

**Evaluation of Methods for Quantifying Cr (VI) and Cr (III)
in Soils and Wastes**

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By

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Executive Summary

Chromium speciation is a two step process and involves complicated chemistry to perform the extraction without interconversion of the two predominant species, followed by multiple analytical methods that are precise, sensitive, and quantitative. While it is the analytical methods that are primarily being examined in this study, it is the development of a reproducible and repeatable extraction protocol that will ultimately determine whether the analytical methodologies are effective at quantifying the actual chromium (VI) content in a soil or waste matrix. The results from this study on extraction protocol improvements, coupled with the interlaboratory study designed to create a certified reference material demonstrate that:

1. The USEPA SW846 extraction protocol 3060A is not effective at removing total chromium and some hexavalent chromium (Cr (VI)) spikes on all matrices
2. EPA method 3060A only targets (CrVI) for extraction and cannot be used for quantitative extraction of trivalent (Cr (III)) due to the solubility chemistries of the extraction method.
3. Effective measurement of chromium reduction and/or loss of the Cr (VI) spike cannot be estimated without an effective extraction protocol for Cr (III) alone
4. The use of stable chromium isotope labels will correct for interconversion either in the extraction or analysis processes up to 80% of the conversion of the spike
5. The use of stable isotope labels will account for potential analyte loss due to complexation or precipitation of chromium (VI) spike
6. The use of a standard reference material for interlaboratory comparison may help in establishing a standard method for extraction and analysis for speciated chromium in soil and waste matrices
7. There was a statistically significant difference in chromium analytical results obtained with method 6800 when compared to either method 7199 or 7196A
8. There was no statistically significant difference in results obtained with method 7199 when compared with method 7196A

An interlaboratory study comparing the three quantitation methods EPA 7196A, 7199 and 6800 demonstrated a statistically significant and consistent 31.6% difference between method 6800 and the results from the other two quantification methods (7196A and 7199) using the same extraction protocol (3060A). Method 6800 had significantly higher values for soluble Cr (VI) than either of the two methods that do not compensate for reduction or loss of Cr (VI) measured with an external spike. Method 6800 uses a stable isotope spike to adjust for loss of

Cr (VI) to reduction during the extraction process. However, method 6800 is however limited by the amount of stable isotope spiked into the matrix. Other methods of quantification (7196A 7199) can underestimate the amount of soluble Cr (VI) if it occurs during the extraction or analysis process. Determination of where in the analytical process the Cr (VI) spike loss occurs cannot be made without the ability to quantitate the Cr (III) species. Therefore, it cannot be assumed that a poor Cr (VI) measurement was caused only by reduction of the Cr (VI). For example, if the Cr (VI) in a sample was either precipitated or absorbed to the soil surface by the addition of the extraction solvent or formed a complex with an organic moiety, it may still be available for oxidation back to Cr (VI) or dissociation to soluble Cr (VI) if conditions in its environment change. While ICP/MS analysis should identify all soluble chromium species, whether or not they had been complexed with an organic ligand, it cannot compensate for Cr (VI) forms that may have been precipitated or absorbed to the soil surface.

Background:

Accurate measurement of Cr species in non-aqueous media such as soils and sediments is complicated by chemical processes that can alter the indigenous amounts of Cr (III), a micronutrient, and Cr (VI), a known carcinogen. The accurate determination of Cr (VI) is critical in order to make informed decisions about remedial actions and to assess the health and safety of the public. For soils or sediments without significant amounts of certain organics, metals or anions, Cr (VI) can be measured with a high degree of accuracy. However, many soils and/or sediments with matrix components including those listed above can oxidize a laboratory spike of Cr(III) species to Cr(VI) species [resulting in the over-reporting the true amount of Cr(VI)], or reduce a laboratory spike of Cr(VI) to Cr(III) [resulting in the under-reporting the true amount of Cr(VI)].

A literature review regarding this topic of method comparability has raised questions as to whether other combinations of methods, such as utilizing 3060a extraction protocols with USEPA method 6800, may generate more reliable and consistent analytical results. These and other issues are currently under review by the Analytical Subgroup of the NJDEP Cr Workgroup to recommend changes to current NJDEP Cr policies and procedures.

General Methodology: USEPA Method 6800 uses ion chromatography (IC) coupled to inductively coupled plasma mass spectrometry (ICPMS) to separate and quantify each chromium species. In addition stable isotope labeled Cr (VI) and Cr (III) are added after sample collection to monitor for species interconversion in all subsequent processes. Method 7199 uses IC with a post column addition of diphenylcarbazide to detect the Cr (VI) after it elutes from the column. Method 7196a uses the same colorimetric complex of chromium for quantification but the assay is performed in situ on the extract with no separation of the chromium species.

A Comparison of Promulgated USEPA Methods for Chromium:

There are three EPA analysis methods 6800, 7199, 7196A (1) currently being used to quantify the amount of extractable Cr (VI) from a solid sample. All three analytical methods utilize the same extraction protocol, EPA 3060a. Method 3060a is an extraction protocol that uses a mixture of sodium bicarbonate and sodium hydroxide as a buffer to remove Cr (VI) from its solid matrix. This method was created to gently extract and stabilize Cr (VI). The extraction protocol limits the amount of chromium that can be solubilized from most soil and waste matrices. The limitations are covered later in this report, but the limitations are critical in trying to assess the true amount of Cr (VI) in the sample. The quantitation methods EPA 6800, 7196A and 7199 cannot compensate for insoluble Cr (III) lost to precipitation during the extraction process because of the chemistry that is utilized for extraction of the chromium species, without making considerable assumptions. Method 6800 can be used to detect changes (up to 80% of the spike) of Cr specie conversions that occur during sample digestion and/or measurement.

In order to evaluate the efficacy of the methods that quantify the Cr once solubilized, the three instrumental techniques should be compared directly, with the same material

containing stable chromium species at known levels. Assuming that the extraction step is reproducible for the material tested, it would then be the quantification process from the instrument that created any differences in the results. By isolating different procedures within the analysis train for chromium, a scientist can determine the uncertainty of each instrument's raw data output by using a representative homogeneous reference material of known chromium species composition. A potential standard reference material (SRM) was used in an interlaboratory study, to measure the concentration of Cr (VI) in a soil type. All laboratories used the same extraction protocol but analyzed the SRM with one of the three methods referenced above in the text. By having a representative SRM utilized by all laboratories reduces the uncertainty in the extraction process and allows the assessment of the instrumental method variability for each of the three techniques. This isolates the extraction efficiency from the collaborative study statistics.

Creation of a Standard Reference Material for Chromium in Soil

There has not been a standard reference material (SRM) that can be used to validate any chromium analytical method in a solid matrix. In an effort to improve the QA of Cr (VI) measurements by any method, a standard reference material was created. NJDEP Office of Quality Assurance initiated the effort in collaboration with National Institutes of Standards and Technology NIST, United States Geological Survey USGS and Rutgers University. A COPR-contaminated soil from behind the Interpretative Center at the Liberty Science Center in Liberty State Park in Jersey City was sampled using a mechanical backhoe excavator. The COPR samples were placed into lined with black polyethylene plastic liners covered sealed and shipped to the United States Geological Survey (USGS) in Arvada, CO for processing. A more detailed description of sample processing by the USGS can be found in an attached manuscript accepted for publication by the Journal of Analytical Atomic Spectroscopy.

An inter-laboratory study was arranged by staff from the NJDEP OQA in conjunction with NIST personnel and a project team that included the lead author of this report. The laboratories initially selected to participate in the characterization were those that could perform method 6800 for quantification of Cr (VI) and possibly other methods as well. Three sub-samples of the principal reference material were sent to each laboratory for analysis. Each sub-sample was analyzed in triplicate. All samples were analyzed by whichever method was most appropriate for that laboratory and many of the laboratories analyzed these samples by more than one method.

