

Optimizing Sample Preservation for Hexavalent Chromium Analyses in Waters



Jane Timm, James Lovick Jr, Raymond Siery,
and Yongtao Li

Underwriters Laboratories

2011 NEMC, Bellevue, Washington

Presentation Outline

Introduction

Background information

Regulatory update

Common analytical methods

EPA Method 218.6

Instrumentation

Optimization & Performance

Sample results

Conclusions



Background Information

- Chromium (Cr) is found naturally in rocks, plants, soil and volcanic dust, humans, and animals. Trivalent chromium Cr(III) is an essential nutrient for the body.
- Water sources can be affected by hexavalent chromium Cr(VI) naturally, or through contamination from industrial centers, landfills, and improper discharge of industrial processing streams.
- Cr(VI) can be removed using a handful of proven treatment techniques, e.g. anion exchange, membrane filtration (nanofiltration and reverse osmosis), reduction-coagulation and precipitation, adsorption, etc.



Background Information

- Cr(VI) is classified as a known human carcinogen via inhalation in EPA's Integrated Risk Information System (IRIS) database (1998) and by the U.S. Occupational Safety and Health Administration (OSHA).
- The California Department of Public Health (CDPH) classified Cr(VI) as an "unregulated chemical requiring monitoring" in 1999.
- National MCL for total chromium = 100 µg/L
- California MCL for total chromium = 50 µg/L
- The National Toxicology Program (NTP) concluded that Cr(VI) is carcinogenic when ingested in drinking water (2007).



Regulatory Update

- The California Office of Environmental Health Hazard Assessment (OEHHA) established a Public Health Goal of 0.02 µg/L Cr(VI) in drinking water (2010).
- Environmental Working Group reported that 31 out of 35 cities evidenced detectible levels of Cr(VI), with samples from 25 cities exhibiting levels of Cr(VI) >0.06 µg/L.
- USEPA released a draft risk assessment of Cr(VI) and stated that it is likely to cause cancer when ingested over a lifetime (IRIS, 9/2010).
- USEPA will release the final version of its “Toxicological Review of Hexavalent Chromium” in the Summer of 2011, and to determine if additional standards and testing requirements are appropriate.



Regulatory Update

- USEPA released a Guidance for Public Water Systems on Enhanced Monitoring for Chromium-6 (Hexavalent Chromium) in Drinking Water (01/2011)
 - EPA Method 218.6
 - Buffered samples, pH = 9.0 – 9.5
 - 5 days of holding time
- USEPA has proposed changes to its Unregulated Contaminant Monitoring Regulation 3 (UCMR 3), which will likely include total Cr and Cr(VI).
- Finally, it is likely that USEPA will tighten drinking water standards to address the health risks posed by Cr(VI) in the near future.



Common Analytical Techniques and Methods

Total Cr	GFAAS	EPA Methods 218.2 and 200.9
	ICP-MS	EPA Method 200.8
	ICP-AES	EPA Method 200.7
Dissolved Cr(VI)	IC-PCR-UV/Vis	EPA Method 218.6 Dionex Application Update 144 SM 3500-Cr C ASTM D5257-11
Cr(III) and Cr(VI) speciation	IC-PCR-UV/Vis LC-ICP-MS IC-ICP-MS Pre-concentration - Sol-gel - SPE cartridges	Dionex Application Update 165



EPA Method 218.6 Instrumentation

Dionex ICS 5000

ICS-5000 SP single pump

AS-DV autosampler

ICS Series VWD variable wavelength detector (UV/Vis)

DC ICS-5000 dual CD and ECD

PC-10 pneumatic post-column reagent delivery system



EPA Method 218.6 Conditions

Analytical column	Dionex IonPac AS7 (4x 250 mm)
Guard column	Dionex IonPac NG1 (4 x 50 mm)
Eluent	250 mM $(\text{NH}_4)_2\text{SO}_4$ and 100 mM NH_4OH Eluent flowrate = 1.0 mL/min Back pressure = 1200-1300 psi Sample loop = 1 mL
PCR	2 mM 1,5-diphenylcarbohydrazide, 10% (V/V) methanol, and 1N H_2SO_4 PCR flowrate = 0.33 mL/min PCR coil = 1 mL PCR coil temperature = 30 °C
Absorbance detection	535 nm
Noise	Auto zero
Run time	10 min
Sample pH buffer	2.5M $(\text{NH}_4)_2\text{SO}_4$ and 1M NH_4OH (pH = 9.0-9.7)



Cr(VI) Method Sensitivity

Spiking Conc. ($\mu\text{g/L}$)	MDL ($\mu\text{g/L}$)	Spiking Conc. ($\mu\text{g/L}$)	LCMRL ($\mu\text{g/L}$)	DL ($\mu\text{g/L}$)	Critical Level ($\mu\text{g/L}$)
0.01	0.006	0.01-0.06	0.027	0.009	0.0064
0.02	0.003				
0.02	0.015				
0.02	0.016				



Cr(VI) Method Accuracy and Precision (n = 4)

Matrix	Spiking Conc. (µg/L)	Mean Recovery (%)	RSD (%)
DI Water	1.0	99	0.6
Chlorinated DW	1.0	103	0.7
Chlorinated SW	1.0	103	0.9
Chlorinated GW	1.0	101	1.0



