

## Application Work AW IC US6-0152-012011

# Determination of Hexavalent Chromium (Chromium(VI)) in drinking water, ground water and surface water by Ion Chromatography followed by Post Column Reaction (PCR) and UV/Vis detection (conforming to USEPA method 218.7)

### Branch

Environmental, Water

### Keywords

850 / 858 / USEPA / ASUPP10 / ASUPP5 / Chromate / Cr(VI) / Chrom-6 / Hexavalent Chromium / PCR / UV-Vis

### Summary

Chromate is determined in potable water, using the 887 Professional UV/VIS detector. Instrument settings and method parameters were optimized, regarding detection wavelength, reference wavelength, column oven temperature, flow rates and most suitable analytical column. Optimal sample preservation chemistries were developed in collaboration with USEPA

### Samples

- Samples were collected from tap water from various cities and contaminated sites in state of Oklahoma, State of Florida, State of Texas and State of California
- These samples contained high total hardness (as CaCO<sub>3</sub>), high levels of anioninc species like Chloride and Sulfate, free chlorine (disinfectant) and other treatment chemicals

### Instruments

881 Compact IC pro – Cation (or 850 Professional IC can be used)	2.881.0010
887 UV-Vis Detector	2.887.0010
858 Professional Sample Processor	2.858.0020
10 mL Dosino <sup>®</sup> Burette	6.3032.210
800 Dosino <sup>®</sup> Drive	2.800.0010
Large volume sample loop (1mL or 2 mL)	SNGIC25310
Metrosep ASUPP5 – 150 (4mm) Column	6.1006.520
Metrosep ASUPP 4/5 Guard Column	6.1006.500

### IC Reagents

#### Eluent for Ion Chromatography:

12.8 mmol/L Na<sub>2</sub>CO<sub>3</sub>

4.0 mmol/L NaHCO<sub>3</sub>

2.5g / L Ammonium Sulfate

### Post Column Reagent

2 mmol/L 1,5-diphenylcarbazine

*[500mg 1,5-diphenylcarbazine was dissolved in 50 mL methanol. 500 mL ultra-pure water was added, then 30mL H<sub>2</sub>SO<sub>4</sub> (98%) was added. The solution was diluted to 1L with ultra-pure water, and it was then degassed]*

### Sample and Standard Preservation Solutions

#### Sample and Standard pH adjustment buffer:

Liquid buffer as per section 7.1.11 of USEPA method 218.7

Dissolve 3.3 g (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> in 75 ml of reagent water. Add 6.5 mL ammonium hydroxide and dilute to 100-mL final volume

- Use 1mL of above solution per 100mL of sample

### Standard solutions

Chromium(VI) in water [µg/L]

Std. 1	Std. 2	Std. 3	Std. 4	Std. 5	Std. 6	Std. 7	Std. 8
0.025	0.05	0.10	0.25	0.50	1.0	2.0	5.0

- All standards prepared according to section 10 of USEPA method 218.7

### Sample preparation

All samples and standards were prepared and preserved as per section 8 of USEPA method 218.7.

### Sample Analysis

- Calibration was established using standards
- MDLs, LCMRL and MRL studies were performed according to USEPA method 218.7

### Parameters

Flow rate column	0.7 mL/min
Flow rate PCR	0.22 mL/min
Injection Volume	2000 µL
Temperature column	40 °C
Light source	VIS (W)
Measuring duration	750 ms
Wavelength	530 ± 15 nm
Reference	650 ± 21 nm

### Calculation

Automatic integration with MagIC Net 2.3 software using peak area.

### Results

Please refer to appendix

### Linearity

The calibration curve is linear over the entire concentration range with a correlation coefficient of 0.999994 with relative standard deviation less than 1.0 %.

