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# Sensitive Determination of Hexavalent Chromium in Drinking Water

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# Outline

- Why do we need a sensitive method for hexavalent chromium analysis?
- U.S. EPA Method 218.6 and optimizations proposed in 2003
- Modifications proposed in 2011 to permit a detection limit of 1 ppt

# Health Effects of Chromium

**Chromium-3**

**A nutritionally essential element**
**often added to dietary vitamin supplements**

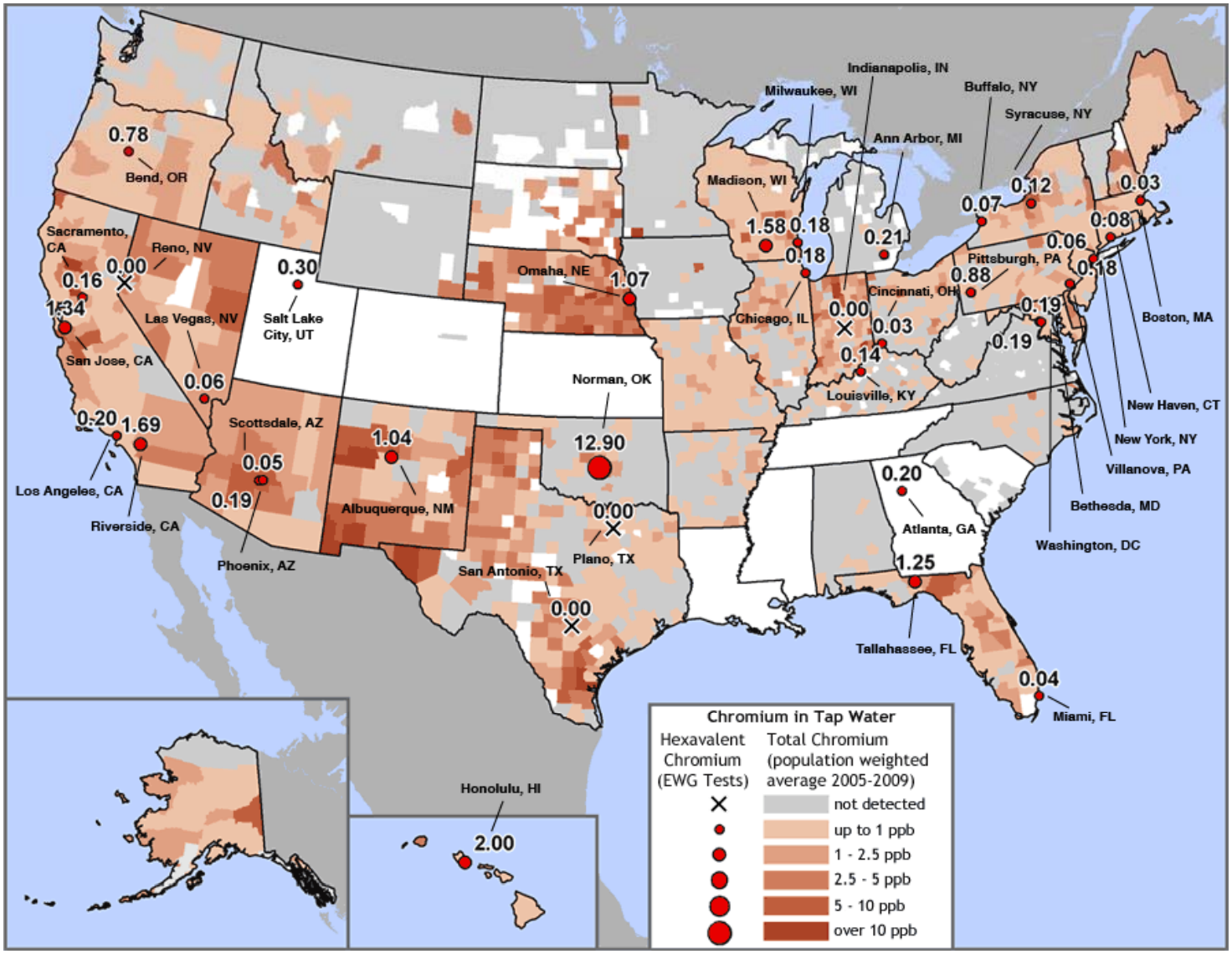
**Chromium-6 (Chromate)**

**Strong oxidizers**
**Genotoxic carcinogens**

# Hexavalent Chromium in the Media

- Original case filed in 1993 (Hinkley, CA, 0.58 ppm)
- Chemical compound in Erin Brockovich case (2000)
- Environmental Working Group Report, December 2010

# Widespread Detection of Chromate in U.S. Tap Water




Environmental Working Group Report, December 2010

**31/35 cities had chromate in their water.**

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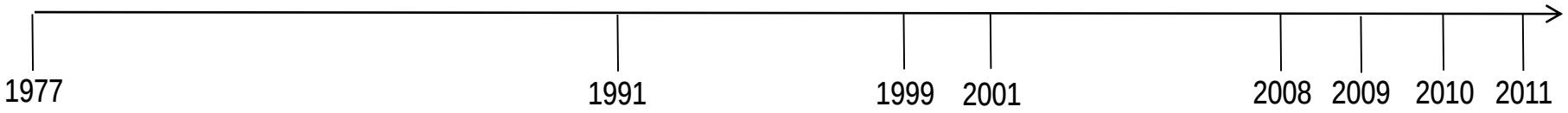
# Chromium Regulations at a Glance




