



Update on New and Modified Extraction Methods for Cr(VI) Determination in Dusts, Ashes, and Soils

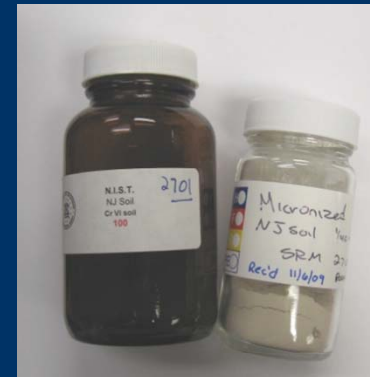
Ruth E. Wolf and Stephen A. Wilson

U.S. Geological Survey, MS 964D, Denver Federal Center, Denver, CO
80225

U.S. Department of the Interior
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Introduction

- One of the difficulties in speciation analyses of solid samples is finding a suitable extraction method for the species of interest
- The extraction method must be compatible with the analytes of interest and be compatible with the analytical determination method(s)
- The extraction method must not cause species interconversion
- The extraction method must also be able to accommodate a limited amount of sample and not generate an excessive amount of waste



**Cr(VI) reference materials
in preparation by USGS
(NIST 2701 and 2700)**

Analytical Method†

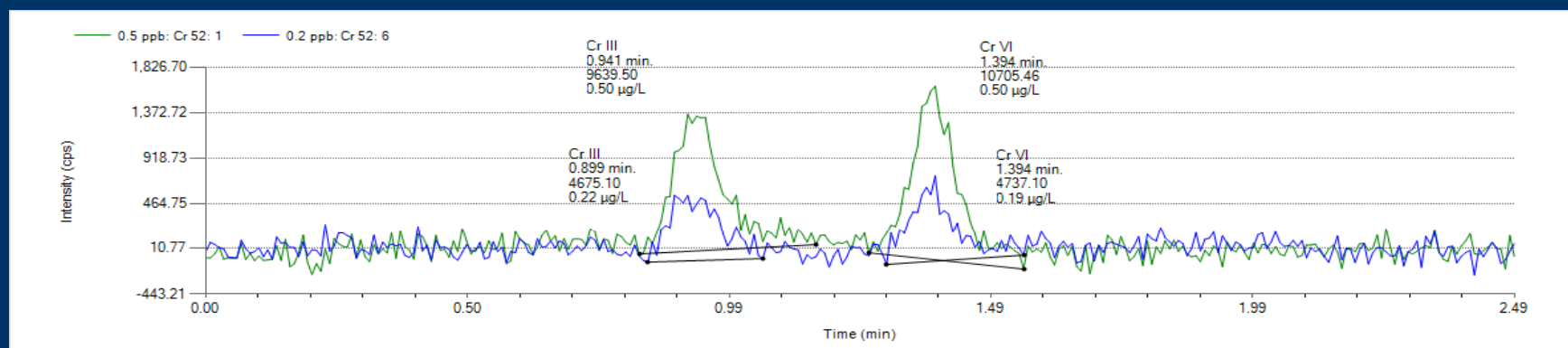
- HPLC – reversed phase, ion-pairing
 - Column: Brownlee C8
 - Column Oven 35 °C
 - Mobile Phase:
 - 2mM tetrabutylammonium hydroxide (TBAOH) + 0.5mM K₂EDTA, pH = 7.4 – 7.6
 - EDTA converts Cr(III) to anionic EDTA-Cr(III)
 - 5% MeOH added on-line
 - Autosampler 10 °C
 - Samples: Diluted minimally 1:1 in mobile-phase, 50 µL injection
- DRC-ICP-MS
 - Reaction gas: N₂ or NH₃
 - Sample Introduction:
 - Baffled quartz cyclonic spray chamber
 - Meinhard TQ-30-A3 nebulizer



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Analytical Figures of Merit:

Parameter	NH ₃ Reaction Gas Flow 0.75, RPq=0.65		N ₂ Reaction Gas Flow 1.0, RPq=0.50	
	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)
Instrument Detection Limit (IDL), µg/L	0.09	0.06	0.1	0.1
Practical Quantitation Limit (PQL), µg/L	0.2	0.2	0.2	0.2



Chromatogram showing low calibration standard at 0.5 µg/L and standard at PQL of 0.2 µg/L