### Influence of Chloride and sulfate

Influence of common anions like chloride and sulfate on chromate is studied (data not shown, ref AW.CH6-01049-102010). 0-200 mg/L of chloride and sulfate is added to the tap water sample spiked with 0.2 µg/L chromate standard. The optimized chromatographic condition provides recovery between 90 to 110 % for anion concentration up to 150 mg/L.

### Spike and recovery

Tap water (n = 4)	Concentration		Recovery Average [%]
	Average [ppb]	RSD [%]	
sample	0.14	4.45	
...spiked with 0.1 ppb chromate	0.24	0.28	99.8
...spiked with 0.2 ppb chromate	0.34	0.35	100.0
...spiked with 0.6 ppb chromate	0.74	0.17	99.2

### Method detection limit (MDL)

Seven replicates of the reagent water fortified with two concentration levels 0.025 µg/L and 0.05 µg/L of chromate were analyzed. From the resulting standard deviation the MDL is calculated. Calculated MDL for 0.025 µg/L level is **0.007 µg/L** and for 0.05 µg/L the MDL is **0.016 µg/L**. The MDL meets the requirement of revised EPA method and is suitable for routine analysis. Precision data is provided in appendix.

### Lowest Concentration Minimum Reporting limit (LCMRL)

Since 2005, a new concept of reporting limit was introduced by ODW/OGW. 7 replicates of low level standards from a calibration curve are plotted using LCMRL software to determine accurate and precise practical quantifiable results for an analyte. (See appendix for graphs and data).

### Conclusion:

Optimal UV/VIS settings were obtained with a detection wavelength of 530 nm and a reference wavelength of 650 nm. With the optimized settings the new 887 Professional UV-VIS detector provides better sensitivity that meets the EPA method requirements.

### Comments

It is important to maintain exact ratio of eluent to post column reagent in PCR box to ensure exact color formation for Chrom(VI) – DPC complex (magenta color). With precise control of reagent delivery using Dosino (low cost high precision liquid handling device), we have proven ruggedness and reproducibility for this application. If required high pressure pump can also be used.

### References

- USEPA Method 218.7, Determination of Hexavalent Chromium by IC-UV/PCR
- Determination of chromate with 886/887 IC Application work –CH6-1049-102010
- LCMRL software link  
[http://water.epa.gov/scitech/drinkingwater/labcert/analytical/methods\\_ogwdw.cfm](http://water.epa.gov/scitech/drinkingwater/labcert/analytical/methods_ogwdw.cfm)
- E.Prince , *Thesis work for graduate study* at University of Houston, Clearlake

### Date

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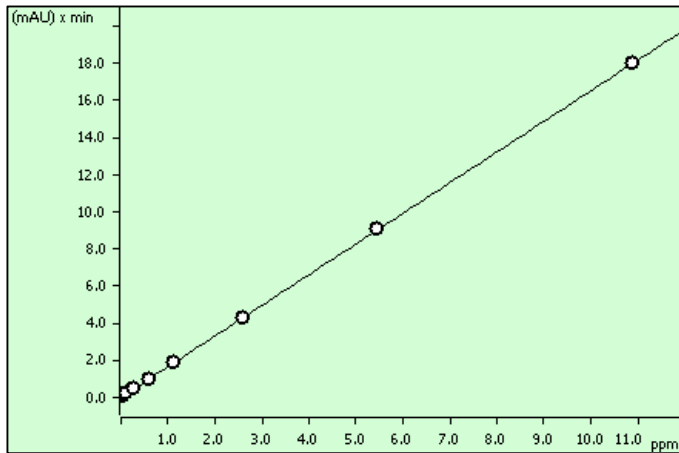
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### Appendix

