Designation: D 4821 – 01a

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 trouble-shooting various test methods.

1.2 This guide establishes the limits within which the statistical calibration procedure of Practice D 3324 shall be applied and establishes the limits for an out-of-calibration condition beyond which the statistical calibration procedure of Practice D 3324 shall not be applied.

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 and provides a format for reporting test data for specified tests on the SRB blacks.

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

1.5 *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 2414 Test Method for Carbon Black—Oil Absorption Number[4]

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

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

D 3324 Practice for Carbon Black—Improving Test Reproducibility Using ASTM Reference Blacks[4]

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

D 3765 Test Method for Carbon Black—CTAB (Cetyltrimethylammonium Bromide) Surface Area[4]

D 4820 Test Methods for Carbon Black—Surface Area by Multipoint B. E. T. Nitrogen Adsorption[6]

D 5816 Test Methods for Carbon Black—External Surface Area by Multipoint Nitrogen Adsorption[6]

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.

3.2 In addition to the calibration of a test method by physicochemical means, Practice D 3324 describes a statistical method for achieving calibration of a test method.

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. These control charts shall be used to validate the testing precision and bias of an individual laboratory.

4. Procedure

4.1 Select six SRBs from the SRB 4, SRB 5, or SRB 6 series to cover the range of interest, being sure to include one each of the A, B, C, D, E, and F (see Note 1) SRBs. 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 DBP 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—SRB 4 and SRB 5 are depleted and not commercially available. However, they are still in use in some laboratories.

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[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 Dec. 10, 2001. Published February 2002. Originally published as D4821 – 88. Last previous edition D4821 – 01.

[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.

[5] Discontinued 1999. See 1998 *Annual Book of ASTM Standards,* Vol 09.01.

[6] Discontinued 2000; replaced by Test Method D 6556; see *1999 Annual Book of ASTM Standards,* Vol 09.01.

4.2 Prepare a control chart for each of the selected SRBs for each test method as presented by Part 3 of ASTM STP 15D.

4.3 The target values given in Table 1 for SRB 6 are the nominal SRB values reported in Practice D 3324. Values are used as control chart limits plus or minus three single test repeatability standard deviations. These values were determined during the validation of the SRB 6s. Comparable data for the SRB 4 set or SRB 5 sets may be obtained from ASTM International Headquarters by requesting research report RR: D24–1043 for SRB 4 data or RR: D24–1042 for SRB 5 data.

NOTE 2—SRB G5 may be used in conjunction with the SRB 6 series.

4.4 Plot the uncorrected values for the selected six SRBs until a repeatability control limit is exceeded (see Note 3). Perform a retest immediately. If the retest falls outside the repeatability control limits, then begin a search for an assignable cause. (See Section 5 for a list of assignable causes.) If the search for an assignable cause and the subsequent action taken still do not produce results within the control limits, then a statistical regression or correction equation shall be calculated as described in Practice D 3324.

NOTE 3—Selected SRBs from SRB 4 and SRB 5 may be plotted on separate charts. Do not plot SRB 4 and SRB 5, for example D-4 and D-5, on the same chart.

4.5 Continuously monitor the selected SRBs and use the most current six data for each selected SRB to construct the correction equation. Otherwise, the correction equation will not be comparable to the corrections made for other instruments and other laboratories.

4.6 Use the correction equation to obtain corrected values for the selected SRBs and plot the corrected values until the repeatability control limit is again 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 six test data for each selected SRB.

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

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
Dibutyl phthalate (DBP) absorption number, 10^{-5} m^3/kg ($cm^3/100$ g)	D 2414	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
DBP absorption number of compressed sample (CDBP), 10^{-5} m^3/kg ($cm^3/100$ g)	D 3493	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	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	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 (N672)	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.

4.8 Apply this procedure only to the interpretation of SRB test data. If problems exist, correct them before making further use of the test method.

4.9 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.

4.10 An example of determining a correction equation for SRBs A-4, B-4, C-4, D-4, E-4, and F-4 for DBP Absorption Number is as follows:

$$\text{The correction equation is: } Y = Ax + B \text{ or}$$
$$\text{Corrected Value } (CV) = A\,(\text{actual value}) + B \qquad (1)$$

where:
B = Y intercept, and
A = slope.

