



National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material[®] 2700

Hexavalent Chromium in Contaminated Soil (Low 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 2700 is a soil matrix, contaminated with chromite ore processing residue (COPR) that has been air-dried, sieved, radiation sterilized, and blended to achieve a high degree of homogeneity. A unit of SRM 2700 consists of approximately 75 g of the dried, radiation-sterilized material in an amber screw-capped glass bottle.

Certified Values: The certified mass fractions on a dry-mass basis of hexavalent chromium, total chromium, iron and manganese in SRM 2700 are provided in Table 1. The certified values are based on critically evaluated independent analytical techniques. 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 taken into account [1]. The measurands are the mass fractions of the elements reported in Table 1. Metrological traceability is to the SI unit for mass, expressed as a mass fraction.

Reference Values: Reference mass fraction values on a dry-mass basis of aluminum, calcium, potassium, magnesium, sodium, silicon, titanium, vanadium and zinc 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]. The measurands in Table 2 are the mass fractions of the elements as determined by the methods indicated. Metrological traceability is to the SI unit for mass, expressed as a mass fraction.

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]. Information values cannot be used to establish metrological traceability.

Expiration of Certification: The certification of **SRM 2700** is valid, within the measurement uncertainty specified, until **01 July 2020**, provided the SRM is handled and stored in accordance with the instructions given in this certificate (see "Instructions for Storage and 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. Registration (see attached sheet or register online) will facilitate notification.

Coordination of the technical measurements leading to the certification of SRM 2700 was provided by S.E. Long of the NIST Chemical Sciences Division.

Analytical measurements at NIST were performed by W.C. Davis, A.F. Marlow, R.O. Oflaz, J.R. Sieber, B.E. Tomlin, and L.J. Wood of the NIST Chemical Sciences Division and J. Malherbe and D.J. O'Kelly formerly of NIST.

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Certificate Issue Date: 02 September 2015

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Information values are based on data supplied by M. Perry of Columbia Analytical Services (Rochester, NY).

Material was collected by S.E. Long and B.S. MacDonald, formerly of NIST, in collaboration with S.J. Nagourney of the New Jersey Department of Environmental Protection (NJDEP), Office of Quality Assurance (OQA).

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

Support aspects involved in the issuance of this SRM were coordinated through the NIST Office of Reference Materials.

NOTICE AND WARNINGS TO USERS

This material is derived from 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 STORAGE AND USE

Storage: SRM 2700 must be stored in its original bottle tightly capped at temperatures less than 30 °C and away from light.

Use: A minimum sample mass of 500 mg should be used for analytical determinations to be related to the certified values on this certificate. 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. The mass fractions of constituents in SRM 2700 are reported on a dry-mass basis. Since chromium is highly susceptible to oxidation state changes, a separate sub-sample should be removed from the bottle at the time of analysis and dried (see "Instructions for Drying") to determine the moisture correction factor.

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 mass loss on drying as bottled was found to be in the range of 0.095 % to 0.117 % (n = 9), with a mean of 0.109 %.

PREPARATION AND ANALYSIS⁽¹⁾

Preparation of Material: The material was processed by S.A. Wilson of the United States Geological Survey (USGS). The original source material for the candidate SRM 2700 was chromite ore contaminated soil from a location in Hudson County, New Jersey. Using a mechanical excavator, samples of soil were collected in metal drums fitted with polyethylene liners. The drums were then sealed and shipped to the USGS in Lakewood, 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 fraction of material less than 2 mm 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 material was then further processed by blending with high-purity quartz sand to bring the chromium mass fraction to the target level, and finally split into 4 oz. brown glass screw-capped bottles using a custom-designed spinning riffler.

⁽¹⁾ Certain commercial equipment, instruments or materials are identified in this certificate to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

Homogeneity: The homogeneity of SRM 2700 was assessed by analyzing duplicate samples of 500 mg from 20 bottles selected by stratified random sampling. The material was fused into borate glass beads and eleven elements were analyzed by wavelength dispersive X-ray fluorescence spectrometry. The data were subjected to analysis of variance (ANOVA) testing. The findings indicated that there was no heterogeneity within-bottle or between bottle for the sample size ($n = 20$) at the 95 % confidence level. An F-test analysis showed that the material is relatively more heterogeneous among bottles than within a single bottle for some of the elements, but the material is considered sufficiently homogeneous for the intended application.

