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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]

D1510 Test Method for Carbon Black—Iodine Adsorption Number

D1513 Test Method for Carbon Black, Pelleted—Pour Density

D1765 Classification System for Carbon Blacks Used in Rubber Products

D2414 Test Method for Carbon Black—Oil Absorption Number (OAN)

D3037 Test Methods for Carbon Black-Surface Area by Nitrogen Adsorption[5]

D3191 Test Methods for Carbon Black in SBR (Styrene-Butadiene Rubber)—Recipe and Evaluation Procedures

D3192 Test Methods for Carbon Black Evaluation in NR (Natural Rubber)

D3265 Test Method for Carbon Black—Tint Strength

D3493 Test Method for Carbon Black—Oil Absorption Number of Compressed Sample (COAN)

D3765 Test Method for Carbon Black—CTAB (Cetyltrimethylammonium Bromide) Surface Area[5]

D4820 Standard Test Methods for Carbon Black-Surface Area by Multipoint B.E.T. Nitrogen Adsorption[5]

D5816 Standard Test Methods for Carbon Black-External Surface Area by Multipoint Nitrogen Adsorption[5]

D6556 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 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.

[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. The last approved version of this historical standard is referenced on www.astm.org.

TABLE 1 SRB 6 Control Chart Limits

NOTE—See Test Method D3765 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	D1510	A6 (N134)	137.2	3.00	134.20	140.20
		B6 (N220)	117.9	2.28	115.62	120.18
		C6 (N326)	82.4	1.08	81.32	83.48
		D6 (N762)	26.5	1.26	25.24	27.76
		E6 (N660)	35.3	1.62	33.68	36.92
		F6 (N683)	33.1	1.44	31.66	34.54
Oil absorption number, 10^{-5} m^3/kg ($cm^3/100$ g)	D2414[B]	A6 (N134)	123.7	1.83	121.87	125.53
		B6 (N220)	114.3	1.11	113.19	115.41
		C6 (N326)	70.3	1.05	69.25	71.35
		D6 (N762)	67.4	1.50	65.90	68.90
		E6 (N660)	88.2	1.80	86.40	90.00
		F6 (N683)	133.6	3.33	130.27	136.93
		G5 (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)	D3493[B]	A6 (N134)	101.0	2.46	98.54	103.46
		B6 (N220)	98.5	1.80	96.70	100.30
		C6 (N326)	68.1	1.59	66.51	69.69
		D6 (N762)	60.2	1.59	58.61	61.79
		E6 (N660)	76.0	2.49	73.51	78.49
		F6 (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)	D4820[C]	A6 (N134)	143.9	2.10	141.80	146.00
		B6 (N220)	110.0	1.59	108.41	111.59
		C6 (N326)	78.3	1.20	77.10	79.50
		D6 (N762)	30.6	0.75	29.85	31.35
		E6 (N660)	36.0	1.20	34.80	37.20
		F6 (N683)	35.3	1.41	33.89	36.71
		G5 (N990)	9.1	0.36	8.74	9.46
Tint strength	D3265	A6 (N134)	129.8	4.11	125.69	133.91
		B6 (N220)	117.8	3.36	114.44	121.16
		C6 (N326)	113.1	1.68	111.42	114.78
		D6 (N762)	56.8	2.01	54.79	58.81
		E6 (N660)	60.0	1.92	58.08	61.92
		F6 (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)	D5816[C]	A6 (N134)	135.7	4.11	131.59	139.81
		B6 (N220)	105.4	2.88	102.52	108.28
		C6 (N326)	79.2	2.07	77.13	81.27
		D6 (N762)	29.6	1.35	28.25	30.95
		E6 (N660)	35.1	2.31	32.79	37.41
		F6 (N683)	34.1	1.83	32.27	35.93
		G5 (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. These target values shall not be used to prepare a statistical correction regression equation.

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

[C] NSA values determined using Test Methods D4820. STSA values determined using Test Methods D5816. Both test methods have been replaced by Test Method D6556, which is technically equivalent to the test methods used to determine the values.

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, Table 2, or Table 3.

