Hexavalent Chromium Determination by Two-Dimensional Capillary Ion Chromatography Using a Monolith Concentrator Column

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Abstract

The Thermo Scientific Dionex ICS-5000 capillary Reagent-Free™ ion chromatography (RFIC™) system is typically offered with an internal 0.4 µL loop, which is the equivalent of a 40 µL loop on a 4 mm standard-bore system. The Dionex ICS-5000 can also be configured with a six-port injection valve, which accommodates external injection loops and concentrator columns.

Capillary systems have the advantage of increased mass sensitivity. To achieve the same sensitivity as a standard bore system, only 1/100 of the sample volume needs to be injected. However, by using a standard-bore system as the first dimension in a two-dimensional (2D) IC system configuration, sample sizes typical of 4 mm systems can be interfaced with the mass sensitivity of a capillary system. Thus a 100-fold increase in sensitivity with a concentration-sensitive detector such as conductivity can be achieved.

This work will show the results of adapting a 2D system for use in hexavalent chromium (chromate or CrO_4^{2-} ion) determination of drinking water samples using suppressed conductivity detection. Minimum detection limits (MDLs) better than existing methods will be demonstrated.

Introduction

Hyphenated, multiple ion chromatography (IC) systems are becoming more prevalent for environmental analyses. This multisystem format can accommodate samples with relatively high matrix content, and simultaneously achieve very low limits of detection (LOD). Recent methods including EPA 314.2 and 302.0 were developed to allow sensitive detection of specific analytes in drinking water samples in the presence of relatively high matrix concentrations. These methods combined a 4 mm system in the first dimension with a 2 mm system in the second dimension. The first dimension was used to separate the targeted analyte from the matrix ions using a 4 mm column, and the selected peak of interest was heart-cut and refocused onto a concentrator column. The second dimension was used to analyze the heart-cut fraction using a 2 mm column. This operational format resulted in a four-fold increase in sensitivity with a concentration-sensitive detector, such as a conductivity detector. However, by interfacing a 4 mm system in the first dimension with a 0.4 mm capillary system in the second dimension, it is possible to achieve a 100-fold increase in sensitivity.

The current method for chromate uses a 4 × 250 mm Thermo Scientific Dionex IonPac™ AS7 column for separation, followed by UV-vis detection in the visible light range after a postcolumn reagent addition of diphenylcarbohydrazide. The postcolumn reaction method is a highly sensitive and selective method for chromate, and detection limits are approximately 0.020 ppb when using a direct injection of 1 mL of sample. However, for best performance the method requires optimization of the postcolumn reagent delivery.

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The maximum contaminant level goals (MCLG) set by the U.S. EPA for chromate (total) is 0.1 mg/L or 100 ppb. California has proposed a health protection goal of 0.02 ppb for chromate. The existing postcolumn derivatization method was recently updated to improve its sensitivity to quantify chromate at these levels, however alternate methods are also being investigated.

Experimental Conditions

All ion chromatographic separations were performed using a hybrid Dionex ICS-5000 system equipped with a Thermo Scientific Dionex IC Cube™ cartridge and capillary pump on one channel and a standard pump on the other. Deionized water with a specific resistance of 18.2 MΩ-cm was used to prepare all eluents and standards. In the first dimension, a Dionex IonPac AS24 (4 mm) column set was used with aThermo Scientific Dionex ASRS™ 300 Anion Self-Regenerating Suppressor™ (4 mm). In the second dimension, a Dionex IonPac AS20 (0.4 mm) or Dionex IonPac AS19 (0.4 mm) column was used with a Thermo Scientific Dionex ACES™ 300 Anion Capillary Electrolytical Suppressor.

Drinking water samples were collected from the cities of San Jose and Sunnyvale, CA. These drinking water samples were treated with a sodium tetraborate-based (borax) sample preservation buffer following a protocol published by the California Department of Public Health (http://cdph.ca.gov/certlic/drinkingwater/Documents/Drinkingwaterlabs/Cr(VI)BorateBufferWebsiteUpdate051810.pdf).

