



# National Institute of Standards & Technology

## Certificate of Analysis

### Standard Reference Material® 2718a

#### Green Petroleum Coke

This Standard Reference Material (SRM) is intended primarily for use in the calibration of apparatus and the evaluation of techniques used in the analysis of green (raw) petroleum coke and other materials of a similar matrix. It can be used to validate value assignment of in-house reference materials. A unit of SRM 2718a consists of 50 g of green petroleum coke ground to pass a 250  $\mu\text{m}$  (60 mesh) sieve, homogenized, packaged in an amber glass bottle under an argon atmosphere, and then sealed in an aluminized bag.

**Certified Mass Fraction Values:** Certified values for iron, sodium, sulfur, and vanadium, expressed as mass fractions [1] on a dry-mass basis, are provided in Table 1. 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 [2]. A certified value is the present best estimate of the true value.

**Reference Mass Fraction Values:** Reference values for aluminum, calcium, chlorine, cobalt, hydrogen, mercury, manganese, and nickel, expressed as mass fractions [1] on a dry-mass basis, are provided in Table 2. A reference value is a non-certified value that is the best estimate of the true value; however, the value does not meet NIST criteria for certification and is provided with an associated uncertainty that may reflect only measurement precision and may not include all sources of uncertainty [2].

**Information Values:** Information values for ash, calorific value, carbon, nitrogen, and silicon are provided in Table 3. An information value is considered to be a value that will be of interest to the SRM user, but insufficient information is available to assess the uncertainty associated with the value or only a limited number of analyses were performed [2]. Information values cannot be used to establish metrological traceability.

**Expiration of Certification:** The certification of **SRM 2718a** is valid, within the measurement uncertainty specified, until **31 July 2036**, provided the SRM is handled and stored in accordance with the instructions given in this certificate (see "Instructions for Handling, Storage, and Use"). This 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 certification of SRM 2718a was provided by T.W. Vetter of the NIST Chemical Sciences Division.

Analytical measurements leading to the certification of this SRM were performed at NIST by S.J. Christopher, K.P. Grogan, S.E. Long, A.F. Marlow, J. Ness, R. Oflaz, D.J. O'Kelly, R.L. Paul, S.A. Rabb, J.R. Sieber, and T.W. Vetter of the NIST Chemical Sciences Division.

Statistical consultation for this SRM was provided by A.L. Pintar of the NIST Statistical Engineering Division.

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

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*Certificate Revision History on Last Page*

## INSTRUCTIONS FOR HANDLING, STORAGE, AND USE

**Storage:** The SRM should be stored in its original bottle, tightly sealed and away from sunlight and intense sources of radiation, under normal laboratory conditions.

**Use:** Before it is sampled, the unit should be thoroughly mixed by carefully inverting and rotating the tightly sealed bottle. A minimum test portion mass of 120 mg for mercury; 200 mg for chlorine, manganese, sodium, sulfur, and vanadium; 300 mg for cobalt and iron; 400 mg for aluminum, calcium, and nickel; and 750 mg for hydrogen should be used for analytical determinations.

**Drying Instructions:** To relate measurements directly to the certified and reference values that are expressed on a dry-mass basis, users should determine a drying correction at the time of the analysis. The correction is determined by oven-drying a separate 1 g sample in a nitrogen atmosphere at  $107\text{ }^{\circ}\text{C} \pm 3\text{ }^{\circ}\text{C}$  to a constant mass [3] or equivalent technique. Attainment of constant mass is defined according to the ASTM thermogravimetric (TG) method as either a mass loss of  $\leq 0.05\%$ , relative, over a nine-minute period or the mass loss after one hour of heating [3]. The mass losses determined in both manners, and in both nitrogen and air, were similar.

The mass loss determined in both a nitrogen and air atmosphere, which is reported *for information purposes only*, was nominally 0.3 %. The mass loss determined by the user may be different, depending on ambient conditions when the bottle is sampled.