After the initial round of analysis, a second round of samples were distributed to the laboratories that participated in the first round as well as other laboratories who agreed to participate. In all 21 laboratories participated in the study. Of those, one laboratory submitted a single result that was eliminated by the Q-Test.

The remaining 20 laboratories that were part of the overall certification data and their contacts and the contact for NJDEP and USGS (who did not analyze the samples) are presented below:

S. Nagourney
New Jersey Department of Environmental Protection,
Office of Quality Assurance
Trenton, NJ, USA

S. Wilson
U.S. Geological Survey
Denver, CO, USA

D. Speis
Accutest Laboratories
Dayton, NJ, USA

L. Call
ALS Laboratory Group
Environmental Division
Smithfield, NSW, Australia

R. Gerads
Applied Speciation and Consulting, LLC
Tukwila, WA, USA

L. Reyes
Columbia Analytical Services
Rochester, NY, USA

D. Thomas
Dionex Corporation
Sunnyvale, CA, USA

H.M. Skip Kingston
Duquesne University
Department of Chemistry and Biochemistry
Pittsburgh, PA, USA

J. DuPont
DHL Analytical, Inc.
Round Rock, TX, USA

B. Goyette
EMT
Morton Grove, IL, USA

C. Huff
Environmental Resource Associates
Arvada, CO, USA

JP. Blouin
Direction du Laboratoire des Pollutions Industrielles
Center D-Expertise en Analyse Environnementale du Quebec
Laval, Quebec, Canada

M. Goss
Kentucky Department of Environmental Protection
Frankfort, KY, USA

A. Doupe
Lancaster Laboratories
Lancaster, PA, USA

J. Ghandi
Metrohm-Peak
Houston, TX, USA

V. Shah
City of New York
Department of Environmental Protection
Wards Island, NY, USA

C. Nowlan
Pace Analytical Services, Inc.
Minneapolis, MN, USA

B. Buckley
Rutgers University
Environmental and Occupational Health Sciences Institute
Piscataway, NJ, USA

C. Armbruster
STL (Test America) Edison
Edison, NJ, USA

D. Dunlap
Test America (STL) Pittsburgh
Pittsburgh, PA, USA

M. Nash
Thermo Electron Corporation
Winsford, Cheshire, UK

O.X.N. Donard
University of Pau,
HELIOPARC
Pau, France

Six months after the original material was distributed, a second round of samples was distributed to the 20 participating laboratories and the NIST analytical laboratory to confirm the stability of the material. Nineteen laboratories submitted data from a second round confirming the product's stability. Most of the laboratories ran the single sample in triplicate or as a single replicate. The analytical results from these studies along with their associated inter and intra-laboratory method variability analysis (both round one and round 2) were used to create the certificate of analysis to accompany the new Standard Reference Material (SRM) (2). The SRM is now commercially available by National Institute of Standards and Technology NIST. The certificate for 2701 (without the aforementioned list of participating laboratories) is found in Appendix 2. This SRM will be available for all future studies to allow laboratories the ability to assess precision and accuracy for their chromium related soil analyses in the future.

The collaborative laboratories that participated in this study analyzed the soil sample by the three principal EPA methods. Eleven laboratories ran the sample by USEPA method 7196A, ten laboratories by USEPA method 7199 and five laboratories by USEPA method 6800. The final results of the three interlaboratory determinations were pooled by their respective analytical method. The collaborative results demonstrated that there was a statistically significant difference in chromium results agreement between EPA method 6800 and the other two federal promulgated analytical techniques. For both rounds of interlaboratory analyses, the distribution of the results from the isotope method (6800) were statistically different in the amount of Cr VI quantified compared to results from the other two promulgated USEPA methods (7196, 7199). The SRM certificate will be issued with a certified value from laboratories using method 6800 and a reference value from laboratories using methods 7196 or 7199. One chromium species concentration for methods 7196A and 7199, and another chromium species concentration for method 6800. Method 6800 detected a greater amount of Cr (VI) than the other two methods. The ability of the stable isotope labeled spike to compensate for any reduction that might occur during the extraction process is believed to be the principal reason why. On average about 31% of the extractable Cr (VI) is not accounted for by methods 7196A and 7199. A summary of the results showing the averages from each lab for each round and their corresponding standard deviations are presented in Table 1 below. Those without standard deviations had only one replicate value reported by the laboratories. Each value reported by the lab was evaluated individually. All values were used to create the average for both round one and round two results as well as the overall average. It should be noted that other NIST SRMs have two values associated with the certificate each based on separate analytical methods such as EPA method 3051 which represents an acid extractable fraction vs. other total assay methods such as an X-ray determination.

The study was an ideal means to evaluate systematic differences in the quantification methods because the material tested was the same in each laboratory and of reasonable concentration to represent real waste samples. These statistically significant differences demonstrate that either methods 7199 and 7196A are not equivalent in their evaluation of the amount of extractable Cr (VI) as compared to Method 6800. The results demonstrate that the methods that do not use stable isotope labels, will underestimate the amount of Cr (VI). This conclusion assumes that the Cr

that is reduced remains soluble or that the losses are not greater than the spike can compensate for.

Discussion of Extraction Protocol Sources of Variability:

Ideally, one method would be used to extract both the Cr (VI) and Cr (III) and the subsequent instrumental analysis of total chromium would match the sum of the measured Cr (III) and Cr (VI) thereby achieving mass balance. If there is a reduction of a Cr (VI) spike, it could be quantified and no assumptions would need to be made about whether the Cr (VI) has just become insoluble in the extracting solution. The total ionic strength could have been surpassed or the Cr (VI) may have been reduced to Cr (III) or complexed and rendered partially insoluble in the extract. It is only the reduction of Cr (VI) that is desired in a remediation strategy. Other outcomes are unsatisfactory because they do not assure that the Cr does not exist in a hazardous form, or cannot be readily converted back to Cr (VI) under ambient conditions. Another possible reason for variability is the differences in cation concentration and the relative number of ions in solution. As more ions are solubilized fewer can enter solution and the ones with the least solubility will fall out. These ion that precipitate may take other less concentrated ions with them either as co precipitates or ion pairs.

The following sections describe the research to create a better method for the extraction of both Cr (III) and Cr (VI).

Chromium exists as both a cation (principal form of Cr (III)) and an anion (principal form of (Cr VI)). With a change in pH it can exist in soils as neutral species in both oxidation states. The oxidation state of the species is dependant on both the pH and eH of the soil or waste solid material and the extraction process can change those conditions

Chromium Speciation by IC-ICP/MS

Soil samples were analyzed for Cr (III) and Cr (VI) using Ion Chromatography-Inductively Coupled Plasma/Mass Spectrometry (IC-ICP/MS) and a modified EPA Method 3060A. The method was optimized using soil samples collected from Liberty State Park around 1997 and stored at 4°C in a cold room. The method was then tested on soil samples collected by the New Jersey Department of Environmental Protection (NJDEP) and labeled: PPG Garfield Ave, Society Hill and Gateway, collected in 2005. For homogeneity all of these samples were sieved using 500 µm pores and then desiccated before method optimization. Both total chromium and chromium speciation was performed on the samples.

Total Chromium Determination

Total chromium was determined by microwave digestion, using a modified EPA method 3051 (CEM MARX5 microwave extractor, Mathews NC) followed by ICP/MS (ThermoElectron X5, Mass.). For the modified EPA method 3051 between 0.08 and 0.10 g of soil was weighted out and then digested using 10 mL of 100% HNO₃. The samples were digested using the "Tool Steel" method in the CEM microwave directory.