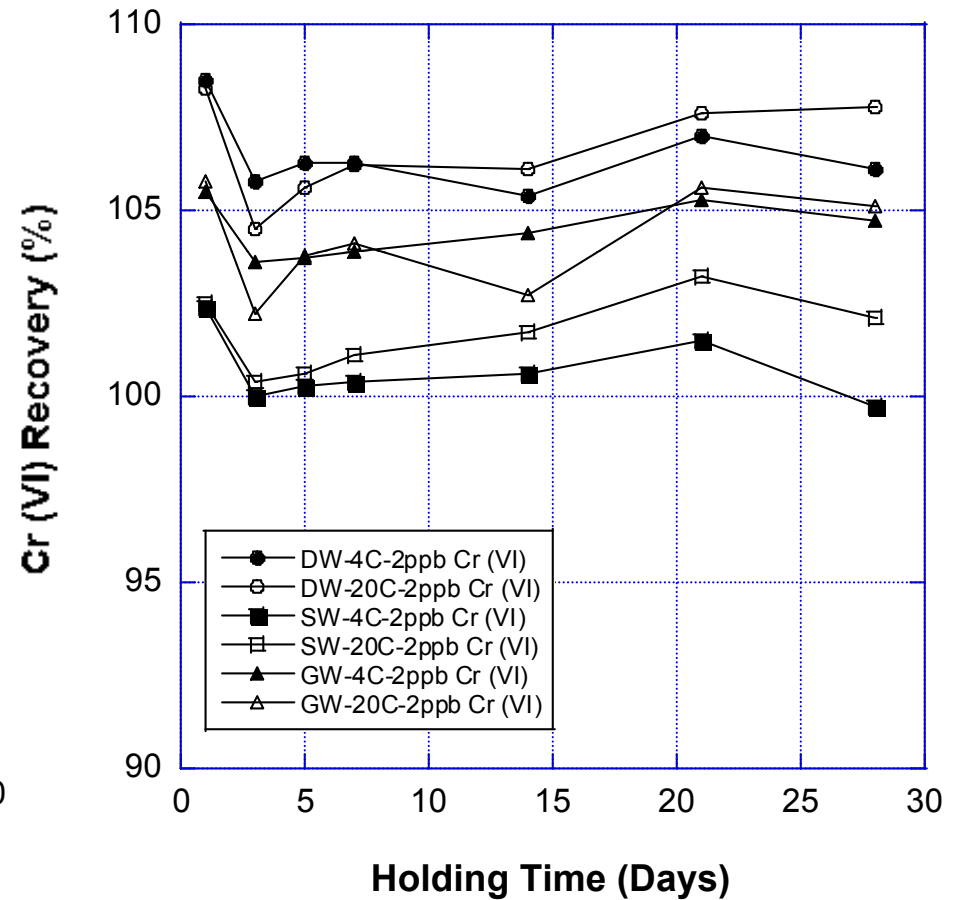
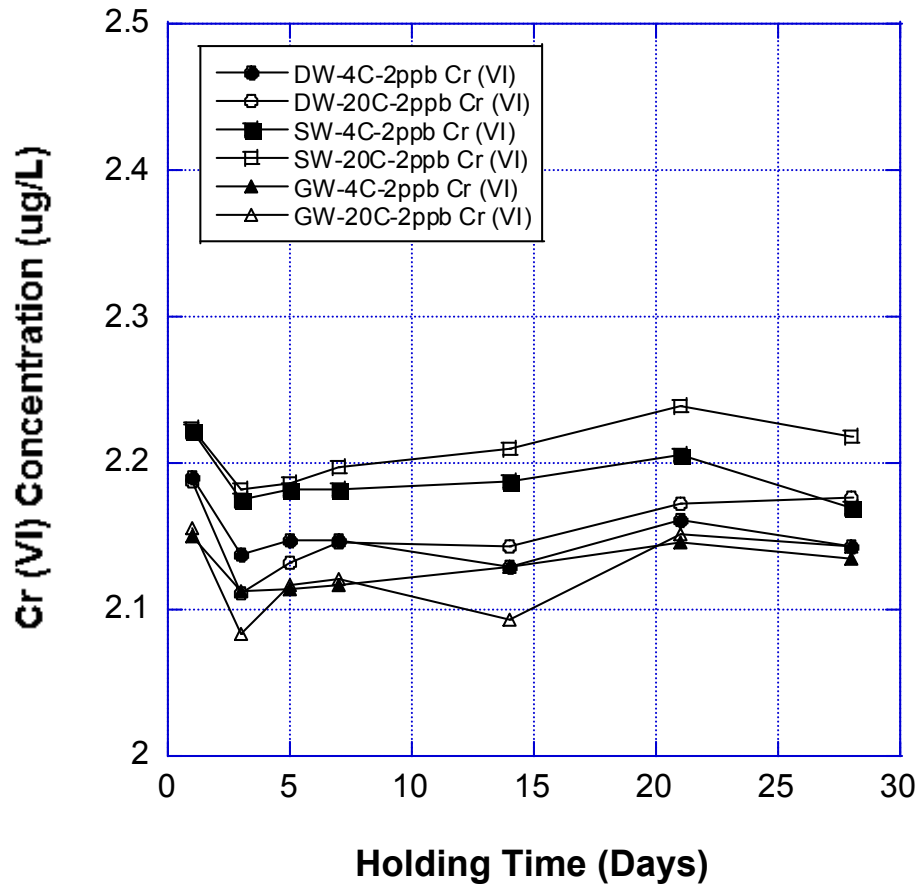
Water Matrix Characterization

Parameter	Drinking Water	Surface Water	Groundwater
Cr (VI)	0.02 µg/L	0.05 µg/L	< 0.02 µg/L
Total Cr	0.17 µg/L	0.21 µg/L	< 0.1 µg/L
Nitrate	< 0.1 mg N/L	2.5 mg N/L	< 0.1 mg N/L
Nitrite	< 0.1 mg N/L	< 0.1 mg N/L	< 0.1 mg N/L
Ammonia	< 0.1 mg N/L	< 0.1 mg N/L	< 0.1 mg N/L
Total cyanide	< 0.02 mg/L	< 0.02 mg/L	< 0.02 mg/L
Total phosphate	< 0.05 mg P/L	0.11 mg P/L	< 0.05 mg P/L
TOC	0.5 mg/L	5.8 mg/L	< 0.5 mg/L
Turbidity	0.23 NTU	11.9 NTU	0.05 NTU
Conductivity	955 umhos/cm	531 umhos/cm	532 umhos/cm
Heterotrophic plate count (HPC)	< 2 MPN/mL	> 738 MPN/mL	40 MPN/mL