## NOTICE TO USERS

NIST strives to maintain the SRM inventory supply, but NIST cannot guarantee the continued or continuous supply of any specific SRM. Accordingly, NIST encourages the use of this SRM as a primary benchmark for the quality and accuracy of the user's in-house reference materials and working standards. As such, the SRM should be used to validate the more routinely used reference materials in a laboratory. Comparisons between the SRM and in-house reference materials or working measurement standards should take place at intervals appropriate to the conservation of the SRM and the stability of relevant in-house materials. For further guidance on how this approach can be implemented, contact NIST by email at [srms@nist.gov](mailto:srms@nist.gov).

## SOURCE, PREPARATION, HOMOGENEITY, AND ANALYSIS<sup>(1)</sup>

**Source and Preparation of Material:** The green petroleum coke for this SRM was obtained from Lake Charles Carbon, a division of Reynolds Metals Company (Lake Charles, LA). The collection of the approximately 230 kg of green petroleum coke was under the direction of R. Jones and R. Morris of Lake Charles Carbon. The gross sample was jaw crushed and subsequently pulverized using ceramic plates to pass a  $250\text{ }\mu\text{m}$  (60 mesh) screen. The entire lot was then divided using the spinning riffle technique into 48 portions. Sixteen portions designated for SRM 2718 were subdivided by the spinning riffle technique into bottles, which were subsequently sealed under an argon atmosphere. The balance of the lot was stored and then eventually subdivided by the spinning riffle technique into bottles, which were subsequently sealed under an argon atmosphere and issued as SRM 2718a.

**Homogeneity Assessment:** Twenty-two bottles of SRM 2718a were selected for homogeneity assessment. Quadruplicate test portions from each bottle were analyzed by wavelength-dispersive X-ray fluorescence spectrometry (WDXRF) for aluminum, calcium, carbon, cobalt, iron, nickel, silicon, sodium, sulfur, and vanadium. Results from duplicate test portions from each of eight bottles analyzed by other methods were also used for homogeneity assessment. These results included calcium and sodium by inductively coupled plasma optical emission spectrometry (ICP-OES), chlorine, cobalt, sodium, and vanadium by instrumental neutron activation analysis (INAA), and hydrogen by prompt gamma activation analysis (PGAA). These tests showed evidence of heterogeneity for chlorine, iron, and nickel based on the recommended minimum test portion mass.

## VALUE ASSIGNMENT

Certified and reference values are expressed with an expanded uncertainty,  $U = ku_c$  and were calculated in a manner that is consistent with the ISO/JCGM Guide [4]. Measurements were modeled using linear mixed effects statistical models, the parameters of which were estimated using the Bayesian inference paradigm [5]. The Monte Carlo method [6] was used to propagate all of the components of uncertainty. For aluminum, calcium, cobalt, hydrogen, manganese, sodium, sulfur, and vanadium, the quantity  $u_c$  represents, at the level of one standard deviation, the

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<sup>(1)</sup> 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.

estimated uncertainty in the mass fraction for the mean of all bottles of SRM 2718a, because the underlying mass fraction is assumed to be the same for each bottle. For chlorine, iron, mercury, and nickel, the quantity  $u_c$  represents, at the level of one standard deviation, the estimated uncertainty for the mean of a single randomly chosen bottle of SRM 2718a, which accounts for possible material heterogeneity. The quantity,  $k$ , is the coverage factor used to obtain an expanded uncertainty that provides a symmetric, approximately 95 % coverage interval.

**Metrological Traceability:** The measurands for the certified values in Table 1 are the total mass fractions for the elements. The measurands for the reference values in Table 2 are the mass fractions for the elements as determined by the indicated methods. Metrological traceability is to the SI derived unit for mass fraction, expressed as milligrams per kilogram for all elements except sulfur and hydrogen, which are expressed as a percentage [1].

**Certified Mass Fraction Values:** The certified values and the corresponding expanded uncertainty are given in Table 1.