| | |
|---|---|
| 1977 | Maximum Contaminant Level (MCL) for total chromium was established at 50 μg/L in California, adopted from what was then a National Interim Drinking Water Standard for chromium. |
| 1991 | Federal MCL for total chromium was raised to 100 μg/L, but California stayed at 50 μg/L. |
| 1999 | California EPA Office of Environmental Health Hazard Assessment (OEHHA) established a PHG at 2.5-μg/L for total chromium. California Department of Public Health identified chromium as a contaminant for possible MCL revision, and included hexavalent chromium among the unregulated chemicals requiring monitoring. |
| 2001 | National Toxicity Program announced it would conduct long-term studies to evaluate the potential carcinogenicity of ingested hexavalent chromium. |
| 2008 | U.S. EPA conducted a review of the health effects of hexavalent chromium based on toxicity studies performed by National Toxicology Program. |
| 2009 | California OEHHA proposed a PHG of 0.06 μg/L for hexavalent chromium. |
| 2010 | U.S. EPA released Toxicological Review of hexavalent chromium.<br>California OEHHA issued new PHG for hexavalent chromium at 0.02 μg/L. |
| 2011 | U.S. EPA will carefully review the conclusions and consider all relevant information to determine if a new standard needs to be set. In the interim period, U.S. EPA provided guidelines for monitoring hexavalent chromium (and continuing to monitor total chromium). |

# Available Methods for Hexavalent Chromium Detection

## U.S. EPA Method 218.4

- Chelation extraction, atomic absorption
- Positive interference from some metals
- Cumbersome, not automated
- Modest detection limits (~5 ppb)

## U.S. EPA Method 218.6 (ASTM Method D5257-03)

- Ion chromatography separation of chromate coupled with postcolumn reaction (diphenylcarbazide) and UV-Vis detection (530 nm)

# Summary of U.S. EPA Method 218.6

An aqueous sample is filtered through a 0.45 μm filter and the filtrate is adjusted to a pH of 9 to 9.5 with a buffer solution.
Buffer Solution: 2500 mM Ammonium Sulfate and 1000 mM Ammonium Hydroxide

A measured volume of the sample (50-250 µL) is introduced into the ion chromatography system.

A guard column removes organics from the sample before the Cr(VI) as $CrO_4^{2-}$ is separated on an anion-exchange-separator column.

Postcolumn derivatization of the Cr(VI) with diphenylcarbazide is followed by detection of the colored complex a 530 nm.

**Samples must be stored at 4 °C and analyzed within 24 hours of collection.

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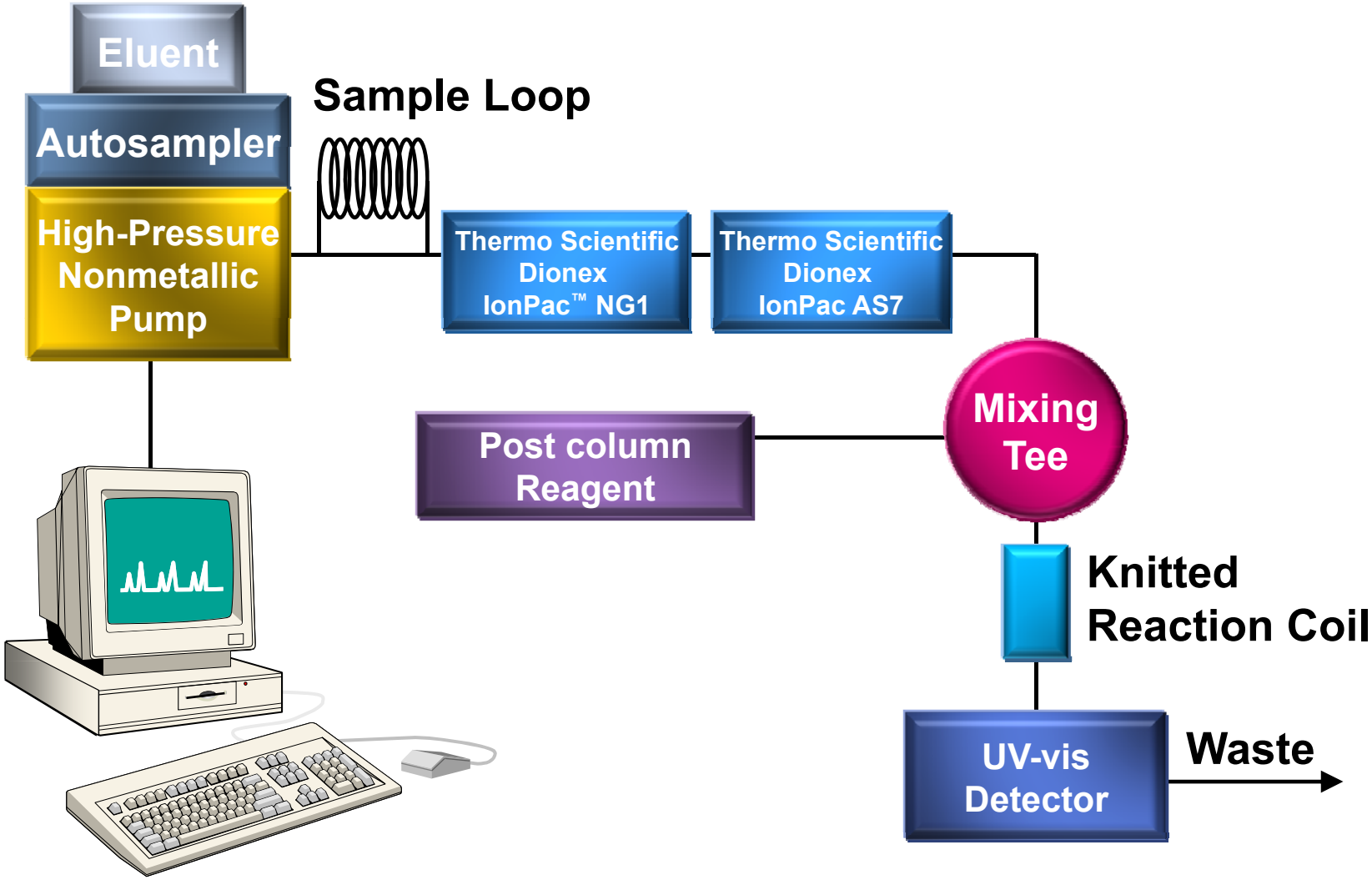
# Chromatography Conditions for U.S. EPA 218.6

| **Columns:** | |
|---|---|
| Guard Column | Thermo Scientific Dionex IonPac™ NG1 |
| Separator Column | Thermo Scientific Dionex IonPac AS7 |
| | |
| Eluent | 250 mM $(NH_4)_2SO_4$<br>100 mM $NH_4OH$ |
| Flow Rate | 1.5 mL/min |
| | |
| Postcolumn Reagent | 2 mM Diphenylcarbohydrazide<br>10% v/v $CH_3OH$<br>1 N $H_2SO_4$ |
| Flow Rate | 0.5 mL/min |
| Detector | Visible 530 nm |
| Retention Time | 3.8 min |

