Documentation Sheet
High Nitrogen Surface Area Reference Material (HNSA)
For Use with ASTM D6556, Carbon Black—Total and External Surface Area by Nitrogen Adsorption and ASTM D3265, Carbon Black—Tint Strength
(Evaluated per ASTM D4483-20 as applied by D24.61)
Accepted by D24 Members Through Email Survey: February 1, 2022[1]
Supersedes: None

Introduction

ASTM Committee D24 on Carbon Black has identified a need for a high surface area, small particle size reference material [High Nitrogen Surface Area (HNSA)] for use by producers and users of this type of carbon black to validate their testing equipment. This reference material is intended for use only with test methods D6556 [Carbon Black—Total and External Surface Area by Nitrogen Adsorption (NSA and STSA)] and D3265 [Carbon Black—Tint Strength]. ***Using the HNSA reference material with other test methods is inappropriate.***

Normalization of the test results is not recommended for D6556, while normalization of the D3265 test results is accomplished using the Industry Tint Reference Black (ITRB) reference materials. Therefore, the use of the HNSA reference material for normalization is inappropriate.

The members of D24 identified a suitable candidate material. An ITP was conducted in March 2021 to establish the reference values for the HNSA material for each test method. The results of the analysis of the ITP data are shown in Table 1.

Table 1 Precision Parameters for HNSA, Mar 2021, NSA, STSA, and Tint, (Type 1 Precision)

		Units	Per test method						
Material	Test	Number of Laboratories (M/H/L)*	Mean Level	Sr	r	(r)	SR	R	(R)
HNSA	NSA	43(5/3/10)	252.7	1.02	2.89	1.1	2.66	7.53	3.0
HNSA	STSA	48(3/3/9)	193.0	1.25	3.55	1.8	3.02	8.55	4.4
HNSA	Tint	47(4/6/5)	151.9	0.57	1.63	1.1	3.17	8.96	5.9

*M = number of outliers for Mean; H = number of outliers for High variation; L = number of outliers for Low variation.

Shelf Life

Per ASTM D6915, Standard Practice for Carbon Black—Evaluation of Standard Reference Blacks, the shelf life of the Standard Reference Black (SRB) carbon blacks is indefinite when properly stored in a manner that protects it from exposure to sources of moisture, such as precipitation, other sources of liquid water, or high humidity environments. The HNSA material

[1] The current version of this document is available from Balentine Enterprises, Inc., 1410 South Cedar Street (Suite 20), Borger, TX, 79007, USA, www.carbonstandard.com, email: mark.derouen@carbonstandard.com, phone: 806.273.3006.

is similar to the SRBs materials so it is expected that its shelf life is also indefinite when properly stored as stated above.

Properties for the HNSA Set

The testing conducted as part of the ITP and evaluation using ASTM D4483-20 as applied by D24.61 generated accepted reference values (means), AR-values, for the D6556 and D3265 test methods as shown in Table 1 and 2 and 3 sigma limits on these values or on individual daily values as obtained by any laboratory using the HNSA reference material as shown in Table 2. The 2 and 3 sigma limits apply to a single measurement of the listed test properties. Two times the 2 or 3 sigma limit equals the total 4 or 6 sigma range, respectively.

Mandel's h and k statistics were used to identify outliers. ASTM D4483-20 uses a one-sided k test to identify outliers having high variability. The ITP evaluation used a two-sided k test to identify outlier laboratories with variation that is statistically too high or too low when compared to the variation within the ITP data set. This approach is thought to better represent expected variability in real-world testing and helps to offset memory-bias from an individual's repeated testing of the same material(s). The outlier mean or standard deviation parameters were deleted and the remaining values were used to calculate the values shown in Tables 1 and 2.

