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Standard Guide for Carbon Black—Validation of Test Method Precision and Bias[1]

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1. Scope

1.1 This guide covers a procedure for using ASTM Standard Reference Blacks[2] (SRBs) to continuously monitor the precision of those carbon black test methods for which standard values have been established. It also offers guidelines for troubleshooting various test methods.

1.2 This guide establishes the x-chart control limits to be used when continuously monitoring those tests listed in Section 2. Alternatively, these control limits may be used as a basis for comparison to testing precision computed within a laboratory.

1.3 This guide uses statistical control chart methodology as discussed in STP-15-D[3] to determine if a laboratory's test results differ significantly from the accepted values of the SRBs.

1.4 This guide provides a statistical procedure for improving test reproducibility when a laboratory cannot physically calibrate its apparatus to obtain the standard values of the ASTM SRBs, within the ranges given in the precision statement of the test method.

1.5 The values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only.

1.6 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:* [4]

D 1510 Test Method for Carbon Black—Iodine Adsorption Number

D 1513 Test Method for Carbon Black, Pelleted—Pour Density

D 1765 Classification System for Carbon Blacks Used in Rubber Products

D 2414 Test Method for Carbon Black—Oil Absorption Number (OAN)

D 3037 Test Methods for Carbon Black-Surface Area by Nitrogen Adsorption[5]

D 3191 Test Methods for Carbon Black in SBR (Styrene-Butadiene Rubber)—Recipe and Evaluation Procedures

D 3192 Test Methods for Carbon Black Evaluation in NR (Natural Rubber)

D 3265 Test Method for Carbon Black—Tint Strength

D 3493 Test Method for Carbon Black—Oil Absorption Number of Compressed Sample (COAN)

D 3765 Test Method for Carbon Black—CTAB (Cetyltrimethylammonium Bromide) Surface Area

D 4820 Test Methods for Carbon Black—Surface Area by Multipoint B.E.T. Nitrogen Adsorption (Discontinued 2000) Replaced by D 6556[5]

D 5816 Test Methods for Carbon Black—External Surface Area by Multipoint Nitrogen Adsorption (Discontinued 2000) Replaced by D 6556[5]

D 6556 Test Method for Carbon Black—Total and External Surface Area by Nitrogen Adsorption

3. Significance and Use

3.1 One of the major causes of poor test precision is the lack of calibration or standardization of instruments, apparatus, reagents, and technique among laboratories. The sum of all sources of testing error is unique for an individual laboratory. A least-squares regression of a laboratory's actual test values for reference materials to the established mean values will result in a unique least-squares regression line (and equation) for that laboratory. Generally, there are two reasons for using the SRBs in testing: (*1*) to monitor testing performance (see Section 4) to ensure that no systematic error or bias is affecting

[1] This guide is under the jurisdiction of ASTM Committee D24 on Carbon Black and is the direct responsibility of Subcommittee D24.61 on Carbon Black Sampling and Statistical Analysis.

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[2] Standard Reference Blacks are available from Laboratory Standards & Technologies, Inc., 227 Somerset St., Borger, TX 79007.

[3] *Symposium on Manual on Presentation of Data and Control Chart Analysis, ASTM STP 15D*, ASTM International, 1976.

[4] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[5] Withdrawn.

TABLE 1 SRB 6 Control Chart Limits

NOTE—See Test Method D 3765 for an algorithm to calculate CTAB values from the STSA values for the SRB 6 set.