Available Cr(VI) Extraction Methods

- U.S. EPA Method 3060A – Alkaline Digestion for Hexavalent Chromium
 - 0.28 M Na_2CO_3 / 0.5 M NaOH with phosphate buffer and MgCl_2 precipitation agent, pH >11.5, hotplate
 - Applicable to soils and solid wastes
 - Requires 2.5 g sample and generates 100 mL of extract
- De-ionized water, buffered and un-buffered extraction
 - Applicable to soils, ashes, other solid materials
- OSHA ID-215 – Hexavalent Chromium in Air Filters
 - 10% Na_2CO_3 / 2% NaHCO_3 with phosphate buffer and Mg sulfate precipitation agent, pH 8, hotplate
 - Applicable to quartz or PVC air filters

Performance of Cr(VI) Extraction Methods with HPLC-ICP-MS Detection:

- Preliminary investigations using various buffer solutions were carried out using spikes of Cr(III) and Cr(VI) in blank extraction solutions and comparing chromatograms to spikes in the HPLC mobile phase
- Phosphate and sulfate extraction solutions were incompatible with HPLC-ICP-MS determination method used

Buffer Solution Tested	Stock Concentrations	Tested Concentration	pH
Phosphate – pH 8	1 M K_2HPO_4 – 0.06M KH_2PO_4	10mM, 20mM	8.4
Carbonate – pH 9	0.1 M Na_2CO_3 – 0.9 M $NaHCO_3$	10mM, 20mM	9.2
Sulfate – pH 10	1M $(NH_4)_2SO_4$ – 1 M NH_4OH	20mM, 50mM	10.3

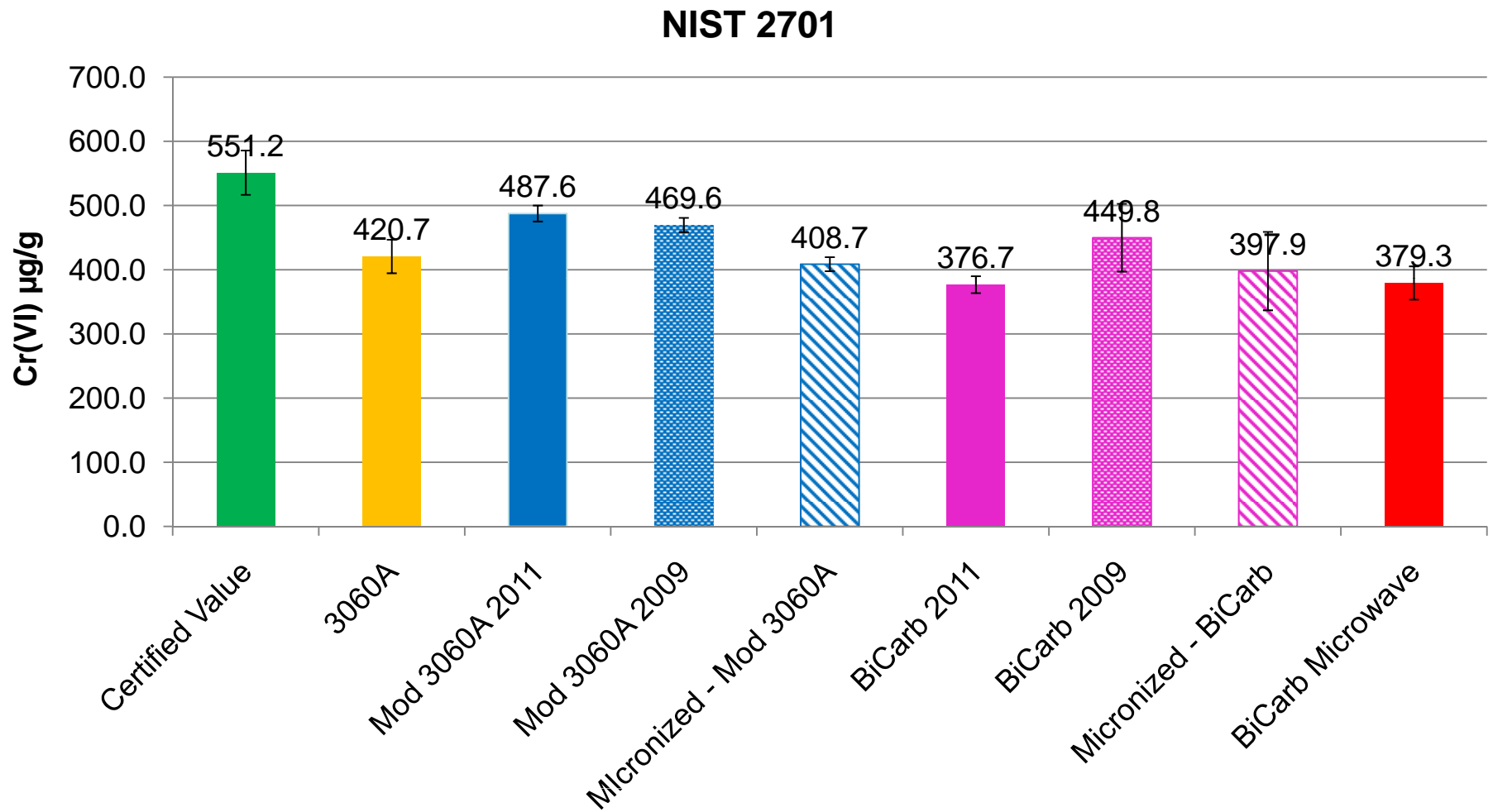
Soil Extraction Study:

- Method 3060A Digestion as written is incompatible with HPLC-ICP-MS detection method
 - Phosphate buffer disrupts ion-pairing chromatography
 - Requires 50x to 100x dilution prior to analysis
 - 2.5 g sample requirement and strong basic (pH ~13) extraction solution results in over 100 mL of digestate for disposal
 - Note: less than 1 mL required for analysis!
 - Mg precipitation agent forms a gelatinous $\text{Mg}(\text{OH})_2$ or $\text{Mg}(\text{CO}_3)_2$ precipitate that is difficult to filter and wash, requires disposal
 - Similar to co-precipitation method used to prepare microanalytical carbonate standards for LA-ICP-MS
 - Could result in analyte loss (need to verify by SEM)
- Desirable to find an extraction method for soils that is compatible with the detection method of choice and easier to use and results in less waste

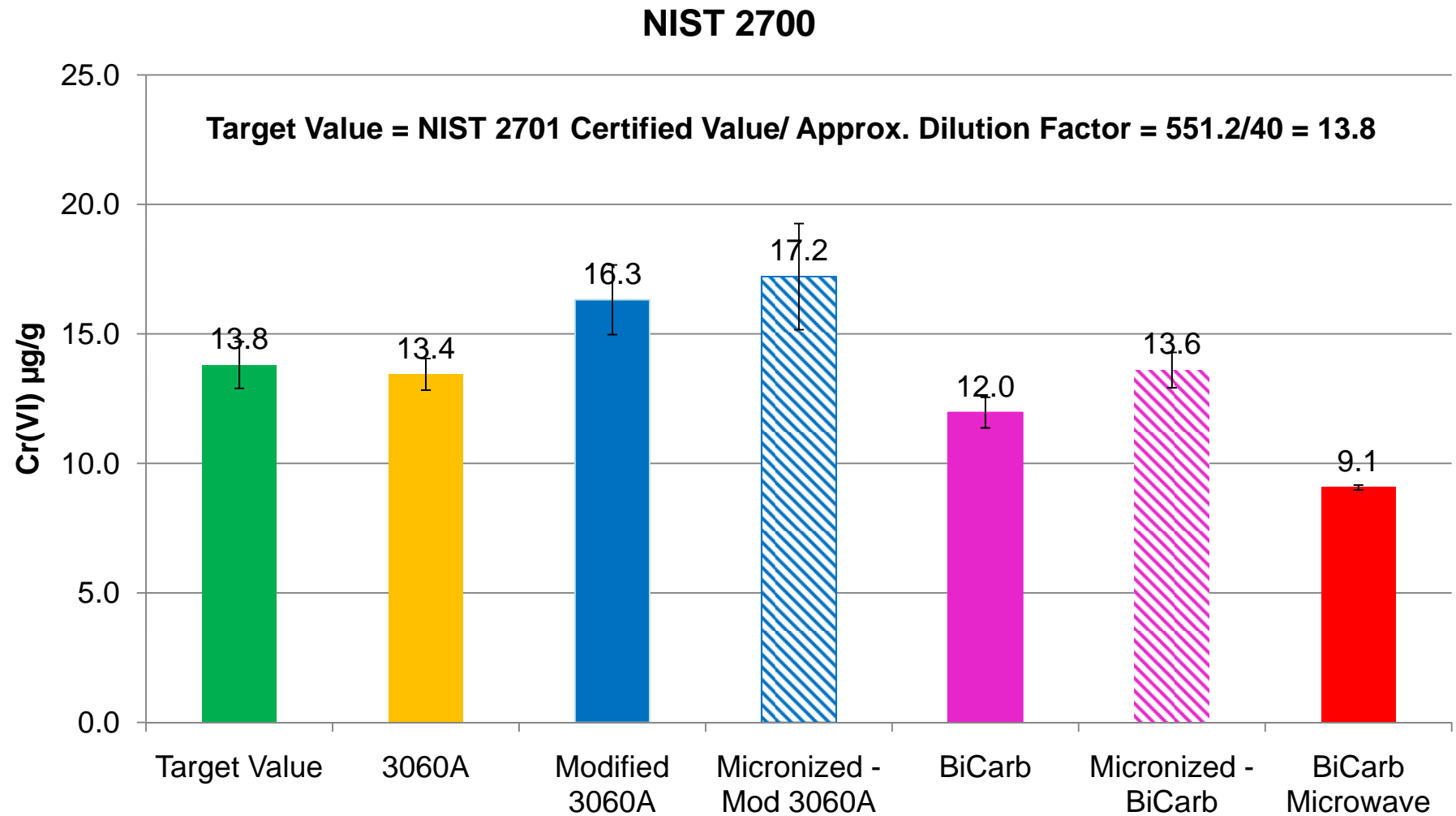
Evaluation of Cr(VI) soil extractions

- Modified 3060A
 - 0.28 M Na_2CO_3 / 0.5 M NaOH, pH > 11.5
 - Omit phosphate buffer and Mg, reduce sample size to 0.5 g and use 50 mL extraction fluid, final volume after pH adjustment 100 mL
- BiCarb Hotplate
 - 1mM Na_2CO_3 /9mM NaHCO_3 , pH~9.2 extraction fluid, 0.5 g sample, 50 mL extraction fluid, 95 °C for 1 hour, centrifuge and filter ~10 mL with 0.45 μm syringe filters into 15 mL tube
- BiCarb Microwave
 - 1mM Na_2CO_3 /9mM NaHCO_3 , pH~9.2 extraction fluid, 0.5 g sample, 50 mL extraction fluid in 100mL Teflon vessels (Anton Paar MW3000, Rotor 16), temperature program ramp to 95 °C (20 min), hold at 95 °C for 1 hour, centrifuge and filter with 0.45 μm syringe filters
- Evaluate effect of particle size on extraction efficiency
 - Extract SRM materials as provided (mean particle size 200 μm)
 - Micronize SRM materials to mean particle size 30 μm