# System Configuration for Hexavalent Chromium by U.S. EPA Method 218.6



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# Thermo Scientific Dionex IonPac AS7 Anion-Exchange Column

## The Dionex IonPac™ AS7:

- Separates a wide variety of polyvalent anions, including polyphosphates, polyphosphonates, and other polyvalent complexing agents such as EDTA and NTA using acidic eluent (eliminating metal interferences) with postcolumn derivatization and UV-Vis detection.

- Has a unique polymer packing that provides superior performance for separating ionic and polar compounds and offers high speed, efficiency, and loading capacity at moderate backpressures.

- Is useful for Cr(VI) in environmental matrices, such as ground water, wastewater, and soil extracts.

# Method Detection Limit (MDL) for Cr(VI) with U.S. EPA Method 218.6

| Matrix Type | Concn. Used to Compute MDL* (µg/L) | MDL* (µg/L) |
|---|---|---|
| Reagent Water | 1 | 0.4 |
| Drinking Water | 2 | 0.3 |
| Ground Water | 2 | 0.3 |
| Primary Sewage Wastewater | 2 | 0.3 |
| Electroplating Wastewater | 2 | 0.8 |

* MDL = (Standard Deviation) × ($t_{s,\,99}$), where $t_{s,\,99}$ = 3.14 for n = 7.

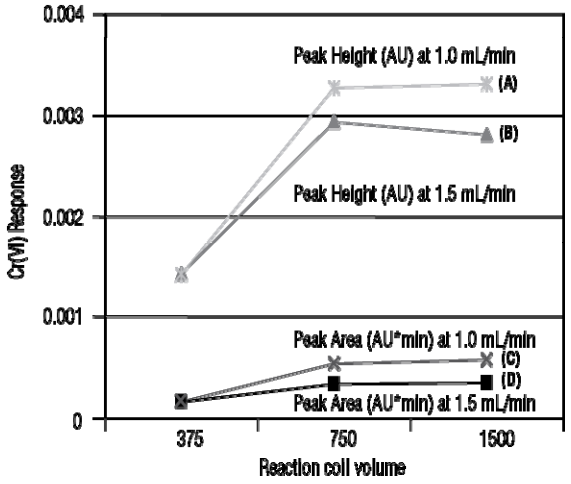
# Modified Version of U.S. EPA 218.6

| Method | Adjustment Buffer | Postcolumn Reaction (PCR) Coil Volume µL | Eluent Flow Rate mL/min | PCR Flow Rate mL/min | Injection Volume µL |
|---|---|---|---|---|---|
| **U.S. EPA 218.6** | 2500 mM $(NH_4)_2SO_4$<br>1000 mM $NH_4OH$ | Not specified | 1.5 | 0.5 | 50-250 |
| **Modified Version of U.S. EPA 218.6** | 250 mM $(NH_4)_2SO_4$<br>1000 mM $NH_4OH$ | 750 | 1.0 | 0.3 | 1000 |

- Use a lower-sulfate buffer to adjust sample pH.
- Increase PCR coil to 750 µL.
- Reduce eluent flow rate to 1 mL/min.
- Reduce PCR flow rate to 0.33 mL/min.
- Increase sample size to 1000 µL.

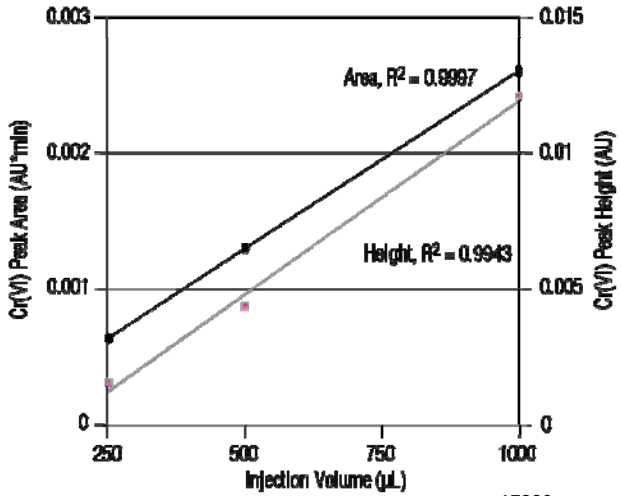
# Effects of Flow Rate, Reaction Coil Volume, and Injection Volume on Hexavalent Chromium Response

| | |
|---|---|
| Columns: | Thermo Scientific Dionex IonPac™ NG1, AS7 |
| Eluent: | 250 mM $(NH_4)_2$ $SO_4$<br>100 mM $NH_4OH$ |
| Inj. Volume: | 250 µL |
| Postcolumn Reagent: | 2 mM diphenylcarbazide<br>10% $CH_3OH$<br>1N $H_2SO_4$ |
| Reaction Coil: | 375, 750, and 1500 µL |
| Detector: | UV-Vis (530 nm) |




