Documentation Sheet
Iodine Number Reference (INR)
For Use with ASTM D1510, Carbon Black—Iodine Adsorption Number
(Evaluated per ASTM D4483-99)
Approved by D24.61: June 26, 2018[1]
Supersedes: None

Introduction

It has long been known by carbon black producers and users that the Iodine Adsorption Number (a.k.a., Iodine Number or Iodine) decreases as the carbon black ages (See Figure 1). This is most likely the result of slow oxygen chemisorption. The rate of the aging effect seems to increase with increasing surface area. This phenomena caused problems in the use of the Standard Reference Blacks (SRBs) as reference materials for the Iodine test because they would be in use for many years. Testing laboratories that used the reference values to track their testing proficiency with control charts would find it to be increasingly difficult to maintain their results within the established control limits. Periodically it would be necessary to conduct an Interlaboratory Test Program (ITP) to determine new Iodine Number reference values for the SRBs. When these new values were published, the testing laboratories would need to update their testing proficiency control charts for the new values.

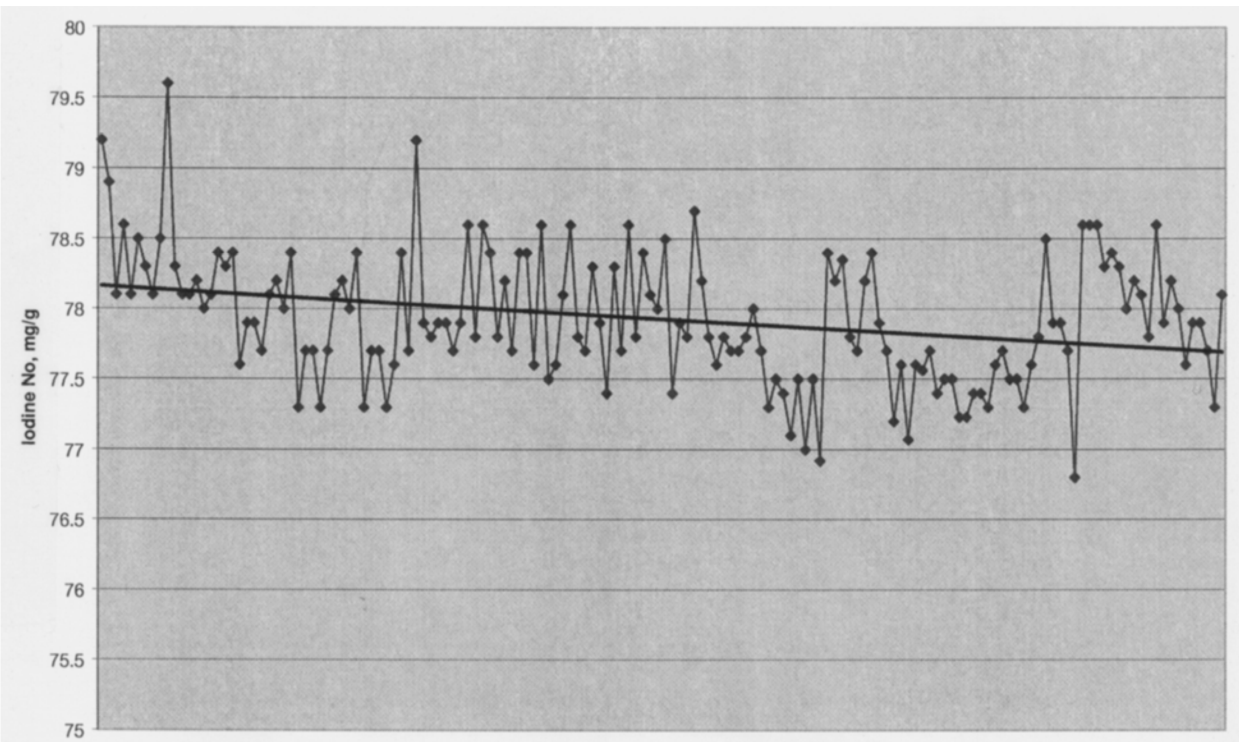

Figure 1. Iodine Number of SRB-5B Decreases with Time (Data Represents Three Years)

[1] The current version of this document is available from Laboratory Standards and Technologies, Inc., 227 Somerset Street, Borger, TX, 79007, www.carbonstandard.com.