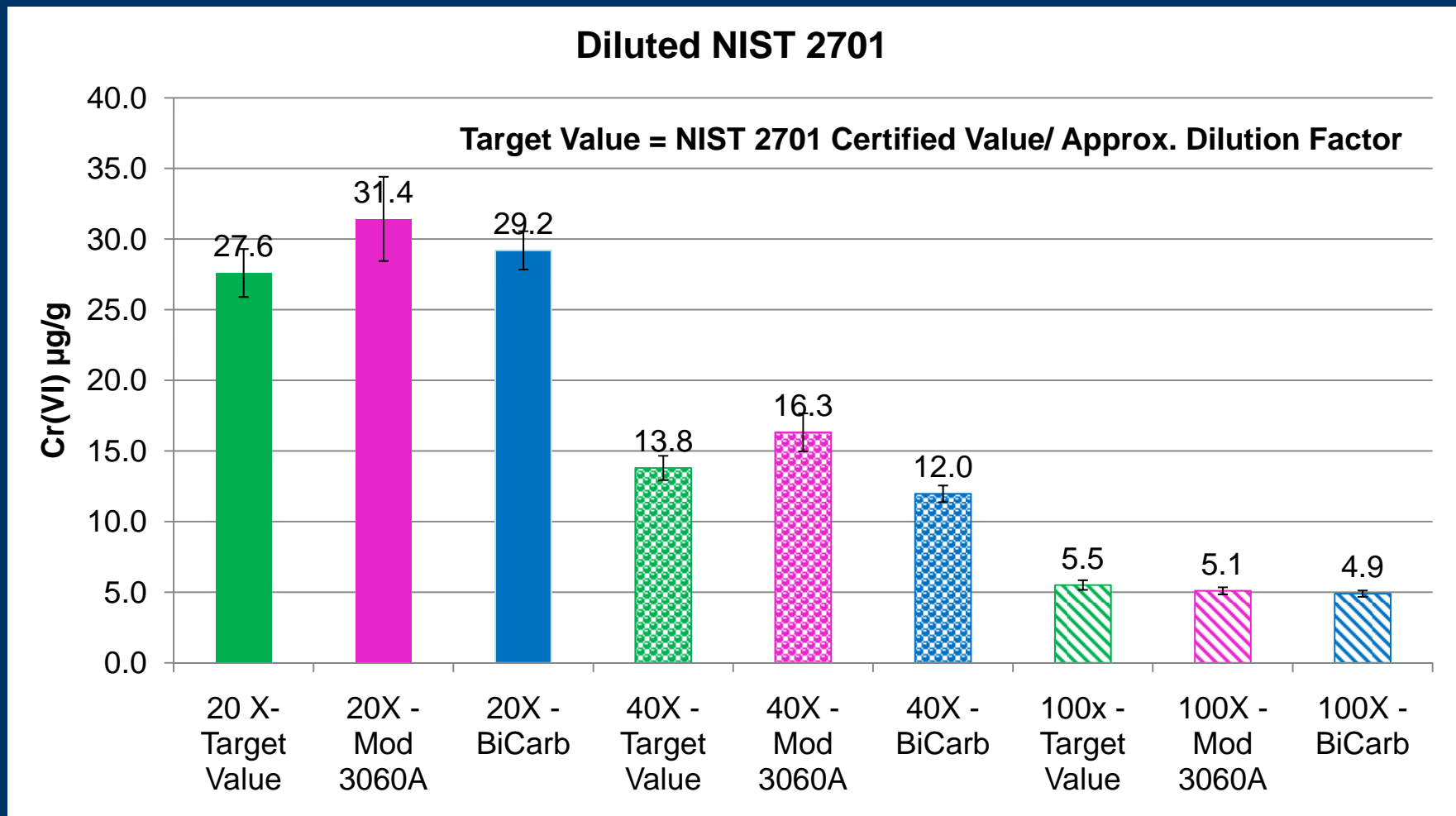
Results – NIST 2701



Results – NIST 2700



Effect of Reduced Matrix

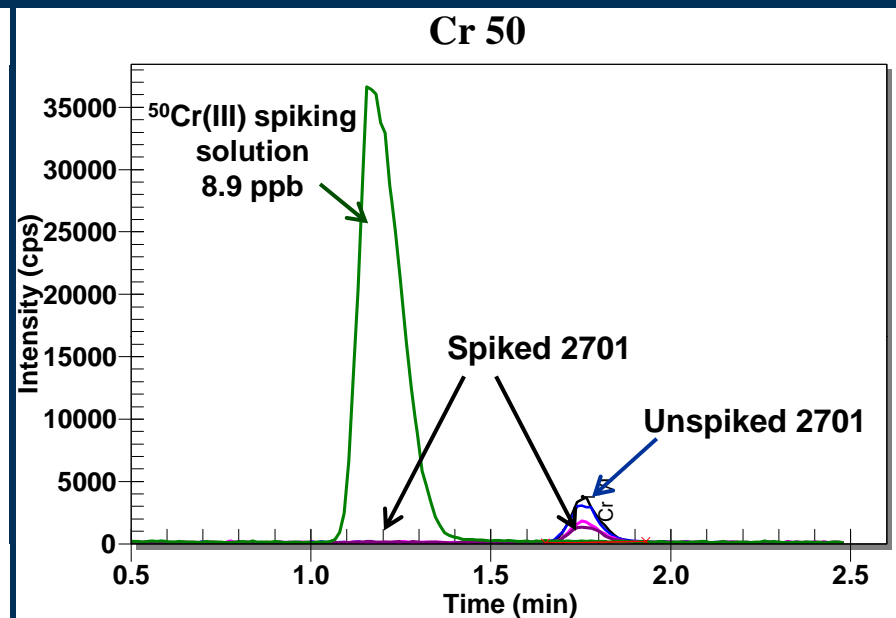
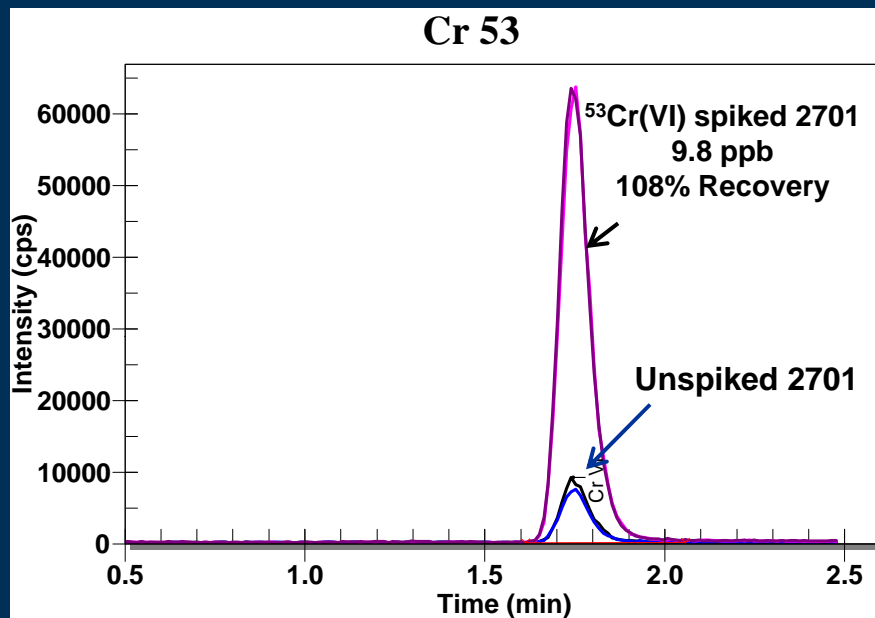


Use of Isotopically Enriched Spikes

- Prepared from Cr metal starting material
 - Dissolved ~ 5 mg in 4 mL 6M HCl in 30 mL PFTE vial
- Cr(III): Transfer to precleaned, tared 500 mL bottle
 - Dilute to 500 g with deionized water (pH=1)
- Cr(VI): transfer to 100 mL PFTE beaker
 - Add 50 μ L 30% H₂O₂ and 4.5 mL conc. NH₄OH (turns yellow), heat to 150 °C to gentle boil, boil 15 minutes (per Method 6800)
 - Transfer to 500 mL bottle and dilute to 500 g with DI water

Cr Isotope	Natural Abundance	⁵⁰ Cr(III) spike	⁵³ Cr(VI) spike
50	4.345	96.05	0.25
52	82.789	3.66	3.73
53	9.501	0.24	95.74
54	2.365	0.05	0.27

