injection volume

The effect of reaction coil volume on peak response was studied, as preliminary investigations by California DHS indicated that the maximum peak response for chromate was not obtained using a standard (375 μl) knitted reaction coil [6]. Fig. 2 shows the effect of reaction coil volume on chromate peak height and area, at eluent flow-rates of 1.0 (a and c) and 1.5 (b and d) ml/min. In both cases, the postcolumn reagent was delivered at the same proportion relative to the eluent flow, i.e., at 0.33 (a and c) and 0.5 (b and d) ml/min, respectively. Increasing the reaction coil volume (hence delay time) increased peak response up to a maximum value, beyond which the peak response remained essentially unchanged. The combination of an eluent flow-rate of 1.0 ml/min with a 750 μl reaction coil was chosen for further work as this provided the maximum peak response and required only a modest pneumatic pressure (70 p.s.i., 1 p.s.i.=6894.76 Pa) to deliver the postcolumn reagent at the necessary flow-rate.

The effect of injection volume on chromate peak response was then studied using the conditions described above. Chromate, at 1.0 μg/l, was injected (in duplicate) at injection volumes of 250, 500, 750 and 1000 μl. Both peak height (R^2=0.9943) and area (R^2=0.9997) increased in a linear manner with injection volume, indicating there was no significant peak distortion at higher injected volumes. A 1000 μl injection volume was used for further investigations.

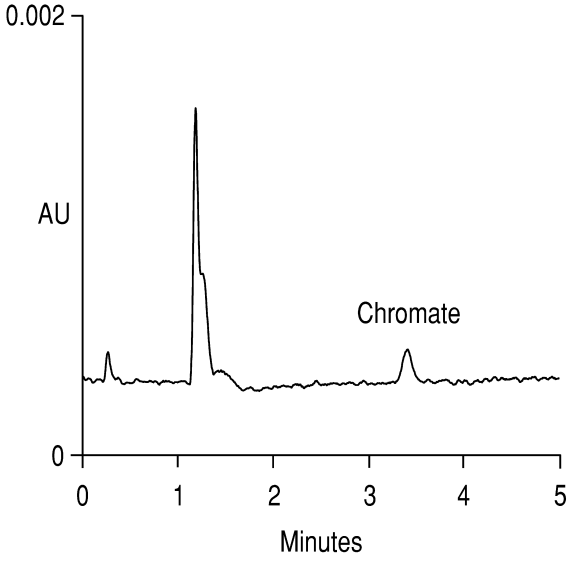

Fig. 1. Determination of chromate using the conditions detailed in EPA Method 218.6. Conditions: guard column, IonPac NG1; analytical column, IonPac AS7; eluent, 250 m*M* ammonium sulfate–100 m*M* ammonium hydroxide; flow-rate, 1.5 ml/min; postcolumn reagent, 2 m*M* diphenylcarbazide–10% methanol–0.5 *M* sulfuric acid; reaction coil volume, 375 μl; postcolumn flow-rate, 0.5 ml/min; detection, UV–Vis at 530 nm; injection volume, 250 μl; solutes, chromate (1.0 μg/l).

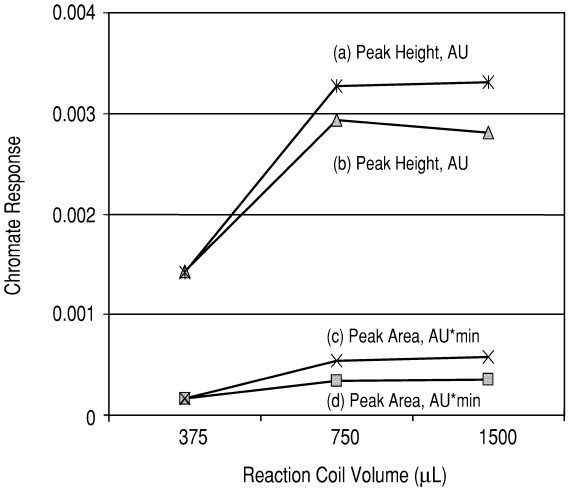

Fig. 2. Effect of reaction coil volume on chromate peak response. Conditions: as for Fig. 1, except: flow-rate, 1.0 (a and c) or 1.5 (b and d) ml/min; postcolumn flow-rate, 0.33 (a and c) or 0.5 (b and d) ml/min: reaction coil volume, 375–1500 μl as indicated; solutes, chromate (10 μg/l).