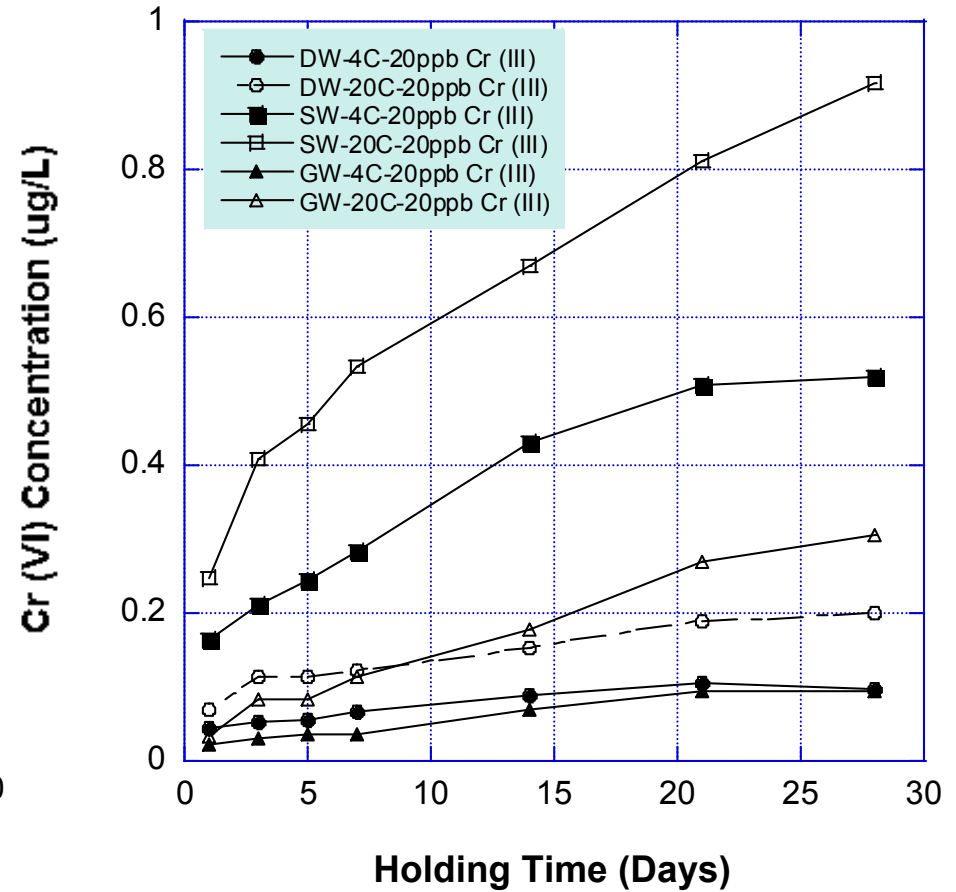
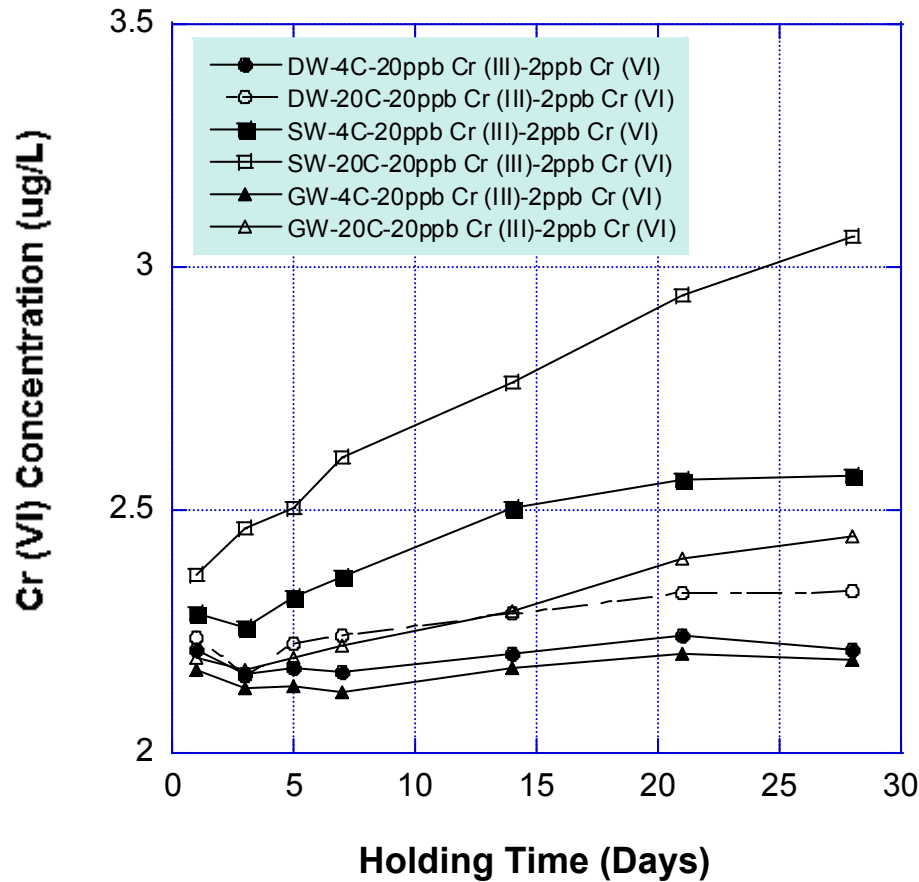
Effects of Holding Time and Temperature

Buffered DW, SW, and GW ($\text{Cl}_2 \approx 0.2 \text{ ppm}$)