Concentrator Selection

Capillary systems require extremely low dead-volume concentrator columns, typically in the order of 10–25 µL. A traditional, packed-bed concentrator column of such low dead volume would be approximately 25 mm in length with an internal diameter of 0.65 mm. The backpressure of such a concentrator at 4 mm column compatible flow rates (typically 1.0 mL/min) would be far too high to act as an interface between the first and second dimensions.

An alternative to a traditional packed-bed concentrator is a monolith-based concentrator. Monoliths have the benefit of producing relatively low backpressures while simultaneously providing high capacities. The Thermo Scientific Dionex IonSwift™ MAC-200 Monolith Anion Concentrator Column is a monolithic anion-exchange concentrator column with a dead volume of approximately 23 µL and a capacity of 0.24 µeq/column in a 0.75 × 80 mm package. At flow rates of 1.0 mL/min, the MAC-200 produces a backpressure of approximately 40 psi, making it ideal for placement as an interface between a 4 mm channel as the first dimension and a 0.4 mm channel as the second dimension.

In this work, a Dionex IonSwift MAC-200 concentrator column was placed immediately after the first dimension's detector cell and in the injection path of the second dimension using a six-port valve.

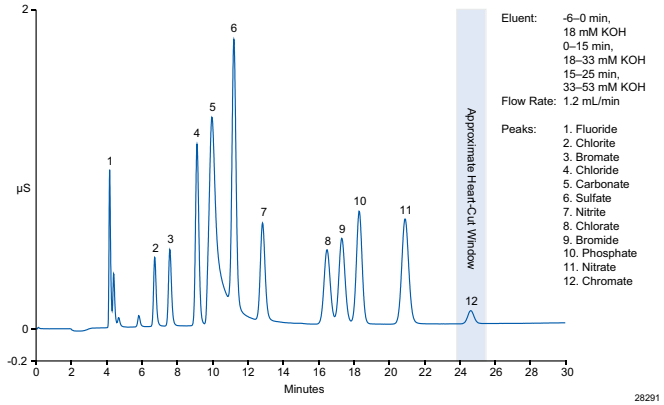
Results and Discussion

Experiments were conducted to optimize the first and second dimension separation, and to evaluate the reproducibility, linearity, and MDL of the chromate analysis. Drinking water samples from San Jose and Sunnyvale and a simulated high-ionic-strength matrix sample were analyzed.

First Dimension

A Dionex IonPac AS24 (4 mm) column was chosen for the first dimension due to its high capacity. By using this column, a 1 mL injection can be made of a relatively high-ionic-strength matrix while still obtaining good separation of the matrix ions from the ion of interest. The eluent gradient was optimized to obtain highest resolution of chromate from matrix ions such as chloride, carbonate, and sulfate, which are typically present in drinking water samples at relatively high concentrations. A two-part linear gradient was chosen as shown in Figure 1.

FIGURE 1. Separation of ten common anions and oxyanions and chromate on a Dionex IonPac AS24 column using a two-step linear gradient.



Second Dimension

A Dionex IonPac AS20 (0.4 mm) column was initially chosen for the second dimension due to its good peak shape and fast resolution of chromate. However, the close proximity of nitrate and chromate in the first dimension under fast elution conditions caused interferences with this column in the second dimension. Attempts to resolve nitrate and chromate satisfactorily with the Dionex IonPac AS20 column resulted in unacceptably long run times. As a result, a different column—a Dionex IonPac AS19 (0.4 mm) column—was chosen with better nitrate/chromate selectivity and similarly fast run times (see Figure 2).

Reproducibility

Nine injections of 50 ppt chromate in the borax-based sample preservation buffer were made. Excellent reproducibility was demonstrated as evident from the % relative standard deviation (RSD) of the peak retention time and peak area response for chromate (see Table 1).