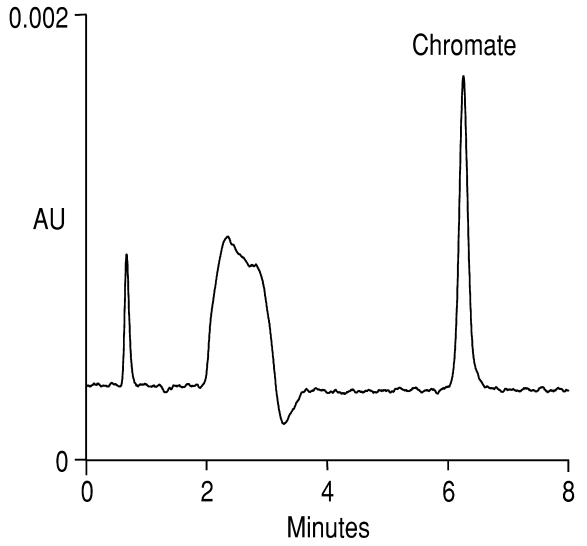

Fig. 3. Determination of chromate using optimized EPA Method 218.6. Conditions: as for Fig. 1, except; flow-rate, 1.0 ml/min; reaction coil volume, 750 μl; postcolumn flow-rate, 0.33 ml/min; injection volume, 1000 μl; solutes, chromate (1.0 μg/l).

3.3. Optimized method performance

The use of a larger volume reaction coil, lower eluent flow-rate and increased injection volume resulted in greater than a 10× increase in the chromate peak area compared to the response obtained using the standard conditions specified in Method 218.6. Fig. 3 shows a chromatogram of a 1.0 μg/l chromate standard, on the same *y*-axis scale as shown in Fig. 1, obtained using the optimized conditions described above. Table 1 shows the results of an MDL study for chromate performed at two concentrations levels of 0.1 and 0.2 μg/l. 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 chromate, which is adequate for routine analysis at the California PHG level of 0.2 μg/l.

Table 1
Method detection limits for chromate based on a 1000 μl injection

Chromate concentration (μg/l)	SD (μg/l)	RSD (%)	MDL[a] (μg/l)
0.1	0.0060	6.986	0.018
0.2	0.0056	3.193	0.018

[a] MDL=SD·$_{ts,99}$ where $_{ts,99}$=3.14 for n=7.

A coefficient of determination of 0.9999 was obtained over the calibration range of 0.1–10 μg/l for chromate. Fig. 4 shows chromatograms obtained using the optimized conditions of a Sunnyvale, CA, tap water blank (a) and tap water sample spiked with chromate at the PHG level of 0.2 μg/l (b). In both cases, the sample was adjusted to pH 9 using the buffer recommended by the California DHS. The presence of the ammonium sulfate–ammonium hydroxide buffer in the sample did not adversely affect the chromate peak shape and a recovery of 96% was obtained for the chromate spike at this level. The tap water blank contained a background level of 0.055 μg/l chromate.

The IonPac AS7 column specified in Method 218.6 is a relatively high-capacity anion exchanger (100 μequiv./column), however the use of a large injection volume increases the possibility of interference from other anions in the sample. Hence, the effect of chloride and sulfate on chromate 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 which had been adjusted to pH 9 with the California DHS buffer and spiked with 0.2 μg/l chromate.

Table 2 shows the effect of common anions on

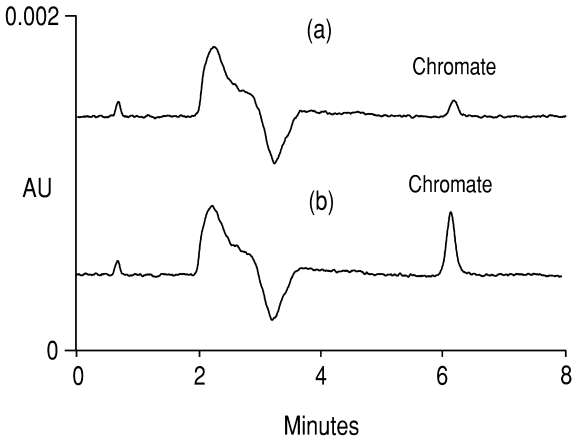

Fig. 4. Determination of chromate in drinking water. Conditions: as for Fig. 3, except: sample, buffered Sunnyvale, CA drinking water (a) and drinking water spiked with 0.2 μg/l chromate; solutes, (a) chromate (0.055 μg/l) and (b) chromate (0.245 μg/l).

Table 2
Effect of common anions on chromate peak area recovery[a]

Anion	Amount added (mg/l)	Chromate recovery (%)
Sulfate	0	100
	250	108
	500	98
	750	97
	1000	96
	2000	99
Chloride	0	100
	250	105
	500	103
	750	93
	1000	87
	2000	59

[a] Relative to 0.2 μg/l chromate spiked in tap water with no added sulfate or chloride.

chromate peak area recovery, relative to the peak area for 0.2 μg/l chromate spiked in tap water containing no added sulfate or chloride. Acceptable method performance, i.e., greater than 80% recovery, was obtained in the presence of up to 1000 mg/l chloride or 2000 mg/l sulfate, which is much higher than would typically be expected in ground and drinking waters.

4. Conclusions

EPA Method 218.6, as published, does not allow sufficient sensitivity to determine hexavalent chromium (i.e., chromate) 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 chromate of 0.02 μg/l. These modifications allow a minimum limit (ML) of quantitation for chromate 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 chromate 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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