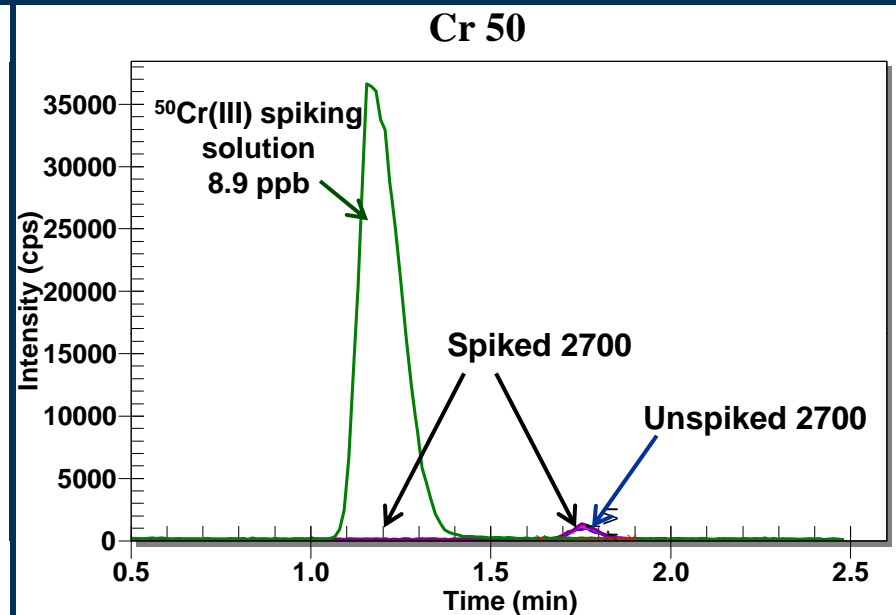
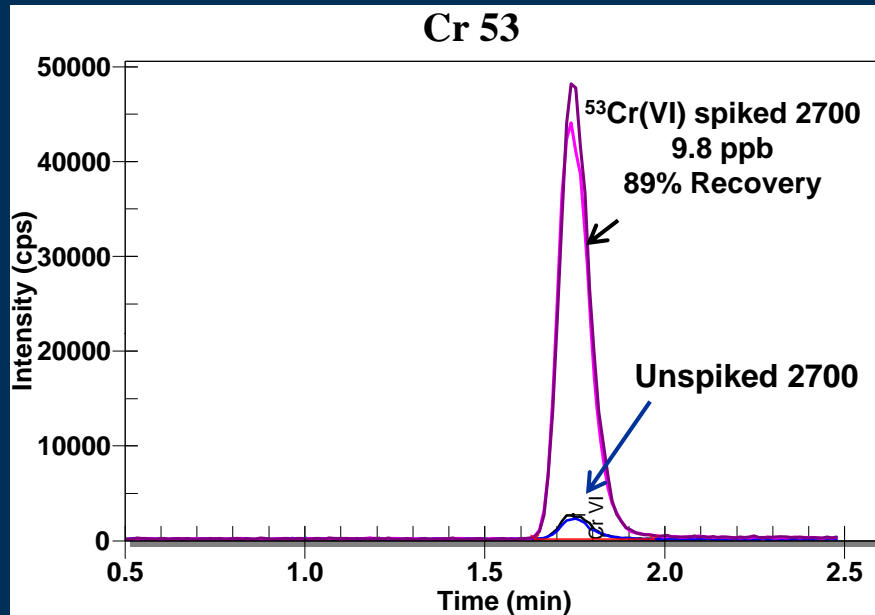
Isotopic Spikes on NIST 2701 (1:100)



Using BiCarb Microwave Digestion

- $^{53}\text{Cr(VI)}$ Spike is recovered
 - No sign of reduction to Cr(III)
- $^{50}\text{Cr(III)}$ Spike is NOT recovered
 - Confirmation Cr(III) removed during filtration step

Isotopic Spikes on NIST 2700 (1:10)



Using BiCarb Microwave Digestion

- $^{53}\text{Cr(VI)}$ Spike is recovered
 - No sign of reduction to Cr(III)
- $^{50}\text{Cr(III)}$ Spike is NOT recovered
 - Confirmation Cr(III) removed during filtration step

Conclusions

- **Modified EPA 3060A extraction achieved best recoveries for NIST 2701 and 2700**
- **1mM Na₂CO₃/9mM NaHCO₃, pH~9.2 extraction fluid (BiCarb) extraction achieved lower recoveries for Cr(VI) in both hot plate and microwave digestion methods**
 - pH might need to be higher (10-11)
 - Lowest recoveries via microwave digestion might be a function of lack of contact via stirring
- **Recoveries obtained for NIST 2701 when diluted with ground quartz were close to “target” values by both Modified 3060A extraction and BiCarb extraction**
 - Indicates that low recoveries on undiluted 2701 might be a function of the sample matrix
- **The use of isotopically enriched spikes of Cr(VI) and Cr(III) with the BiCarb microwave digestion do not indicate any reduction of Cr(VI) to Cr(III)**
 - Verifies that Cr(III) is removed during filtration step

Next Steps

- Perform extractions using sodium bicarbonate extraction fluid adjusted to a higher pH (10-11)
- Evaluate effects of possible oxidation/reduction reactions during Modified 3060A extraction using isotopically enriched spikes
- Contact: Ruth E. Wolf (303) 236-2470, rwolf@usgs.gov