National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material® 2484

Multiwall Carbon Nanotubes
(Raw Soot)

This Standard Reference Material (SRM) is intended primarily for use in evaluating chemical and instrumental methods of analysis of carbon nanotubes. A unit of SRM 2484 contains 6 g of multiwall carbon nanotube soot.

Certified Mass Fraction Value: The certified value (dry-mass basis) of cobalt (Co) is listed in Table 1 and reported as a mass fraction [1]. The value reported is based on the results of analyses performed at NIST using instrumental neutron activation analysis (INAA) and cold neutron PGAA (CNPGAA). 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 [2].

Reference Mass Fraction Values: Reference value for the iron mass fraction (dry-mass basis) is provided in Table 2. Table 3 reports values measured for the material via thermogravimetry. Reference values are non-certified values that are the best estimate of the true value. However, the values do not meet the 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 [2].

Information Values: Scanning electron microscopy (SEM) images are provided in Figures 1, 2, and 3 and Table 4 reports the length measured by SEM. Additional elemental composition is given in Table 5. Tables 6 and 7 summarize the distributions of inner and outer diameter of the nanotubes, as well as the number of walls per tube. Transmission electron microscopy (TEM) images are provided in Figure 4. An information value is a value that may 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 a value derived from a limited number of analyses. Information values cannot be used to establish metrological traceability.

Expiration of Certification: The certification of **SRM 2484** is valid, within the measurement uncertainty specified, until **31 October 2021,** provided the SRM is handled and stored in accordance with the instructions given in this certificate (see "Instructions for Handling, 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 for certification was accomplished under the direction of E. Mansfield of the NIST Applied Chemicals and Materials Division.

Analytical measurements for homogeneity testing and certification of this SRM were performed by E. Mansfield, A.N. Chiaramonti-Debay, J. Holm, R. White of the NIST Applied Chemicals and Materials Division and R. Paul and R. Oflaz of the NIST Chemical Sciences Division.

Statistical consultation for this SRM was provided by J. Wang of the NIST Statistical Engineering Division.

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

James Fekete, Chief
Applied Chemicals and Materials Division

Gaithersburg, MD 20899
Certificate Issue Date: 11 May 2017

Steven J. Choquette, Director
Office of Reference Materials

NOTICE AND WARNING TO USERS

This material should be handled as recommended by the National Institute for Occupational Safety and Health (NIOSH). According to NIOSH, currently there are no studies reported in the literature of adverse health effects in workers producing or using carbon nanotubes or carbon nanofibers. The concern about worker exposure to these materials arises from results of animal studies. Several studies in rodents have shown an equal or greater potency of carbon nanotubes compared to other inhaled particles known to be hazardous to exposed workers in causing adverse lung effects including pulmonary inflammation and fibrosis [3]. Currently, the adverse effects of skin penetration or ingestion of nanoparticles have not been fully studied. For further information, refer to the Safety Data Sheet (SDS).

INSTRUCTIONS FOR HANDLING, STORAGE AND USE

Until required for use, the SRM should be **stored at room temperature** in its original bottle and package, and protected from intense direct light or ultraviolet radiation. NIST recommends a minimum sample mass of 25 mg to 40 mg of the material when relating the analytical determinations to the certified values in this certificate. The SRM does not require preparation prior to weighing. Length measurements and wall counts on smaller sample quantities may indicate material microheterogeneities in electron microscopy analyses due to the small sample sizes inherent to those techniques.

PREPARATION AND ANALYSIS[(1)]

Material Preparation: Material for SRM 2484 was obtained from Nanocyl (Belgium). One kilogram of a single lot of material was received at NIST where it was homogenized via mechanical agitation and placed into amber glass bottles with screw tops.

Value Assignment and Uncertainty Analysis: Analyses to establish reference values were conducted at NIST using best practices as determined independently for each measurement method. All elements for which certified and reference values are provided were determined using INAA or CPGAA. Mass fraction values are reported on a dry-mass basis. Moisture loss was determined by CPGAA to be 0.258 %– 0.269 % and the material was determined to not be hydroscopic.

Instrumental Neutron Activation Analysis (INAA): INAA was carried out by a forming pellets in a 5 mm diameter die with 2,000 pounds force for 2 s to 3 s. Pellets were irradiated for 1 hr at 20 MW at the NIST reactor. Elemental standards were used to calculate mass fractions. SRM 2483 *Single-Wall Carbon Nanotubes (raw soot)* was used at a control material. Corrections for moisture content were applied to the sample masses for SRM 2483. All count rates were corrected for radioactive decay and spectral interference.