Effects of Holding Time and Temperature

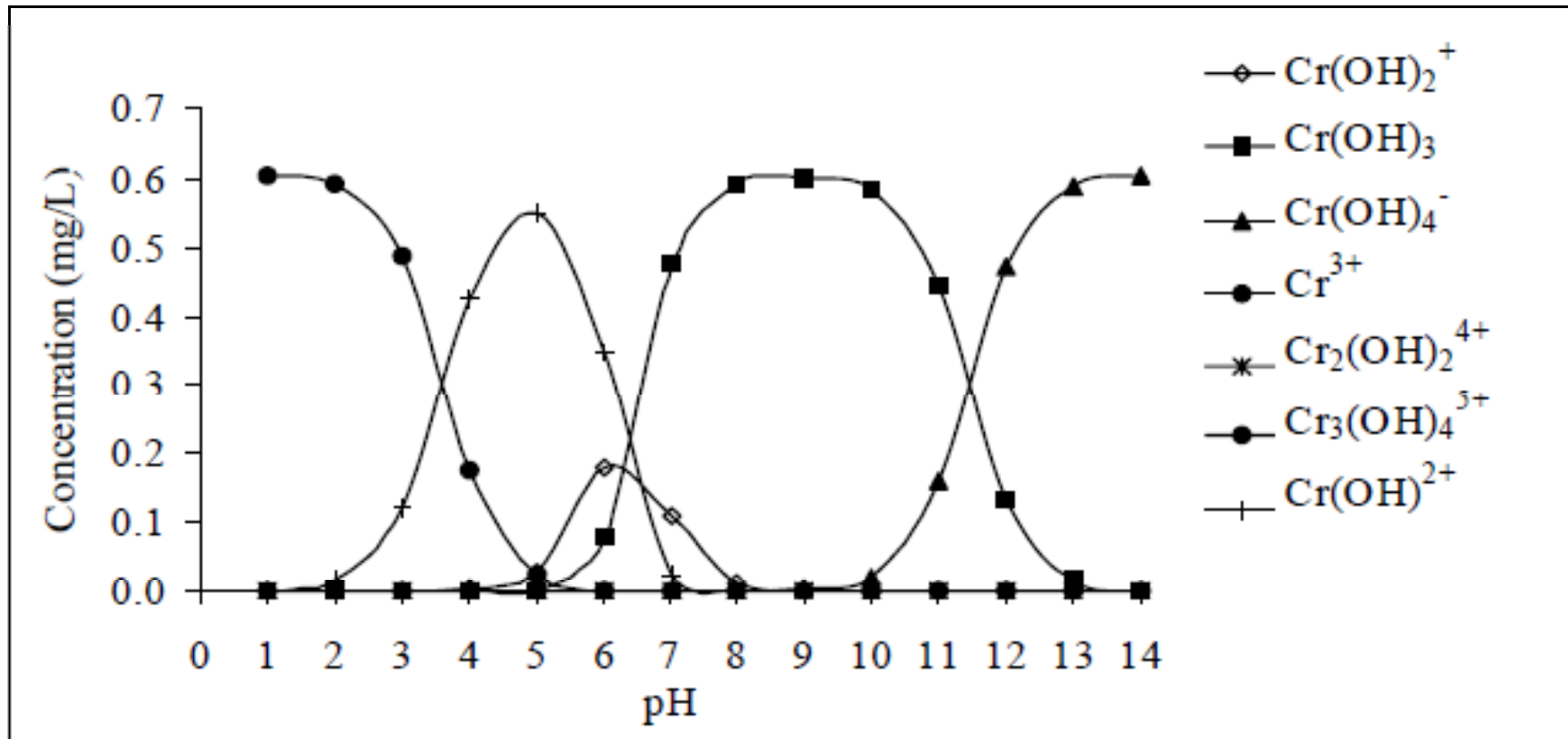
Buffered DW, SW, and GW ($\text{Cl}_2 \approx 0.2 \text{ ppm}$)



Cr(III) Speciation as a Function of pH

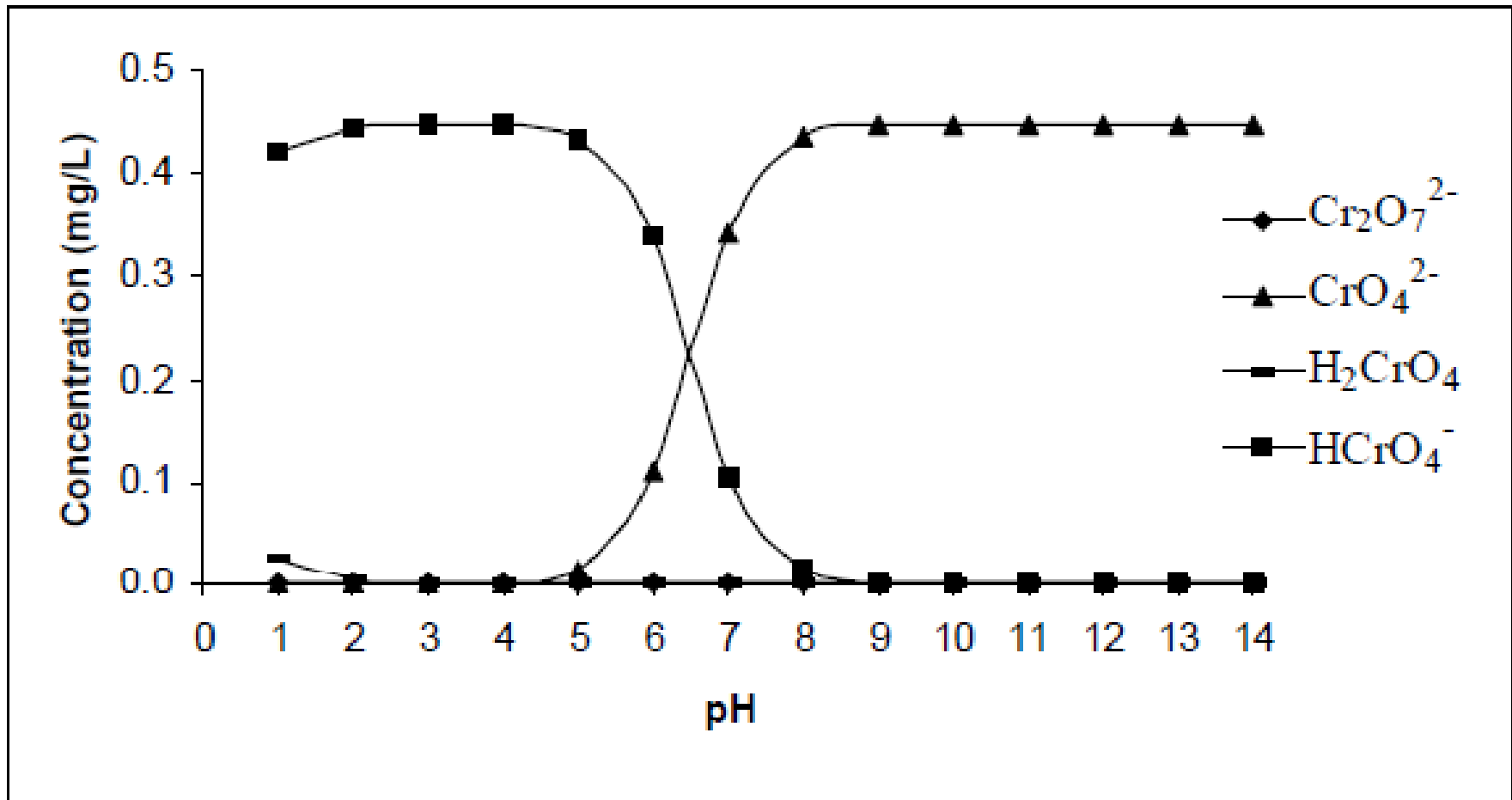
Ionic strength of ~ 0.01 M and Cr(III) = 1.0 mg/L