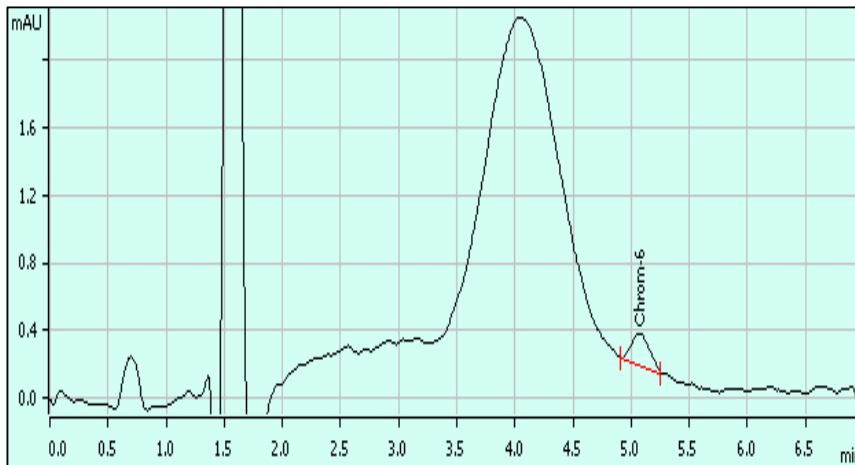
- Calibration curves and chromatograms
- LCMRL and MDL study data
- MRL Study Data
- Results tables

### Calibration curves and chromatograms

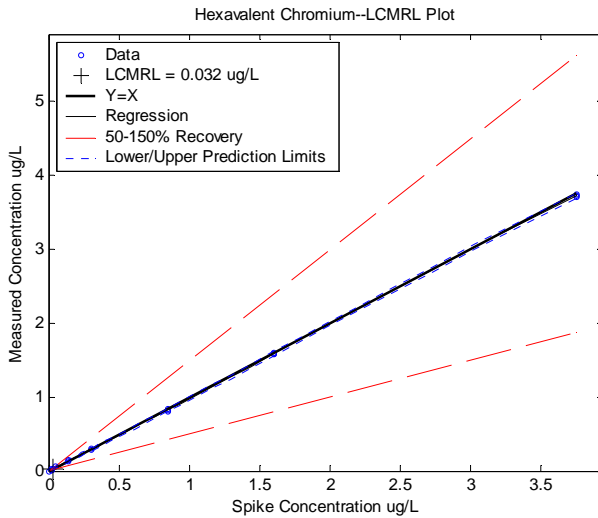


Calibration Range 0.025ppb to 5.0 ppb

Function:	A = 9.09859E-3 + 8.25694E-4 × Q		
Relative standard deviation	0.595%		
Correlation coefficient	0.999994		
Curve type	Linear		
Weighting	1		



0.025 ppb Chromium(VI) standard



According to LCMRL calculations, a lab or analyst must be able to quantitate at least ½ value of software calculated LCMRL

In this case software calculated LCMRL = 0.032 ug/L AND

One of the calibration standard is 0.025 ug/L

### **Explanation of LCMRL (section 13 - Method Performance of USEPA method 218.7)**

#### **Lowest Concentration Minimum Reporting Level (LCMRL)**

For the past several years, EPA has been working on a procedure to determine the Lowest Concentration Minimum Reporting Level (LCMRL). The LCMRL is defined as the lowest spiking concentration such that the probability of spike recovery in the 50% to 150% range is at least 99%. LCMRLs are laboratory- and method-specific, and were used by EPA to determine Minimum Reporting Levels (MRLs) for use in the second Unregulated Contaminant Monitoring Regulation (UCMR 2). In addition, EPA's Technical Support Center (TSC) personnel are looking into the potential to expand the use of the LCMRL in EPA programs. Laboratories will only be required to demonstrate their ability to quantitate at the MRLs specified in 40 CFR 141.40. Therefore, there is no requirement, nor associated financial burden, for laboratories to determine LCMRLs.

EPA recently revised the equations within the LCMRL calculator that perform the data regression. Rather than using linear or weighted linear regressions, the revised LCMRL calculator uses advanced statistics to minimize the error at each concentration.