The Tool Steel method has the following parameters:

- 1200 W power
- 350 psi pressure
- 180°C temperature
- 10 minute ramp time
- 15 minute hold time

After digestion the samples were allowed to cool to room temperature before diluting (1:200 dilution). The diluted samples were then analyzed by ICP/MS. The total metals assay method has been previously described (3). This methodology gives total chromium. The chemical conditions for this extraction technique would be expected to convert all of the chromium present in the sample into Cr (III) because of the very low pH and reductive properties of the concentrated acid, and therefore this method of extraction cannot be used for chromium speciation.

Total Chromium as Determined by Tool Steel Method

Sampling Location	ppm Cr
Liberty State Park	504
Gateway	6556
Society Hill	5305
PPG Garfield Ave	2950

Table 1: Total Cr as measured by acid extraction and ICP/MS quantitation

Sixteen other elements were measured in the four soil samples by ICP/MS and the Tool Steel method.

Element	Gateway	Garfield Ave	Society Hill	Liberty
	ppm	ppm	ppm	ppm
Mg	16845	11829	14211	21967
Al	22891	24829	18134	17790
Ti	1124	934	861	1591
V	419	140	353	694
Mn	562	542	474	816
Co	66	119	57	104
Ni	209	88	181	327
Cu	163	131	143	162
Zn	643	131	398	676
Sr	776	57	581	97
Cd	0.60	0.20	0.60	1.30

Cs	1.20	2.30	0.90	0.60
Ba	509	137	200	123
Pb	1086	71	332	1118
Bi	0.60	0.50	0.30	1.20
U	0.70	1.20	0.50	0.80

Table 2: Concentration of other elements in the four soil types examined. Measurement was by direct ICP/MS and during the same assay as that for total chromium.

Elements such as manganese, lead and barium can affect the concentration of chromium in the soil by either complexing chromium or electrochemically participate in an oxidation/reduction due to their respective activity potential. This possibility can change the state of the chromium and negatively effect recoveries. Table 2 lists the concentrations, in parts per million (ppm), of the other elements examined.

Chromium Isotopic Ratio Measurements

In nature chromium has four isotopes: ^{50}Cr , ^{52}Cr , ^{53}Cr and ^{54}Cr . For experimental purposes only the isotopes at mass to charge ratios (m/z) of ^{50}Cr , ^{52}Cr and ^{53}Cr are examined by mass spectrometry. The scientifically accepted natural isotopic ratios are as follows:

$$\begin{aligned} 50/52 &= 0.051856 \\ 50/53 &= 0.45732 \\ 53/52 &= 0.113391 \end{aligned}$$

It is critically important to the success of the isotopic analysis that the ICP/MS measure these chromium ratios with as much precision and accuracy as possible so that a comparison to the known natural abundance ratios can be made (one part in ten thousand mass resolution is typically required). This is because the trivalent and Hexavalent chromium species interconvert in nature under acidic or basic ambient conditions. To fully quantify this interconversion, stable isotope standards have been developed. Different ICP/MS parameters were tested and varied to see which configuration yielded chromium isotopic ratios closest to those found in nature. For each configuration experiment, the ICP/MS was allowed to equilibrate for two minutes. After equilibration, five measurements were taken of a 10 ppb Cr (III) standard with natural isotopic abundance. The operating conditions were optimized by minimizing the error between the measured isotopic ratios to those scientifically accepted ratios listed above. Optimized parameters included; the number of channels (5 or 7) and the dead time (30, 35, 40, 45, 50 and 55 ns). The best configuration was 5 channels and a dead time of 50 ns.

	Ratio	Percent Error
50/52	0.0496	4.20%
50/53	0.4366	4.50%
53/52	0.1138	0.40%

The channels and dead time were selected because they were thought to be the most likely parameters to affect isotope ratios. Other parameters that can be examined are dwell time; minimum settle time and maximum settle time.

Chromium Speciation and Extraction Recovery Studies

Liberty State Park soil was used for chromium speciation analysis. Three extraction experiments were accomplished to optimize the speciation of chromium in the soil matrix. All of the experimental extraction protocols used 0.5 g of soil and identical microwave extraction program conditions. Microwave extraction has been previously used for chromium speciation experiments (4). The difference was the chemical composition of the extraction solution.

The three extraction solutions are as follows:

1. 40 mL of dilute HNO₃ (pH = 4)
2. 5 mL of 2.5 M NaOH with 20 mL of H₂O
3. 5 mL of 2.5 M NaOH with 20 mL of H₂O with 0.74 g Sodium Bicarbonate added

The microwave extraction method conditions were:

- 300 W power
- 95°C temperature
- 5 minute ramp time
- 60 minute hold time

The sample extracts were stored at 4°C until they were analyzed. Prior to injection, the pH of the samples that were extracted, (using extraction conditions two and three, with NaOH) were adjusted to a pH of 6 with 6 M HNO₃ addition. The samples were injected into an Ion Chromatograph (Dionex DX 600) coupled to an Inductively Coupled Plasma /Mass Spectrometer (ThermoElectron PQ3) creating an IC-ICP/MS system.

The Ion Chromatographic (IC) conditions were as followed:

- Column: CG5A Guard Column (Dionex)
- 100 µL injection loop(Valco,)
- 1.5 mL/min flow rate
- 0-1.5 minute 30%:70% 1M HNO₃:H₂O mobile phase gradient
- 1.5 – 4.0 minute 100% 1M HNO₃ mobile phase gradient

Cr (III) and Cr (VI) concentrations were calculated by applying the instrument response, based on an integrated area under curve, to a 7 point calibration curve. After a concentration was determined based on the calibration curve the proper dilution factors were added for the final Cr (III) and Cr (VI) concentrations. The concentrations of Cr (III) and Cr (VI) were summed together to determine the total chromium in the sample extracted by the method. This was then compared to the total chromium determined by the Tool Steel digestion method to determine recoveries. All extraction methods gave recoveries below 15% using the extraction methodology outlined above.

Organic Free Sand Experiment

Concurrently with the soil extraction, sands (Fischer Scientific, Fairlawn NJ) spiked with both Cr (III) and Cr (VI) was analyzed. While much of the chromium may be in an organically bound fraction in soils (5) the presence of organic constituents may also interfere with extraction efficiencies. To develop a method for modification after extraction efficiencies have been optimized, these experiments were performed without potential organic interferences. Initially 20 ppm spikes were analyzed. A 20 ppm spike was chosen to simulate a concentration in the same order of magnitude as the Liberty soil samples. Recoveries of 0.2% and 40% were obtained for Cr (III) and Cr (VI) respectively. The lower recoveries were attributed to two parameters: 1. the concentrations examined were too high; the signal overwhelmed the mass spectrometer and 2. Cr (III) visibly precipitated out of solution upon NaOH addition. A 100 ppb spike was then analyzed.

Recoveries for all three extractions are described below:

	Acid	Base	Base + Bicarb
Cr (III)	114%	25%	86%
Cr (VI)	114%	142%	598%

Lowering the concentration of the chromium spike improved recoveries for all methods. The lower recoveries for the Cr (III) for the basic methods are most likely a result of precipitation combined with specie interconversion. The higher recoveries for the basic method with bicarbonate are most likely a result of interferences from ArC+. This significant interference leads to samples being diluted before injection to lower the concentrations entering the mass spectrometer. Samples were first diluted 20 times. With a 1:20 dilution the recoveries for the Base plus bicarbonate rose from 10% to 26%. With an improved recovery upon dilution being discovered it was determined to experiment with even further dilutions, including an increase in the liquid to solid ratio of the extraction.