ASTM D4483-20 has a two-level process of evaluation for outliers. The first evaluation is performed at a 95% significance level. If no outliers are identified at the 95% level, the analysis is complete and the data is used to prepare the precision and bias tables and statements. If outliers are identified at the 95% level, the outliers are treated per the D4483-20 instructions to produce a reduced data set. Because the outliers have already been identified and treated at the 95% significance level, the second evaluation is performed at a 98% significance level on the reduced data set remaining after the 95% level outlier treatment. The critical h and k values are calculated at 98% significance for the number of laboratories remaining in the reduced data set. If no outliers are identified at the 98% level, the analysis is complete and the reduced data set is used to prepare the precision and bias tables and statements. If outliers are identified at the 98% level in the reduced data set, the outliers are treated per the D4483-20 instructions to produce the final data set. The final data set is used to prepare the precision and bias tables and statements.

'Accepted Reference Value' or AR-value; this is the average (mean), for the D6556 or D3265 test methods as listed below in Table 2, obtained in an ITP for a large group of typical laboratories using samples taken from the candidate material lot. See page 5 for more details on the ITP.

'Within Typical Laboratory' 2 and 3 sigma value; this is the within laboratory ± 2 and ± 3 standard deviation (Sr) value (for single measurements) on the HNSA reference material with the process centered on the AR-values for the D6556 or D3265 test methods, as obtained from the same group of typical ITP laboratories.

'Between Typical Laboratory' 2 and 3 sigma value); this is the between laboratory ± 2 and ± 3 standard deviation (SR) value (for single measurements) on the HNSA reference material with the process centered on the AR-values for the D6556 or D3265 test methods, as obtained from the same group of typical ITP laboratories.

2 sigma versus 3 sigma use considerations: Most carbon black test properties (with the exception of pellet hardness maximum) have an acceptable approximation to a normal distribution. With a normal distribution, 95.5% of all the test values are expected to fall within the limits of mean ± 2 sigma and 99.7% will fall within the limits of mean ± 3 sigma. This means that with only random variation present, approximately 1 in 20 results will fall outside the 2 sigma limits and 3 in 1000 will fall outside the 3 sigma limits. This means that when using 2 sigma limits the laboratory will be looking for a problem 1 in 20 test results when there is no problem to be found. This is a waste of valuable resources. On the other hand, when using 3 sigma limits the laboratory will be looking for a problem when there is not a problem only 3 in 1000 test results. However, if the consequences of allowing a problem to go undetected for a long time are too high, using 3 sigma limits may not give adequate warning in sufficient time to implement timely corrective action. Using 2 sigma limits will give an earlier warning of the presence of a problem. It is up to the user to balance the costs of untimely warnings versus the costs of searching for problems that do not exist.

Special consideration for bias: When no absolute reference material exists, such as is the case with carbon black testing, a laboratory's bias can be defined as the difference between its results and the mean result from an ITP involving many laboratories. Every laboratory can be expected to have some level of bias due to the unique combination of testing conditions (equipment, materials, manpower, environment, etc.) that exists within a given laboratory. The level of bias for a given laboratory may or may not be critical. A laboratory that did not participate in the ITP may find that it cannot maintain control within the control limits due to factors unique to that laboratory causing bias in its values, increased variation, or both. The laboratory should conduct an investigation to identify the presence and cause(s) of the bias and variation and eliminate them so that it is aligned with the ITP data. Participation in a multi-laboratory precision study, such as D24's LPRS program, may help to identify the unique sources of bias and variation. The HNSA reference material can be used to assist a laboratory in determining the presence and magnitude of bias and variation using the values given in Tables 2 below.

Using the HNSA Set – When using the D6556 or D3265 test methods, it is strongly recommended that laboratories determine if they are operating in an "in control" manner, by the use of the ± 2 or ± 3 sigma within-laboratory limits as the laboratory may choose to use. Despite rigorous analysis of the ITP data for the AR-value(s) and associated standard deviation(s), the group of laboratories in this (and any) ITP do not represent a typical "in statistical control system" to which the usual 6 sigma limits are applied. All the assignable causes of variation that are typically eliminated to attain 'statistical control' have not and cannot be, eliminated for the AR testing.

Normalization of the NSA or STSA in carbon black test results is not recommended. Tint test results are normalized using the ITRB reference material.