**Method Detection Limit Study (USEPA method 218.7 section 9.2.6)**

A method detection limit (MDL) is the minimum concentration of a specified analyte that can be detected and quantified with a 99% confidence level. The MDL was determined by injecting 7 replicates of known concentration near the expected limit of detection. The standard deviation is determined from the results and multiplied by the t value. The t value for 7 replicates is 3.14 at a 99% confidence level. An MDL study was performed for Chromium(VI) over three days.

**MDL study (0.025ppb and 0.050ppb)**

	Chromium(VI) parts per billion
MDL-1 day 1	0.026
MDL-1 day 1	0.028
MDL-1 day 2	0.029
MDL-1 day 2	0.028
MDL-1 day 2	0.031
MDL-1 day 3	0.030
MDL-1 day 3	0.024
<b>average</b>	<b>0.028</b>
<b>std dev</b>	<b>0.0024</b>
<b>calculated MDL</b>	<b>0.007</b>

\*MDL = 3.14 x SD

	Chromium(VI) parts per billion
MDL-2-Day 1	0.051
MDL-2-Day 1	0.044
MDL-2-Day 2	0.040
MDL-2-Day 2	0.046
MDL-2-Day 2	0.055
MDL-2-Day 3	0.051
MDL-2-Day 3	0.047
<b>average</b>	<b>0.048</b>
<b>std dev</b>	<b>0.005</b>
<b>calculated MDL</b>	<b>0.016</b>

\*MDL = 3.14 x SD

**Minimum Reporting Limit (MRL) study (USEPA method 218.7 section 9.2.4)**

Analyze seven replicate at or below the proposed MRL concentration. Calculate the mean (Mean) and standard deviation for these replicates. Determine the Half Range for the Prediction Interval of Results (HRPIR) using the equation

$$HR_{PIR} = 3.963S$$

Where S is the standard deviation and 3.963 is a constant value for seven replicates.

Confirm that the Upper and Lower limits for the Prediction Interval of Results (PIR = Mean + HRPIR) meet the upper and lower recovery limits as shown below.

The Upper PIR Limit must be ≤150 percent recovery.

$$\frac{Mean + HR_{PIR}}{Fortified\ Concentration} \times 100 \leq 150\%$$

The Lower PIR Limit must be ≥50 percent recovery.

$$\frac{Mean - HR_{PIR}}{Fortified\ Concentration} \times 100 \geq 50\%$$

	Chromium(VI), ppb
analysis-1	0.018
analysis-2	0.018
analysis-3	0.019
analysis-4	0.020
analysis-5	0.018
analysis-6	0.022
analysis-7	0.018
<b>Mean</b>	<b>0.0190</b>
<b>std.Dev</b>	<b>0.0015</b>
<b>HP<sub>PIR</sub></b>	<b>0.0061</b>
<b>True Concentration</b>	<b>0.020</b>
Upper HP <sub>PIR</sub>	125.2679
Lower HP <sub>PIR</sub>	64.73208

**Disclaimer:**

\*Reference herein to any specific commercial products or nonprofit organization, process, or service by trade name, trademark, manufacturer, or other-wise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government and shall not be used for advertising or product endorsement purposes.