**Reaction Coil Volume and Chromate Response**

| | |
|---|---|
| Columns: | Dionex IonPac NG1, AS7 |
| Eluent: | 250 mM $(NH_4)_2$ $SO_4$<br>100 mM $NH_4OH$ |
| Flow Rate: | 1.0 mL/min |
| Inj. Volume: | 250–1000 µL |
| Postcolumn Reagent: | 2 mM diphenylcarbazide<br>10% $CH_3OH$<br>1N $H_2SO_4$ |
| Reaction Coil: | 750 µL |
| Detector: | UV-Vis (530 nm) |




**Injection Volume and Chromate Response**

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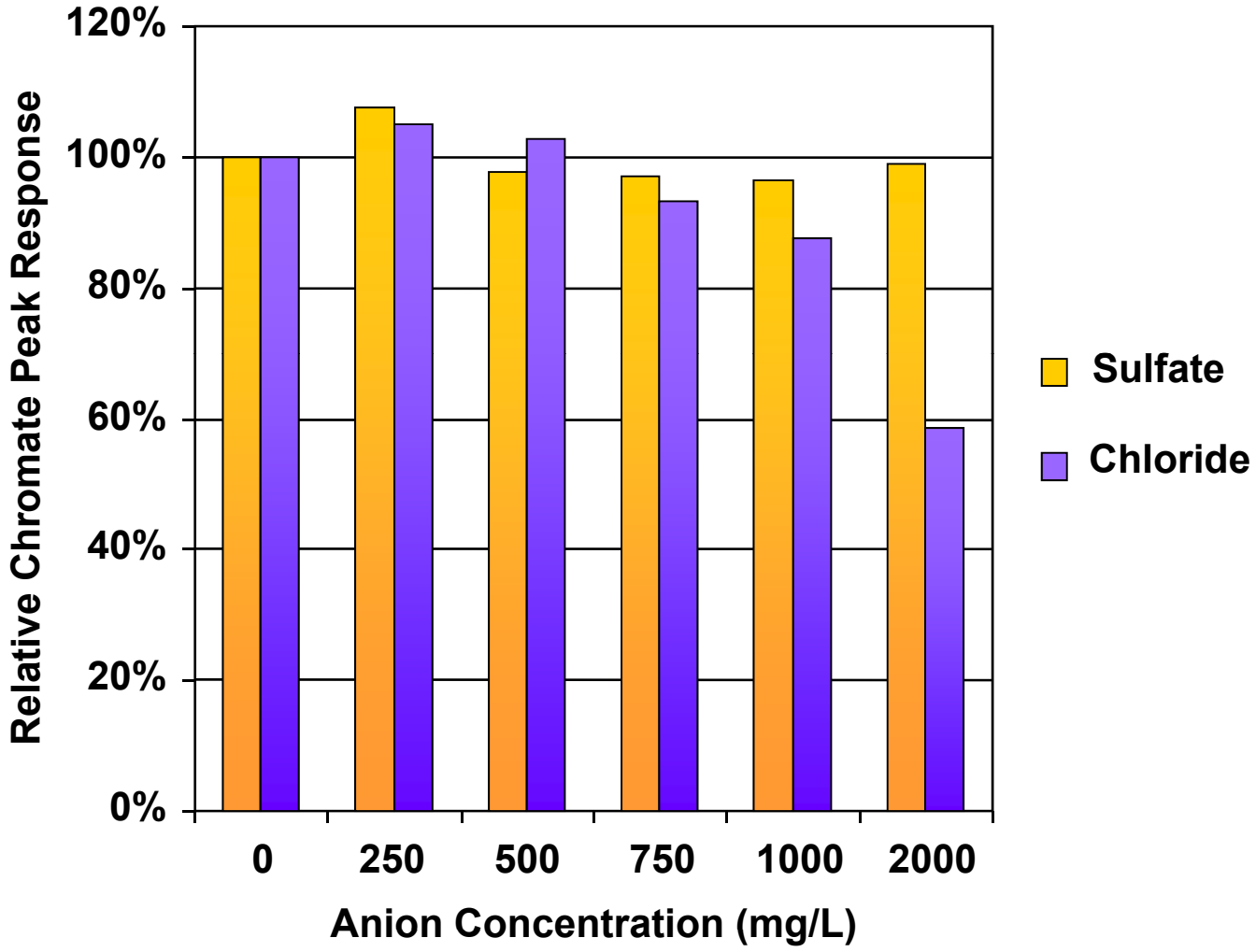
# Effect of Sulfate and Chloride on Chromate Peak Response Using Modified Version of U.S. EPA Method 218.6



# Hexavalent Chromium Determination Using Modified Version of U.S. EPA Method 218.6

| | |
|---|---|
| Columns: | Thermo Scientific Dionex IonPac™ NG1, AS7 |
| Eluent: | 250 mM $(NH_4)_2$ $SO_4$<br>100 mM $NH_4OH$ |
| Flow Rate: | 1.0 mL/min |
| Inj. Volume: | 1000 µL |
| Postcolumn Reagent: | 2 mM diphenylcarbazide<br>10% $CH_3OH$<br>1N $H_2SO_4$ |
| Reaction Coil: | 750 µL |
| Detector: | UV-Vis (530 nm) |
| Sample: | 1.0 µg/L Cr(VI) |

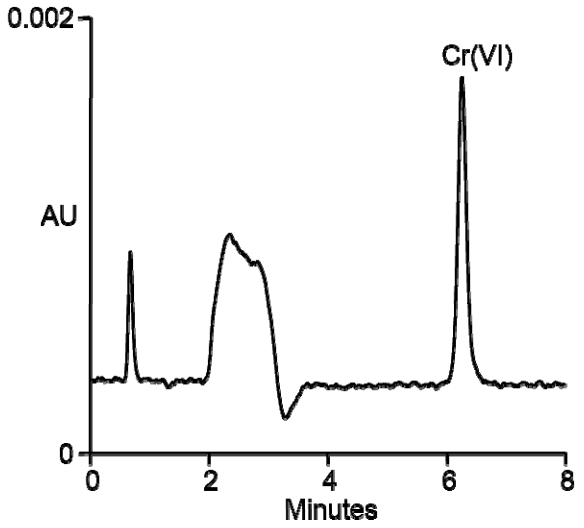



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**Table 1. Method Detection Limit (MDL) for Chromate Based on a 1000 µL Injection**

| Chromate Concn. (µg/L) | Std. Dev. (µg/L) | RSD (%) | MDL* (µg/L) |
|---|---|---|---|
| 0. 1 | 0.0060 | 6.996 | 0.018 |
| 0.2 | 0.0056 | 3.193 | 0.018 |

* MDL = (Standard Deviation) × ($t_{s, 99}$), where $t_{s, 99}$ = 3.14 for n = 7.