Table 2 HNSA Mean (AR-value) and Limit Values for NSA, STSA, and Tint testing

Units per test method	Percent	Within Laboratory			Between Laboratories		
Test Method	Mean (AR-value)	Sr	2 x Sr	3 x Sr	SR	2 x SR	3 x SR
D6556 NSA	252.7	1.02	2.04	3.06	2.66	5.32	7.98
D6556 STSA	193.0	1.25	2.51	3.76	3.02	6.04	9.06
D3265 Tint	151.9	0.57	1.15	1.72	3.17	6.33	9.50

Background and Interlaboratory Test Program Details:
HNSA Reference Material

Background - The HNSA reference material is similar to the Standard Reference Blacks (SRBs) used for a number of test methods under the jurisdiction of ASTM Committee D24. The members of D24 decided that the HNSA reference material would not be classified as a member of the SRB sets but would be a stand-alone reference material similar to the INR and STRM materials.

A producer of high surface area, small particle size carbon blacks agreed to produce a lot of material for evaluation to become the HNSA reference material.

Evaluation of the HNSA Reference Material – The covid-19 pandemic caused delays in receiving data from other LPRS programs operated by OkStats, which caused delays in analysis and reporting of the HNSA data. The analysis was started in November but not completed until January 2022. Two reports based on partial data analyses were issued during that period.

The values listed in Table 1 were obtained through the ITP and were analyzed per D4483-20 as practiced by subcommittee D24.61.

Fifty-four laboratories reported NSA and STSA data and fifty-one laboratories reported tint data. Besides collecting the test results, information regarding the testing conditions was also collected in the ITP. This information was used to determine whether a laboratory performed the testing per the ASTM test method instructions. Eleven laboratories either reported testing condition that did not comply with the NSA testing instructions or did not provide the requested information that would permit validation of their data. Six laboratories either reported testing condition that did not comply with the STSA testing instructions or did not provide the requested information that would permit validation of their data. Four laboratories either reported testing condition that did not comply with the Tint testing instructions or did not provide the requested information that would permit validation of their data. The data from these laboratories was removed from the data set for each test method before performing any outlier analysis. The laboratory count for outlier analysis was forty-three for NSA, forty-eight for STSA, and forty-seven for Tint.

Outlier evaluation was performed at a 95% significance level for mean and variability. A 2-sided k test was used for the variability outliers to remove laboratories with variability that was statistically too high or too low based on the variability within the data set. Outliers were detected at the 95% level. Per D4483-20, the preferred outlier treatment for data sets with nine or more laboratories is parameter deletion. For laboratories with high or low outlier mean values, those outlier mean values were deleted from the data set. For laboratories with high or low outlier variability values, those outlier variability values were deleted from the data set.

The data set remaining after the outlier treatment at 95% significance level was then subjected to outlier evaluation at the 98% significance level. Additional outliers were detected at the 98% significance level. Parameter deletion was applied to those outliers. The data set remaining after 95% and 98% outlier treatment was used to prepare the precision values shown in Table 1.

The values in Table 2 are an expansion of values in Table 1 to show the 2-standard deviation (sigma) and 3-standard deviation (sigma) limits to be used if a laboratory wishes to practice control charting of the HNSA reference material for the NSA, STSA, or Tint test methods.

Interlaboratory Test Program (ITP) – A sample of the HNSA candidate material was distributed with the 2021 CB LPRS samples. Only NSA, STSA, and Tint was tested on the material. A data file using the CB LPRS format was distributed to all 2021 CB LPRS participants to collect the test results and information for the HNSA candidate material. Since this testing was in addition to the regular CB LPRS samples, performing these tests was voluntary. The testing was to be done during March/April 2021 with a data reporting deadline of May 1, 2021. The last data was received May 24th.

The testing and reporting protocols for the HNSA candidate material were the standard testing and reporting protocols used in the CB LPRS program.

To report corrections or request changes to this document, contact Balentine Enterprises, the chairman of ASTM subcommittee D24.61, or the chairman of ASTM subcommittee D24.21.