Cold Neutron Prompt Gamma Activation Analysis (CNPGAA): CNPGAA was carried out by forming pellets using a 12.7 mm stainless steel die and hydraulic press at 10,000 pounds force for 3 s to 5 s. A high purity cobalt foil was used as the cobalt standard. Hydrogen sensitivity was determined by measuring the H/Ti sensitivity ratio of a standard sample, then using comparisons for titanium sensitivity to determine the hydrogen sensitivity as described in reference 4. Standards were used for comparison and to monitor changes in neutron fluence rate. Background was also collected and corrected for, if necessary. Quality control was achieved by measuring Co and H in SRM 2483 *Single Wall Carbon Nanotubes (raw soot).*

Thermogravimetry: Samples of soot were measured during heating in an air environment until the combustible material was consumed. Sample pans were equilibrated to 30 °C before heating. The heating rate was 10 °C/min to 1000 °C. Air was introduced at 10 mL/min with 20 mL/min protective nitrogen flow. The rate of mass loss during this process, and the amount of residual mass at 1000 °C were recorded. The oxidation temperature is defined as the temperature with the peak mass loss.

Microscopy: Images of SRM 2484 were acquired using SEM. A Zeiss LEO 1525 FEG-SEM equipped with an EDAX Genesis 400 energy dispersive X-ray spectrometer was used for imaging and point X-ray analyses of the samples prepared on adhesive carbon tabs. For dry preparation, adhesive carbon tabs were attached to an SEM stub and carbon nanotube soot was deposited onto the adhesive tabs. Loose material was removed from the tabs by gently tapping the stub against a hard surface. For length measurements, dry powder was selected using sharp tweezers and added to a clean vial. N-methylpyrrolidone was added and the vial was gently sonicated in a bath sonicator for 15 min. The suspended nanotubes were dropped onto copper sample support grids with an ultrathin carbon film and allowed to dry 8 hours. The SEM magnification calibration was performed with NIST RM 8820 *Scanning Electron Microscope Scale Calibration Artifact.* In addition, images of SRM 2484 were acquired using TEM. Dry powder

[(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.

was selected using sharp tweezers and added to a clean vial. Chloroform was added and the vial was gently sonicated in a bath sonicator for 15 min. The suspended nanotubes were dropped onto support grids and allowed to dry 1 hr. Inner and outer diameter as well as number of walls were measured on a JEOL 2000FX transmission electron microscope equipped with a LaB_6 filament and operated at 200 kV. Magnification calibration was performed with a crocidolite calibration artifact. Diameter was measured to the walls of the nanotube, excluding any amorphous carbon coating. Walls were counted separately on both sides of a nanotube.

Certified Mass Fraction Value: The certified value of cobalt on a dry-mass basis is listed in Table 1. The assigned value is an unweighted mean of the results from two analytical methods [5]. The uncertainty listed with the value is an expanded uncertainty about the mean, with coverage factor $k = 2$, following the JCGM and NIST Guides [6,7]. The measurand is the total concentration value for cobalt in Table 1. The certified value is metrologically traceable to the derived SI unit for mass fraction (expressed as percent).

Table 1. Certified Mass Fraction of Cobalt (Dry-Mass Basis) for SRM 2484

Element	Mass Fraction (%)
Cobalt (Co)	0.1821 ± 0.0071

Reference Values: The reference mass fraction value for iron on a dry-mass basis is listed in Table 2 and is the result of the INAA analysis performed at NIST. The measurand is the mass fraction of iron as determined by the method listed above. Metrological traceability is to the derived SI unit for mass concentration (expressed as micrograms per kilogram). The assigned value is an unweighted mean of the results from a single analytical method [5–7]. Table 3 reports values measured for the material via thermogravimetry. The measurands are the values listed in Table 3 as determined by the method listed above. Metrological traceability for the oxidation temperature is to the derived SI unit for temperature (expressed as degrees Celsius); metrological traceability for the residual mass is to the derived SI unit for mass concentration (expressed as percent).

Table 2. Reference Mass Fraction Value (Dry-Mass Basis) SRM 2484

Element	Mass Fraction (mg/kg)
Iron (Fe)	1892 ± 42

Table 3. Reference Thermogravimetry Derived Values for SRM 2484

Measurand	Value[(a)]
Oxidation Temperature	653.5 °C
Residual Mass (dry-mass basis)	6.22 % ± 0.13 %

[(a)] The uncertainty listed with the value is an expanded uncertainty about the mean, with coverage factor, $k = 2$, following the JCGM and NIST Guides [6,7].