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, Table 2, or Table 3 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, SRB 6, SRB 7, or SRB HT materials (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

TABLE 2 SRB 7 Control Chart Limits

Test Property	ASTM Standard	SRB	Target Value	3 s Value	Lower Control Limit	Upper Control Limit
Iodine adsorption number, g/kg	D1510	A7 (N326)	81.7	0.90	80.80	82.60
		B7 (N134)	136.3	1.50	134.80	137.80
		C7 (HS-Tread)	143.0	1.83	141.17	144.83
		D7 (LS-Carcass)	21.0	0.93	20.07	21.93
		E7 (N660)	35.1	0.93	34.17	36.03
		F7 (N683)	35.6	0.93	34.67	36.53
Oil absorption number (OAN), 10^{-5} m^3/kg ($cm^3/100$ g)	D2414	A7 (N326)	72.6	1.05	71.55	73.65
		B7 (N134)	124.2	1.26	122.94	125.46
		C7 (HS-Tread)	172.0	1.89	170.11	173.89
		D7 (LS-Carcass)	39.3	0.99	38.31	40.29
		E7 (N660)	88.1	1.47	86.63	89.57
		F7 (N683)	129.4	1.74	127.66	131.14
		G7 (N990)	36.2	0.75	35.45	36.95
Oil absorption number of compressed sample (COAN), 10^{-5} m^3/kg ($cm^3/100$ g)	D3493	A7 (N326)	68.6	1.35	67.25	69.95
		B7 (N134)	101.0	1.44	99.56	102.44
		C7 (HS-Tread)	130.9	1.80	129.10	132.70
		D7 (LS-Carcass)	39.0	0.93	38.07	39.93
		E7 (N660)	75.9	1.23	74.67	77.13
		F7 (N683)	88.3	1.35	86.95	89.65
Surface area by multipoint B.E.T. nitrogen adsorption (NSA), 10^3 m^2/kg (m^2/g)	D6556	A7 (N326)	77.2	0.96	76.24	78.16
		B7 (N134)	143.7	1.44	142.26	145.14
		C7 (HS-Tread)	129.8	1.41	128.39	131.21
		D7 (LS-Carcass)	21.0	0.57	20.43	21.57
		E7 (N660)	36.0	0.69	35.31	36.69
		F7 (N683)	36.2	0.78	35.42	36.98
		G7 (N990)	9.1	0.36	8.74	9.46
Tint strength	D3265	A7 (N326)	109.6	1.95	107.65	111.55
		B7 (N134)	129.2	2.13	127.07	131.33
		C7 (HS-Tread)	111.4	2.04	109.36	113.44
		D7 (LS-Carcass)	41.7	0.78	40.92	42.48
		E7 (N660)	59.9	1.35	58.55	61.25
		F7 (N683)	52.7	1.41	51.29	54.11
External surface area by multipoint nitrogen adsorption (STSA), $10^3 m^2/kg$ (m^2/g)	D6556	A7 (N326)	78.0	1.35	76.65	79.35
		B7 (N134)	135.3	2.46	132.84	137.76
		C7 (HS-Tread)	119.2	1.86	117.34	121.06
		D7 (LS-Carcass)	20.6	0.87	19.73	21.47
		E7 (N660)	35.1	0.96	34.14	36.06
		F7 (N683)	35.1	1.05	34.05	36.15
		G7 (N990)	8.4	0.60	7.80	9.00

TABLE 3 SRB HT Iodine Standards Control Chart Limits

SRB	Mean mg/g	Sr mg/g	3s mg/g	LCL mg/g	UCL mg/g
HT-1	44.0	0.25	0.76	43.2	44.8
HT-2	91.1	0.29	0.88	90.2	92.0
HT-3	127.1	0.35	1.05	126.0	128.2

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 or F7 must be checked with other members of the 6 or 7 set, respectively.