4.11 Examples of control charts for the six SRBs are shown in Fig. 1 and Fig. 2.

5. Assignable Causes

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

5.1.1 *Test Method D 1510 Iodine Adsorption Number*:

5.1.1.1 Incorrect normality of iodine and sodium thiosulfate solutions,

5.1.1.2 Volumetric glassware not calibrated correctly,

5.1.1.3 Purity of water insufficient,

5.1.1.4 Incorrect pipet size, and

5.1.1.5 Incorrect cleaning and rinsing of glassware with dirty water.

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

5.1.1.7 The known decline in iodine number as the carbon black ages.

5.1.2 *Test Method D 2414 DBP Absorption Number*:

5.1.2.1 Incorrect cooling time between samples,

5.1.2.2 Incorrect setting of torque spring and collar,

5.1.2.3 Incorrect setting of torque limit switch,

5.1.2.4 Excessive blade and bowl clearance,

5.1.2.5 Incorrect finish roughness,

5.1.2.6 Incorrect dashpot oil level,

5.1.2.7 Incorrect rate and volume of DBP delivery,

5.1.2.8 Air bubbles in the DBP delivery tube, and

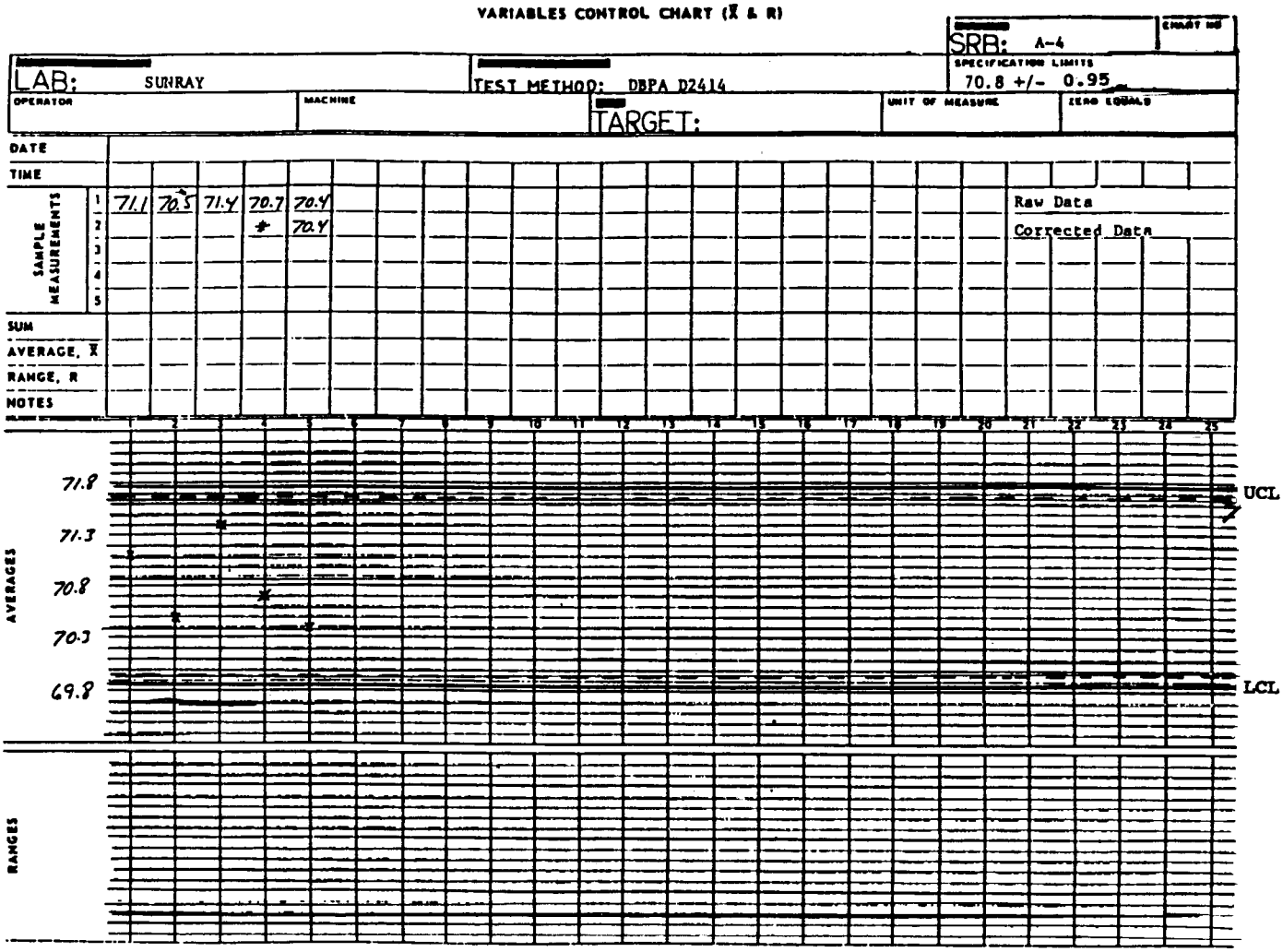

FIG. 1 Control Chart SRB A-4

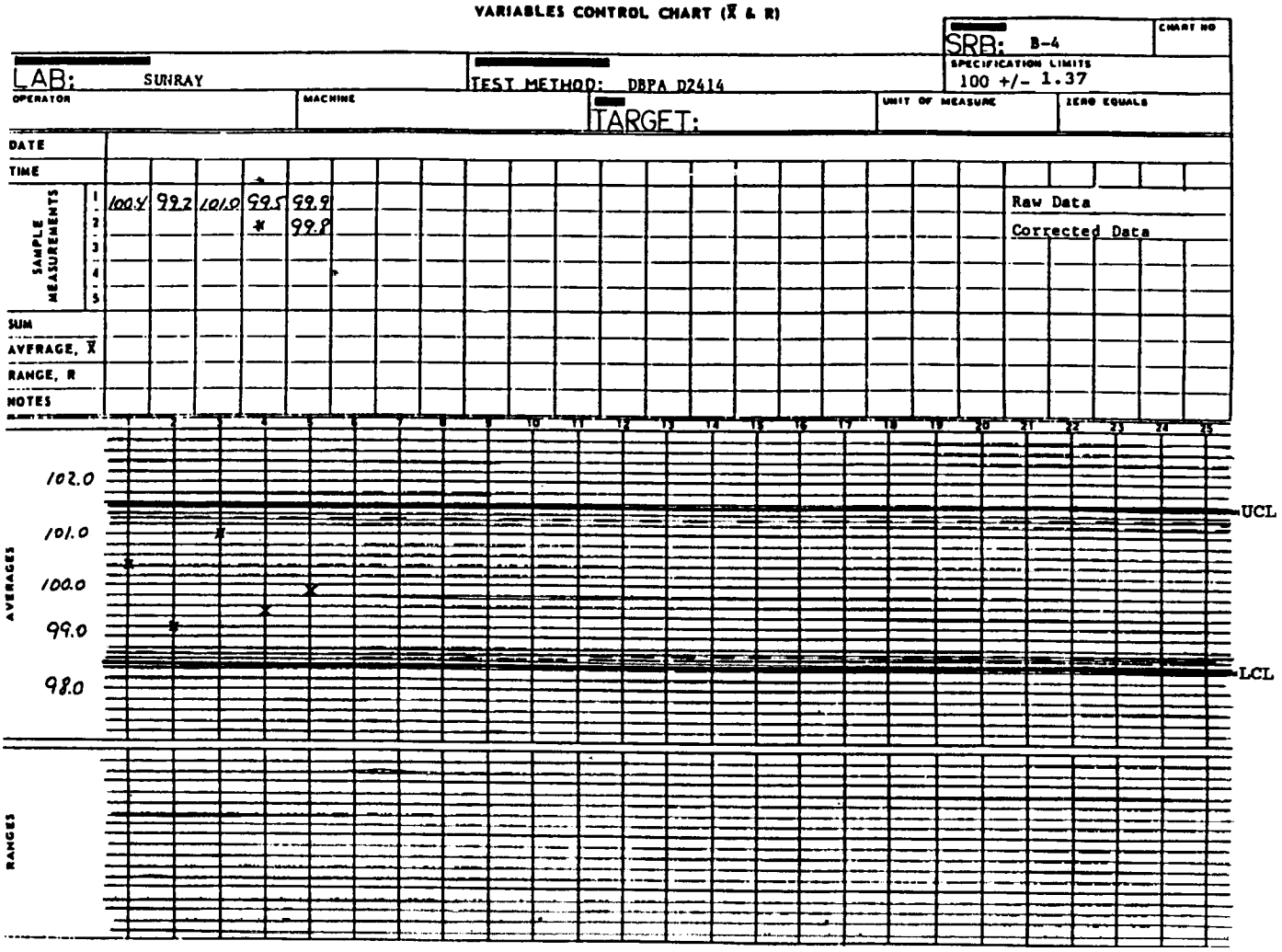

FIG. 2 Control Chart SRB B-4

DBP Absorption Number

SRB A-4		SRB B-4		SRB C-4		SRB D-4		SRB E-4		SRB F-4	