Sample Dilution Experiment

For all sample extraction experiments a minimum of three replicates were used. Using a Dionex AS11 analytical column in the ion chromatograph, different dilution factors and liquid to solid ratios were examined. Dilution factors of 1:50, 1:100 and 1:125 were tested along with soil weights of 0.5 g, 0.25 g, 0.1 g and 0.08 g. The basic extraction method without bicarbonate addition had a total recovery of 30% while the acid extraction method gave concentrations below detection limits. The highest recoveries were obtained using the basic extraction method with bicarbonate addition. The recovery for the basic extraction using bicarbonate was 41%. The method gave 107.9 ppm of Cr (III) with a coefficient of variance of 17% and 100.1 ppm of Cr (VI) with a coefficient of variance of 4%. To further improve recoveries the volume of the extracting solvent was increased to further increase the liquid to solid ratio. Solvent volumes of 36.25 mL and 42.5 mL were tested. Table 3 below illustrates the results.

Mass	Vol ml	Cr (III)	%CV	Cr (VI)	%CV	Total	Recovery
0.1g	25	108	17%	100	4%	208	41%

0.1g	36.25	83	28%	170	17%	253	50%
0.1g	36.25	104	26%	200	9%	303	60%
0.1g	42.5	179	83%	195	5%	374	74%
0.1g	42.5	192	72%	211	9%	403	80%

Table 3 affect of liquid to solid ratios on recovery

The Table illustrates, as the liquid to solid volumes are increased, the recoveries are also increased. However this also leads to an increase in the variance seen in the method. The statistics are based on a sample size of 3 (N=3).

Extract Variable Volume Experiment

To further improve recoveries, the same liquid to solid ratios were maintained but with an increase in the volume of extract solution and sample size. Total extraction solutions of 42.5 mL, 68 mL and 75 mL were tested with sample sizes of 0.1 g, 0.16 g and 0.2 g respectively. The results are listed in Table 4 below.

Mass	Vol. ml	Dilution Factor	Cr (III) ppm	Cr (VI) ppm	Total Cr	%CV	Recovery
0.1 g	42.5	1:100	195	206	401	17%	79.7%
0.1 g	42.5	1:125	233	187	420	4%	83.5%
0.16 g	68	1:100	240	181	421	11%	83.8%
0.16 g	68	1:125	268	190	458	11%	91.0%
0.2 g	75	1:100	225	154	379	4%	75.3%
0.2 g	75	1:125	260	168	428	2%	85.1%

Table 4: Affect of sample size on recovery efficiency

Based on the highest recoveries, in conjunction with the lowest variance, a 75 mL extract solution (60 mL H₂O and 15 mL NaOH), 0.2 g soil sample size and 1:125 dilution factor was selected for further experimentation because they results indicated that these were the optimum conditions for the extraction. The optimized extraction method was then used on the other three soils sampled by NJDEP to demonstrate how well the method performs on different soil types. Table 5 below illustrates the results.

Sample Name	Cr (III)	Cr (VI)	Total Cr	%CV	Recovery
Gateway	247	248	495	0.10	8%
Society Hill	291	53	344	0.15	7%
PPG Garfield Ave	229	60	289	0.04	10%

Table 5: Optimized liquid to solid ratio extraction conditions on recovery of chromium from other soil types

These optimized extraction conditions did not translate well to the other soil sample types. It is possible that the type of soil is playing a role. The Garfield Avenue soil was visually comparable to the Liberty State Park Soils, The Gateway soil had the consistency of sand and appeared to be primarily inorganic material while the Society Hill sample had a high percentage of organic or plant matter.

To increase recoveries the pressure was increased to 20 psi. The results are shown in Table 6 below.

Sample Name	Cr (III)	Cr (VI)	Total Cr	%CV	Recovery
Gateway	328	266	536	14.8%	8.2%
Society Hill	332	70	403	4.5%	7.6%
PPG Garfield Ave	313	57	369	2.0%	12.5%

Table 6: Recovery with increased pressure in extraction vessel

While the recoveries did increase, the increase was only slight. To further improve recoveries the same soil sample and extract was run through the microwave extraction program three times.

Sample Name	Cr (III)	Cr (VI)	Total Cr	%CV	Recovery
Gateway	267	778	1045	17.6%	15.9%
Society Hill	499	57	556	50.6%	10.5%
PPG Garfield Ave	265	288	553	35.0%	18.7%

Table 7: Effect of recovery with multiple replicate extraction steps using the microwave technique.

The recoveries increased but are still considerably lower when compared to the recoveries for the Liberty State Park samples. To increase recoveries an acidic extraction was initiated. The rationale was that a large portion of trivalent chromium is complexed to hydroxyl groups and that sodium hydroxide could not extract hydroxides out of the soil. Nitric acid solutions of varying strengths were tried. The same liquid to solid ratio was kept as outlined above but 50 mL of extract solution was used. The acid solutions in order of most acidic to least examined were: 7%, 3.5%, 1%, 0.5%, pH 3 and pH4. The PPG Garfield Avenue soil was selected for the experiment. Only trivalent chromium was recovered from these samples. The solutions were too acidic for Hexavalent chromium to be recovered. The recoveries range from 22.7% for a 7% nitric acid extract solution to 15.3% for the pH of 4 nitric acid solution.

Serial Extraction Experiment

To further improve recoveries a serial extraction scheme was examined. The serial extraction scheme would first extract chromium from the soil using basic extraction methods, to remove Hexavalent chromium. The soil would then be extracted using an acidic extraction scheme to remove trivalent chromium. Table 3 lists the extraction schemes that were tested. For basic extractions the samples were prepared as outlined

in the Table. After the extraction the samples pH was lowered to 6 by HNO₃ addition and then injected into the IC-ICP/MS system.

		Basic Extractions	
Acid Extraction	Digestion	Method A	Method B
25 mL H ₂ O	(Tool Steel)	2.2 g Na ₂ CO ₃	2.2 g Na ₂ CO ₃
25 mL HNO ₃	10 mL HNO ₃	60 mL H ₂ O	60 mL H ₂ O
60 min	25 min	75 mL NaOH	75 mL NaOH
105C	180C	60 min	60 min
25 psi	no press monitor	95C	105C
300 W	1200W	no press monitor	25 psi
		300W	300W

Table 8: Acid and Basic Extraction Protocols

Basic Extraction	Acid Extraction	Base Cr (III)	Base Cr (VI)	Acid Cr (III)	Total Cr	Percent Recoveries
A	n	47	227	1107	1382	46.8
A	Digestion	89	222	1743	2054	69.6
A	n	103	243	845	1190	40.4
A	Digestion	0	303	1371	1674	56.8
B	n	40	215	1048	1304	44.2
B	Digestion	0	233	1298	1531	51.9
B	n	47	228	937	1212	41.1
B	Digestion	84	235	1824	2143	72.7

Table 9: Recoveries of Total Chromium with Acid Extraction Following Basic Extraction

The solution was then filtered, under slight vacuum. The soil was collected on Whatman Hardened Ashless Circles (70 mm diameter). The filter paper was weighted pre and post filtering to measure the amount of soil collected. The filter paper was then desiccated for 24 hours before being extracted using the acid extraction methods listed in Table 8.

Acid Strength Modification Experiment

Recoveries are increased considerably over the single extraction method. The recoveries are still less than that for the Liberty State Park samples. The Tool Steel

method was used for both the measuring of total chromium and here in the serial extraction. Despite this the recoveries for the serial extraction are still well below the total amount determined by the Tool Steel method. It has been noted that upon addition of base, trivalent chromium forms a precipitate. The recoveries of total chromium were expected to be greater because the Cr (III) remaining after extraction with base should have been solubilized by the rigorous acid extraction conditions described in Table 9. Poorer recoveries for these samples suggest that the matrix plays a much greater role in extraction efficiency than either acid or base used to extract the chromium species.

To see if recoveries could be improved, aqua regia, in conjunction with the Tool Steel method, instead of nitric acid alone. Aqua regia is 3 parts hydrochloric acid and one part nitric acid, or in this case 7.5 mL of hydrochloric and 2.5 mL of nitric acid. This acid extraction solution should be more aggressive in extracting the chromium form the soil sample matrix.

