Designation: D 4821 – 03

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

This standard is issued under the fixed designation D 4821; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

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:*

D 1510 Test Method for Carbon Black—Iodine Adsorption Number[4]

D 1765 Classification System for Carbon Blacks Used in Rubber Products[4]

D 2414 Test Method for Carbon Black—Oil Absorption Number[4]

D 3265 Test Method for Carbon Black—Tint Strength[4]

D 3493 Test Method for Carbon Black—Oil Absorption Number of Compressed Sample[4]

D 6556 Test Methods for Carbon Black—Total and External Surface Area by Nitrogen Adsorption[4]

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.

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

[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.

Current edition approved Jan. 10, 2003. Published February 2003. Originally approved in 1988. Last previous edition approved in 2001 D 4821 – 01a.

[2] Standard Reference Blacks are available from Laboratory Standards & Technologies, Inc., 227 Somerset St., Borger, TX 79007. Phone/fax: (806) 273-3006. E-mail: jwbal@infinitytx.net.

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

[4] *Annual Book of ASTM Standards*, Vol 09.01.

TABLE 1 SRB 6 Control Chart Limits

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 Methods D 6556, which is technically equivalent to the test methods used to determine the values.

"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.

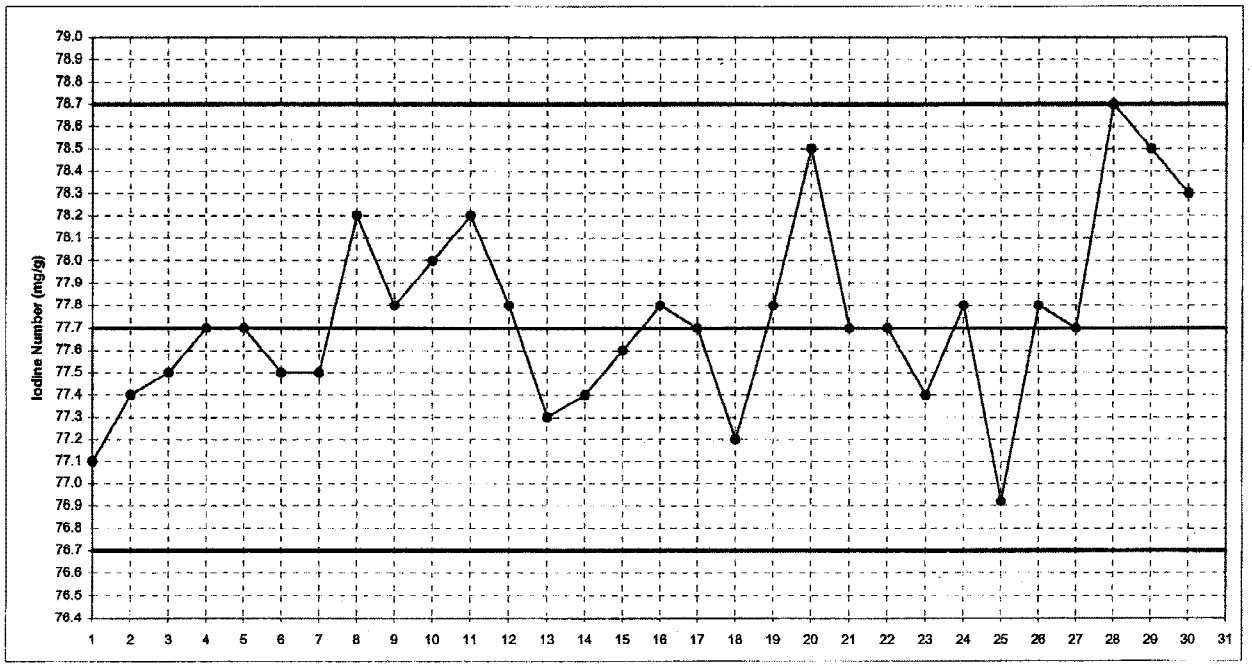
4.2 Select one (or more) SRBs from the SRB 4, SRB 5, or SRB 6 series (see Note 1) or a "local reference" to cover the range of interest. Because of the differing grades in each SRB set and material ages, do not mix materials from different SRB sets. For example, do not use A, B, and C from set 4 with 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 ASTM STP 15D. 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.