Test Property	ASTM Standard	SRB	Target Value	3 s Value	Lower Control Limit	Upper Control Limit
Iodine adsorption number,[A] g/kg	D 1510	A 6 (N134)	137.2	3.00	134.20	140.20
		B 6 (N220)	117.9	2.28	115.62	120.18
		C 6 (N326)	82.4	1.08	81.32	83.48
		D 6 (N762)	26.5	1.26	25.24	27.76
		E 6 (N660)	35.3	1.62	33.68	36.92
		F 6 (N683)	33.1	1.44	31.66	34.54
Oil absorption number, 10^{-5} m^3/kg ($cm^3/100$ g)	D 2414[B]	A 6 (N134)	123.7	1.83	121.87	125.53
		B 6 (N220)	114.3	1.11	113.19	115.41
		C 6 (N326)	70.3	1.05	69.25	71.35
		D 6 (N762)	67.4	1.50	65.90	68.90
		E 6 (N660)	88.2	1.80	86.40	90.00
		F 6 (N683)	133.6	3.33	130.27	136.93
		G 5 (N990)	36.2	0.75	35.45	36.95
Oil absorption number of compressed sample (24M4), 10^{-5} m^3/kg ($cm^3/100$ g)	D 3493[B]	A 6 (N134)	101.0	2.46	98.54	103.46
		B 6 (N220)	98.5	1.80	96.70	100.30
		C 6 (N326)	68.1	1.59	66.51	69.69
		D 6 (N762)	60.2	1.59	58.61	61.79
		E 6 (N660)	76.0	2.49	73.51	78.49
		F 6 (N683)	88.6	2.58	86.02	91.18
Surface area by multipoint B.E.T. nitrogen adsorption (NSA), 10^3 m^2/kg (m^2/g)	D 4820[C]	A 6 (N134)	143.9	2.10	141.80	146.00
		B 6 (N220)	110.0	1.59	108.41	111.59
		C 6 (N326)	78.3	1.20	77.10	79.50
		D 6 (N762)	30.6	0.75	29.85	31.35
		E 6 (N660)	36.0	1.20	34.80	37.20
		F 6 (N683)	35.3	1.41	33.89	36.71
		G 5 (N990)	9.1	0.36	8.74	9.46
Tint strength	D 3265	A 6 (N134)	129.8	4.11	125.69	133.91
		B 6 (N220)	117.8	3.36	114.44	121.16
		C 6 (N326)	113.1	1.68	111.42	114.78
		D 6 (N762)	56.8	2.01	54.79	58.81
		E 6 (N660)	60.0	1.92	58.08	61.92
		F 6 (N683)	51.7	1.47	50.23	53.17
External surface area by multipoint nitrogen adsorption (STSA), $10^3 m^2/kg$ (m^2/g)	D 5816[C]	A 6 (N134)	135.7	4.11	131.59	139.81
		B 6 (N220)	105.4	2.88	102.52	108.28
		C 6 (N326)	79.2	2.07	77.13	81.27
		D 6 (N762)	29.6	1.35	28.25	30.95
		E 6 (N660)	35.1	2.31	32.79	37.41
		F 6 (N683)	34.1	1.83	32.27	35.93
		G 5 (N990)	8.4	0.60	7.80	9.00

[A] The iodine adsorption number of carbon black has been shown to decrease in value as the black ages. Generally, the higher the surface area the faster the rate of change. Therefore, the target values given in this table may not be obtained due to this aging effect. The most current standard value may be obtained by contacting the chairman of Subcommittee D24.61.

[B] Values determined using *n*-Dibutyl Phthalate (DBP) oil.

[C] NSA values determined using Test Methods D 4820. STSA values determined using Test Methods D 5816. Both test methods have been replaced by Test Method D 6556, which is technically equivalent to the test methods used to determine the values.

the test results, or (2) to establish a statistical calibration (see Section 5) when the correction of assignable causes (see Section 6) does not yield in-control test results.

3.2 In addition to the calibration of a test method by physicochemical means, a statistical method for achieving calibration of a test method is presented.

3.3 This guide outlines the use of control charts to graphically present calibration test data determined for the ASTM SRBs for those test methods given in Section 2. All laboratories are encouraged to utilize statistical control charts and the SRBs because this allows a comparison of testing precision within a laboratory to the "industry average" values found in Table 1.

3.4 The techniques of this guide can be used to continuously monitor testing execution and precision for other tests that are not listed in Section 2 or for materials that fall outside the range of the SRBs for those tests listed in Section 2. In these cases, each laboratory will have to establish the applicable mean and control limit values for the "local reference." The monitoring will then consist of a comparison of present test results for the "local reference" to past performance within that laboratory instead of to "industry average" values.

4. Procedure for Continuously Monitoring Testing

4.1 For each test of interest, test each SRB listed for that test in Table 1 in duplicate. Use the mean value for each SRB to establish the baseline values. A new baseline should be determined whenever the test equipment or conditions change. If a "local reference" is going to be used for test monitoring, it should be tested at the same time and included in the baseline data.

4.2 Select one (or more) SRBs from the SRB 4, SRB 5, or SRB 6 series (see Note 1) or a "local reference" to cover the range of interest. Because of the differing grades in each SRB set and material ages, do not mix materials from different SRB sets. For example, do not use A, B, and C from set 4 with D, E, and F from set 5. This is especially critical for oil absorptometer calibration. An absorptometer calibrated with F5 (or F5A) must be checked with other members of the 5 set. Likewise, an absorptometer calibrated with F6 must be checked with other members of the 6 set.