Samples were first extracted using the basic extraction method at 105°C and 25 psi. After injection into the IC-ICP/MS system the extract was passed through filter paper (70 mm, Whatman Hardened Ashless Circles). Ten milliliters of aqua regia was then added to the soils and digested using Tool Steel. The extracts were diluted 200 times before injection. Results are summarized in Table 10 below.

	Cr (VI) Base	Cr (III) Base	Cr (III) Acid	Total Cr	Recovery
ppm	172	174	1382	1727	58.50%
%CV	47.5%	55.4%	6.1 %		

Table 10: Recovery of Total Chromium Using Acid to Extract Residual Cr (III)

The recoveries are still less than with the previous serial extraction scheme (72.7%). The missing chromium could be in the form of the trivalent precipitate. The precipitate is too small to be contained by the filter paper used and thus passes through with the filtrate.

Base Strength Modification Experiment

The strength of the basic extraction solution was varied to see if chromium recoveries improved. An increase in the strength of the acidic extraction solution did increase recoveries for trivalent chromium in the various soils; therefore it may be possible that an increase in basic strength utilized in the extraction could increase recoveries for Hexavalent chromium. The possibility also existed that an increase in the strength of the sodium hydroxide would lead to more trivalent chromium precipitating out, thus lowering recoveries. The previous extraction had 15 mL of 2.5 M NaOH and 60 mL of H₂O as the extraction solution, or a 20% NaOH solution. This was tested along with a 50% NaOH solution (30 mL of each 2.5 M NaOH and H₂O) as well as a 100% 2.5 M NaOH solution (20 mL of 2.5 M NaOH, 0 mL of H₂O).

Dilution factors also have played a role in recoveries, as discussed previously. With the greater the dilution factor greater chromium recoveries were observed. The Garfield Avenue soils were diluted ten times using silica, i.e. 0.2 g of soil was mixed with 1.8 g of silica. The soils were first extracted using the increased in base concentration with the microwave conditions at 130°C and 50 psi. After extraction was completed the samples were acidified with nitric acid and then injected into the IC-ICP/MS system. The extracts were then passed through filter paper and desiccated to collect the soil/silica. After desiccation for 24 hours the samples were digested using acid and the Oyster Tissue method, a method that is not as rigorous as Tool Steel to prolong the lifetime of the reaction vessels. Oyster Tissue digests the samples for 30 minutes at 300 psi and 200°C. Results are shown in the Table 11 below.

20% NaOH					
	Cr (VI) Base	Cr (III) Base	Cr (III) Acid	Total Cr	Recovery
PPM	398	42	54	495	16.80%
%CV	6.5%	92.4%	18.6%		
50% NaOH					
	Cr (VI)	Cr (III)	Cr (III) Acid	Total Cr	Recovery
PPM	307	41	29	377	12.80%
%CV	2.6%	43.1%	52.1%		
100% NaOH					
	Cr (VI)	Cr (III)	Cr (III) Acid	Total Cr	Recovery
PPM	100	126	23	248	8.40%
%CV	4.6%	52.8%	63.1%		

Table 11 Effect of base strength on extraction efficiency for Cr species

This series of experiments demonstrated that an increase in the strength of base does not increase the recoveries for Hexavalent chromium; in fact the recoveries were decreased. The variability in replicate analysis was also increased, most likely because of the silica sand addition to the soil sample matrix. It is clear from this experimental sequence that the dilution of soil samples using silica sand did not increase chromium recoveries. The Oyster Tissue acid digestion method also provided lower recoveries when compared to Tool Steel method of extraction. Using the Tool Steel method the PFA Teflon hi pressure vessels can be used about 15 to 20 times before they begin to warp, this method complication adds significant cost to any high throughput chromium analysis.

Alternative Buffered Base Chromium Extraction Experiment

In an effort to explore alternative extractant solutions, a buffer solution of boric acid and borax (sodium tetraborate) provided an alternative to the extraction solutions outlined above. The first soil extraction uses a Na₂B₄O₇·10H₂O (borax) solution containing 9.5 g of borax dissolved in 500 mL of water as a stock solution. This primary extraction was accomplished on the three soil types provided by NJDEP (Gateway, Society Hill, and Garfield Ave). Fifty milliliters (50 ml) of the solution was used for extraction on 0.2 g of each soil. The microwave extraction conditions were 60 minutes, 105°C at 25 psi. The results are shown below in Table 12.

Sample Name	Cr (VI)	%CV	Cr (III)	%CV	Total	Recovery
Gateway	106.7	8.1%	8.4	28.2%	115.1	1.80%
Society Hill	40.6	8.8%	13.6	17.6%	54.2	1.00%
PPG Garfield Ave	32.7	21.8%	12.8	21.2%	45.5	1.50%

Table 12: Total Cr extraction efficiency using the optimized extraction method for multiple samples collected from Locations in Jersey City.

Total recovery is based on a sum of the Cr III and Cr VI values as compared to the Cr recovered from a concentrated acid extraction. From these experimental results the borax extract solution is not adequate enough for the recovery of chromium.

Ionic Strength and Insoluble Complex Formation Effects on Recovery of Chromium in Soil

The ionic strength of the solution plays an important role in what state chromium is in, reduced or oxidized, and how much is recoverable. The elements of the most concern are titanium, vanadium, lead, barium, manganese and iron. Titanium and vanadium are of concern because they create an isobaric interference with ⁵⁰Cr. Lead and barium form insoluble complexes with hexavalent chromium, PbCrO₄ and BaCrO₄ respectively. Under alkaline conditions, in the presence of a bicarbonate buffer, the complexes will free the hexavalent chromium and form either BaCO₃ or Pb(OH)₂ (4). Iron, as well as fulvic and humic acids, sulfides and various microorganisms will reduce hexavalent chromium to trivalent chromium (5). Manganese will oxidize trivalent chromium to hexavalent chromium (6). In addition Cr III can be converted in the dry solid form to Cr VI by atmospheric oxygen (6). This reaction happens over the course of a few days under a wide range of pH and chromium concentrations.

As reported previously, the concentrations of sixteen elements were determined for all four soils using ICP/MS. The highest recoveries were obtained for the Liberty State Park soils, so its elemental composition was compared to that of the other three soils. The Liberty State Park soils had lower concentrations of aluminum, strontium and barium compared to the majority of other soil types.

Cation Spike Experiments

To test the affect of ionic strength on chromium recoveries, aluminum, in the form of aluminum nitrate, was added to Liberty State Park soils. To increase the concentration of aluminum in the solutions 0.2 g of soil was mixed with 0.8 g of aluminum nitrate and extracted using the basic extraction method. The experiment was run in triplicate and the results are presented below in [Table 13](#). All values are present in parts per million (ppm).

Liberty	Cr (VI)	Cr (III)	Total	Recov
Replicate 1	439.1	24.7	463.8	92.2%
Replicate 2	61.4	725.4	786.8	156.4%
Replicate 3	85.1	155.5	240.6	47.8%
Average	195.2	301.9	497.1	98.8%
%CV	108.4%	123.4%	55.2%	

Table 13: Effect of Aluminum on extraction efficiency for three replicate samples

Aluminum addition increases the variability of the method. Its effects on recoveries aren't certain since the average of the three runs, 497.1 ppm, is close to the actual value, 503 ppm.