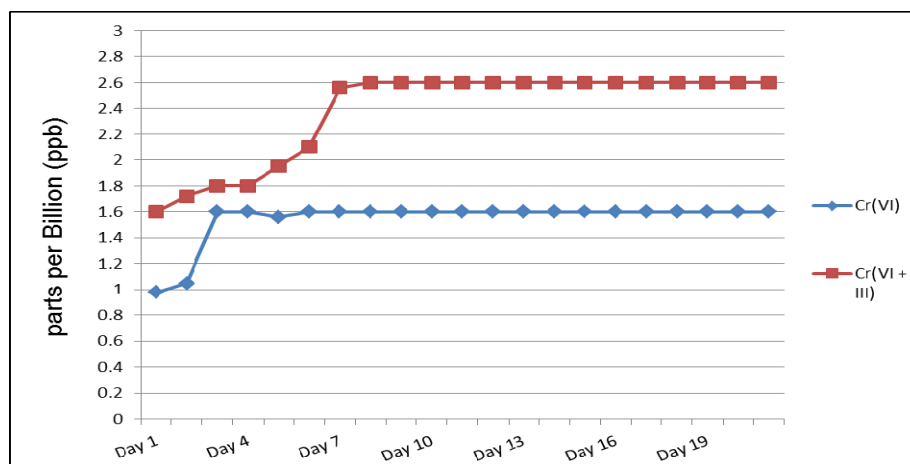
**Optimal buffer for sample preservation study** (collaborated with USEPA and University of Houston – Clearlake)

**Preparation of sample preservation buffer:** Five buffer solutions were tested for their potential as the preserving reagent for Chromium(VI). Buffer A was selected because it is suggested by USEPA method 3060A and 1636, whereas buffer C was used in USEPA method 218.6 (References). As noted in below table, all buffers have pH of higher than 9.0

Buffer	Chemical Composition	Initial measured pH
A	2 mM Na <sub>2</sub> CO <sub>3</sub> + 10 mM NaOH in 1000 mL	12.0
B	1.25 mM Na <sub>2</sub> CO <sub>3</sub> + 1.25 mM NaHCO <sub>3</sub> in 1000 mL	10.2
C	0.4 g (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> + 0.65 mL NH <sub>4</sub> OH in 1000mL	10.0
D	1.25 mM Na <sub>2</sub> CO <sub>3</sub> + 1.25 mM NaHCO <sub>3</sub> + 0.15 g/L (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> in 1000 mL	9.25
E	5 mM NaHCO <sub>3</sub> + 10 mM Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> in 1000 mL	9.10

1 Liter of each buffer solutions was prepared in two separate 1 Liter plastic containers. One bottle was fortified with 1 part per billion Chromium(VI) and other bottle with 1 part per billion each of Chromium(III) and Chromium(VI). Every day for consecutive 21 days this solution was analyzed for Chromium(VI) stability. This solution was preserved at 4°C in refrigerator.

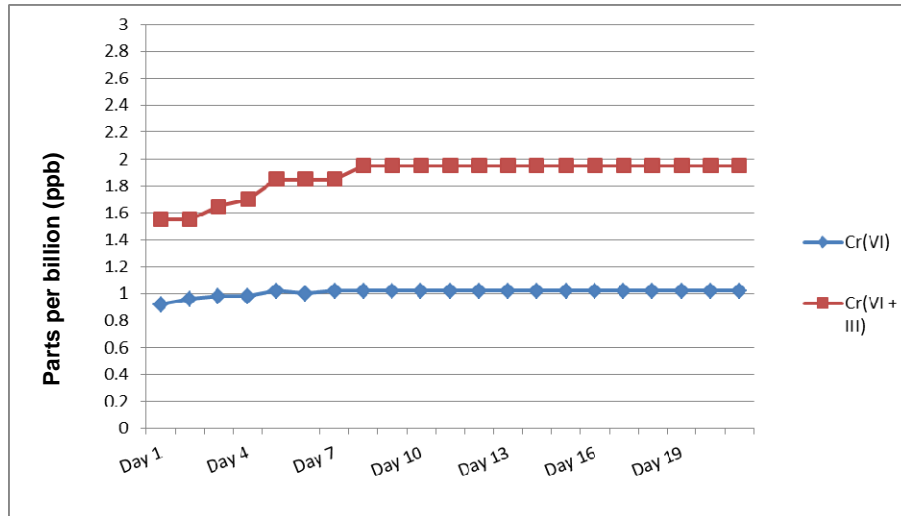
**1. Buffer – A (2mM Na<sub>2</sub>CO<sub>3</sub> + 10mM NaOH)**



**Buffer A data for Chromium(III)→ Chromium(VI) conversion**

Buffer A data demonstrated that even at Day1 there is almost 52% oxidation of Chromium(III) into Chromium(VI) due to high pH of buffer (pH = 12). Progressively, oxidation is increased and on Day 6 it is 100% conversion. Also, please make a note that data from Day 7-21 indicates more than 100% conversion to Chromium(VI). This is due to original Total Chromium (Cr) contamination in Sodium Hydroxide pellets. This total Chromium converted to Chromium(VI) with favorable pH in the solution.