NOTE 1—The SRB 4 set is depleted and not commercially available. Some members of the SRB 5 set are depleted and not commercially available. SRB F5A and G5 are commercially available. SRB G5 is used as a member of the SRB 6 set. The SRB 4 and SRB 5 sets may still be in use in some laboratories. Because of the known effects of material aging, it is recommended that the most current set of SRBs be used for test monitoring.

4.3 Prepare a control chart for each of the selected SRBs or "local reference" material(s) for each test method as presented by Part 3 of STP-15-D. It is an accepted practice to control chart one reference material on each day of testing and rotate through each selected reference material on successive days of testing.

4.4 The target values given in Table 1 for SRB6s were determined during the validation of the SRB6 materials. Values are used as control chart limits (x-chart) plus or minus three single test repeatability standard deviations.[6] The mean and control chart limits (three standard deviations) for use on the x-charts must be determined by each laboratory for any "local reference" material(s).

4.5 Plot the uncorrected values for the selected reference materials (see Note 2). If a control limit is exceeded, perform a retest immediately. If the retest falls outside the control limits, stop testing and begin a search for an assignable cause (see Section 6 for a list of possible assignable causes). Once the cause is corrected and the reference material's values are within the established control limits, testing can resume.

4.6 Examples of typical x-charts are found in Figs. 1 and 2.

4.7 If only one reference material is used to regularly monitor testing performance, additional reference materials must be tested periodically to ensure that no systematic error or bias is affecting the test results. Test one or more of the reference materials not routinely used and compare the test results to the original baseline values to ensure that the testing system is still stable. Deviation from the original baseline values indicates the possibility of systematic testing error. If instability is suspected, all the reference materials should be tested and the results compared to the original baseline values. On a longer time frame basis, all the reference materials should be tested and compared to the original baseline values to determine the long-term testing stability. Initiate corrective action as indicated (see Section 6). If stability cannot be demonstrated, it may be necessary to apply a statistical correction (see Section 5).

[6] Supporting data for the SRB4 or SRB5 sets have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR: D24-1043 for SRB4 or RR: D24-1042 for SRB5.

4.8 A laboratory can estimate its testing precision relative to the "industry average" by calculating the three standard deviation values from its actual test data and comparing this to the control limit values for those tests given in Table 1.

NOTE 2—Selected SRBs from SRB4, SRB5, and SRB6 must be plotted on separate charts. Do not plot SRB4 and SRB5, for example D-4 and D-5, on the same chart.

5. Procedure for Continuously Monitoring Testing Using SRB Normalized Data

5.1 If the search for an assignable cause and the subsequent action taken still does not produce results within the control limits, then, only as a last resort, a statistical regression or correction equation may be calculated as described below. This action should not be considered to be a substitute for maintaining good laboratory testing practices, the proper use of a test as described within each test method, or implementing corrective actions, such as those described in Section 6. Section 7 provides the user with a quick guide to the accepted normalization practices for the test methods or properties used as target and typical properties in accordance with Classification D 1765.

5.2 Physically calibrate the test apparatus using the instructions in the test method or the manufacturer's instructions, or both.

5.3 Test the ASTM Standard Reference Blacks at least four (six preferred) times to establish firm measured values.

5.4 Calculate the least-squares linear regression of the standard values on the measured values. This relationship has usually been observed to be linear, although a curvilinear function might conceivably sometimes exist.

5.5 Correct the measured values on all subsequent samples by substituting each measured value into the equation and calculating the corrected value.

5.6 Alternatively, a nomograph or a table of numbers may be used to find the correspondence between a measured value and a corrected value.

5.7 Recheck the regression equation whenever replacement apparatus or a new lot of materials is put into use. Also, recheck it periodically to find changes due to wear or aging.

5.8 The form of the correction equation (linear regression) for SRBs is as follows:

$$\text{The correction equation is: } Y = Ax + B \quad (1)$$

$$\text{or Corrected Value } (CV) = A(\text{actual value}) + B$$

where:

B = Y intercept, and

A = slope.

5.9 A statistical correction may be applied to any of the tests listed in Table 1. For the iodine number test (Test Method D 1510), if corrective actions, such as those listed in 6.1.1, do not bring the measured value(s) within the control limits delineated in Table 1, do not use the target values in Table 1 to prepare a statistical correction for the iodine number. Instead, a statistical correction must be prepared using the target values from Table 2 for reporting iodine number results (see Test Method D 1510 for details). Corrections are applied individually only for those tests where physical calibration is not