Next the affects of iron, lead and barium on recoveries of chromium were tested. Two pseudo-soil samples were created. The first contained iron and aluminum (in the form of ferric oxide and aluminum nitrate). These two elements were diluted using silica so that they both had a concentration of 17,700 ppm, or the concentration the respective elements have in the Liberty State Park soils. The second sample contained lead and barium (in the form of lead acetate and barium nitrate). They were diluted with silica so that they had concentrations of 1118.4 and 123.3 ppm respectively, to mimic the same concentration as encountered in Liberty State Park soils. The soils were then divided in half and spiked with hexavalent and trivalent chromium. Half a gram of soil was then extracted using the basic method. Each chromium sample had an initial concentration of 20 ppb. Before the extracts were analyzed a 20 ppb spike of hexavalent and trivalent chromium was injected into the IC-ICP/MS. The two soils were spiked separately with 20 ppb trivalent and hexavalent chromium each and injected into the IC-ICP/MS before extraction to determine the affect of the ions on chromium prior to extraction. All experiments were performed in triplicate.

First the ability to recover the species from a liquid matrix was examined. Without extraction hexavalent chromium had a recovery of 94.7% with a CV of 0.9%. Trivalent chromium had a recovery of 119.1% with a CV of 2.2%, showing that both species can be recovered reproducibly. Upon extraction hexavalent chromium had a recovery of 80.6% while trivalent chromium had a recovery of 40.0%. The low recoveries for trivalent chromium once again reflect the formation of the precipitate.

Lead and Barium Spikes

The lead and barium pseudo-soil was then tested. No hexavalent chromium was recovered from the hexavalent chromium spike sample that was applied before extraction. After extraction 8.3 ppb of the 20 ppb, (41.5 %), hexavalent chromium spike was recovered, with a CV of 71.7%. These preliminary results indicate that lead and barium bind hexavalent chromium and make it unavailable for extraction as seen in the first experiment. The addition of bicarbonate and base should free the hexavalent chromium by competitive ion exchange. In this experiment less than half of the

Hexavalent chromium was freed from the complexes formed with barium and lead. As seen by the coefficient of variance, the amount recovered was not reproducible. The soil spiked with trivalent chromium had a recovery of 103.6% with a CV of 6.7% before extraction. This shows that lead and barium do not exert an effect on the recovery of trivalent chromium. After extraction only 8.7 ppb of the 20 ppb spike of trivalent chromium was recovered. This is a 43.5% recovery for Cr (III) and on par to the recoveries seen for trivalent chromium extracted with a basic extraction protocol.

Aluminum and Iron Spikes

The aluminum and iron pseudo-soil was then tested. Before extraction 4.6 ppb of hexavalent chromium and 3.2 ppb of trivalent chromium, with CVs of 1.1% and 6.3% respectively, were recovered from the 20 ppb hexavalent chromium spike. Iron reduces hexavalent chromium to the trivalent state so it is not surprising to recover trivalent chromium. It is a bit surprising that only 7.8 ppb of the total chromium spike was recovered, or 39%. The trivalent chromium spiked sample had a recovery of 99.7% with a CV of 3.3% for trivalent chromium. The recoveries and reproducibility are acceptable meaning that aluminum and iron probably do not have that much of an effect on trivalent chromium.

Upon extraction under basic conditions 5.9 ppb of hexavalent and 5.7 ppb of trivalent chromium were recovered from the 20 ppb hexavalent chromium spike. It is seen that hexavalent chromium is once again reduced to trivalent chromium. The recovery is also increased, to 58%, upon basic extraction. The CVs however were large, 115% for hexavalent chromium and 56.6% for trivalent chromium. This is also observed in an experiment where aluminum nitrate was mixed with the Liberty State Park soils, demonstrating that aluminum, upon basic extraction, produces conditions in the extract that increase the experimental variability.

The most surprising results were obtained for the basic extraction of the trivalent chromium spike. More hexavalent chromium, 7.7 ppb, was recovered than in any of the other experiments involving aluminum and iron. The CV was quite high again, 64.5%. The amount of trivalent chromium recovered was low, 1.6 ppb with a CV of 17.3%. It is possible that the basic extraction conditions precipitated out the trivalent chromium once again.

Stable Isotopes

Stable isotopes of $^{53}\text{Cr(VI)}$ and $^{50}\text{Cr(III)}$ can be used to measure the interconversion between the two species during the extraction process. A four point calibration curve (2, 5, 10 and 20 ppb) was created for each of the stable isotope solutions ($^{53}\text{Cr(VI)}$ and $^{50}\text{Cr(III)}$), and direct injection of standard into the IC-ICP/MS.

Next the ability to recover the stable isotopes from a liquid matrix and then spiked onto silica was examined. The solutions were spiked into separate vessels and done in triplicate. The basic extraction scheme was used for extraction. A spike of 10 ppb was used for all samples. The area and recoveries, after correction for abundance and masses, is shown in the Table 14 below.

	Cr (III)	Cr (VI)	Recovery
53 Cr (VI) no silica	97587.7	100774.4	123.4%
53 Cr (VI) silica	95651.5	57082.8	95.0%
50 Cr (III) no silica	162140.9	2116.0	69.7%
50 Cr (III) silica	80685.4	16862.1	41.4%

Table 14: Extraction efficiency measured with stable isotopes spiked onto silica

Recoveries are within acceptable ranges for the ⁵³Cr(VI) spikes. Recoveries were lower than acceptable for the ⁵⁰Cr(III) spikes, most likely due to the precipitate that forms when base is added to trivalent chromium.

Comparing the silica blank chromatogram to that of the ⁵⁰Cr(III) spike shows that some interconversion, in the form of oxidation of trivalent chromium to hexavalent chromium occurs. This oxidation seems to take place more so when silica provides a surface for the reaction to occur. Using the extraction method no interconversion, in the form of reduction of hexavalent chromium to trivalent chromium, occurs.

Next the standards were spiked onto the Liberty State Park soils. Two milliliters of the 10 ppb standards were separately spiked onto Liberty soils diluted with silica. This spike provided a 266 ppb concentration of ⁵⁰Cr(III) and ⁵³Cr(VI). Figure 8 shows a chromatogram of an unspiked Liberty soil sample. Figure 9 and 10 shows chromatograms of the ⁵³Cr(VI) and ⁵⁰Cr(III) spikes respectively. Once again the graphs show that trivalent chromium will oxidize to hexavalent chromium but hexavalent chromium does not reduce to trivalent chromium, under the basic extraction conditions attempted here. Table 15 below, shows the corrected counts and concentrations of the species when dilution factors and calibration curves are applied.

⁵⁰ Cr (III) spike	Counts	%CV	% Recovery
⁵⁰ Cr (III)	139833	6.6%	
⁵⁰ Cr (VI)	12763	9.9%	63.8%
⁵³ Cr (VI) spike	Counts	%CV	% Recovery
⁵³ Cr (III)	0	0.0%	
⁵³ Cr (VI)	38436	23.0%	30.7%

Table 15 Stable Isotope Recovery from Liberty State Park Soil

From the corrected counts it can be calculated that 8.4% of the total Chromium recovered interconverted from ⁵⁰Cr(III) to ⁵⁰Cr(VI). It was expected that under the basic conditions used here some of the trivalent chromium would convert to hexavalent chromium. The recoveries for the trivalent chromium spike are on par with those recoveries for extraction from a liquid matrix and spiked onto silica. The missing chromium in that experiment has likely been precipitated out of solution.