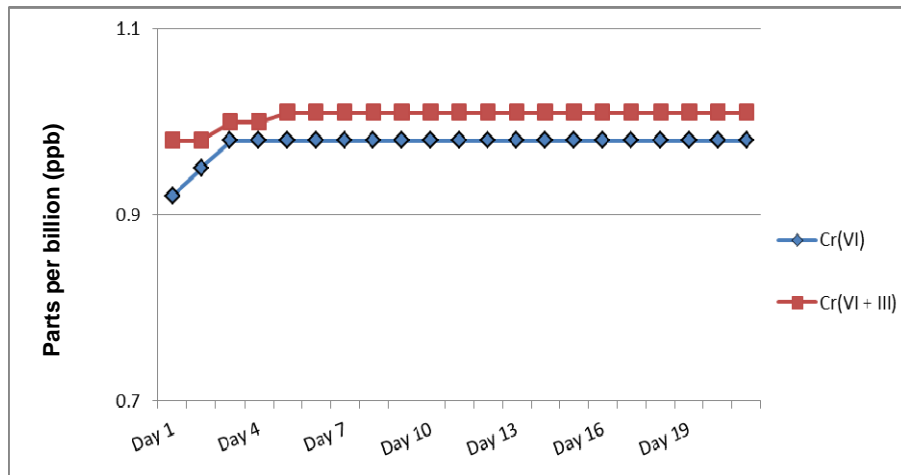
**2. Buffer – B (1.25mM Na<sub>2</sub>CO<sub>3</sub> + 1.25mM NaHCO<sub>3</sub>)**



**Buffer B data for Chromium(III)--> Chromium(VI) conversion**

Buffer B data demonstrated that even at Day1 there is almost 59% oxidation of Chromium(III) into Chromium(VI) due to high pH of buffer (pH = 10.5). Progressively, oxidation is increased and on Day 8 it is 92% conversion. Sodium Carbonate/Bicarbonate buffer preserves Chromium(VI) at a stable rate but if native Chromium(III) is present in drinking water, then it will also convert to Chromium(VI) very quickly.

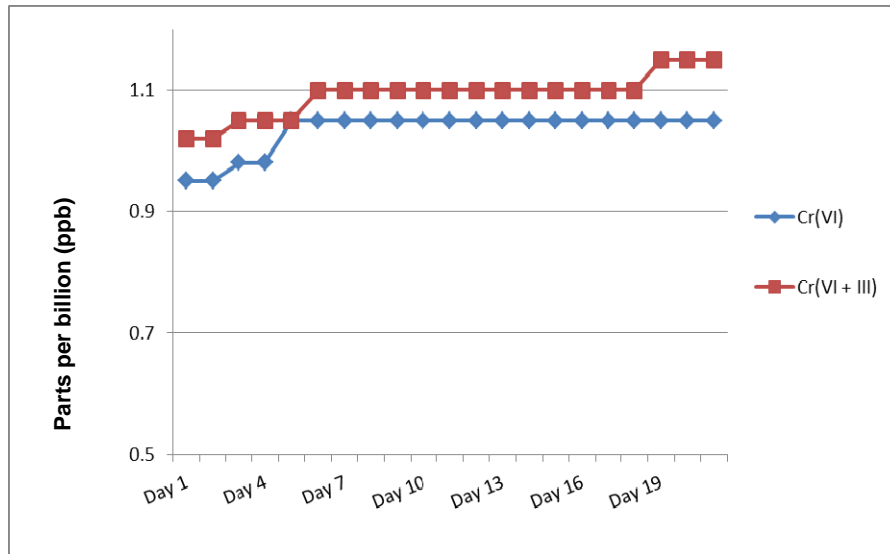
**3. Buffer – C (0.4g (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> + 0.65ml NH<sub>4</sub>OH)**