**New MDL in reagent water is 0.018 µg/L**

**15× lower than 218.6.**

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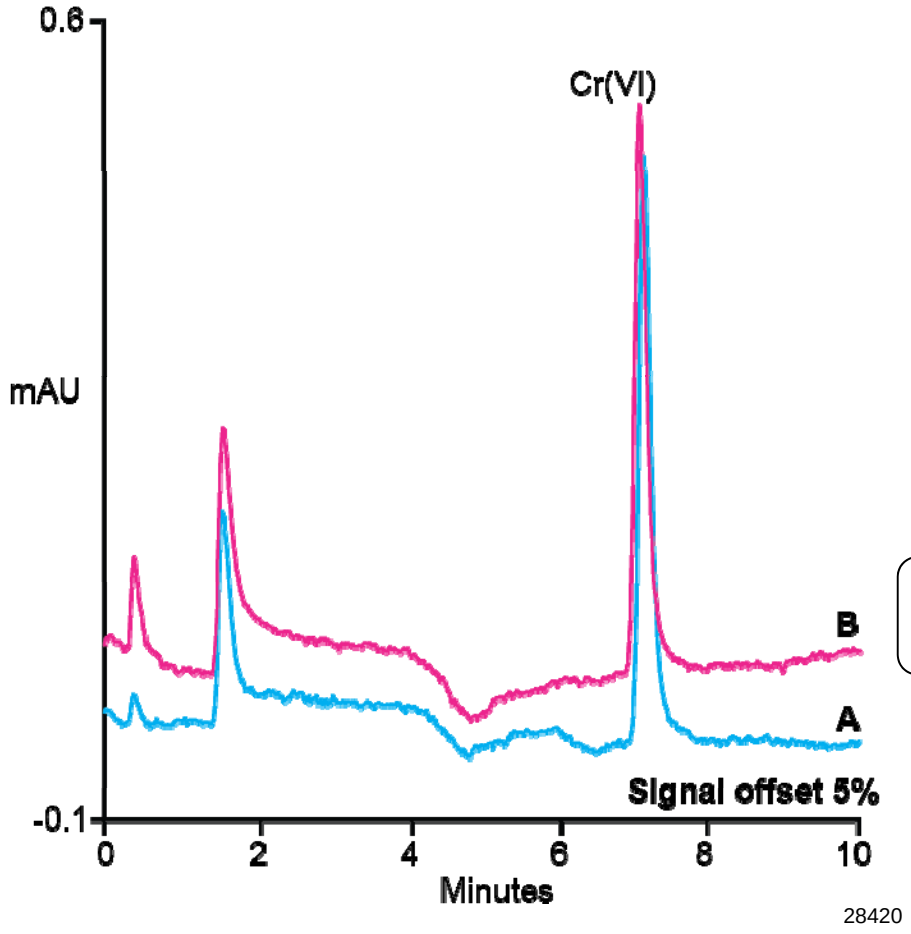
# How to Achieve a Lower Method Detection Limit?

# Achieving a Lower Method Detection Limit (MDL)

| Method | Column Set | Reaction Coil Volume (µL) | Eluent Flow Rate (mL/min) | Postcolumn Flow Rate (mL/min) |
|---|---|---|---|---|
| **Modified Version of 218.6** | Thermo Scientific Dionex IonPac™ NG1 Guard 4 × 50 mm<br><br>Dionex IonPac AS7 Analytical 4 × 250 mm | 750 | 1.0 | 0.3 |
| **Current Study** | Dionex IonPac AG7 Guard 2 × 50 mm<br><br>Dionex IonPac AS7 Analytical 2 × 250 mm | 125 | 0.36 | 0.12 |

# Chromate Determination Using a 2 mm Column Format




| | |
|---|---|
| Columns: | Thermo Scientific Dionex IonPac™ AG7 (2 × 50 mm), AS7 (2 × 250 mm) |
| Eluent: | 250 mM $(NH_4)_2 SO_4$<br>100 mM $NH_4OH$ |
| Flow Rate: | 0.36 mL/min |
| Inj. Volume: | 1000 µL |
| Postcolumn Reagent: | 2 mM diphenylcarbazide<br>10% methanol<br>1N sulfuric acid |
| Reaction Coil: | 125 µL |
| Flow Cell: | Semi-micro (PEEK) 2.5 µL |

