National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material® 2719

Calcined Petroleum Coke

This Standard Reference Material (SRM) is intended primarily for use in the calibration of apparatus and the evaluation of techniques employed in the analysis of calcined petroleum coke and other materials of a similar matrix. SRM 2719 consists of 50 g of calcined petroleum coke ground to pass a 250 μm (60 mesh) sieve, homogenized, and bottled under an argon atmosphere.

Certified Values: The certified values, expressed as mass fractions [1] on a dry 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 accounted for by NIST. The certified values for aluminum, calcium, iron, nickel, and vanadium are based on two independent NIST methods. The certified value for sulfur is based on a single NIST primary method.

Reference Values: The reference values, expressed as a mass fraction on a dry basis, for cobalt and sodium are provided in Table 2. The reference values for cobalt and sodium are based on one NIST method. Reference values are noncertified 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 and may not include all sources of uncertainty.

Information Values: Information values are reported in Table 3. The silicon, ash content, and gross caloric values are based on an interlaboratory analysis study for this SRM, administrated on behalf of NIST by Laboratory Quality Services International. The values for carbon, hydrogen, and nitrogen are based on a single method performed by LECO Corporation (St. Joseph, MI) and corroborated by results from the interlaboratory analysis program. These values are provided without uncertainty for information purposes only.

Expiration of Certification: The certification of SRM 2719 is valid, within the measurement uncertainties specified, until **30 January 2008**, provided the SRM is handled in accordance with the instructions given in this certificate (see Instructions for Use). This certification is nullified if the SRM is damaged, contaminated, or modified.

The overall direction and coordination of the technical measurements leading to certification were performed by J.D. Fassett and R.L. Watters, Jr., of the NIST Analytical Chemistry Division.

Statistical analysis of the certification data was performed by L.M. Gill of the NIST Statistical Engineering Division.

The technical and support aspects involved in the preparation, certification, and issuance of this SRM were coordinated through the NIST Standard Reference Materials Program by B.S. MacDonald.

Willie E. May, Chief
Analytical Chemistry Division

Gaithersburg, MD 20899
Certificate Issue Date: 20 May 2002
See Certificate Revision History on Last Page

John Rumble, Jr., Acting Chief
Standard Reference Materials Program

NOTICE AND WARNINGS TO USERS

Maintenance of SRM Certification: NIST will monitor representative samples of 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.

Instructions for Use: The unit should be thoroughly mixed by rotating the bottle before sampling. A minimum sample mass of 250 mg should be used for analytical determinations to be related to the certified values, and cobalt and sodium reference values. The SRM should be stored in its original, tightly sealed bottle away from sunlight and intense sources of radiation.

Instructions for Drying: In order for users to directly relate their measurements to the certified and reference values, drying corrections should be measured and applied at the time of analysis. The correction is determined by drying separate 1 g samples in a nitrogen atmosphere at 107 °C ± 3 °C to a constant mass. Air is also an acceptable carrier gas for drying this material. The average mass loss measured at NIST for SRM 2719 was 0.07 % (standard deviation = 0.04 %, n = 6).

PREPARATION, HOMOGENIETY, AND ANALYSIS

Source and Preparation of Material: The calcined petroleum coke for this SRM was donated by VENCO, Moundsville, WV. The collection of the approximately 240 kg of calcined petroleum coke was under the direction of R.B. Murzyn, Environmental Coordinator, VENCO.

The gross sample was jaw crushed and subsequently pulverized using ceramic plates to pass a 250 μm (60 mesh) screen. The entire lot was then divided using the spinning riffle technique into 48 portions. Sixteen portions were subdivided by the spinning riffle technique into bottles, which were subsequently sealed under an argon atmosphere. The balance of the lot is being retained in long term storage at NIST under an argon atmosphere.

Homogeneity: No evidence of inhomogeneity was noted during certification from replicate measurements using the minimum sample size.

Table 1. Certified Values (Dry Basis)

Elements	Mass Fraction (mg/kg)		
Aluminum	58.9	±	5.7
Calcium	57.7	±	4.4
Iron	201.6	±	5.4
Nickel	204	±	12
Sulfur	8 877	±	10
Vanadium	58.6	±	3.4

Certified Values and Uncertainties: Certification analyses for aluminum, calcium, iron, nickel, vanadium, and sulfur were performed by the NIST Analytical Chemistry Division. The certified values for aluminum, calcium, iron, nickel, and vanadium are the equally weighted mean of two independent analytical methods. Aluminum, calcium, and vanadium values are based on inductively coupled plasma optical emission spectrometry (ICP-OES), performed by L.J. Wood, and instrumental neutron activation analysis (INAA), performed by D.A. Becker. Iron and nickel values are based on ICP-OES, performed by L.J. Wood, and INAA performed by R. Demiralp. The certified value for sulfur is based on a single NIST primary method, isotope dilution thermal ionization mass spectrometry (ID-TIMS) [2] performed by W.R. Kelly, J.L. Mann, and R.D. Vocke.

The uncertainty in the concentrations certified by two NIST methods is calculated as, $U = ku_c + B$ as described by Schiller and Eberhardt [3]. The quantity, u_c, is the combined standard uncertainty calculated according to ISO Guide [4], which accounts for the combined effect of the variance for the two methods at one standard deviation. The coverage factor, k, is determined from the Student's t-distribution corresponding to the appropriate associated

degrees of freedom and 95 % confidence for each analyte. B is a bias adjustment for the difference between methods, which is the maximum difference between the certified value and the method means [3].

