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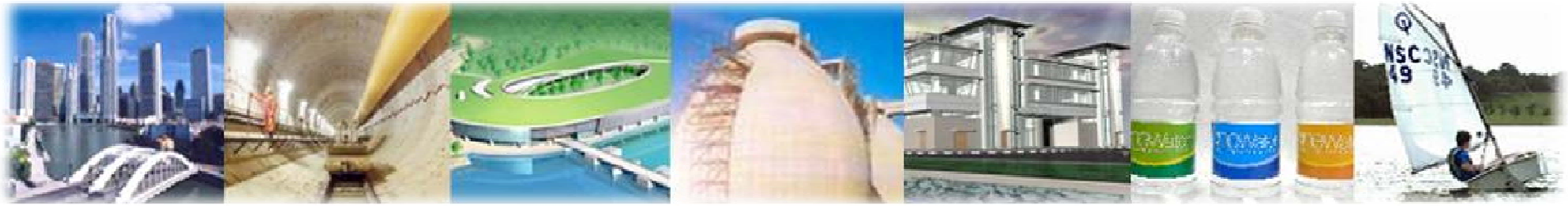

Determination of Hexavalent Chromium in Drinking Water by SPE-ICP-MS and IC-ICP-MS

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Outline

- Chromium: presence and regulations
- Analytical methods of chromium-6
- Method development: IC-ICP-MS & SPE-ICP-MS
- Analytical characteristics
- Preliminary application

Chromium in environment

	Chromium-3	Chromium-6	Chromium (0)
Form	Occur naturally as cation Cr^{3+} in food, agricultural products	Exists as anion CrO_4^{2-} or $Cr_2O_7^{2-}$ (pH related), from industrial processes	Metal, produced by industrial processes
Health effect	Essential trace element, needed for carrying out lipid and sugar metabolism	Harmful to our body, Mutagenic and potentially carcinogenic, under toxicological review	

Regulation in drinking water:

Total chromium regulated, but no standard for Cr-6

U.S. EPA	WHO	Singapore
100 µg/L	50 µg/L	50 µg/L

Removal of Chromium in drinking water

Effective for removing chromium (total) to below 100 µg/L:

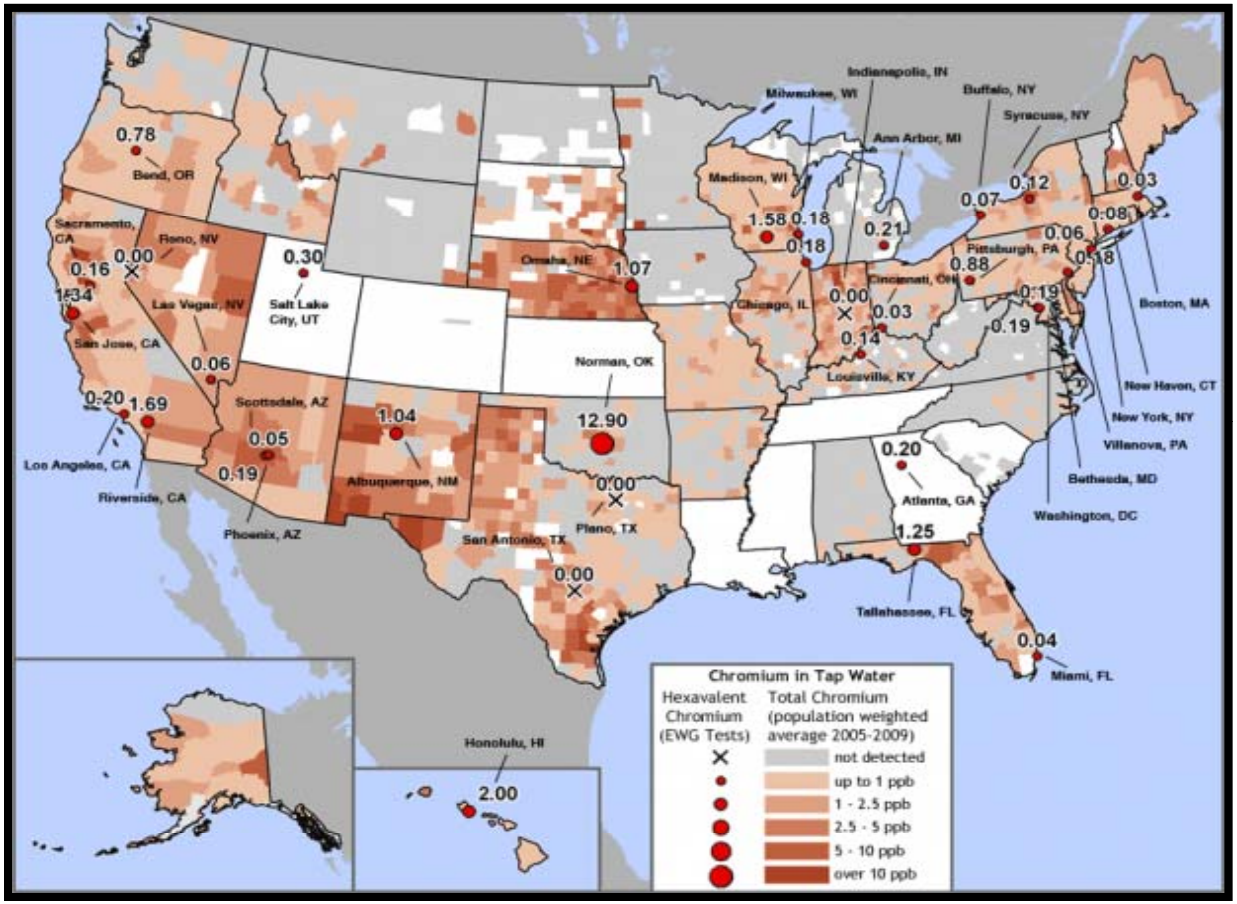
- Coagulation/filtration
- Ion exchange
- Reverse osmosis
- Lime softening