A. 0.1 µg/L Cr(VI) in DI water
B. 0.1 µg/L Cr(VI) in HIW

**0.1 µg/L Cr(VI) in (A) DI water and (B) high ionic-strength water (HIW)**

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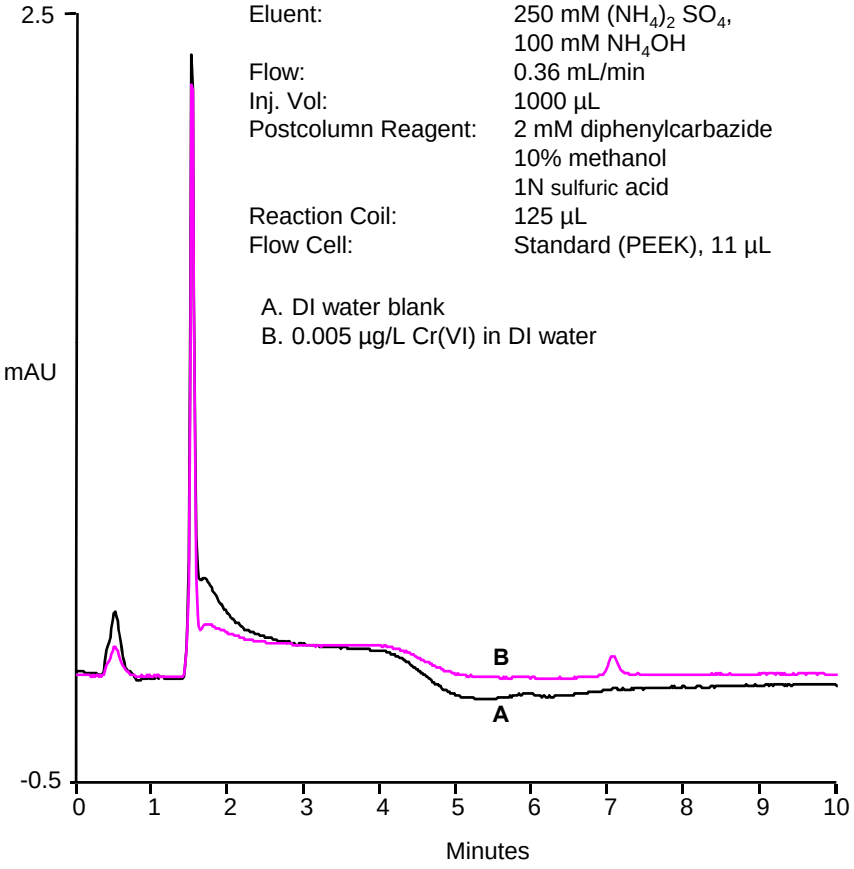
# Chromate Detection

| | |
|---|---|
| Column: | Thermo Scientific Dionex IonPac™ AS7 (2 × 50 mm), AS7 ( 2 × 250 mm) |
| Eluent: | 250 mM $(NH_4)_2 SO_4$, 100 mM $NH_4OH$ |
| Flow: | 0.36 mL/min |
| Inj. Vol: | 1000 µL |
| Postcolumn Reagent: | 2 mM diphenylcarbazide<br>10% methanol<br>1N sulfuric acid |
| Reaction Coil: | 125 µL |
| Flow Cell: | Standard (PEEK), 11 µL |

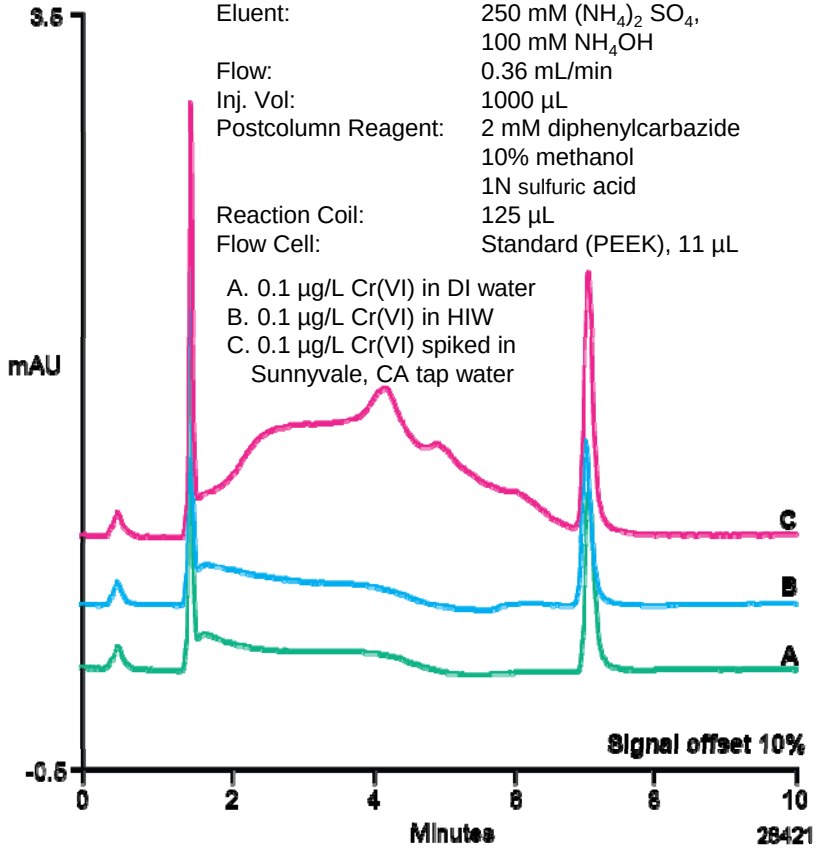
A. DI water blank
B. 0.005 µg/L Cr(VI) in DI water