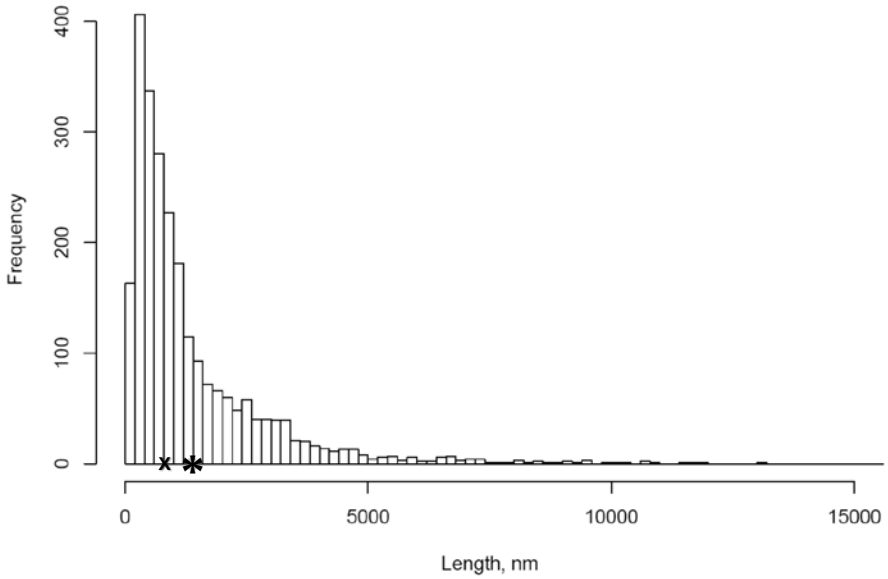


Figure 1: Histograms of all length data. Length is shown on the x-axis, with frequency shown on the y-axis. The width of each box represents 200 nm. The x represents the median of 830 nm and the ∗ is the mean of 1370 nm.

Information Values: Additional measurements and data were obtained to further characterize the material and are provided as information values. Additional elemental composition is given in Table 5. Scanning electron microscopy images are provided in Figures 2 and 3. Transmission electron microscopy images are provided in Figure 4. Table 6 and 7 summarize the distributions of inner and outer diameter of the nanotubes, as well as the number of walls per tube.

Table 4: Length measurements as determined by SEM for SRM 2484

Mean (nm)	Median (nm)	Mode (nm)	LMS (nm)
1370 nm	830 nm	300 nm	475 nm

Table 5: Informational Elemental Mass Fraction Values (Dry-Mass Basis) for SRM 2484

Measurand	Value
Thorium (Th)	<1.495 mg/kg
Aluminum (Al)	4.102 %

Table 6: Information values of inner and outer diameter for SRM 2484

	Mean (nm)	Median (nm)	Mode (nm)	LMS (nm)
Inner diameter	5.45	5.30	5.50	5.25
Outer diameter	10.56	9.95	9.50	9.50