Around 2002, a carbon black producer brought information to D24 regarding a special material they had had in storage for twelve years whose iodine number had dropped by only 0.1 g/kg. This material was a N121 carbon black that had been heat treated at high temperature in an inert atmosphere to graphitize the carbon. After investigation and confirmation, D24 began a program to use this technology to produce an iodine number reference material that would be stable over long periods of time.

The first reference materials were produced in 2004 having three levels that covered the expected range of iodine values. This first material was designated as HT (Heat Treated) reference materials. An ITP was conducted in November 2004 to determine the precision parameter values. There is no record of the number of participating laboratories or the number of outliers identified for each material during this ITP. The three materials in the HT set were designated HT-1 with a mean iodine value of 44.0, HT-2 with a mean of 91.1, and HT-3 at a mean of 127.1. The repeatability standard deviations from this ITP were: HT-1 0.25, HT-2 0.29, and HT-3 0.35. The reproducibility standard deviation values from this ITP are unknown. This material was approved for use by D24 at its June 2005 meeting. The resulting precision values were posted on the D24 webpage.

During the time that the HT materials were being developed, there were also other activities to improve the D1510 test method. Those activities specifically focused on the impact of the potassium iodide (KI) concentration in the iodine solution on the iodine test results and the need to have good validation of the iodine and sodium thiosulfate solutions through the running of blanks. A test method for determining the KI concentration was added to D1510 as an annex and the language regarding the running of blanks was improved.

The D24 members thought that these improvements were significant enough that they may affect the HT values so another ITP was conducted in 2009. Forty-nine laboratories participated in this ITP. The mean values did change and, perhaps more importantly, the repeatability standard deviations dropped and were more consistent. This helps to confirm the importance of maintaining proper KI concentrations and having blank values within the established limits for the iodine and sodium thiosulfate solutions. See Table 1 for the HT precision parameters from the 2009 ITP.

Table 1 HT Precision Parameters for D1510, Method A & B, (Type 1 Precision)							
Units	g/kg						
Material	Mean Level	Sr	**r**	(r)	SR	**R**	(R)
HT-1	43.7	0.24	**0.68**	1.50	0.49	**1.38**	3.20
HT-2	90.7	0.23	**0.65**	0.70	0.68	**1.94**	2.10
HT-3	126.6	0.23	**0.64**	0.50	0.61	**1.73**	1.40
Average	87.0						
Pooled Values		0.23	**0.66**	0.80	0.60	**1.70**	2.00

Table 1. HT Iodine Reference Materials Precision Parameters.

By late 2011 the HT materials available for commercial sales were nearing depletion so D24 began the process of preparing the HT-2 set of materials. During the time the HT-2 set was being produced and validated, ASTM D7849, Standard Classification for Nomenclature of Reference Materials of Committee D24 was approved. Following the guidelines of D7849, the HT-2 set was redesignated as INR, Iodine Number Reference. The INR set has three materials at nearly the same mean values as the HT set. The three materials were designated as INR-A at 41.5 iodine number, INR-B with a 90.8 iodine number, and INR-C at 125.8 iodine number. See Table 2 for the INR precision parameters.

Table 2 INR Precision Parameters for D1510, Method A & B, (Type 1 Precision)							
Units	g/kg						
Material	Mean Level	Sr	**r**	(r)	SR	**R**	(R)
INR-A	41.5	0.31	**0.88**	2.1	1.19	**3.37**	8.1
INR-B	90.8	0.33	**0.95**	1.0	0.63	**1.77**	2.0
INR-C	125.8	0.31	**0.87**	0.7	1.00	**2.84**	2.3
Average	86.0						
Pooled Values		0.32	**0.90**	1.0	0.97	**2.74**	3.2

Table 2. INR Iodine Reference Materials Precision Parameters.