Blank and low-level chromate

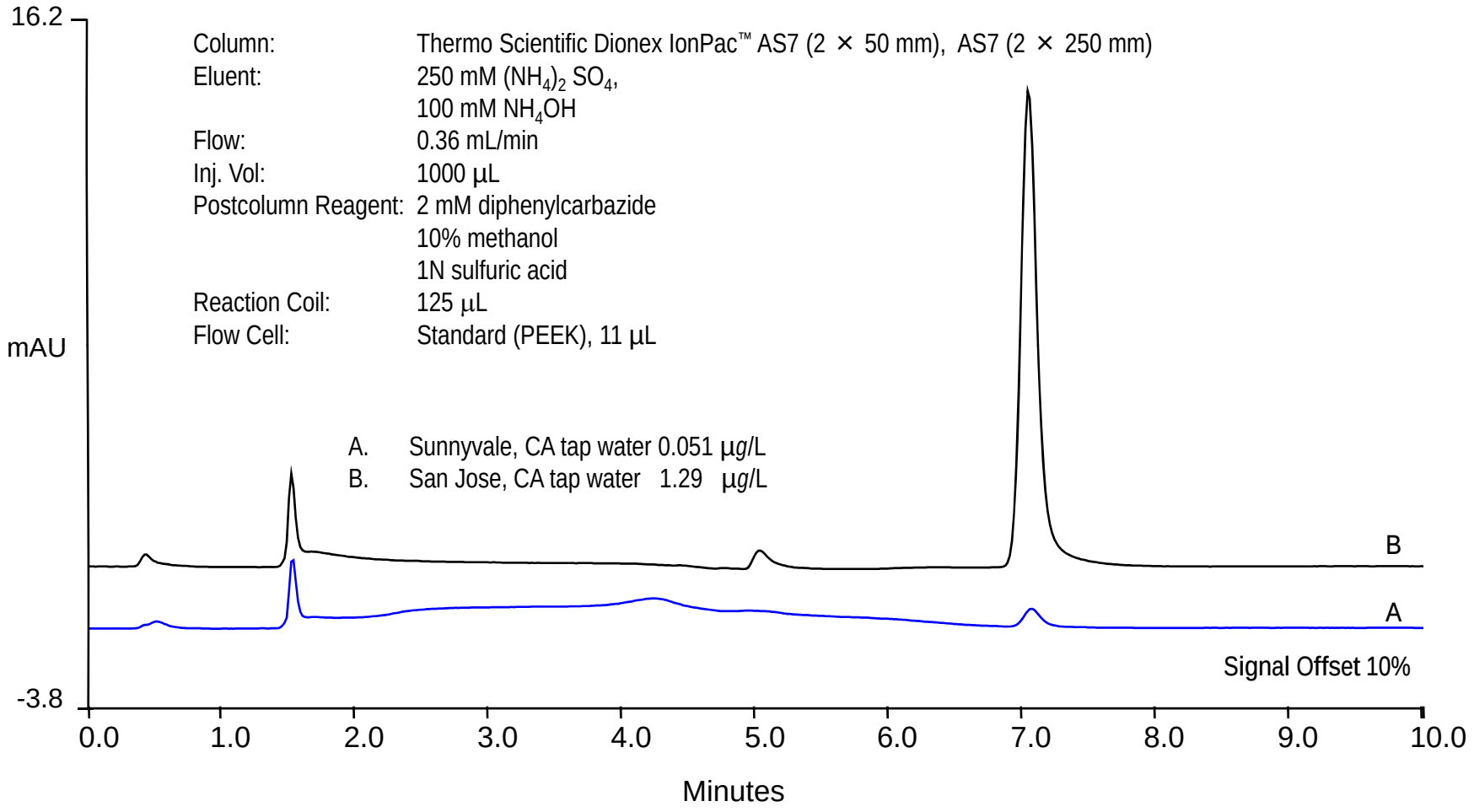
| | |
|---|---|
| Column: | Dionex IonPac™AS7 (2 × 50 mm), AS7 ( 2 × 250 mm) |
| Eluent: | 250 mM $(NH_4)_2 SO_4$, 100 mM $NH_4OH$ |
| Flow: | 0.36 mL/min |
| Inj. Vol: | 1000 µL |
| Postcolumn Reagent: | 2 mM diphenylcarbazide<br>10% methanol<br>1N sulfuric acid |
| Reaction Coil: | 125 µL |
| Flow Cell: | Standard (PEEK), 11 µL |

A. 0.1 µg/L Cr(VI) in DI water
B. 0.1 µg/L Cr(VI) in HIW
C. 0.1 µg/L Cr(VI) spiked in Sunnyvale, CA tap water




Comparison of chromate in high ionic-strength water (HIW) and Sunnyvale tap water

# Chromate in Tap Water




| | | | |
|---|---|---|---|
| Sunnyvale, CA | 0.051 µg/L | San Jose, CA | 1.3 µg/L |

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# LCMRL and Method Detection Limit (MDL)

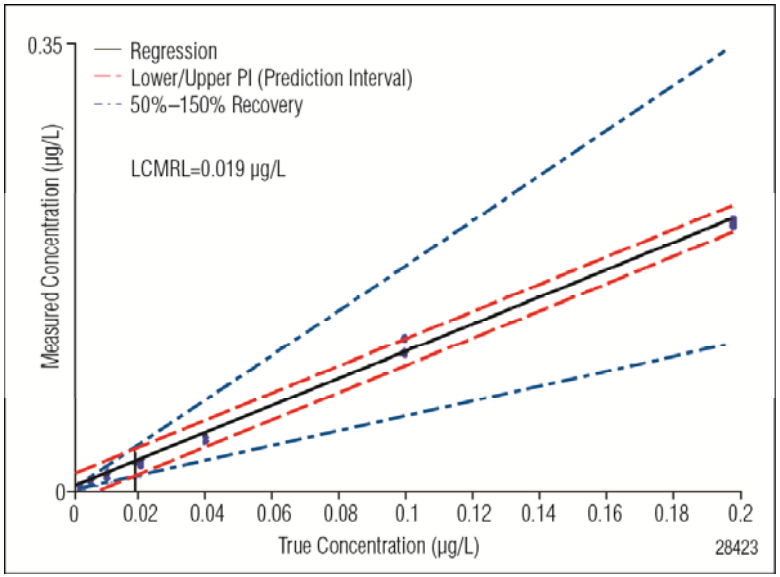


**Table 1. MDL for Chromate in High Ionic-Strength Water Based on a 1000 µL Injection**

| Chromate Concn. (µg/L) | Std. Dev. (µg/L) | RSD (%) | MDL* (µg/L) |
|---|---|---|---|
| 0.001 | 0.0003 | 10.03 | 0.0009 |
| 0.005 | 0.0004 | 6.62 | 0.0013 |

* MDL = (Standard Deviation) × ($t_{s,\,99}$), where $t_{s,\,99}$ = 3.14 for n = 7.