Certified Mass Fraction Values: The certified value for hexavalent chromium is based on a single NIST primary method consisting of speciated isotope dilution inductively coupled plasma mass spectrometry (SID-ICP-MS). The value is based on the extraction of hexavalent chromium from the material using an approved U.S. Environmental Protection Agency (EPA) SW-846 analytical method (Method 3060A). The certified values for total chromium, iron and manganese are based on two independent analytical methods at NIST. The uncertainty provided with each value is an expanded uncertainty about the mean to cover the measurand with approximately 95 % confidence, consistent with the ISO/JCGM Guide [2]. The expanded uncertainty is calculated as $U = ku_c$, where u_c is the combined uncertainty that incorporates within-method uncertainty, bottle to bottle heterogeneity, and uncertainty components related to the analysis, and k is the coverage factor ($k = 2$) corresponding to approximately 95 % confidence for each measurand [2]. For estimates based on multiple methods, the combined uncertainty also incorporates between-methods uncertainty.

Table 1. Certified Values for Mass Fractions (Dry-Mass Basis) of Hexavalent Chromium and Elements

| | Mass Fraction | | | Unit |
|---------------|---------------|---|--------|-------|
| Hexavalent Cr | 14.9 | ± | 1.2 | mg/kg |
| Total Cr | 0.1055 | ± | 0.0024 | % |
| Fe | 0.595 | ± | 0.056 | % |
| Mn | 0.0060 | ± | 0.0005 | % |

Reference Mass Fraction Values: The reference mass fraction values are the means of results from a single method. The uncertainty provided is an expanded uncertainty about the mean to cover the measurand with approximately 95 % confidence, consistent with the ISO/JCGM Guide [2]. The expanded uncertainty is calculated as $U = ku_c$, where u_c is the combined uncertainty that incorporates within-method uncertainty, bottle to bottle heterogeneity, and uncertainty components related to the analysis, and k is the coverage factor corresponding to approximately 95 % confidence for each measurand, where $k = 2$.

Table 2. Reference Values for Mass Fractions (Dry-Mass Basis) of Selected Elements

| Element | Mass Fraction (%) | | | Element | Mass Fraction (%) | | |
|---------|-------------------|---|--------|---------|-------------------|---|---------|
| Al | 0.3058 | ± | 0.0093 | Si | 45.80 | ± | 0.36 |
| Ca | 0.1985 | ± | 0.0071 | Ti | 0.0338 | ± | 0.0015 |
| K | 0.0368 | ± | 0.0014 | V | 0.0063 | ± | 0.0011 |
| Mg | 0.1937 | ± | 0.0061 | Zn | 0.00269 | ± | 0.00018 |
| Na | 0.0086 | ± | 0.0003 | | | | |

Information Values: Information values are single method results provided by a collaborating laboratory.

Table 3. Information Values for Selected Species and Properties

| Species/Property | Value | Unit |
|------------------------------|-------|-------|
| Chemical oxygen demand (COD) | 11700 | mg/kg |
| Redox potential | 281.3 | mV |
| Sulfide (acid soluble) | <19 | mg/kg |
| Total organic carbon (TOC) | 810 | mg/kg |
| pH | 9.33 | |

Multi-laboratory Study: A multi-laboratory test on the usage of EPA SW-846 methods for hexavalent chromium, and leachable total chromium in SRM 2700 was conducted by NIST in collaboration with S.J. Nagourney of the NJDEP OQA. The results of the study are summarized in Appendix A.

Analytical Methods: The analytical methods used for the analysis of SRM 2700 are listed in Table 4.

Table 4. Analytical Methods Used for Determination of Certified and Reference Values in SRM 2700