FIGURE 2. Analysis of 100 ppb chromate in a 10 anion standard using a Dionex IonPac AS19 column and a simple linear gradient; direct injection of 4 µL.

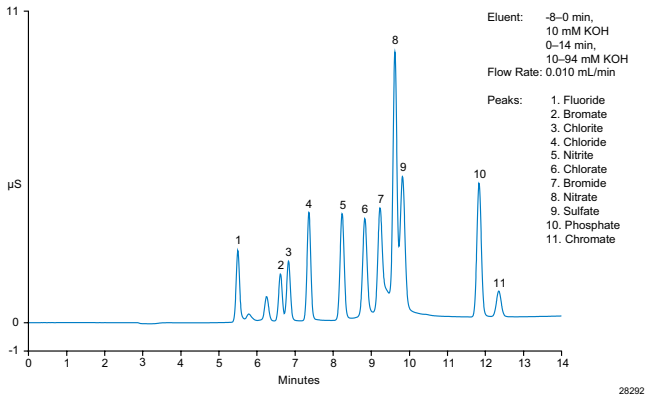


Table 1. Retention Time and Peak Area Response for 50 ppt Chromate in Borax-Based Sample Preservation Buffer

	Retention Time for 50 ppt Chromate in Sample Preservation Buffer	Area Response for 50 ppt Chromate in Sample Preservation Buffer
1	39.797	0.05484
2	39.790	0.05507
3	39.817	0.05499
4	39.810	0.05501
5	39.803	0.05529
6	39.800	0.05519
7	39.810	0.05524
8	39.783	0.05504
9	39.807	0.05521
Average	39.802	0.05510
St. Dev.	0.011	0.00014
% RSD	0.03%	0.26%

Linearity

Linearity was determined for chromate by injecting standards of chromate at levels of 10, 20, 50, 100, 200, and 500 ppt. The correlation coefficient was found to be 0.99999. A Cassidy curve was plotted; ideally the response should remain constant across the entire range of standards. The RSD of the Cassidy curve was 2.7% (see Figure 3).

Minimum Detection Limit

Seven injections of 5.0 ppt chromate in the borax-based sample preservation buffer were made to determine the MDL. The experiment was repeated using 10 ppt chromate in the borax-based sample preservation buffer with 100 ppm each of chloride, bicarbonate, and sulfate, and 10 ppm nitrate and phosphate. See Table 2.

FIGURE 3. Calibration curve (A) and offset area/ response curve (B) for chromate in borax-based sample preservation buffer.