Lower concentrations [1]:

- Weak base anion exchange and reduction-coagulation-filtration could remove Cr-6 to below 5 µg/L
- Slow oxidation of Cr-3 by dissolved O_2 and chloramine
- Cl_2 and $KMnO_4$ are effective oxidants of Cr-3
- Residual Cl_2 in drinking water distribution system may oxide soluble Cr-3 to Cr-6 due to long contact time

[1] Lai. H, McNeill, L.S. J. Environ. Eng. 2006,132(8): 842-851.

New Concerns on Chromium-6



Cr-6: detected (> 0.02 µg/L) in the tap water from 31 of 35 U.S. cities, > 0.06 µg/L (California's public health goal, PHG) in 25 cities, 0.18 µg/L as the average.

[2] Environmental Working Group, Chromium-6 in U.S. Tap Water, 2010.

New Concerns on Chromium-6

- U.S. EPA released the draft of the Toxicological Review of Hexavalent Chromium in its Integrated Risk Information System (IRIS) database in September 2010
- U.S. EPA issued on 22 Dec 2010 a guidance to public water systems for enhanced monitoring of Cr-6, and will decide if a new standard is necessary to be set
- California proposed an even more stringent PHG of 0.02 µg/L of Cr-6 for public comment, will set MCL for Cr-6 after the PHG is finalized
- WHO Guidelines (4th edition, 4 July 2011): maintain a guideline value of 50 µg/L for total Cr

Analytical Methods of Chromium-6 in water

- Colorimetry
  - Nearly specific reaction of Cr-6 with 1,5-diphenylcarbazide (DPC)
  - For Cr-6 in the range of 10-100 µg/L (SM3500-Cr B)

- Ion chromatography (IC)
  - Often UV-Vis detection after post column reaction (PCR) with DPC
  - MDL of dissolved Cr-6: 0.4 µg/L as CrO_4^{2-}
  - USEPA 218.6 and 7199; SM3500-Cr C, ISO 23913
  - Further improvements by Dionex:
    1. AU144: 1000 µL sample loop, 1.0 mL/min eluent, 0.33 mL/min PCR reagent, 750 µL reaction coil, MDL: 0.02 µg/L
    2. AU179: 2-mm column, 125 µL reaction coil, MDL: 0.001 µg/L

Analytical Methods of Chromium-6 in water

- HPLC-ICP-MS [3]
  - Ion-pair HPLC (e.g., using tetrabutylammonium hydroxide - EDTA) on C8 column
  - Collision/reaction cell to reduce interference and baseline noise

- IC-ICP-MS [4,5]
  - Cr-3: pre- or on-column derivatization with EDTA
  - No organic solvent involved in the eluent
  - Method more rugged

[3] Neubauer, K., Reuter, W., Perrone, P. PerkinElmer Application Note, 2003.
[4] Gurleyuk, H., Wallschlager, D. J. Anal. At. Spectrom. 2001,**16**, 926.
[5] Sakai, T., McCurdy E., Wilbur, S., Agilent Application Note 5989-2481EN, 2005