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

REFERENCES

- [1] May, W.; Parris, R.; Beck II, C.; Fassett, J.; Greenberg, R.; Guenther, F.; Kramer, G.; Wise, S.; Gills, T.; Colbert, J.; Gettings, R.; MacDonald, B.; *Definitions of Terms and Modes Used at NIST for Value-Assignment of Reference Materials for Chemical Measurements*; NIST Special Publication 260-136; U.S. Government Printing Office: Washington, DC (2000); available at: <http://www.nist.gov/srm/publications.cfm> (accessed Sep 2015).
- [2] JCGM 100:2008; *Evaluation of Measurement Data - Guide to the Expression of Uncertainty in Measurement*; (GUM 1995 with Minor Corrections), Joint Committee for Guides in Metrology (JCGM) (2008); available at http://www.bipm.org/utls/common/documents/jcgm/JCGM_100_2008_E.pdf (accessed Sep 2015); see also Taylor, B.N.; Kuyatt, C.E.; *Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results*; NIST Technical Note 1297, U.S. Government Printing Office: Washington, DC (1994); available at <http://www.nist.gov/pml/pubs/index.cfm> (accessed Sep 2015).
- [3] *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*; United States Environmental Protection Agency, Office of Solid Waste, Washington D.C; also available at <http://www.epa.gov/epaoswer/hazwaste/test/main.htm> (accessed Sep 2015).
- [4] Huo, D.; Kingston, H.M.; *Correction of Species Transformations in the Analysis of Cr(VI) in Solid Environmental Samples Using Speciated Isotope Dilution Mass Spectrometry*; Anal. Chem. Vol. 72, pp. 5047–5054 (2000).

Users of this SRM should ensure that the Certificate of Analysis in their possession is current. This can be accomplished by contacting the SRM Program: telephone (301) 975-2200; fax (301) 948-3730; e-mail srminfo@nist.gov; or via the Internet at <http://www.nist.gov/srm>.

APPENDIX A

Multi-Laboratory Testing Using Approved U.S. Environmental Protection Agency (EPA) Analytical Methods: Method 3060A, Method 7196A, Method 7199 and Method 6800 (Hexavalent Chromium), and Method 3050 (Leachable 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 mass fraction of each measurand in the given SRM matrix. The certified mass fractions 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 microwave. Alternatively, and where applicable, the sample may also be analyzed nondestructively.

For environmental monitoring purposes, the mass fractions of labile or extractable fractions of elements are often more useful than total mass fractions. Mass fractions of labile or extractable fractions are generally determined using relatively mild leach conditions, which are unlikely to totally decompose the sample. Reported mass fractions of labile or extractable fractions of elements are generally lower than total absolute mass fractions; 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. 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 accordance with the 1976 Resource Conservation and Recovery Act (RCRA). SW-846 Methods 3060A, 7196A and 7199 and 6800 are applicable to the measurement of hexavalent chromium, while Method 3050 is applicable to measurements of total chromium. 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 2700. Method 3050 is a strong acid leachable digestion method intended for the dissolution of elements which are environmentally available.

To assess the performance of these SW-846 methods for the determination of hexavalent chromium and total chromium in SRM 2700 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 2700 were distributed to a number of participating laboratories who were asked to measure the hexavalent chromium mass fraction in the material and/or the total chromium. The names of the participating laboratories are listed in Table A1. 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 A2 and include summary statistics together with the percent recovery relative to the certified value. For completeness, some data sets submitted for non-SW-846 methods, involving ion chromatography (IC) coupled to inductively coupled plasma mass spectrometry (ICP-MS) are also listed in Table A2.

Please note that none of the values in Table A2 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 2700. The data should not be used for any other purpose. **The certified values, provided in Table 1 of the Certificate of Analysis, are the best estimates of the true mass fractions.**