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Appendix 1

Data from Interlaboratory Study on Quantitation Chromium Species in Standard Reference Material

	6800 aver	Round 1		Round 2		7196A ave	Round 1		Round 2		7199 ave	Round 1		Round 2	
		sd	6800 ave	sd			sd	7196A ave	sd			sd	7199 ave	sd	7199 ave
Lab 1	543	14.6	534	1.0											
Lab 2											348	15.7			
Lab 3						404	25.2				384	17.0			
Lab 4								392	15.0						
Lab 5												547	5.8		
Lab 6								75							
Lab 7								320							
Lab 8								261				269			
Lab 9								491							
Lab 10								345							
Lab 11								358	31.5						
Lab 12								334	80.8						
Lab 13			534												
Lab 14								265	36.1						
Lab 15								332							
Lab 16			509								352	20.4	361	11.4	
Lab 17	548	21.3	558	9.0		494	38.8								
Lab 18	514	21.1	539	4.0		308	18.4								
Lab 19											398	3.0	431	24.3	
Lab 20						404	19.0	460	6.7		453	15.9	386	12.2	
Lab 21											360	50.6	406	6.1	
						eliminated by Q test									
Overall mean Std	540	24.9	540	15.0		403	80.1	378	64.1		383	38.8	429	79.5	

	Method			Percent difference	
	6800	7196A	7199	$\frac{6800 - 7196}{7196}$	$\frac{6800 - 7199}{7199}$
Total R1 + R2	540	393	394	31.6%	31.6%
Average	540	393	394	31.6%	31.6%
STD	22.2	81.3	54.6		

Appendix 2

Abridged version of NIST 2701 SRM Chromium VI in a Contaminated Soil Matrix



National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material[®] 2701

Hexavalent Chromium in Contaminated Soil (High Level)

This Standard Reference Material (SRM) is intended primarily for use in the analysis of waste, soils, sediments, or other materials of a similar matrix. SRM 2701 is a soil, heavily contaminated with chromite ore processing residue (COPR) that has been air-dried, sieved, radiation sterilized, and blended to achieve a high degree of homogeneity. All constituents in SRM 2701 for which certified reference and information values are provided were naturally present in the material before processing. A unit of SRM 2701 consists of approximately 75 g of the dried, radiation-sterilized material in a brown screw-capped glass bottle.

Certified Values: The certified concentrations of hexavalent chromium, total chromium and iron in SRM 2701 are given in Table 1. The certified values are based on the agreement of results from two or more independent analytical measurements at NIST and collaborating expert laboratories. A NIST certified value is a value for which NIST has the highest confidence in its accuracy in that all known or suspected sources of bias have been investigated or accounted for by NIST [1]. The certified value for hexavalent chromium is the un-weighted mean of analytical measurements by NIST and three participating expert laboratories. The value is based on the extraction of hexavalent chromium from the material using an approved U.S. Environmental Protection Agency (U.S. EPA) SW-846 analytical method (Method 3060A) which was used by all participating laboratories. The certified values for both total chromium and iron are the un-weighted means of three independent analytical methods at NIST. Each result is expressed as the certified value \pm expanded uncertainty, U , calculated as $U = ku_c$, where u_c is the combined standard uncertainty calculated according to the ISO and NIST guides [2]. The value of u_c is intended to represent, at the level of one standard deviation, the combined effects of inherent sources of uncertainty of the measurements and corrections for interferences and species inter-conversions (hexavalent chromium). The value of the coverage factor, k , is equal to 2, which corresponds to a level of confidence of approximately 95 %.

Expiration of Certification: The certification of SRM 2701 is valid within the measurement uncertainties specified until **31 December 2013**, provided the SRM is handled and stored in accordance with the instructions given in this certificate (see *Instructions for Use*). The certification is nullified if the SRM is damaged, contaminated or otherwise modified.

Maintenance of SRM Certification: NIST will monitor this SRM over the period of its certification. If substantive technical changes occur that affect the certification before the expiration of this certificate, NIST will notify the purchaser. Return of the attached registration card will facilitate notification.

Coordination of the technical measurements leading to the certification of SRM 2701 was provided by S.E. Long of the NIST Analytical Chemistry Division.

Analytical measurements at NIST were performed by W.C Davis, W.R. Kelly, S.E. Long, J.L. Mann, A.F. Marlow, K.E. Murphy, R.L. Paul and J.R. Sieber of the NIST Analytical Chemistry Division.

Stephen A. Wise, Chief
Analytical Chemistry Division

Gaithersburg, MD 20899

Certificate Issue Date: 1 July 2008

See Certificate Revision History on Last Page

The material was collected by S.E. Long of the NIST Analytical Chemistry Division and B.S. MacDonald of the NIST Measurement Services Division in collaboration with S.J. Nagourney of the New Jersey Department of Environmental Protection (NJDEP), Office of Quality Assurance (OQA).

Robert L. Watters, Jr., Chief
Measurement Services Division

Statistical consultation was provided by Z.Q.J. Lu of the NIST Statistical Engineering Division.

The technical and support aspects involved in the issuance of this SRM were coordinated through the NIST Measurement Services Division.

Table 1: Certified Values for SRM 2701

Hexavalent Cr	551.2	mg/kg	±	34.5	mg/kg
Total Cr (mass fraction)	4.26	%	±	0.12	%
Fe (mass fraction)	23.73	%	±	0.19	%

Reference Values: Reference concentration values for aluminum, calcium, potassium, magnesium, manganese, sodium, silicon, titanium and vanadium are provided in Table 2. Reference values are non-certified values that are the best estimate of the true value; however, the values do not meet NIST criteria for certification and are provided with associated uncertainties that may reflect only measurement precision, may not include all sources of uncertainty, or may reflect a lack of sufficient statistical agreement among multiple analytical methods [1].

Table 2: Reference Values for Concentrations of Selected Elements

Element	Mass Fraction, %	Element	Mass Fraction, %
Al	5.05 ± 0.15	Na	0.255 ± 0.005
Ca	7.47 ± 0.09	Si	4.17 ± 0.04
K	0.174 ± 0.007	Ti	0.547 ± 0.008
Mg	7.47 ± 0.17	V	0.236 ± 0.011
Mn	0.213 ± 0.006		

Information Values: Information values for sulfide, total organic carbon (TOC), chemical oxygen demand (COD), pH and oxidation/reduction potential are provided in Table 3 as additional information on the composition and properties of the material. An information value is considered to be a value that will be of interest and use to the SRM user, but for which insufficient information is available to assess adequately the uncertainty associated with the value, or only a limited number of analyses were performed [1].

Table 3: Information Values for Selected Species and Properties

Species/Property	Value	Unit
Chemical oxygen demand (COD)	<10	mg/kg
Redox potential	526	mV
Sulfide	<10	mg/kg
Total organic carbon (TOC)	36900	mg/kg

pH

9.57

std. units

Analytical Methods: The analytical methods used for the analysis of SRM 2701 are listed in Table 4.

Table 4: Analytical Methods Used for Certified and Reference Values in SRM 2701

Analyte	Methods
Hexavalent Cr	U.S. EPA Method 3060A [3] and U.S. EPA Method 6800 [3] U.S. EPA Method 3060A [3] and speciated isotope dilution inductively coupled plasma mass spectrometry (SID-ICP-MS) [4]
Total Cr	Isotope dilution inductively coupled plasma mass spectrometry (ID-ICP-MS) [5] X-Ray fluorescence spectrometry (XRF) following borate fusion preparation Instrumental neutron activation analysis (INAA)
Fe	X-Ray fluorescence spectrometry (XRF) following borate fusion preparation Instrumental neutron activation analysis (INAA) Prompt gamma activation analysis (PGAA)
Al, Ca, K, Mg, Mn, Na, Si, Ti, V	X-Ray fluorescence spectrometry (XRF) following borate fusion preparation

NOTICE AND WARNINGS TO USERS

Storage: SRM 2701 must be stored in its original bottle tightly capped at temperatures less than 30 °C and away from light.

Handling: This material is a waste ore that contains a significant amount of hexavalent chromium. **HEXAVALENT CHROMIUM IS A KNOWN CARCINOGEN.** Due caution and care should be exercised during its handling and use. This material has been processed to maintain homogeneity and is composed of a particle size distribution that is readily respirable. Stringent precautions should be taken to avoid inhalation of dust during material transfer and in the event of bottle breakage or compromise of the lid seal.