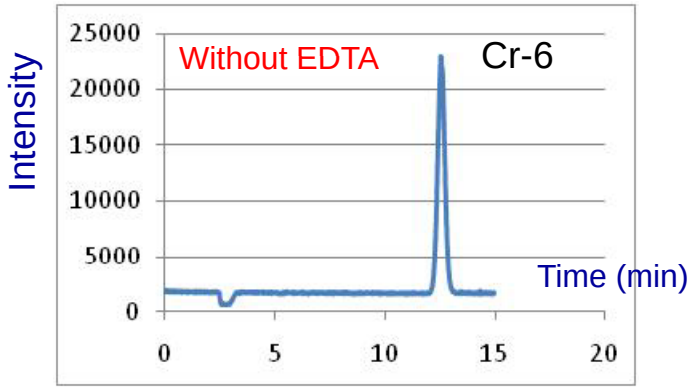
Study on IC-ICP-MS

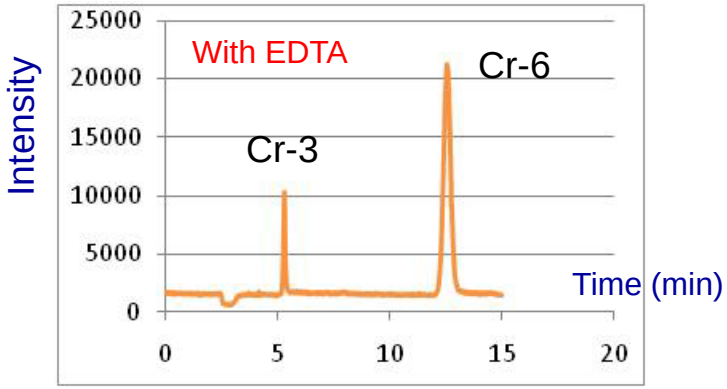
IC-ICP-MS configuration and parameters	
ICP-MS equipment	Agilent 7500a
Chromatograph	Agilent 1100 HPLC (with pump, degasser, sample injector only)
Guard Column	Dionex IonPac AG-19, 4 x 50 mm
Analytical column	Dionex IonPac AS-19, 4 x 250 mm
Eluent	25 mM KOH
Eluent flow rate	1.0 mL/min
Sample injection volume	500 µL
Carrier gas flow rate	1.13 mL/min
RF forward power	1450 W

Study on IC-ICP-MS

Without EDTA

- A mixture of Cr-6 and Cr-3 had a peak only (for Cr-6).
- Where was Cr-3? Cr-3 stayed in the column (guard) as Cr_2O_3, which may affect the column life time.





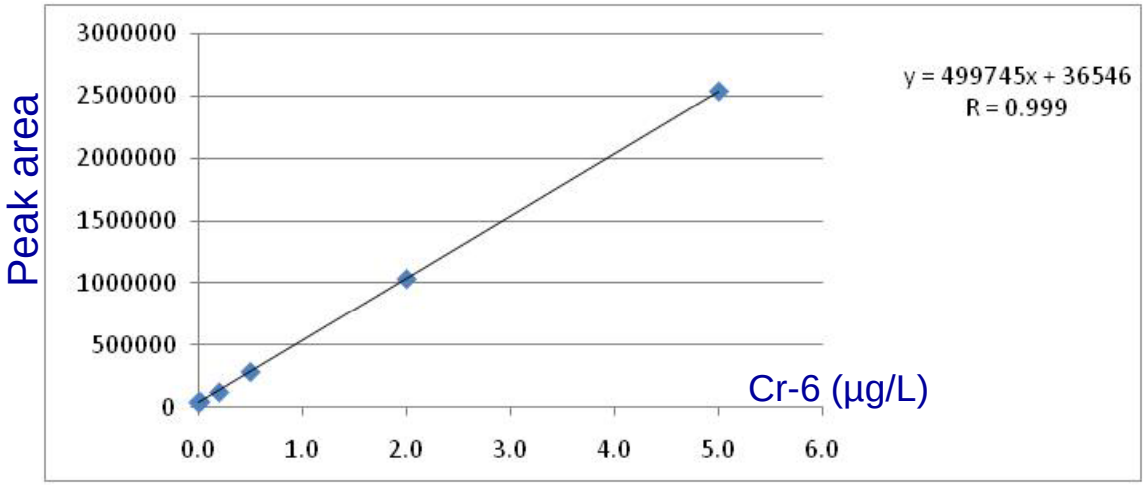
Eluent: 25 mM KOH, 0.8 mL/min

With EDTA

- Reaction of sample (adjusted to pH 9.0-9.5) with 0.5 mM EDTA at 40°C water bath for 60 min
- Simultaneous quantitation of Cr-3 and Cr-6