Anticipating that the INR materials available for commercial sales would be depleted by 2018 or 2019, D24 began planning for the INR2 set in 2016. The three materials were produced in 2017 with nominal targets of 47, 93, and 147 iodine number. An ITP was conducted in June 2018 to establish the precision values. See Table 3 for the INR2 precision parameters.

Table 3 INR2 Precision Parameters for D1510, Method A & B, (Type 1 Precision)							
Units	g/kg						
Material	Mean Level	Sr	r	**(r)**	SR	R	**(R)**
INR-2A	48.1	0.30	0.85	**1.76**	0.56	1.58	**3.29**
INR-2B	96.7	0.31	0.87	**0.90**	0.77	2.18	**2.26**
INR-2C	150.7	0.49	1.40	**0.93**	1.35	3.81	**2.53**
Average	98.5						
Pooled Values		0.38	1.07	**1.09**	0.95	2.70	**2.74**

Table 3. INR2 Iodine Reference Materials Precision Parameters.

While the HT reference materials are no longer commercially available and the INR reference materials will soon be no longer commercially available, to be replaced by the INR2 set of reference materials, values for all three sets of reference materials are presented because some laboratories are still using the HT materials and the INR materials are expected to be in use in laboratories for many years. As these materials are depleted in the laboratories, they will be replaced with the INR2 materials.

The HT material has been in use for nearly 20 years. It is possible that the INR and INR2 sets will be in use for 20 years or more. At least 2 years before the INR2 set nears depletion for commercial sales, planning and production of the INR3 set will need to begin.

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. (See ASTM D8043, Standard Guide for Carbon Black—Shelf Life for similar information on other carbon blacks.) It is expected that for the HT, INR, and INR2 materials, their shelf life is also indefinite when properly stored as stated above.

Properties for the HT, INR, and INR2 Sets

The testing data for the HT, INR, and INR2 sets were evaluated using ASTM D4483-99. This evaluation generated accepted reference values (means), AR-values for the HT, INR, and INR2 sets for use with the D1510 Method A and Method B test methods as shown below, and 2 and 3 sigma limits on these values or on individual daily values as obtained by any laboratory using the HT, INR, or INR2 sets. The 2 and 3 sigma limits apply to a single iodine number measurement of the listed reference materials. Two times the 2 or 3 sigma limit equals the total 4 or 6 sigma range, respectively.

ASTM D4483-99 uses a one-sided k test to identify outliers having high variability. The analysis of the HT materials used the one-sided k test of D4483. The analysis of the INR and INR2 reference materials used a two-sided k test developed for D24 to identify outliers having high and low variability. 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).

'Accepted Reference Value' or AR-value; this is the average (mean), for the HT, INR, and INR2 reference materials listed below in Tables 4 through 6 for use with D1510 Methods A and B. These values were obtained in an interlaboratory test program (ITP) for a large group of typical laboratories using samples taken from the various material lots. See page 7 for more details on the ITPs.

'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 HT, INR, or INR2 set AR-values for the D1510 Method A or B 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 HT, INR, or INR2 set AR-values for the D1510 Method A or B 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, such as is the case with the testing done on the HT, INR, and INR2 sets. 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 the LPRS program, may help to identify the unique sources of bias and variation. The HT, INR, or INR2 reference materials can be used to assist a laboratory in determining the presence and magnitude of bias and variation using the values given in the Tables 4 to 6 below. See ASTM D4821 for specific instructions on how to use these values to evaluate a laboratory's testing proficiency (bias and variability).

Using the HT, INR, or INR2 Sets

When using either of the D1510 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 been, and cannot be, eliminated for the AR testing.

If any one of the three reference materials in the selected set (See Tables 4, 5, or 6) falls outside the established limits for iodine number of carbon black, normalization of the test results MUST be performed. See D1510 and/or D4821 for specific details for performing the normalization.