INSTRUCTIONS FOR USE

Use: A minimum sample weight of 200 mg (dry weight - see Instructions for Drying) should be used for analytical determinations to be related to the certified values on this Certificate of Analysis. Prior to use, the contents of the bottle should be thoroughly mixed by gently rotating the bottle by hand and inverting several times. As this process may generate electrostatic charges, caution should be observed when opening the bottle to avoid accidental exposure to the contents.

Instructions for Drying: Samples should be dried for 2 h at 110 °C in a laboratory convection oven to obtain a correction factor for moisture. Correction for moisture is to be made to the data before comparison with the certified values. The approximate weight loss on drying has been found to be in the range of 1.9 % to 2.3 % (n=6), with a mean of 1.93 %.

Source and Preparation of Material: The material was processed by S.A. Wilson of the United States Geological Survey (USGS) under contract to NIST. The source material for the candidate SRM 2701 was

chromite ore contaminated soil from a location in Hudson County, New Jersey. Material was acquired from a three acre site behind the Interpretative Center at the Liberty Science Center in Liberty State Park in Jersey City. Using a mechanical excavator, samples of soil were collected in metal drums fitted with polyethylene liners to prevent contact between the material and the surface of the drums. The drums were then sealed and shipped to the USGS in Arvada, CO for processing. At the USGS, the soil was removed from the drums, transferred onto plastic lined cardboard trays and dried in a forced air oven operating at room temperature for three days. Once dry, the material was transferred into a series of plastic-lined, five-gallon buckets. The material was then mechanically disaggregated using a ceramic auger and grinding bowl. The oversized material was separated from the soil fraction by sieving through a vibrating 2 mm screen. The less than 2 mm fraction was then ground in 25 kg batches using a ceramic lined ball mill and corundum grinding media for a period of 8 h. The ground material was transferred to a series of five-gallon containers and sealed prior to gamma radiation sterilization at an average dosage rate of 39.1 kGy per container. Upon return to the USGS, the material was transferred to a 10 ft³ cross-flow V-blender and allowed to mix for 24 h. The blended material was then finally split into 4 oz. brown glass screw-capped bottles using a custom-designed spinning riffler.

Homogeneity: The homogeneity of SRM 2701 was assessed by analyzing duplicate samples from twenty bottles selected by stratified random sampling. The material was pressed into briquettes and analyzed by wavelength dispersive X-ray fluorescence spectrometry using 20 selected elemental constituents as indicators. The data were subjected to analysis of variance (ANOVA) testing. The findings for between bottle heterogeneity indicated that, at the 95 % confidence level, none of the bottles exhibited statistically significant differences from the rest of the population of the sampled bottles with the exception of Cu. For chromium, the relative standard deviation (RSD) of the measurements was less than 1 % for an estimated sample size of 170 mg. All elements listed in Table 2 also had RSDs of less than 1 % with the exception of sodium which had an RSD of 1.9 % for an estimated sample size of 3 mg.

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Appendix A

Multi-laboratory Testing Using Approved U.S. EPA Analytical Methods: Method 3060A, 7196A, Method 7199 (Hexavalent Chromium), Method 3050 (Leachable Chromium) and Method 3052 (Total Chromium)

The certified values of inorganic constituents in most National Institute of Standards and Technology (NIST) chemical composition Standard Reference Materials (SRMs) reflect the total absolute concentration of each measurand in the given SRM matrix. The certified concentrations are based on rigorous measurements obtained by well-characterized primary methods, or two or more independent methods or techniques. If dissolution of the matrix is necessary, the measurement approach generally requires complete sample decomposition, which can usually be achieved in a high-pressure digestion system such as a Carius tube. Alternatively and where applicable, the sample may also be analyzed nondestructively.

For environmental monitoring purposes, the concentrations of labile or extractable fractions of elements are often more useful than total concentrations. Concentrations of labile or extractable fractions are generally determined using relatively mild leach conditions, which are unlikely to totally decompose the sample. Reported concentrations of labile or extractable fractions of elements are generally lower than total absolute concentrations; recovery can be total only if an element in a given sample is completely labile. The recovery of an element as a percentage of the total concentration is a function of several factors which are defined by the sample matrix and the measurement method conditions.

In its monitoring programs, the U.S. Environmental Protection Agency (EPA) has promulgated a number of analytical methods to determine toxic elements, or element species, in soils, sediments and sludges. The EPA publication SW-846, entitled *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*, [3] is the official compendium of analytical and sampling methods compiled by the EPA Office of Solid Waste (OSW). The methods have been evaluated and approved for use in permit monitoring in accordance with the 1976 Resource Conservation and Recovery Act (RCRA). SW-846 Methods 3060A, 7196A and 7199 are applicable to the measurement of hexavalent chromium, while Methods 3050 and 3052 are applicable to measurements of leachable chromium and total chromium respectively. Method 3060A is currently the best available analytical method for the extraction of hexavalent chromium from solid matrices, and preservation of the oxidation state prior to analytical determinations using other finishing methods such as 7196A (colorimetric) and 7199 (ion chromatography with post-column derivatization). Method 3060A was used as the common basis for the certified value of hexavalent chromium in SRM 2701. Method 3050 is a strong acid leachable digestion method intended for the dissolution of elements which are environmentally available, while Method 3052 employs microwave assisted digestion of solid samples, which is intended to provide almost complete decomposition of the sample, including silica, primarily using concentrated nitric acid and hydrofluoric acid combined with microwave heating.

To assess the performance of these SW-846 methods for the determination of hexavalent chromium and total chromium in SRM 2701 and to provide data which are relevant to users of these SW-846 methods, a multi-laboratory testing program was established jointly by NIST and the New Jersey Department of Environmental Protection (NJDEP), Office of Quality Assurance (OQA). Stratified random samples of SRM 2701 were distributed to a number of cooperating laboratories who were asked to measure the hexavalent chromium concentration in the material and/or the total chromium. The names of the cooperating laboratories are listed in Table 5 of the Certificate of Analysis. Several laboratories provided replicate analyses for each data set from which the mean was calculated. The means of all the data sets forwarded by each laboratory are compiled by method in Table A1 and include summary statistics together with the % recovery relative to the certified value.

Please note that none of the values in Table A1 are certified, but are given as information on the typical relative performance of the various EPA SW-846 methods for the determination of hexavalent chromium and total chromium in SRM 2701. The data should not be used for any other purpose. **The certified values, provided in the Certificate of Analysis, are the best estimates of the true concentrations.**

Table A1. Multi-laboratory Concentration Data for SRM 2701 by SW-846 Methods

Data Set	Method 7196A Hexavalent Cr mg/kg	Method 7199 Hexavalent Cr mg/kg	Method 3050 Leachable Cr % mass fraction	Method 3052 Total Cr % mass fraction
1	503.8	389.1	0.294	1.025
2	314.3	354.4	0.384	
3	415.7	461.6	0.465	
4	408.7	391.1	0.514	
5	399.9	405.7	0.317	
6	326.2	363.3	0.255	
7	266.0	358.6	0.360	
8	500.5	557.2	0.597	
9	351.7	414.2	0.441	
10	364.9	274.2	0.833	
11	336.7	393.8	0.236	
12	469.2	439.3	0.235	
13	338.4	270.4		
14		368.3		
Mean	384.3	388.7	0.411	1.025
SD ^a	73.5	72.1	0.175	
RSD ^b	19.1	18.5	42.7	
Median	364.9	390.1	0.372	
Minimum	266.0	270.4	0.235	1.025
Maximum	503.8	557.2	0.833	1.025
# Labs ^c	12	10	10	1
# Measurements ^d	13	14	12	1
Recovery (%) ^e	69.7	70.5	9.6	24.1

^a standard deviation

^b relative standard deviation

^c number of laboratories reporting data sets

^d number of data sets reported by all laboratories

^e mean recovery for the method relative to the certified value expressed as a percentage