NOTE 1—The SRB 4 and 5 sets are depleted and not commercially available. Some members of the SRB 6 set are depleted and not commercially available. SRB G5 is used as a member of the SRB 6 and 7 sets. The SRB 4 and SRB 5 sets may still be, and the SRB 6 set is known to 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.[1] 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 SRB6, Table 2 for SRB7, and Table 3 for SRB HT materials were determined during the validation of the respective 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

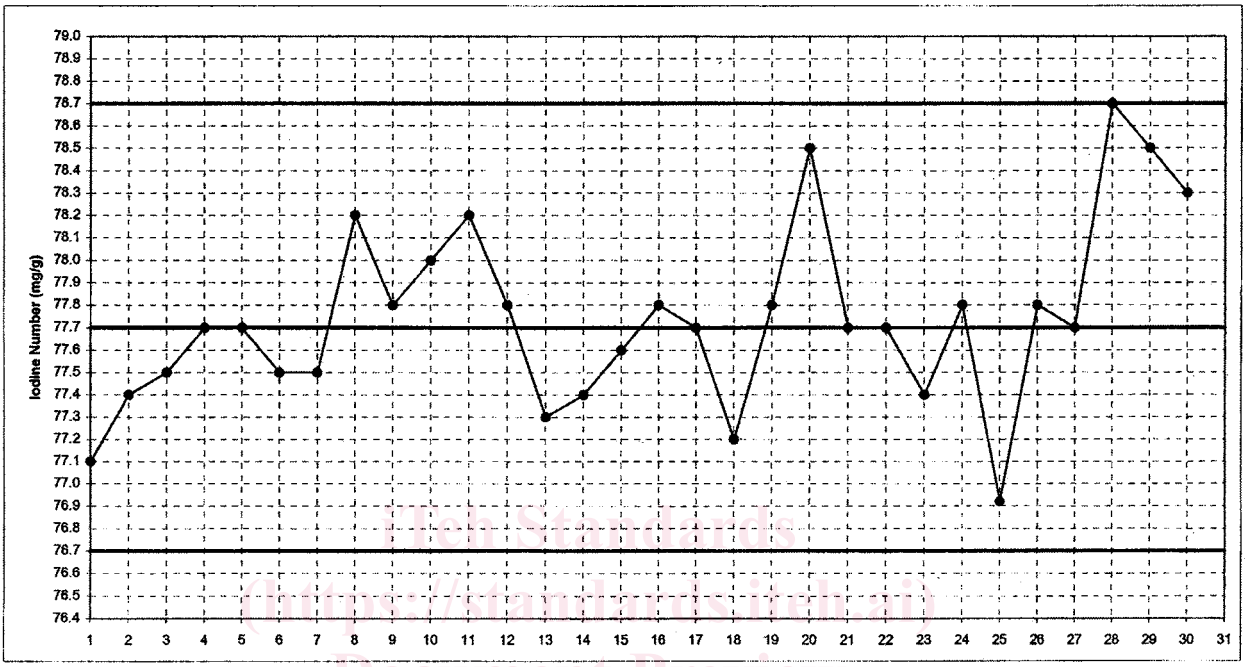
[6] Supporting data for the SRB4 and SRB5 sets have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D24-1043 for SRB4 and RR:D24-1042 for SRB5. Research reports will soon be filed for SRB6 and SRB7 data.

CARBON BLACK-IODINE ADSORPTION NUMBER X-CHART

Test	Iodine Number (D1510)	Equipment	Dosimat 665 Manual Titration	Materi	SRB B5 (N330)	Std. Value	77.7

N	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31
Date																															
Analyst																															
X	77.1	77.4	77.5	77.7	77.7	77.5	77.5	78.2	77.8	78.0	78.2	77.8	77.3	77.4	77.6	77.8	77.7	77.2	77.8	78.5	77.7	77.7	77.4	77.8	76.9	77.8	77.7	78.7	78.5	78.3	

Control Limits	Mean	77.7	UCL	78.7	LCL	76.7	Date Initiated		Date Completed	



NOTES:

Limits based on ASTM D4821
ASTM B-5 Control Limits = 77.7 ± 1.0 mg/g
Note the iodine number drops with sample aging - previous target value for B-5 was 79.1 mg/g

FIG. 1 X-Chart Using Guide D4821 Control Limits

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.

NOTE 2—Selected SRBs from SRB4, SRB5, SRB6, and SRB7 must be plotted on separate charts. Do not plot SRB6 and SRB7, for example D-6 and D-7, on the same chart.

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).

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, Table 2, or Table 3.

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