The uncertainty in the value certified by a NIST primary method is expressed as an expanded uncertainty, U, and is calculated according to the method described in the ISO Guide [4]. The expanded uncertainty is calculated as $U = ku_c$, where u_c is intended to represent, at the level of one standard deviation, the combined effect of uncertainty components associated with the measurement and material inhomogeneity, and k is a coverage factor corresponding to 95 % confidence.

Table 2. Reference Values (Dry Basis)

Elements	Mass Fraction (mg/kg)
Cobalt	18.6 ± 0.5
Sodium	15.1 ± 0.9

Reference Value and Uncertainty: The reference value for cobalt was determined from INAA performed by R. Demiralp. The reference value for sodium is based on INAA performed by D.A. Becker.

The uncertainty in the reference values is expressed as an expanded uncertainty, U, and is calculated according to the method described in the ISO Guide [4]. The expanded uncertainty is calculated as $U = ku_c$, where u_c represents, at the level of one standard deviation, the combined effect of uncertainty components associated with the measurement uncertainty and material inhomogeneity, and k is a coverage factor. The coverage factor, k, is determined from the Student's t-distribution corresponding to the appropriate associated degrees of freedom and 95 % confidence for each analyte.

Table 3. Information Values (Dry Basis)

Silicon	138 mg/kg
Carbon [5]	97.1 %
Hydrogen [5]	0.17 %
Nitrogen [5]	1.17 %
Ash [6,7]	0.12 %
Volatile Matter [7,8]*	0.54 %
Gross Calorific Value [9,10]	32.90 $Mj \cdot kg^{-1}$ (14146 $Btu_{th} \cdot lb^{-1}$)

* Samples having a thermal history above 600 °C, such as SRM 2719, are excluded from the scope of ASTM D 4421-89 [8]. The volatile matter reported may include a loss of mass associated with sample oxidation.

Information Values[1]: The information values given in Table 3 for silicon, ash, volatile matter, and gross caloric value are based on an interlaboratory analysis study for SRM 2719, administrated on behalf of NIST by Laboratory Quality Services International. The values for carbon, hydrogen, and nitrogen are based on measurements performed according to a NIST experimental plan by the LECO Corporation using ASTM D 5373-93, Standard Test Methods for Instrumental Determination of Carbon, Hydrogen, and Nitrogen in Laboratory Samples of Coal and Coke [5]. These results were corroborated by the SRM 2719 interlaboratory analysis program. Information values are provided without uncertainty for information purposes only.

[1]Certain commercial organizations, services, equipment, or materials are identified in this report in order 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 organizations, services, materials, or equipment identified are necessarily the best available for the purpose.

REFERENCES

[1] Taylor, B.N., "Guide for the Use of the International System of Units (SI)," NIST Special Publication 811, 1995 Ed., (April 1995).

[2] Kelly, W.R., Paulsen, P.J., Murphy, K.E., Vocke, R.D., and Chen, L.-T., "Determination of Sulfur in Fossil Fuels by Isotope Dilution Thermal Ionization Mass Spectrometry," Anal. Chem., Vol. 66, p. 2505, (1994).

[3] Schiller, S.B. and Eberhardt, K.R., "Combining Data from Independent Analysis Methods," Spectrochemical Acta, Vol. 12, pp. 1607-1613, (1991).

[4] *Guide to the Expression of Uncertainty in Measurement*, ISBN 92-67-10188-9, 1st Ed., ISO, Geneva, Switzerland, (1993); see also Taylor, B.N. and 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://physics.nist.gov/Pubs/.

[5] ASTM D 5373-93, "Standard Test Methods for Instrumental Determination of Carbon, Hydrogen, and Nitrogen in Laboratory Samples of Coal and Coke," Vol. 05.05, ASTM Book of Standards, West Conshohocken, PA.

[6] ASTM D 3174-93, "Test Method for Ash in the Analysis Sample of Coal and Coke from Coal," Vol. 05.05 ASTM Book of Standards, West Conshohocken, PA.

[7] ASTM D 5142-90, "Standard Test Methods for Proximate Analysis of the Analysis Sample of Coal and Coke by Instrumental Procedures," Vol. 05.05, ASTM Book of Standards, West Conshohocken, PA.

[8] ASTM D 4421-89, "Test Method for Volatile Matter in Petroleum Coke," Vol. 05.02, ASTM Book of Standards, West Conshohocken, PA.

[9] ASTM D 2015-93, "Test Method for Gross Calorific Value of Coal and Coke by Adiabatic Bomb," Vol. 05.05, ASTM Book of Standards, West Conshohocken, PA.

[10] ASTM D 3286-91a, "Test Method for Gross Calorific Value of Coal and Coke by the Isoperibol Bomb Calorimeter," Vol. 05.05, ASTM Book of Standards, West Conshohocken, PA.

Certificate Revision History: 20 May 2002 (Note regarding volatile matter and disclaimer added); 15 July 1999 (Original certificate date).

Users of this SRM should ensure that the certificate in their possession is current. This can be accomplished by contacting the SRM Program at: telephone (301) 975-6776; fax (301) 926-4751; e-mail srminfo@nist.gov; or via the Internet http://www.nist.gov/srm.