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 D 4821 Control Limits

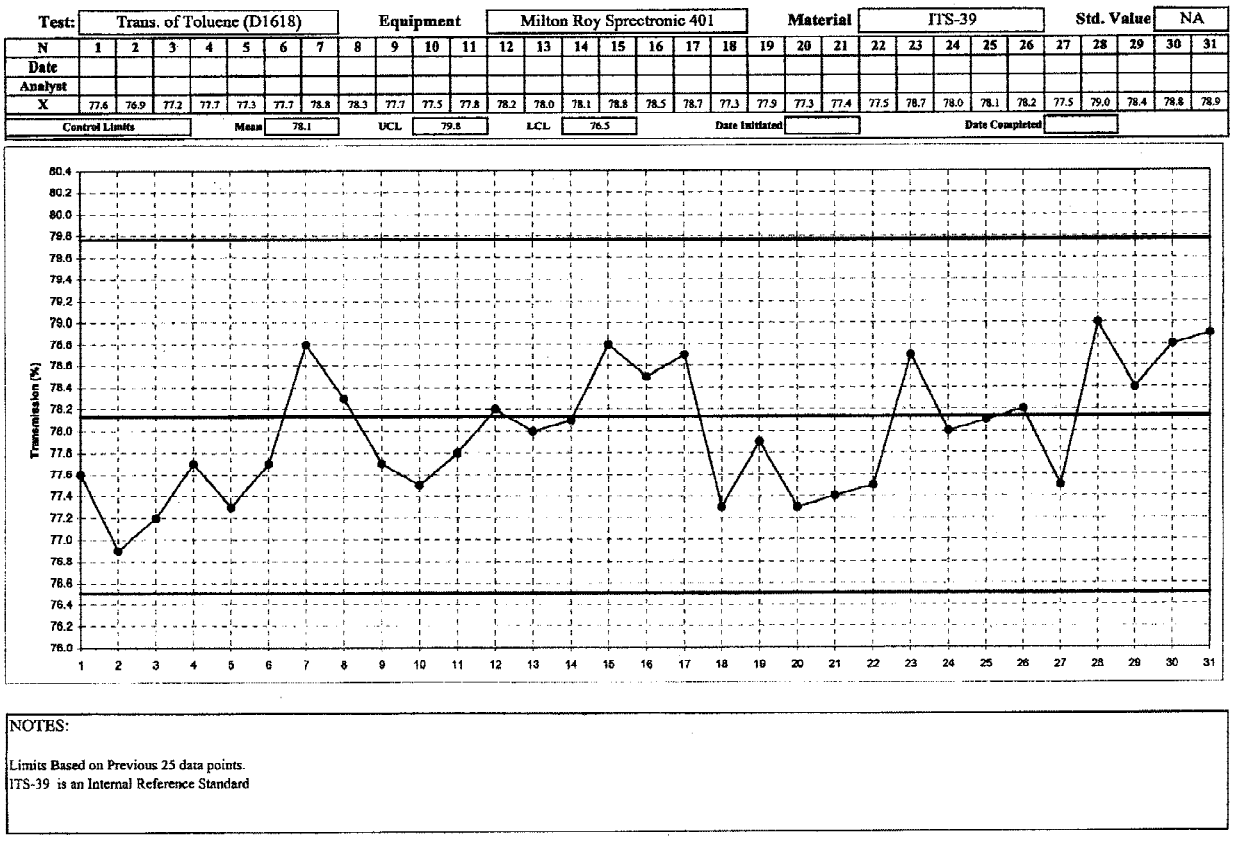
4.4 The target values given in Table 1 for SRB6s were determined during the validation of the SRB 6 materials. Values are used as control chart limits (x-chart) plus or minus three single test repeatability standard deviations. Comparable data for the SRB4 or SRB5 sets may be obtained from ASTM Headquarters by requesting research report RR: D24-1043 for SRB4 or RR: D24-1042 for SRB5. 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).

