Determination of Hexavalent Chromium in Drinking Water Using Segmented Flow Analysis

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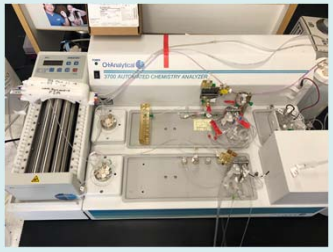
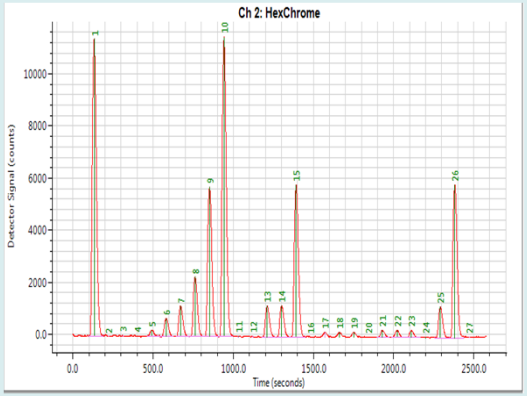
Introduction

Segmented Flow Analysis (FIA) is a cost and time effective alternative procedure for a wide range of analytical techniques, specifically hexavalent chromium (Cr VI) in drinking water. It is advantageous to have alternative methods other than ion chromatography (EPA 218.6 or 218.7), which are currently the only approved methods for drinking water. The use of FIA to determine Cr VI is substantially more efficient than other methods. It has a run time of 120 seconds per sample and can consistently produce low-level results with minimized prep time and analyst work load. After the acceptance of Cr VI for wastewater (Standard Method 3500 Cr B) in our laboratory, the goal of acquiring acceptance for drinking water was initiated. Method detection limit studies, initial demonstration of accuracy and precision and total reporting limit verification were competed. It was determined that the MDL is 0.35ug/L, with a reporting level of 0.5ug/L. In California, the required detection limit for reporting is currently 1.0ug/L; which is above the method detection limit and the reporting level acquired when using the FIA system. While this method is not yet approved, it is vital to bring attention to this possible alternative procedure because it has the capability to drastically improve efficiency and lower costs.

Objective

The goal of this study is to present information about this method and the capabilities of the flow through automated analyzer that could lead to a broader acceptance of this method for drinking water analysis. This method was initially explored as California and other states begin to develop more stringent guidelines for hexavalent chromium. While the use of flow analysis is approved for determining Cr VI in wastewater, the use of this methodology is not yet approved by the EPA for drinking water.





The graph above is an example of a calibration, quality control samples and laboratory samples typically produced when analyzing hexavalent chromium on our flow analyzer.

Method

1. *Sample should be collected in a 250ml unpreserved container if sample is to be analyzed within 48hours. If hold time is to be extended to 28 days the sample should be preserved with an ammonium sulfate buffer.*
2. *Prepare a six point calibration curve. 1ppb to 50ppb provides a wide range of possible analyte concentration, while still allowing for linearity.*
3. *Follow warm-up procedures specified by the manufacture of the automated analyzer and prepare all reagents and standards.*
   - *Rinse Solution*
   - *Diphenylcarbazide Solution*
   - *Quality Control Standards and Second Source Quality Control*
4. *Transfer all calibration points, quality control standards and samples into their appropriate test tubes and place in the autosampler rack.*
5. *Begin analysis and allow all samples to be analyzed.*
6. *Follow instrument shut down procedure.*

Method Detection Limit Studies

Method Blank MDL Study

Replicate Number	Analysis Date	True Value (ug/L)	Measured Value (ug/L)
1	1/23/2017	0.00	0.1027
2	1/23/2017	0.00	0.1993
3	1/23/2017	0.00	0.0579
4	1/23/2017	0.00	-0.0288
5	1/24/2018	0.00	-0.3151
6	1/24/2018	0.00	-0.3544
7	1/26/2018	0.00	0.1509
8	1/26/2018	0.00	0.0657
9	1/26/2018	0.00	0.0513
10	1/26/2018	0.00	0.0715

Average: 0.00001 ug/L
Standard Deviation: 0.186835679
RSD: 5.35%
MDL: 0.516 ug/L

Sample MDL Study

Replicate Number	Analysis Date	True Value (ug/L)	Measured Value (ug/L)	Percent Recovery (50-150%)
1	1/24/2017	0.75	0.6026	80.3
2	1/24/2017	0.75	0.4707	62.8
3	1/24/2017	0.75	0.4748	63.3
4	1/26/2017	0.75	0.4172	55.6
5	1/26/2018	0.75	0.7291	97.2
6	1/26/2018	0.75	0.6943	92.6
7	1/26/2018	0.75	0.6524	87.0
8	1/26/2018	0.75	0.6327	84.4
9	1/30/2018	0.75	0.7505	100.1
10	1/30/2018	0.75	0.7287	97.2
11	1/30/2018	0.75	0.7989	106.5

Average: 0.63 ug/L
Standard Deviation: 0.1275571
RSD: 20.2%
MDL: 0.35 ug/L

External Reference Sample Analysis

Matrix	Analysis Date	Lot Number	Assigned Value	Analyzed Value	% Recovery	Acceptance Limits
WS (Drinking Water)	1/23/2018	050516	16.0 µg/L	16.5 µg/L	103.1	12.8-19.2 µg/L
WP (Waste Water)	1/23/2018	050416	624 µg/L	621 µg/L	100.5	522-712 µg/L
Internal WP (Waste Water)	1/23/2018	022316	741 µg/L	756 µg/L	102.0	623-848 µg/L

An External Reference Sample was analyzed for both drinking water (WS) and wastewater (WP) matrices with acceptable results. This was conducted through the Absolute Grade PT Program by Absolute Standards for both matrices.

Conclusion

While this methodology is not yet approved by the EPA for the determination of hexavalent chromium in drinking water, the information presented gives validity to the future acceptance of the method. Major advantages of the study include low detection limits; higher throughput; minimized prep time and decreased analyst workload, which ultimately lower costs. It is ultimately the goal of the presenters and our laboratory to acquire EPA acceptance of this method.

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