(Source: visual MINTEQ program)



Cr(VI) Speciation as a Function of pH

Ionic strength of ~ 0.01 M and Cr(VI) = 1.0 mg/L
(Source: visual MINTEQ program)



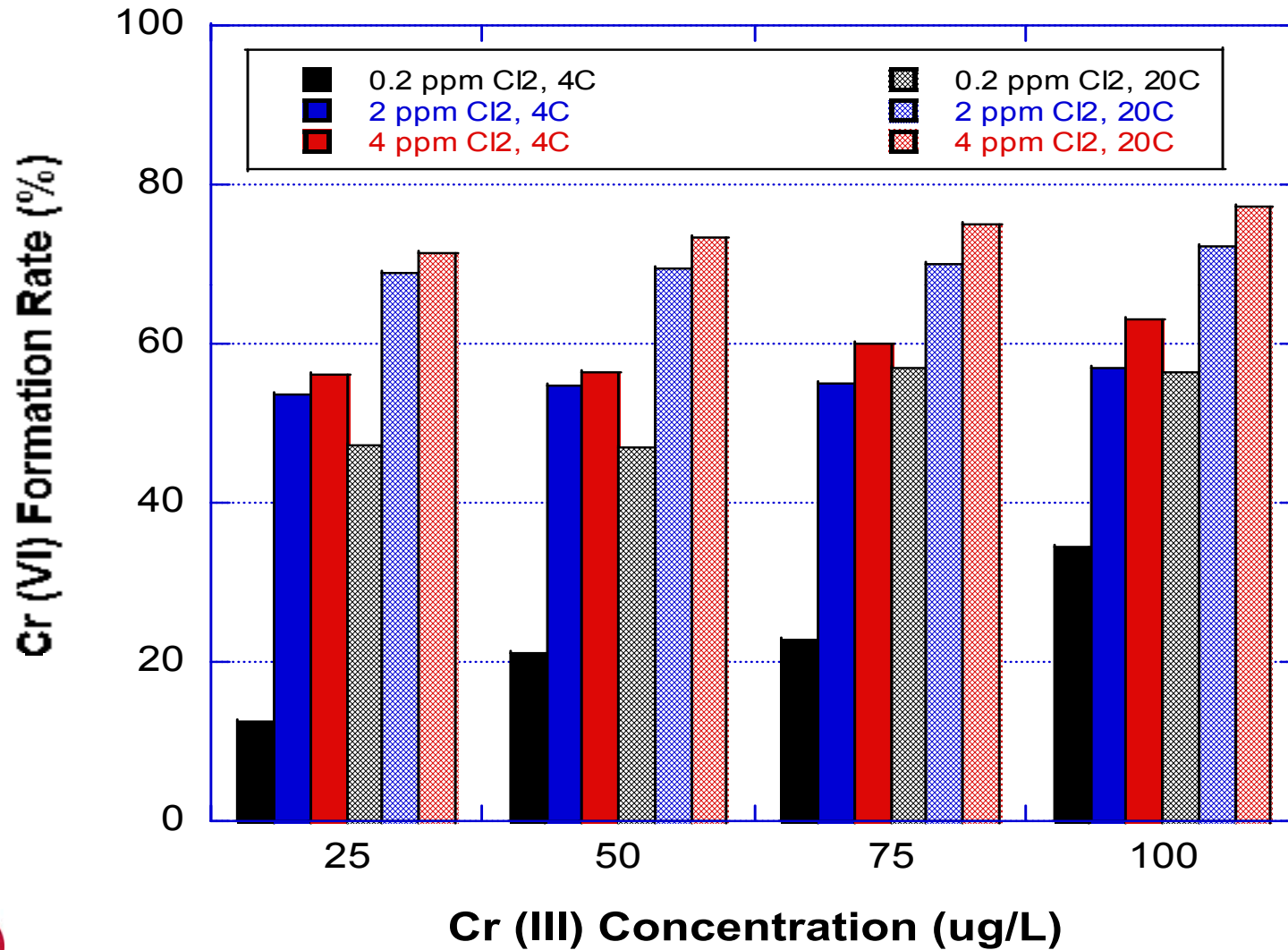
Formal Reduction Potential