CARBON BLACK EXTRACTABLES-TRANSMITTANCE OF TOLUENE X-CHART



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	77.6	76.9	77.2	77.7	77.3	77.7	78.8	78.3	77.7	77.5	77.8	78.2	78.0	78.1	78.8	78.5	78.7	77.3	77.9	77.3	77.4	77.5	78.7	78.0	78.1	78.2	77.5	79.0	78.4	78.8	78.9

FIG. 2 X-Chart Using Control Limits Based on Test Data (Three Sigma Limits)

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 per 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 except for iodine number (Test Method D 1510). A statistical correction must not be used 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 successful in maintaining the test within the control limits; not to all the tests in Table 1 if any one test requires correction.

5.10 When it becomes necessary to use a statistical correction factor, all the SRBs for the range of interest (A-F or A-G) must be used to develop the linear regression equation, even if some of the SRBs fall outside the range of interest. At least four values (six preferred) should be used for each SRB. An equal number of results must be used for each SRB. If these instructions are not followed, the correction equation will not be comparable to the corrections made for other instruments and other laboratories. For the Oil Absorption test (Test Method D 2414), it is acceptable to develop a separate linear regression equation for the tread (A-C) and carcass (D-F) SRBs.

5.11 Continuously monitor the selected SRBs and use the most current data to construct the correction equation.

5.12 Use the correction equation to obtain corrected values for the SRBs and plot the corrected values until the control limit is exceeded. When a test value exceeds the control limit, perform a retest immediately, and if the average of the two remains outside the control limit, then recalculate the statistical correction equation using the most recent test data, excluding the value that was outside the control limit, for each selected SRB.

5.13 If the corrected data using the new correction equation still fall outside the control limits, then no further use should be made of the test method until corrective action (see Section 6) brings the SRBs back inside the three standard deviation control chart limits.

5.14 Apply this procedure only to the interpretation of SRB test data. If problems exist, correct them before making further use of the test method. “Local reference” materials do not have established “industry average” values to be used in a linear regression equation.

5.15 This procedure prescribes only the minimum action needed to continuously monitor test precision. Additional SRB testing may be done and correction equations regularly recalculated at individual discretion.

5.16 Discontinue using a statistical correction equation when new or repaired test equipment is put into service, a new lot of SRBs are purchased and put into use, or other corrective actions yield uncorrected test results that fall within the control limits. Resume using a statistical correction equation only when the conditions of Section 4 and 5.1 have again been satisfied.

6. Assignable Causes

6.1 The following lists suggest several assignable causes as possible reasons for a test to be out of statistical control.

6.1.1 *Test Method D 1510 Iodine Adsorption Number*:

6.1.1.1 Incorrect normality of iodine and sodium thiosulfate solutions,

6.1.1.2 Volumetric glassware not calibrated correctly,

6.1.1.3 Purity of water insufficient,

6.1.1.4 Incorrect pipet size,

6.1.1.5 Incorrect cleaning and rinsing of glassware with dirty water,

6.1.1.6 Incorrect potassium iodide (KI) concentration. This is especially suspect if using commercial iodine solutions,

6.1.1.7 The known decline in iodine number as the carbon black ages, and

6.1.1.8 Sample not dried.

6.1.2 *Test Method D 2414 Oil Absorption Number*:

6.1.2.1 Incorrect cooling time between samples,

6.1.2.2 Incorrect setting of torque spring and collar,

6.1.2.3 Incorrect setting of torque limit switch,

6.1.2.4 Excessive blade and bowl clearance,

6.1.2.5 Incorrect finish roughness,

6.1.2.6 Incorrect dashpot oil level,

6.1.2.7 Incorrect rate and volume of oil delivery,

6.1.2.8 Air bubbles in the oil delivery tube,

6.1.2.9 Improper cleaning and lubrication of the area between the blades and the backplate,

6.1.2.10 Sample not dried, and

6.1.2.11 SRB calibration curves need updating.

6.1.3 *Test Method D 3493 Oil Absorption Number, Compressed Sample*:

6.1.3.1 Same as in 6.1.2,

6.1.3.2 Hydraulic press system pressure not properly corrected for diameter of piston, and

6.1.3.3 Incorrect number of compressions.

6.1.4 *Test Method D 3265 Tint Strength*:

6.1.4.1 Incorrect or contaminated ITRB,

6.1.4.2 Incorrect number of mullings,

6.1.4.3 Muller glass plates excessively scratched or scored,

6.1.4.4 Reflectance meter not properly calibrated, and

6.1.4.5 Sample not dried.

6.1.5 *Test Methods D 3037 Nitrogen Surface Area*:

6.1.5.1 Leaks in apparatus, and

6.1.5.2 Faulty O-rings.

6.1.6 *Test Method D 3765 CTAB Surface Area*:

6.1.6.1 Incorrect ITRB for scaling,

6.1.6.2 Incorrect manifold pressure,

6.1.6.3 Incorrect filters,

6.1.6.4 Failure to check standardization curve daily, and

6.1.6.5 Insufficient light intensity on automatic titrator.

6.1.7 *Test Method D 6556 Total and External Surface Area*:

6.1.7.1 Leaks in apparatus,

6.1.7.2 Faulty O-rings,

6.1.7.3 Incorrect sample size,

6.1.7.4 P/P_o not in the linear range of the B.E.T. equation, and

6.1.7.5 STSA greater than NSA.

NOTE 3—*All Test Methods:* If contamination or unusual aging degradation of an SRB is suspected, try using a different SRB sample.