Study on IC-ICP-MS

Calibration for Cr-6: 0.02-5.0 µg/L



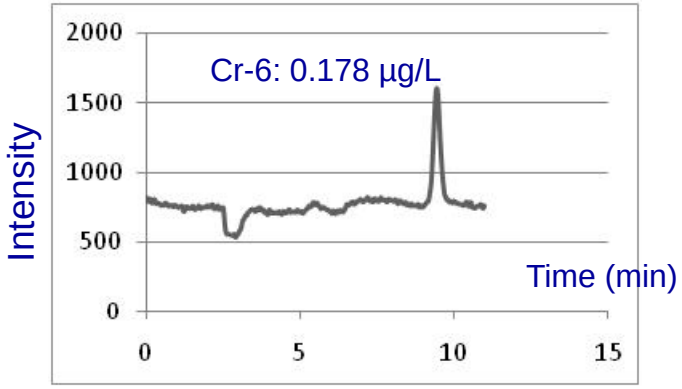
Method detection limit: 0.032 µg/L (from 7 replicate tests of fortified reagent water at 0.050 µg/L, SD = 0.01µg/L)

Spike recovery (R):
1.0 µg/L spike into a treated water sample containing 0.178 µg/L Cr-6:
R = 105.6%

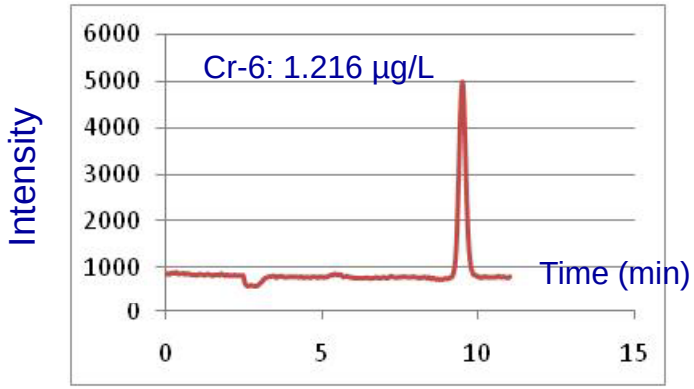
Study on IC-ICP-MS

Chromatograms

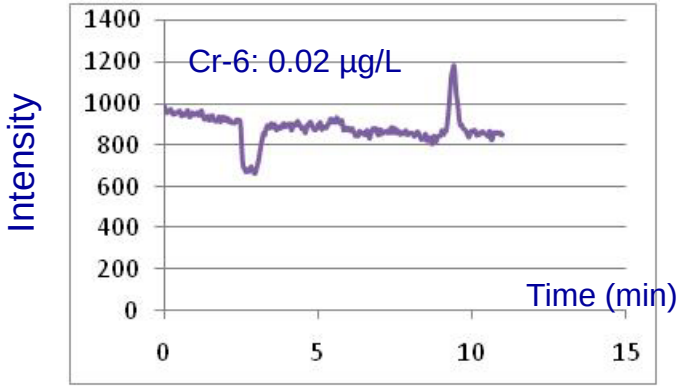
Sample test results should be corrected by subtracting blank value