pH = 9.0 - 9.5

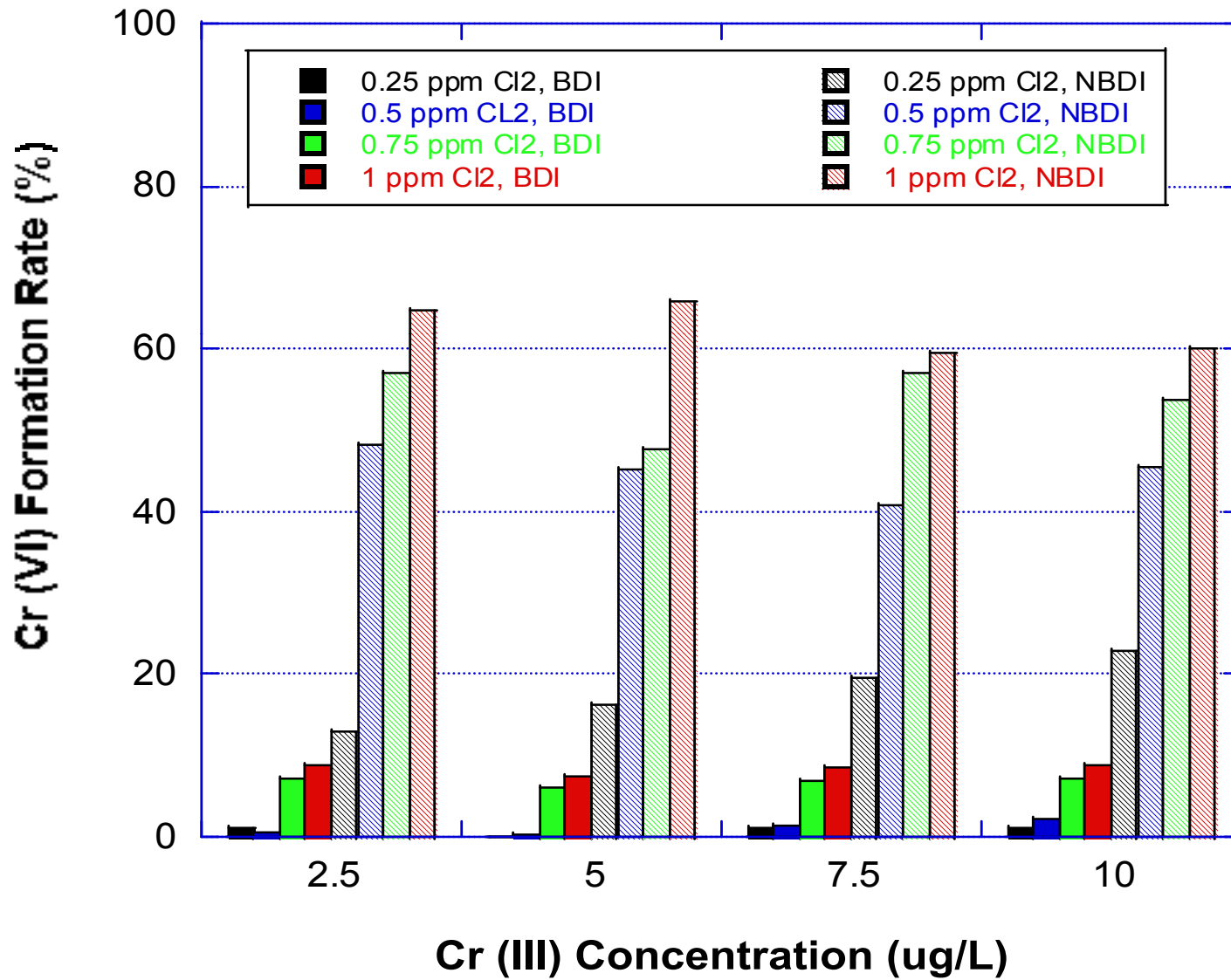


Effects of Chlorine, Cr(III), and Temperature

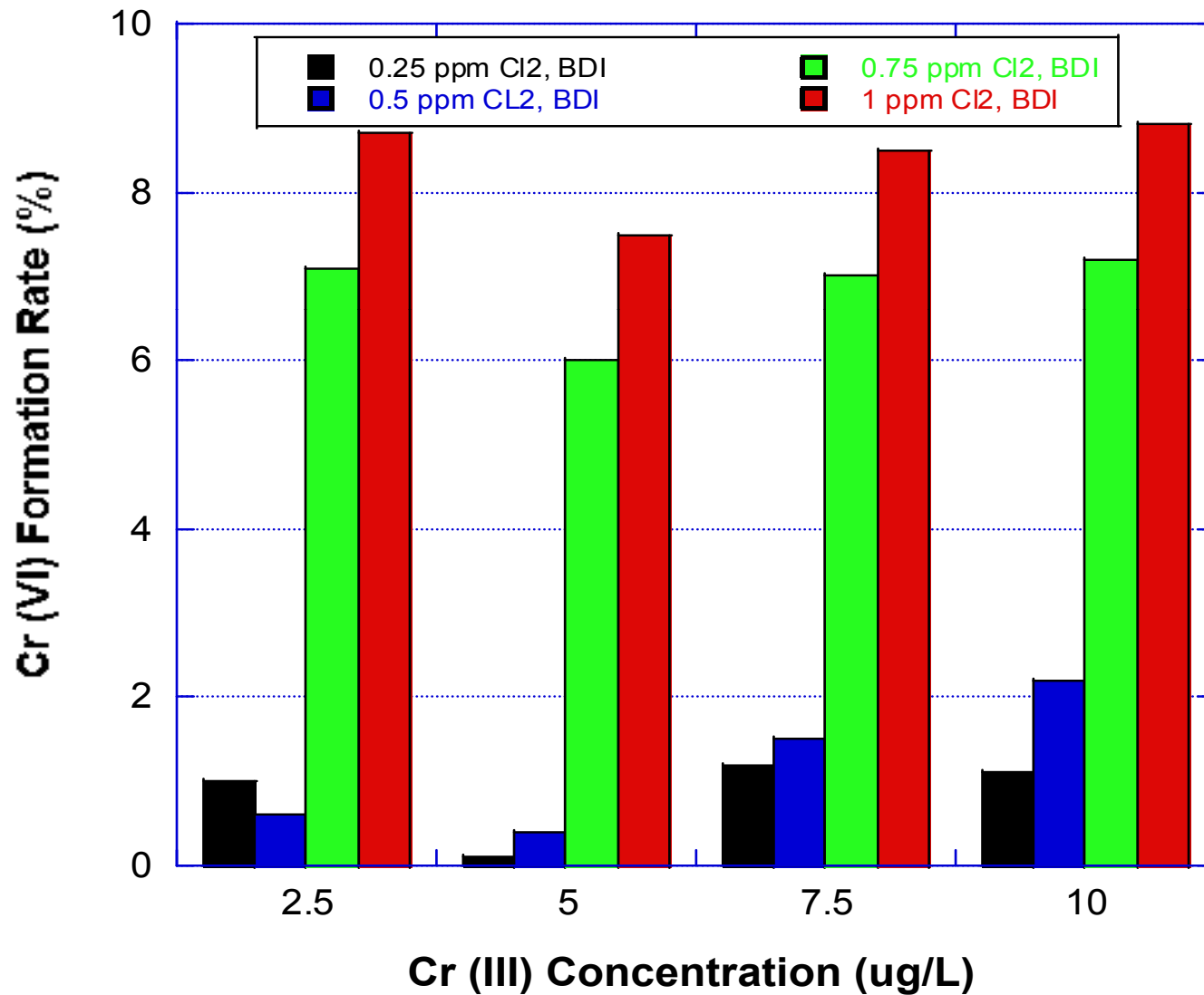
24 hrs of chlorination, buffered prior to analysis