The certified value and expanded uncertainty for iron, sodium, and vanadium were calculated by combining two sets of results, the first from sample decomposition by microwave-oven digestion with measurements by ICP-OES, and the second by INAA. For ICP-OES, the major source of uncertainty was measurement replication for iron and sodium, and the major source of uncertainty for vanadium was calibration standards. For INAA, the major sources of uncertainty for iron and vanadium were measurement replication and calibration standards, and the major source of uncertainty for sodium was measurement blank. In addition, the iron uncertainty includes a heterogeneity component.

The certified value and expanded uncertainty for sulfur were calculated by combining two sets of results using the approach in [7], the first from sample decomposition by microwave-oven digestion with measurements by isotope dilution sector field inductively coupled plasma mass spectrometry (ID-SF-ICP-MS), and the second from a Laboratory Quality Services International (LQSi) inter-laboratory study (ILS). For the determination of sulfur by ID-SF-ICP-MS, the major source of uncertainty was measurement replication. For the LQSi ILS, the sources of uncertainty explicitly accounted for were between-lab and within-lab variability.

Table 1. Certified Mass Fraction Values (Dry-Mass Basis) for SRM 2718a

Element	Mass Fraction (mg/kg)			Coverage Factor, $k$
Iron (Fe)	287	±	44	3.18
Sodium (Na)	83.0	±	9.3	3.64
Vanadium (V)	310	±	12	3.24
	(%)			
Sulfur (S)	4.690	±	0.083	2.87

**Reference Mass Fraction Values:** The reference values and the corresponding expanded uncertainty are given in Table 2. The reference values and expanded uncertainties for aluminum, calcium, and nickel are based on measurements by ICP-OES. The major source of uncertainty for aluminum and calcium was measurement replication. The major sources of uncertainty for nickel were measurement replication, calibration standards, and heterogeneity. The reference values and expanded uncertainty for chlorine and manganese are based on measurements by INAA. The major source of uncertainty for chlorine and manganese was measurement replication. In addition, the chlorine uncertainty includes a heterogeneity component. The reference values and expanded uncertainty for hydrogen are based on measurements by PGAA. The major sources of uncertainty for hydrogen were measurement replication and calibration standards. The reference values and expanded uncertainty for mercury are based on measurements by direct combustion atomic absorption spectrometry (DC-AAS). The major sources of uncertainty for mercury were measurement replication and possible heterogeneity.

Table 2. Reference Mass Fraction Values (Dry-Mass Basis) for SRM 2718a

Element	Mass Fraction (mg/kg)			Coverage Factor, <i>k</i>
Aluminum (Al)	15.4	±	1.2	2.13
Calcium (Ca)	165.5	±	8.6	2.13
Chlorine (Cl)	62	±	10	2.71
Cobalt (Co)	5.71	±	0.19	1.99
Manganese (Mn)	2.11	±	0.10	2.13
Nickel (Ni)	144.06	±	0.91	2.38
(%)				
Hydrogen (H)	3.725	±	0.042	2.05
(μg/kg)				
Mercury (Hg)	0.197	±	0.093	2.32

**Information Values:** The information values given in Table 3 are provided without an uncertainty estimate because insufficient information is available to assess the uncertainty. The values are given as additional information on the matrix and should **NOT** be used as substitutes for certified or reference values.

Table 3. Information Values for SRM 2718a

	Value
Ash	1 %
Calorific Value <sup>(a)</sup>	35 MJ/kg
Carbon (C)	90 %
Nitrogen (N)	1 %
Silicon (Si)	50 mg/kg

<sup>(a)</sup> 15000 Btu/lb

Particle size measurements were made using a laser-based light scattering system. Approximately 0.5 g of material (refractive index: 1.68, absorption index: 0.1) was measured using water as the dispersant, (refractive index: 1.33) and 0.1 % Triton X-100 as a pre-wetting surfactant. Calculated 10th percentile ( $d_{0.1}$ ) and 90th percentile ( $d_{0.9}$ ) particle sizes (percent volume of particles smaller than the value) are  $d_{0.1} = 5 \mu\text{m}$  and  $d_{0.9} = 160 \mu\text{m}$ . The volume weighted mean is  $43 \mu\text{m}$ . The fraction of material smaller than  $10 \mu\text{m}$  in diameter is 19 %. The particle size distribution is shown in Figure 1.