Table A1. Laboratories Participating in the Multi-laboratory Study of SRM 2700

| | | |
|---|--|---|
| S. Nagourney New Jersey Department of Environmental Protection, Office of Quality Assurance Trenton, NJ, USA | L. Reyes Columbia Analytical Services Rochester, NY, USA | C. Zhang Univ. Of. Houston-Clearlake Friendswood, TX, USA |
| J-P. Blouin Laboratoire des Pollutions Industrielles Center D-Expertise en Analyse Environnementale du Quebec Laval, Quebec, Canada | D. Dunlap STL Pittsburgh Pittsburgh, PA, USA | W. Chamberlin EMSL Westmont, NJ, USA |
| L. Call ALS Laboratory Group, Environmental Division Smithfield, NSW, Australia | A. Doupe Lancaster Laboratories Lancaster, PA, USA | G. Apostolopoulos. Clean Earth of North Jersey Kearny, NJ, USA |
| C. Armbruster STL Edison Edison, NJ, USA | B. Buckley Rutgers University Environmental and Occupational Health Sciences Institute Piscataway, NJ, USA | R. Wolf U.S. Geological Survey Denver Federal Center Denver, CO, USA |
| R. Jack Dionex Corporation Sunnyvale, CA, USA | J. DuPont DHL Analytical, Inc. Round Rock, TX, USA | NASA Johnson Space Center Houston, TX, USA |
| R. Gerads Applied Speciation and Consulting, LLC Bothell, WA , USA | C. Nowlan Pace Analytical Services, Inc. Minneapolis, MN, USA | J. Rossi Hampton Clark Veritech Fairfield, NJ, USA |
| V. Shah City of New York Department of Environmental Protection Wards Island, NY, USA | B. Goyette EMT Morton Grove, IL, USA | S. Reddy Chemtex Environmental Labs Port Arthur, TX, USA |
| M. Goss Inorganic Branch Manager Kentucky Department of Environmental Protection Frankfort, KY, USA | R. Lieckfeld Bureau Veritas North America Inc. Novi, MI, USA | R. Siebert Maxxam Mississauga, ON, Canada |
| J. Ghandi Metrohm-Peak Houston, TX, USA | J. Morgan Environmental Sciences Corporation Mt. Juliet, TN, USA | G. Gill Pacific Northwest National Laboratory Marine Sciences Laboratory Sequim, WA, USA |
| K. Smith ElementOne, Inc. Wilmington, NC, USA | Z. Fan EOHSI Piscataway, NJ, USA | |
| J. Swift ERG Morrisville, NC, USA | A. Carroll USEPA Region 4 Athens, GA, USA | |
| P. Hopke Clarkson University Potsdam, NY, USA | A. Shearrow Metrohm USA lab Riverview FL, USA | |
| F. Awanya USEPA Region 5 Chicago, IL, USA | J. Mathew USEPA Region 6 lab Houston, TX, USA | |

Table A2. Multi-Laboratory Data (Dry-Mass Basis) for SRM 2700

| Data Set | Method 7196A Hexavalent Cr (mg/kg) | Method 7199 Hexavalent Cr (mg/kg) | Method 6800 Hexavalent Cr (mg/kg) | IC/ICP-MS ^(a) Hexavalent Cr (mg/kg) | Method 3050 Cr (mg/kg) |
|-----------------------------|--|---|---|--|------------------------------|
| 1 | 10.9 | | | | |
| 2 | 10.6 | | | | |
| 3 | 11.0 | | | | 90.3 |
| 4 | | 11.2 | | | |
| 5 | 8.9 | | | | |
| 6 | | 11.3 | | | |
| 7 | | 8.9 | | | |
| 8 | | 9.6 | | | |
| 9 | 13.0 | | | | |
| 10 | | 10.2 | | | |
| 11 | 11.0 | | | | |
| 12 | 9.5 | | | | 71.3 |
| 13 | 12.4 | | | | |
| 14 | 10.8 | 10.9 | | | 137.5 |
| 15 | 6.8 | | | | |
| 16 | 8.2 | 8.9 | | | |
| 17 | 7.5 | | | | 103.1 |
| 18 | | | 14.8 | | |
| 19 | | 10.6 | | | |
| 20 | | 9.3 | | | |
| 21 | 12.3 | | | | |
| 22 | | | 16.4 | | |
| 23 | | | 18.2 | | |
| 24 | 11.7 | | | | |
| 25 | | | | 11.7 | |
| 26 | | 15.6 | 13.7 | | |
| 27 | | | | 13.5 | |
| 28 | | 14.0 | 14.9 | | |
| 29 | 7.5 | 10.3 | | | |
| 30 | | | | 12.2 | |
| 31 | | | 9.7 ^(b) | | |
| Mean | 10.1 | 10.9 | 14.6 | 12.5 | 100.6 |
| SD ^(c) | 1.97 | 2.01 | 2.87 | 0.90 | 27.9 |
| % RSD ^(d) | 19.5 | 18.5 | 19.6 | 7.2 | 27.7 |
| Median | 10.8 | 10.5 | 14.9 | 12.2 | 96.7 |
| Minimum | 6.8 | 8.9 | 9.7 | 11.8 | 71.3 |
| Maximum | 13.0 | 15.6 | 18.2 | 13.5 | 137.5 |
| # Labs | 15 | 12 | 6 | 3 | 4 |
| Recovery (%) ^(e) | 68.1 | 73.1 | 98.3 | 83.7 | 9.5 |

^(a) Ion chromatography ICP-MS methods (see text in Appendix A)^(b) Analytical method equivalent to EPA Method 6800^(c) Standard deviation^(d) Relative standard deviation^(e) Mean recovery for the method relative to the certified value expressed as a percentage