Effects of Chlorine, Cr(III), and pH Buffer

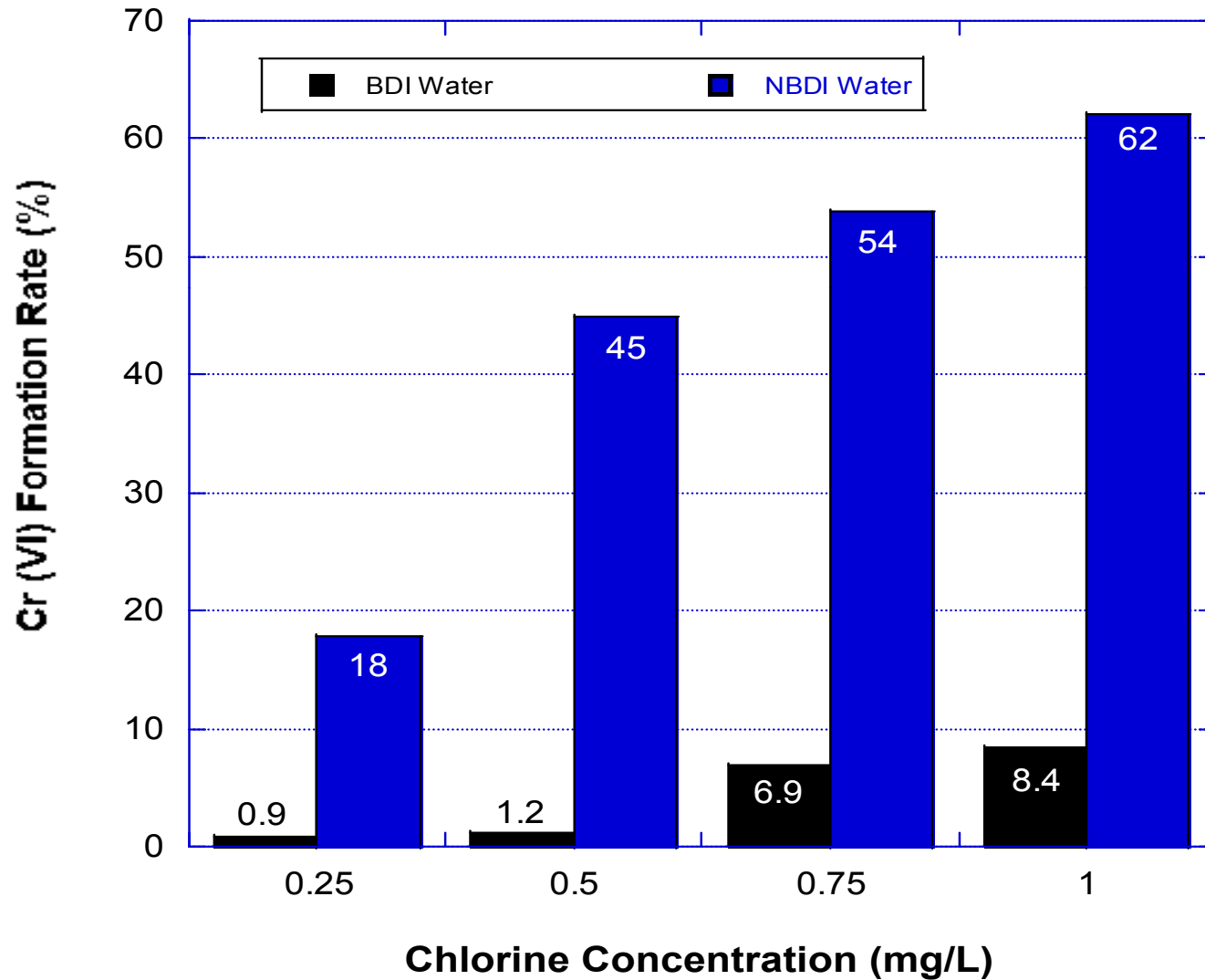


Effects of Chlorine, Cr(III), and pH Buffer



Effects of Chlorine and pH Buffer

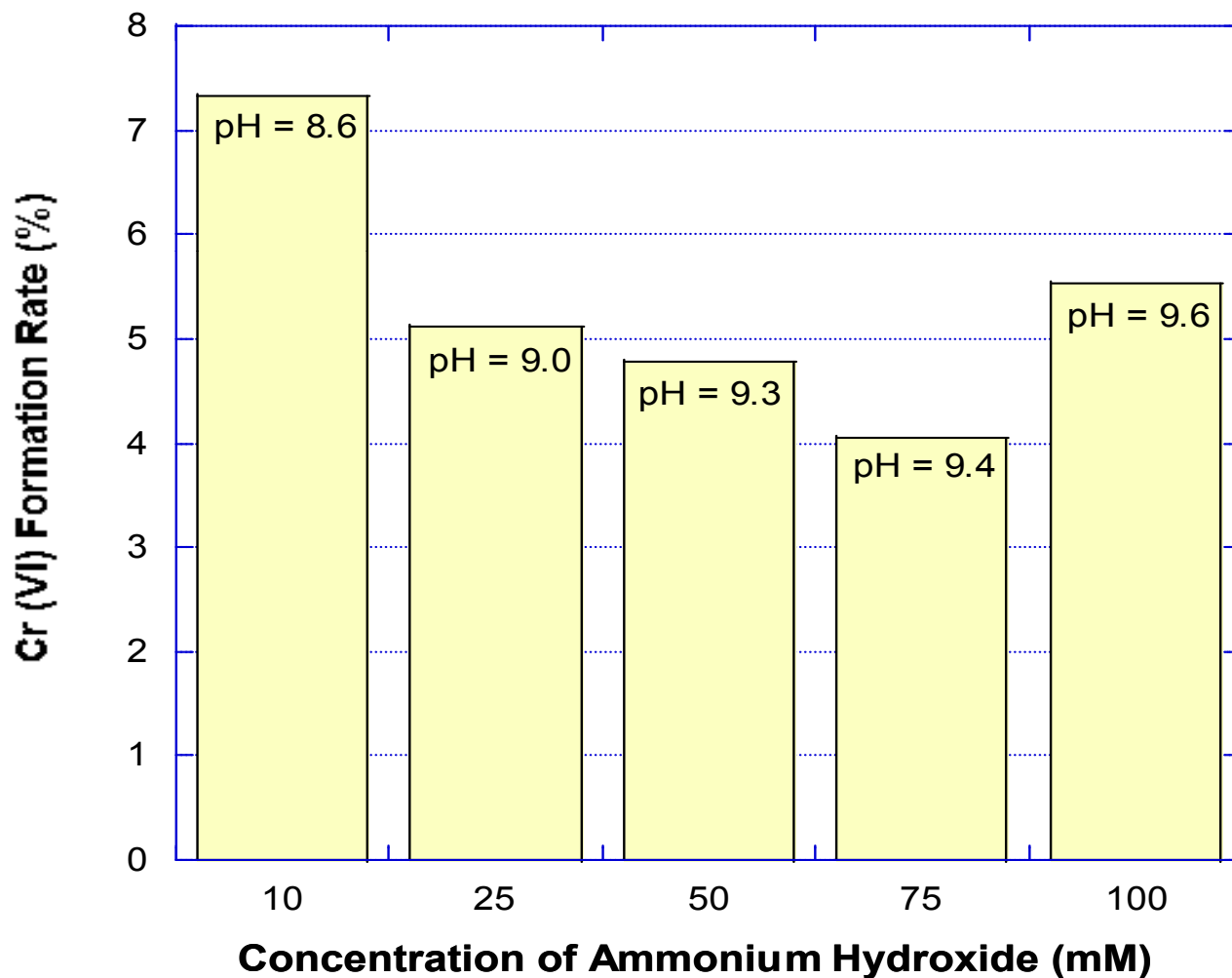
Average conversion rate of Cr(III) (0.25, 5, 7.5, 10 ppb)



Effects of Chlorine and pH Buffer (n=4)

$\text{Cl}_2 = 1 \text{ ppm}$, pH buffered, >12 hrs

Cr(III) = 10 ppb, Cr(VI) = 1 ppb, >6 hrs at ambient temperature



Cr(VI) Field Sample Results

Matrix	Total Sample #	Sample # (≥ 0.02 µg/L)	Lowest Conc. (µg/L)	Median Conc. (µg/L)	Highest Conc. (µg/L)	Mean Conc. (µg/L)
DW	307	277	0.020	0.021	38.8	2.32
GW	33	20	0.024	0.088	10.7	1.17
SW	101	87	0.024	0.15	10.2	0.61



Conclusions

- EPA Method 218.6 is applicable for analyzing Cr(VI) with an MRL of 0.02-0.03 $\mu\text{g/L}$.
- EPA Method 218.6 can provide good accuracy ($\pm 10\%$ recovery) and precision ($\leq 20\%$ RSD).
- The presence of Cr(III) may affect sample results.
- Cr(III)-to-Cr(VI) conversion is dependent on total Cr(III), Cl_2 and NH_4OH concentrations, temperature, and holding time.
- When Cl_2 concentrations varied from 0.25 mg/L to 1 mg/L, Cr(III)-to-Cr(VI) conversion rates were 18% to 62% for non-buffered samples and 0.9% to 8.4% for buffered samples.



Conclusions

- The use of $(\text{NH}_4)_2\text{SO}_4\text{-NH}_4\text{OH}$ buffer to adjust sample pH to 9.0-9.5 cannot completely stop the oxidation of Cr(III). Cr(VI) formation rates were generally less than 10%.
- General recommendations for Cr(VI) control in drinking water include:
 - Remove Cr(III) before disinfection.
 - Use alternative disinfection techniques, such as chloramination instead of chlorination.
 - For a chlorination system, consider to reduce Cl_2 doses.



THANK YOU!



Dr. Yongtao Li

Yongtao.Li@us.ul.com

1-574-472-5562

Underwriters Laboratories