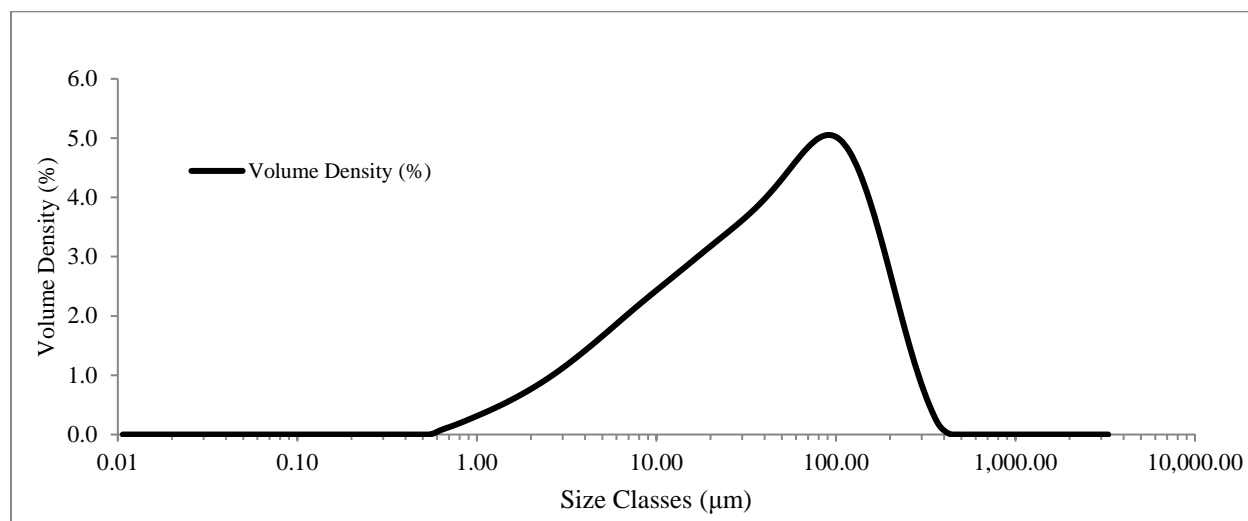


Figure 1. Particle size distributions in SRM 2718a

#### REFERENCES

- [1] Thompson, A.; Taylor, B.N.; *Guide for the Use of the International System of Units (SI)*; NIST Special Publication 811; U.S. Government Printing Office: Washington, DC (2008); available at <https://www.nist.gov/physical-measurement-laboratory/special-publication-811> (accessed Aug 2017).
- [2] May, W.; Parris, R.; Beck, 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 Aug 2017).
- [3] ASTM D7582-10; *Standard Test Methods for Proximate Analysis of Coal and Coke by Macro Thermogravimetric Analysis*; Annu. Book ASTM Stand., Vol 05.06, pp. 812–820 (2012).
- [4] 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](http://www.bipm.org/utls/common/documents/jcgm/JCGM_100_2008_E.pdf) (accessed Aug 2017); 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 Aug 2017).
- [5] Gelman, A.; Carlin, J.B.; Stern, H.S.; Rubin, D.B.; *Bayesian Data Analysis*; Chapman & Hall (2004).
- [6] JCGM 101:2008; *Evaluation of Measurement Data — Supplement 1 to the “Guide to the Expression of Uncertainty in Measurement” — Propagation of Distributions Using a Monte Carlo Method*; JCGM (2008); available at <http://www.bipm.org/en/publications/guides/gum.html> (accessed Aug 2017).
- [7] Stone, M.; *The Opinion Pool*; Ann. Math. Stat., Vol. 32, pp. 1339–1342 (1961).

**Certificate Revision History:** 09 August 2017 (Updated units for mercury; editorial changes); 26 July 2016 (Original certificate date).

*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](mailto:srminfo@nist.gov); or via the Internet at <http://www.nist.gov/srm>.*