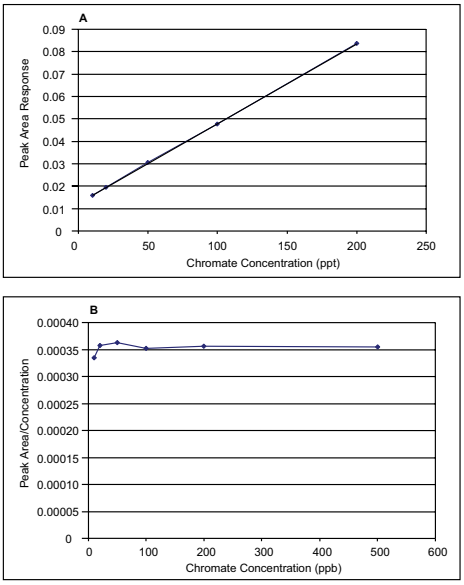


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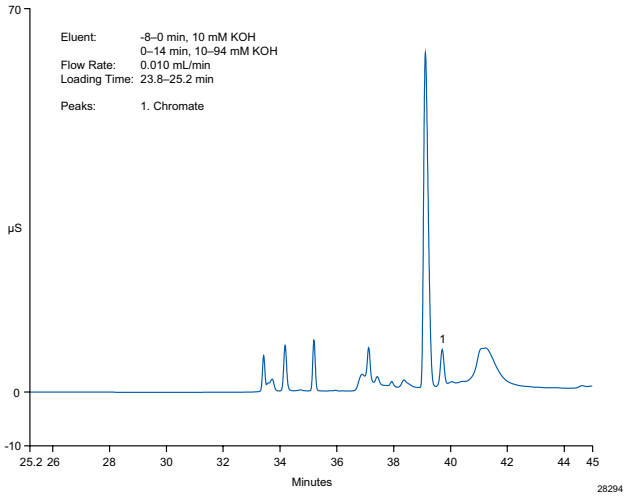
Table 2. Peak Area Response, Reported Concentration Values, and MDL for Chromate in Borax-Based Sample Preservation Buffer and High-Ionic-Strength Matrix

	Area Response for 5.0 ppt Chromate in Sample Preservation Buffer	Reported Concentration Value for 5.0 ppt Chromate in Sample Preservation Buffer	Area Response for 10 ppt Chromate in High-Ionic-Strength Matrix	Reported Concentration Value for 10 ppt Chromate in High-Ionic-Strength Matrix
1	0.01442	5.536	0.02539	10.856
2	0.01387	3.988	0.02483	9.839
3	0.01426	5.086	0.02506	10.257
4	0.01330	2.384	0.02491	9.984
5	0.01414	4.748	0.02500	10.148
6	0.01347	2.862	0.02485	9.876
7	0.01479	6.577	0.02439	9.040
Average	0.01404	4.454	0.02492	10.000
St. Dev.	0.00053	1.483	0.00030	0.545
MDL		4.66		1.711

Drinking Water

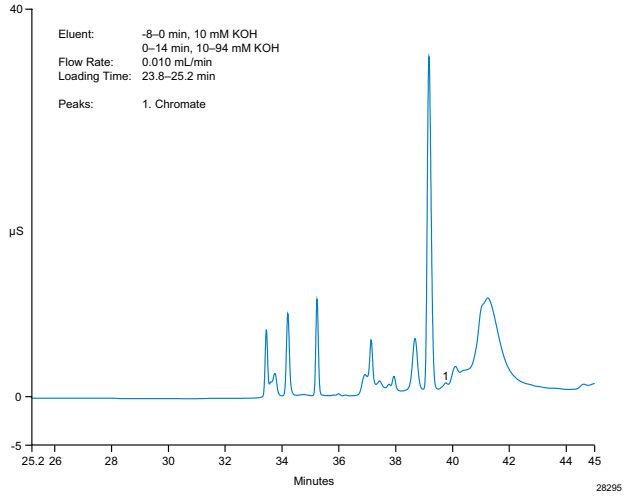
A sample of San Jose drinking water was analyzed (Figure 4). The amount of chromate detected in the sample was 2.6 ppb.

FIGURE 4. Second-dimension chromatogram of San Jose drinking water. Analysis reveals approximately 2.6 ppb chromate.



A sample of Sunnyvale drinking water was analyzed (Figure 5). The amount of chromate detected in the sample was 0.047 ppb.

FIGURE 5. Second-dimension chromatogram of Sunnyvale drinking water. Analysis reveals approximately 47 ppt chromate.



Conclusion

The results shown in this poster demonstrate that a 2D-IC method with suppressed conductivity detection can be used for chromate analysis and provides several advantages over the current postcolumn derivatization method.

- Using the same injection volume, sensitivity is improved with the suppressed conductivity method when compared to the postcolumn reagent method.
- The method is simple since it is a direct conductivty measurement versus a postcolumn derivatization protocol.
- The first dimension can be used to determine the composition of the common anions within the same sample, or operated independently for other types of analyses.
- The method is fully automated, as the RFIC system with eluent generation only requires deionized water for operation with suppressed conductivity detection.

The most significant drawback of the method is the relatively long run time (approximately 50 min) compared to the existing method (approximately 10 min).

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