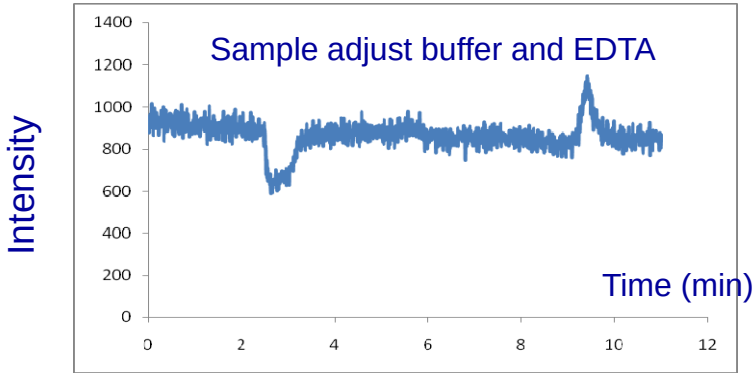
Treated water



Spiked treated water



Standard solution

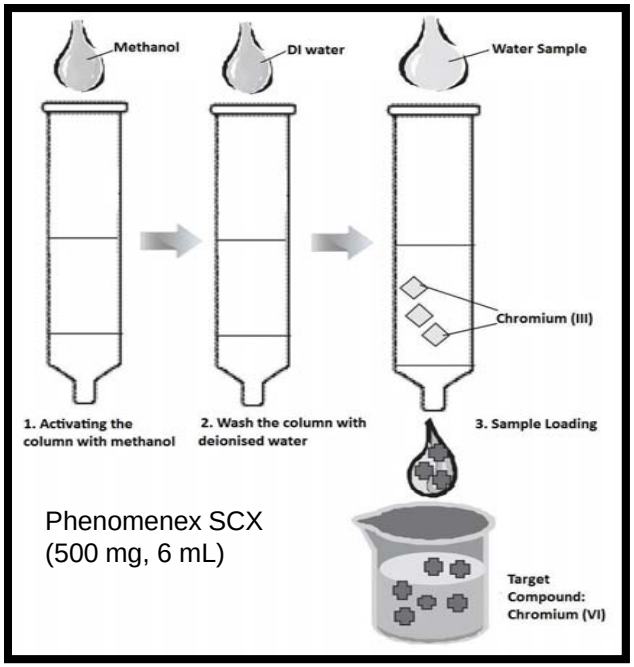


Reagent blank

Study on SPE-ICP-MS

- Solid phase extraction (SPE): simple, rapid separation
- Assumption of the separation on strong cation exchange (SCX) cartridge
  - Cr-6: negatively charged, not retained
  - Cr-3: positively charged, retained
  - Effluent: acidified, quantified by ICP-MS

Procedure:



Study on SPE-ICP-MS: Experimental Verification

- Pure Cr-6: passing through SCX without loss
  - 0.25 µg/L Cr-6: 0.250 ±0.010 µg/L (n=2)
  - 0.50 µg/L Cr-6: 0.491±0.008 µg/L (n=2)
  - 1.0 µg/L Cr-6: 1.14 ±0.04 µg/L (n=7)
  - 2.0 µg/L Cr-6: 2.17±0.08 µg/L (n=8)

- Pure Cr-3: retained on SCX cartridge completely
  - Original 0.25, 0.5 or 2.0 µg/L Cr-3, non-detected (< 0.012 µg/L)

- Mixture: 1.0 µg/L Cr-6, 10 µg/L each of Cr-3 and other 47 elements
  - Through 1 cartridge: 1.11 ±0.05 µg/L (n=4)
  - Through 2 cartridges: 1.11±0.01 µg/L (n=4)

- Mixture: 1.0 µg/L Cr-6, 100 µg/L each of Cr-3 and other 67 elements: detected as 1.15±0.02 µg/L (n=4)

Study on SPE-ICP-MS: Experimental Verification

- Mixture of Cr-6 and Cr-3

Mixture (µg/L)	Cr-6 detected	Spike level	Recovery (%)
Cr-6 (0.25), Cr-3 (0.25)	0.214, 0.218		
Cr-6 (0.25), Cr-3 (0.25), buffer	0.240, 0.260	0.1	107
Cr-6 (0.50), Cr-3 (0.50)	0.477, 0.456	0.5	98.7
Cr-6 (0.50), Cr-3 (0.50), buffer	0.548, 0.535	0.5	100
Cr-6 (2.0), Cr-3 (2.0)	1.82, 1.91	1.0	93.5
Cr-6 (2.0), Cr-3 (2.0), buffer	1.96, 1.95	1.0	88.4
Cr-6 (10.0), Cr-3 (10)	9.41		
Cr-6 (1.0) , Cr-3 (1000)	1.85 ±0.19 (n=6)		

Buffer: $(NH_4)_2SO_4$ - NH_4OH, pH 9.0-9.5

Study on SPE-ICP-MS

- Comparison of SCX cartridges: Phenomenex Strata, Varian Chromoband, Agilent Bond Elut
- Detection: background at m/z = 52 from polyatomic ions, blank subtraction needed
- Reproducibility: mainly dependent on manual SPE process, still acceptable

Hexavalent Chromium in treated water

Reservior location	IC-ICP-MS	SPE-ICP-MS
A	0.160	0.209
B	0.080	0.103
C	0.128	0.159
D	0.055	0.090
E	0.064	0.129
F	0.050	0.083
G	0.089	0.136
H	<0.032	<0.012
I	<0.032	0.032

Unit: µg/L

Cr-6 in treated water at sub-µg/L level

Conclusions

- Enhanced monitoring of Cr-6 in drinking water for needs sensitive analytical methods
- IC-ICP-MS method: comparable to IC-PCR-UV in sensitivity and selectivity
- SPE-ICP-MS method: simple, sensitive, but less reproducible than IC-ICP-MS
- Treated water: Cr-6 at trace levels


THANK YOU!☺
Water for All: Conserve, Value, Enjoy