**Buffer C data for Chromium(III)--> Chromium(VI) conversion**

Buffer C data demonstrates that this buffer preserves Chromium(VI) very well for at least 21 days.

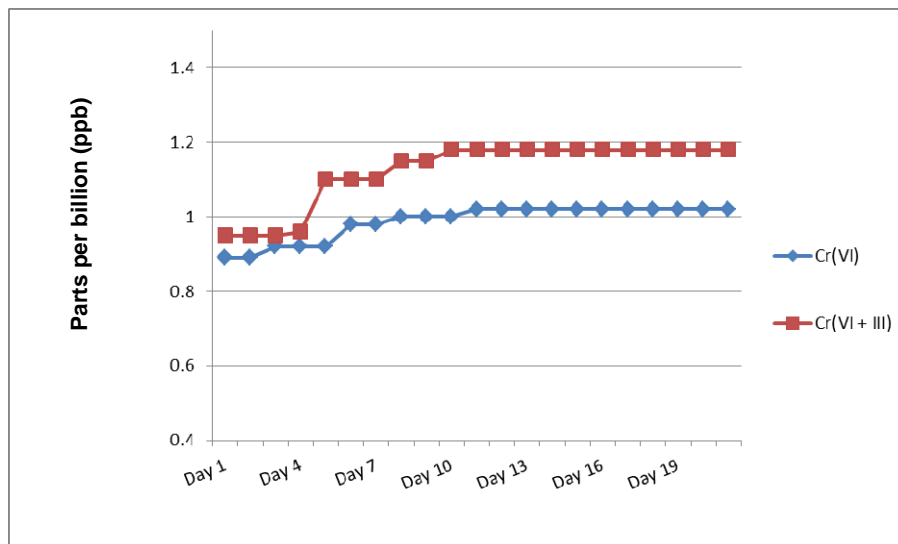
**4. Buffer – D (1.25mM Na<sub>2</sub>CO<sub>3</sub> + 1.25mM NaHCO<sub>3</sub> + 0.15g/L (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>)**



**Buffer D data for Chromium(III)--> Chromium(VI) conversion**

Buffer D data demonstrated that this buffer preserves Chromium(VI) very well for at least 21 days. It is believed that Ammonium Salt in the buffer system forms Chloramine products due to free chlorine in drinking water samples and hence prevents Chromium(III) oxidation to Chromium(VI).

**5. Buffer – E (5mM NaHCO<sub>3</sub> + 10mM Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>)**



**Buffer E data for Chromium(III)--> Chromium(VI) conversion**

Buffer E data demonstrated that this buffer preserves Chromium(VI) very well for at least 4 days. Up to 20% Chromium(III) oxidizes to Chromium(VI). This may be due to native total Chromium present in Tetraborate salt. Analyst had to validate each batch of pure buffer chemicals purchased.

**Conclusion of Buffer study (accepted by USEPA for updating method 218.7)**

This study concludes that there are several choices and flexibility in the selection buffers for the preservation of Chromium(VI) in water matrix. We also conclude that buffers containing ammonium salt is favorable for drinking water samples as it contains free chlorine which can serve as a strong oxidizer. Buffer D containing 1.25 mM Na<sub>2</sub>CO<sub>3</sub>, 1.25 mM NaHCO<sub>3</sub>, and 0.15 g/L (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> added in the solid form of field samples is recommended. This preserving chemical is also recommended in USEPA method 218.7.