X ACTUAL	*Y* NOMINAL	*X* ACTUAL	*Y* NOMINAL	*X* ACTUAL	*Y* NOMINAL	*X* ACTUAL	*Y* NOMINAL	*X* ACTUAL	*Y* NOMINAL	*X* ACTUAL	*Y* NOMINAL
71.1	70.8	100.4	100.0	128.2	130.8	65.0	64.8	88.7	90.1	131.0	130.0
70.5	70.8	99.2	100.0	131.4	130.8	63.8	64.8	90.9	90.1	129.4	130.0
71.4	70.8	101.0	100.0	130.6	130.8	65.4	64.8	91.3	90.1	130.6	130.0
70.7	70.8	99.5	100.0	131.7	130.8	64.6	64.8	89.3	90.1	129.1	130.0

$\Sigma X = 2344.8$ $\Sigma Y = 2346.0$ $\Sigma XY = 245197.7$
$\Sigma X^2 = 245061.4$ $n = 24$

$$B = Y \text{ intercept} = \frac{\Sigma Y \Sigma X^2 - \Sigma X \Sigma XY}{n\Sigma X^2 - (\Sigma X)^2} = -0.067$$

$$A = \text{slope} = \frac{n\Sigma XY - \Sigma X \Sigma Y}{n\Sigma X^2 - (\Sigma X)^2} = 1.0012$$

Example: For SRB B-4 test value of 99.9
$CV = 1.0012\ (99.9) + 4 - 0.067 = 100.0$

5.1.2.9 Improper cleaning and lubrication of the area between the blades and the backplate.

5.1.3 *Test Method D 3493 DBP Absorption Number, Compressed Sample*:

5.1.3.1 Same as in 5.1.2,

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

5.1.3.3 Incorrect number of compressions.

5.1.4 *Test Method D 3265 Tint Strength*:

5.1.4.1 Incorrect or contaminated ITRB,

5.1.4.2 Incorrect number of mullings,

5.1.4.3 Muller glass plates excessively scratched or scored, and

5.1.4.4 Reflectance meter not properly calibrated.

5.1.5 *Test Methods D 3037 Nitrogen Surface Area*:

5.1.5.1 Leaks in apparatus, and

5.1.5.2 Faulty O-rings.

5.1.6 *Test Method D 3765 CTAB Surface Area*:

5.1.6.1 Incorrect ITRB for scaling,

5.1.6.2 Incorrect manifold pressure,

5.1.6.3 Incorrect filters,

5.1.6.4 Failure to check standardization curve daily, and

5.1.6.5 Insufficient light intensity on automatic titrator.

NOTE 4—*All Test Methods:* If contamination or unusual aging degradation of an SRB is suspected, try using a different SRB sample.

6. Report

6.1 Report the following information:

6.1.1 Proper identification of the test method standard,

6.1.2 The value of the bias ($\bar{x} - x$ASTM) as determined in 7.1, and

6.1.3 The standard deviation, *s*, using the values from 7.1.

7. Precision and Bias

7.1 The bias of testing an SRB for certain tests may be determined by taking an average, $\bar{x}$, of the most recent 25 test results for a test (corrected, uncorrected, or both) and calculating the bias or difference from the ASTM accepted value ($\bar{x} - x$ASTM).

7.2 The precision of testing an SRB for a certain test may be determined by calculating the standard deviation, *s*, of the 25 points in 7.1.

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

8. Keywords

8.1 carbon black; SRBs; standard reference blacks; validation; variables control charts