Table 4 Mean (AR-value) and Limit Values for D1510, Iodine Number Methods A & B, HT Reference Materials

Units	g/kg	**Within Laboratory**			**Between Laboratories**		
Material	Mean (AR-value)	Sr	2 x Sr	3 x Sr	SR	2 x SR	3 x SR
HT-1	43.7	0.24	0.48	0.72	0.49	0.98	1.47
HT-2	90.7	0.23	0.46	0.69	0.68	1.36	2.04
HT-3	126.6	0.23	0.46	0.69	0.61	1.22	1.83

Table 5 Mean (AR-value) and Limit Values for D1510, Iodine Number Methods A & B, INR Reference Materials							
Units	g/kg	**Within Laboratory**			**Between Laboratories**		
Material	Mean (AR-value)	Sr	2 x Sr	3 x Sr	SR	2 x SR	3 x SR
INR-A	41.5	0.31	0.62	0.93	1.19	2.38	3.58
INR-B	90.8	0.33	0.66	1.00	0.63	1.26	1.88
INR-C	125.8	0.31	0.62	0.92	1.00	2.00	3.01

Table 6 Mean (AR-value) and Limit Values for D1510, Iodine Number Methods A & B, INR2 Reference Materials							
Units	g/kg	**Within Laboratory**			**Between Laboratories**		
Material	Mean (AR-value)	Sr	2 x Sr	3 x Sr	SR	2 x SR	3 x SR
INR-2A	48.1	0.30	0.60	0.90	0.56	1.12	1.68
INR-2B	96.7	0.31	0.62	0.93	0.77	1.54	2.31
INR-2C	150.7	0.49	0.98	1.47	1.35	2.70	4.05

Background and Interlaboratory Test Program Details: HT, INR, or INR2 Sets

Background - The HT, INR, and INR2 reference materials are used for test method D1510, Iodine Adsorption Number, methods A and B under the jurisdiction of ASTM Committee D24. These materials are evaluated according to the practices of D6915, "Evaluation of Standard Reference Blacks" with statistical analysis per D4483-99, “Standard Practice for Evaluating Precision for Test Method Standards in the Rubber and Carbon Black Manufacturing Industries”. Three materials were selected for use in each of the HT, INR, and INR2 sets.

Evaluation of the HT, INR, and INR2 Sets – The selection of the materials for the HT, INR, and INR2 sets was based on their expected iodine number value following heat treatment. The Accepted Reference Value (ARV) for each material was determined from an ITP and analyzed per D4483-99.

The values listed in Tables 1 to 3 were obtained through an Interlaboratory Test Program (ITP) conducted by D24. The data was analyzed per D4483-99 with the exception that a two-sided test was used 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). Mandel’s h and k statistics were used to identify outliers. Replacement values were calculated and substituted for outlier values. All three materials in each set were analyzed at the same time in each laboratory and evaluated at the same time. The values in Tables 4 to 6 are an expansion of values in Tables 1 to 3 to show the 2 standard deviation (sigma) and 3 standard deviation (sigma) limits to be used if a laboratory wishes to do control charting of the D1510 test methods.

Interlaboratory Test Program (ITP) – See Table 7 for a list of the various iodine reference number materials and when they were tested in an ITP. Table 7 also shows how many laboratories participated in the testing for each set and how many were removed as outliers for mean (M), high variation (H), or low variation (L).

Table 7 Iodine Number Reference Materials Information			
		Number of Laboratories (M/H/L)[1]	
Material	Test Period		
HT	2009		
HT-1		49 (1/3/0)	
HT-2		49 (3/4/0)	
HT-3		49 (3/3/0)	
INR	Mar-Jun 2012		
INR-A		51 (0/2/3)	
INR-B		51 (2/2/1)	
INR-C		51 (0/2/4)	
INR2	June 2018		
INR-2A		33 (1/0/0)	
INR-2B		43 (0/2/0)	
INR-2C		33 (0/0/0)	
[1]M = number of outliers for Mean; H = number of outliers for High variation; L = number of outliers for Low			

To report corrections or request changes to this document, contact Laboratory Standards and Technologies, the chairman of ASTM subcommittee D24.61, or the chairman of ASTM subcommittee D24.21.