Table 7: Informational value of number of walls for SRM 2484

	Mean	Median	Mode
Wall A	7.7	7	6
Wall B	7.8	7	7

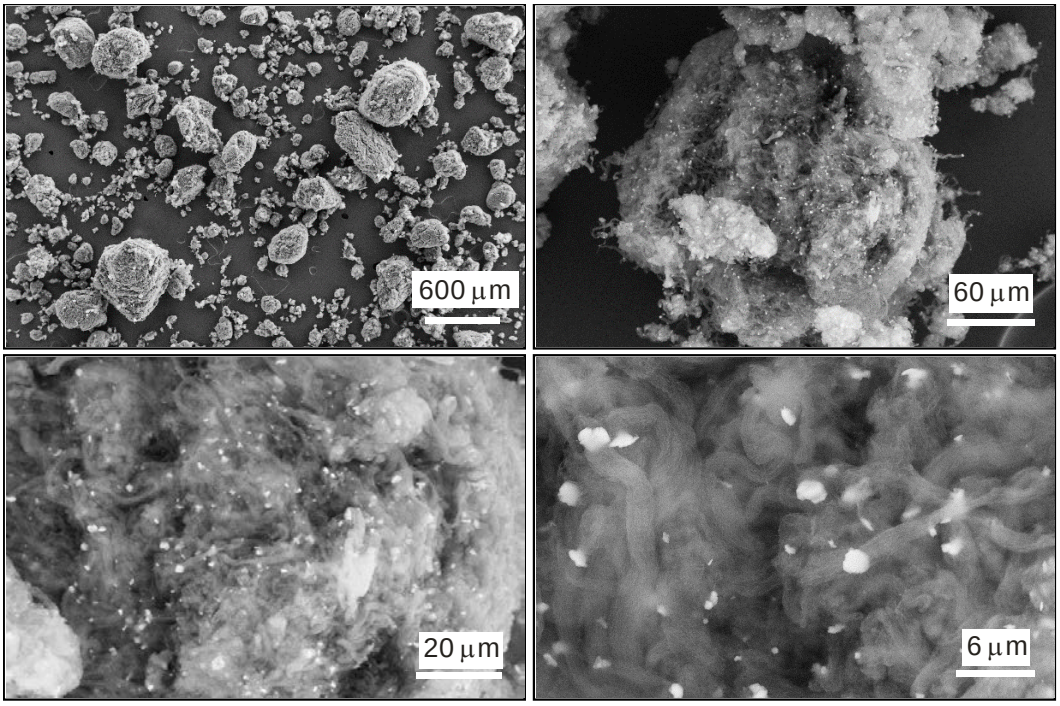
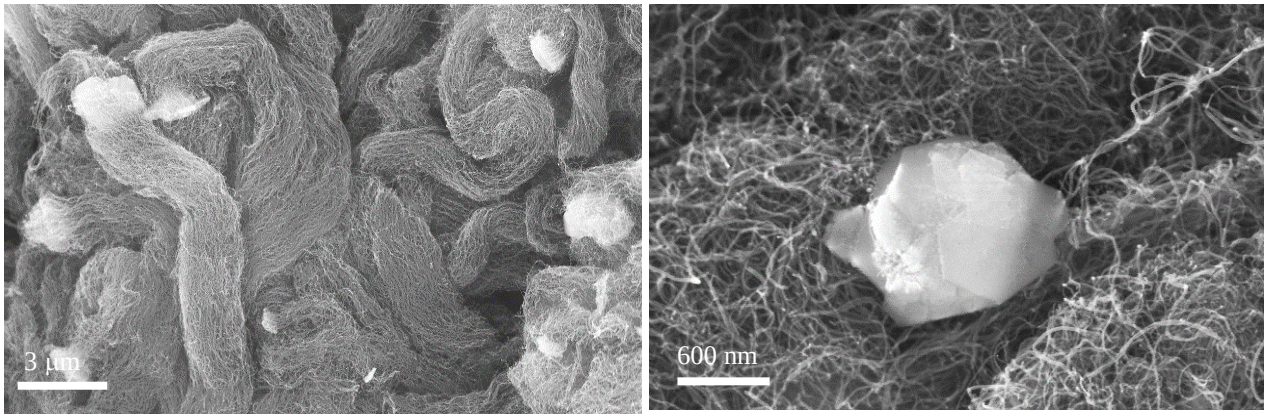


Figure 2: Representative images of the raw soot recorded at different magnifications using an Everhart-Thornley secondary electron detector. Images were generated using 10 keV primary electrons, a 30 µm condenser aperture, at approximately 10 mm working distance.



(a) (b)

Figure 3: Representative SEM images recorded with an in-lens secondary electron detector. (a) an image showing MWCNT bundles presumably terminated by catalyst, and (b) a higher magnification image of the presumed catalyst. Spot measurements by Energy-dispersive X-ray spectroscopy identified the predominant materials in the catalyst as carbon, oxygen, and aluminum, and the predominant material in the MWCNTs as carbon.

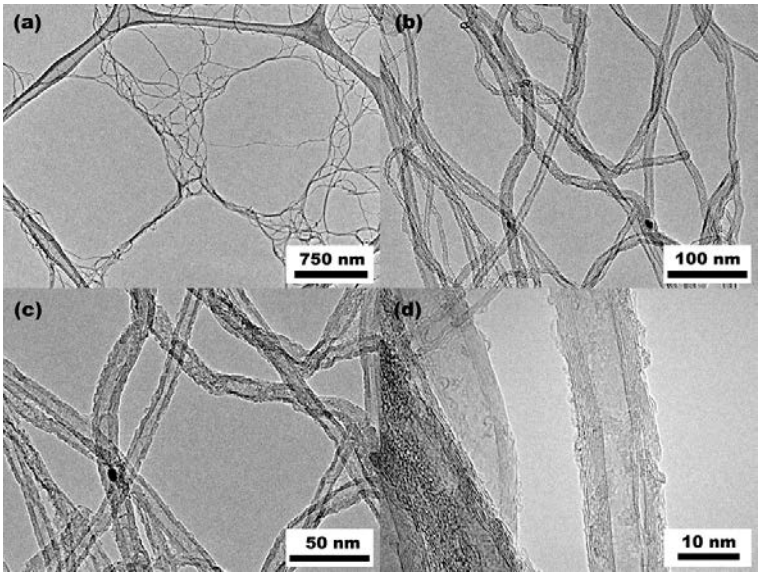


Figure 4: Representative TEM images of SRM 2484 at increasing magnification. The lacey carbon support film can be seen in (a); residual catalyst particles and other defects such as kinks and internal caps can be observed in images (b) and (c). Image (d) is a high-resolution phase contrast image of the type used for wall counting. The thin, irregular coating on the MWCNT is amorphous carbon contamination from either the fabrication or the sample preparation process.

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[7] Paul, R. L.; Lindstrom, R. M.; *Metall. Mater. Trans. A*, 43A, 4888–4895 (2012).

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.