7. Guide to Accepted Normalization Practices for Carbon Black Test Methods

7.1 Accepted normalization practices for test methods found in Classification D 1765 are described below:

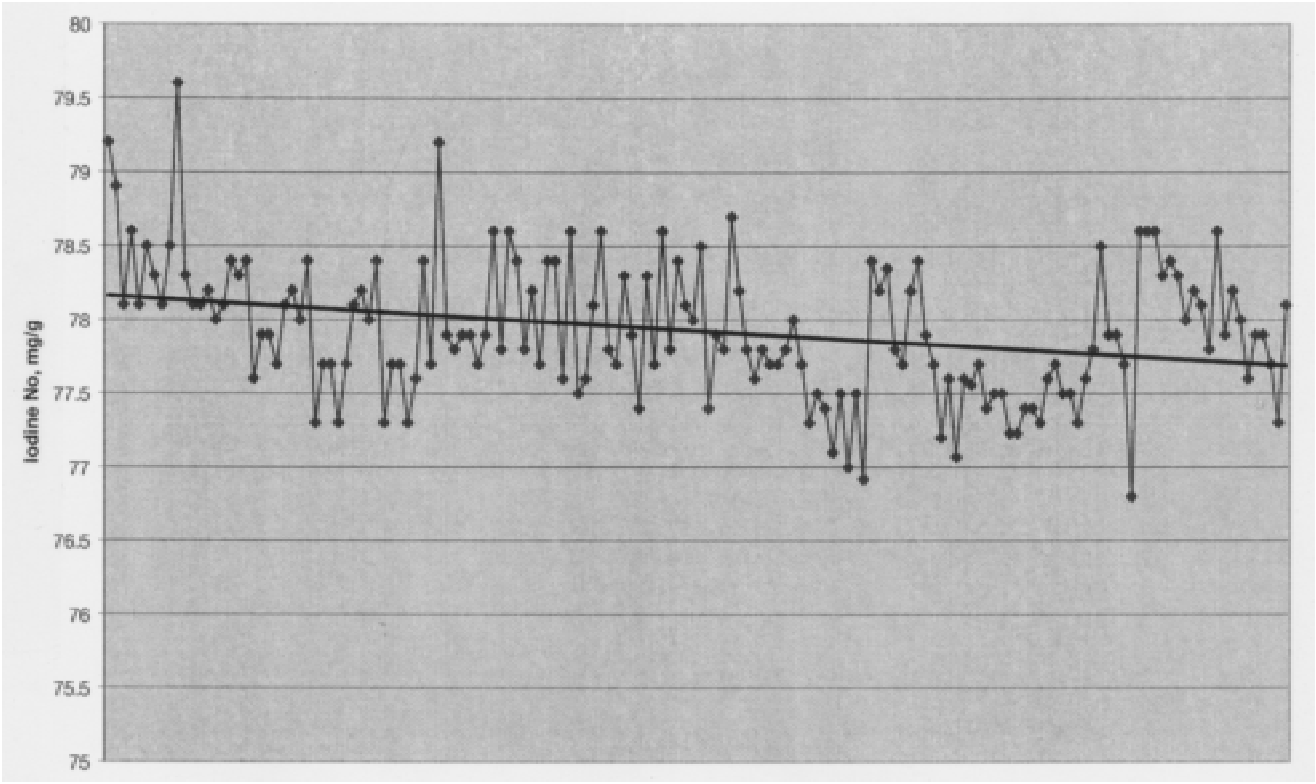


FIG. 3 Iodine Number of SRB B-5 Decreases with Time (Data Represents Three Years)

7.1.1 *Test Method D 1510, Iodine Number*—Should not require normalization. A statistical correction factor per Section 5 should not be used due to the known phenomenon that the iodine number can decrease due to aging. See Fig. 3 for an example of sample aging.

7.1.2 *Test Method D 1513, Pour Density*—No normalization required.

7.1.3 *Test Method D 2414, Oil Absorption*—The only normalization required is that using the tread or carcass SRBs as discussed in the test method.

7.1.4 *Test Method D 3265, Tint Strength*—The only normalization required is that using the ITRB as discussed in the test method. Normalization to the SRBs is not recommended.

7.1.5 *Test Method D 3493, Oil Absorption of Compressed Sample*—The only normalization required is that using the tread or carcass SRBs as discussed in the test method.

7.1.6 *Test Method D 3192, Stress-strain in Natural Rubber*—(Also applies to Test Method D 3191, stress-strain in SBR.). Normalization not recommended.

7.1.7 *Test Methods D 6556, NSA and STSA*—Should not require normalization.

8. Report

8.1 Report the following information on statistical control charts:

8.1.1 Proper identification of the test method standard.

8.1.2 Proper identification of the reference material.

8.1.3 Indicate whether the mean and control limits are from Guide D 4821 Table 1 or calculated from test data.

8.1.4 If the mean and control limits are calculated from test data, identify the number of data points used for the calculations.

8.1.5 Identify test data as “SRB Normalized per Guide D 4821 Section 5 or 7” if either procedure has been applied to the data.

9. Precision and Bias

9.1 The bias of testing an SRB for certain tests may be determined by taking an average, $\bar{x}$, of the most recent 20 to 30 test results for a test (corrected, uncorrected, or both) and calculating the bias or difference from the ASTM accepted value ($\bar{x} - x$ASTM). To reduce the uncertainty associated with the mean value, at least 20 data points should be used to estimate the mean value. Using more than 30 data points does not significantly reduce the uncertainty.

9.2 The precision of testing an SRB for a certain test may be determined by calculating the standard deviation, s, of the data points used in 9.1.

$$s = \sqrt{\frac{(x_1 - \bar{x})^2 + \ldots + (x_n - \bar{x})^2}{n - 1}} \quad (2)$$

10. Keywords

10.1 carbon black; continuously monitoring testing; SRBs; standard reference blacks; statistical control charts

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