**Lowest Concentration**
**Minimum Reporting Limit = 0.019 µg/L**

**MDL = 1 ppt**

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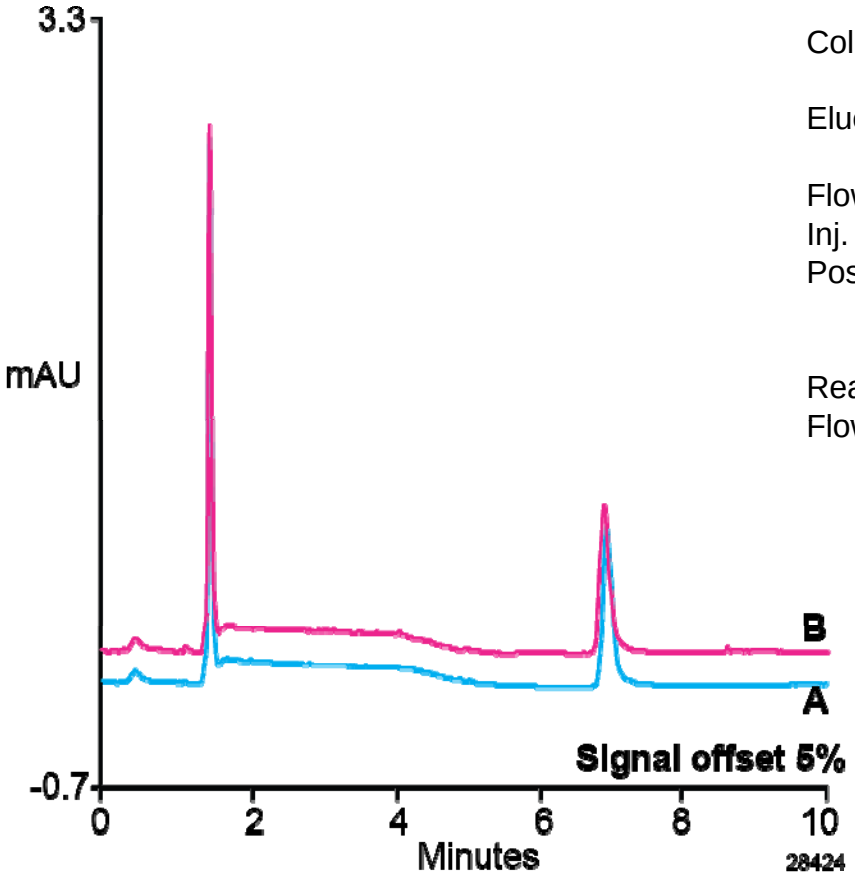
# Postcolumn Delivery Options

- Pneumatic delivery—a pressurized chamber that uses pressure to deliver reagent
  - Advantages
    - Lower baseline noise
  - Disadvantages
    - Not software controlled
    - Requires monitoring to maintain accurate flow rate
- Single Piston Pump (e.g., AXP)
  - Reliable flow rate
  - Software controlled
- Dual Piston Pump
  - Flexibility for additional applications
  - Software controlled

# Alternative Mode of Postcolumn Reagent Delivery




| | |
|---|---|
| Column: | Thermo Scientific Dionex IonPac™ AS7 (2 × 50 mm), AS7 (2 × 250 mm) |
| Eluent: | 250 mM $(NH_4)_2 SO_4$, 100 mM $NH_4OH$ |
| Flow: | 0.36 mL/min |
| Inj. Vol: | 1000 µL |
| Postcolumn Reagent: | 2 mM diphenylcarbazide<br>10% methanol<br>1N sulfuric acid |
| Reaction Coil: | 125 µL |
| Flow Cell: | Standard (PEEK), 2.5 µL |

A. 0.1 µg/L Cr(VI) in DI water
B. 0.1 µg/L Cr(VI) in HIW

A) DI water and B) high ionic-strength water (HIW) on a Thermo Scientific Dionex ICS-2100 system

**Postcolumn reagent delivered by an AXP pump**

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# Detection Limit Using Different Postcolumn Delivery Mechanisms

| Method Detection Limit (MDL) Comparison Between Postcolumn Pumps | | | | |
|---|---|---|---|---|
| Column Format | Chromate Concn. (µg/L) | Pneumatic Pump MDL* (µg/L) | Single Piston MDL* (µg/L) | Dual Piston MDL* (µg/L) |
| 4 mm | 0.1<br>0.2 | 0.018<br>0.018 | NA | NA |
| 2 mm | 0.005 | 0.0013 | | |

* MDL = (Standard Deviation) × ($t_{s, 99}$), where $t_{s, 99}$ = 3.14 for n = 7.

# Column Dimension Comparison

| Method Detection Limit (MDL) for Chromate Based on a 1000 µL Injection | | | | |
|---|---|---|---|---|
| Column Format | Chromate Concn. (µg/L) | Std. Dev. (µg/L) | RSD (%) | MDL* (µg/L) |
| 4 mm | 0.1<br>0.2 | 0.0060<br>0.0056 | 6.986<br>3.193 | 0.018<br>0.018 |
| 2 mm | 0.005 | 0.0004 | 6.62 | 0.0013 |

* MDL = (Standard Deviation) × ($t_{s,\,99}$), where $t_{s,\,99}$ = 3.14 for n = 7.

1 ppt Detection Limit with 2 mm Column Format

# Summary

- Modifications proposed: use 2 mm column format and proportional reduction of the flow rates and reaction coil volume.
- Postcolumn reagent delivery can be configured three ways.
- Method detection limit for chromate at 1 ppt will allow a minimum quantitation limit of 3 ppt.
- Modifications allow sufficient sensitivity for determining hexavalent chromium at the proposed California PHG level of 20 ppt.
- We are working with the U.S. EPA Office of Ground Water and Drinking Water to incorporate these configurations into a new U.S. EPA Method 218.7.